# ORGANIC REACTIVITY

English Edition

of

## Реакционная способность органических соединений

# ORGANIC REACTIVITY

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Comparison of $pK_{BH^+}$ -Values for Weak
Bases Calculated by Marziano and Cox-Yates
Methods.

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$pK_{BH^+}$ -Values for 28 hypothetical weak bases
have been calculated, using the methods of N. C.
Marziano ($M_c$ -function) and of R. A. Cox (X-func-
tion).The $H_2SO_4$ % (wt/wt) at half-protonation of
weak bases studied lies in the range from 20% to
80%. The solvation parameter in R.A. Cox treatment
$m^*$ has been varied from 0.4 to 1.6. Comparison of
$pK_{BH^+}$ - values obtained by $M_c$ and X - functions
shows that they are essentially the same, if $H_2SO_4$%
at half-protonation of bases is 20, 40 or 60%
(wt/wt). Very weak bases, half-protonating in 80%
$H_2SO_4$ (wt/wt) have been found to give different
$pK_{BH^+}$ - values in N.C.Marziano and in R.A. Cox
treatments. These differences are about 2 $pK_{BH^+}$-
- units in some cases. Therefore a conclusion has
been drawn that at least one of the functions $M_c$
and X needs to be corrected for the range of 60 -
95% $H_2SO_4$ (wt/wt)

Two research groups (H. C. Marziano et al.[1,2] and
R. A. Cox, K. Yates [3] ) have suggested essentially
the same method for estimating $pK_{BH^+}$ -values of weak bases
which only become significantly protonated in strongly
acidic solutions. Both of these groups used the free energy
linear relationship [2,3]

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$$\log \frac{f_{H^+} \cdot f_B}{f_{BH^+}} = m^* \log \frac{f_{H^+} \cdot f_{B^*}}{f_{B^*H^+}} \tag{1}$$

as a common starting point. In Eq. 1 the B and $B^*$ are two arbitrary weak bases. The validity of Eq. 1 has been tested in a number of papers. [2 - 7] In order to derive a generally applicable method for estimating $pK_{BH^+}$ - s one needs a scale of $\log (f_{H^+} \cdot f_{B^*} / f_{B^*H^+})$ values for a hypothetical common reference base $B^*$. This scale should range from water to concentrated solutions of strong acid. Both groups mentioned above were able to solve this problem, using most of available data about protonation of weak bases and iteration procedures. [2,3] N. C. Marziano et al [1,2] denoted

$$- \log \frac{f_{H^+} \cdot f_{B^*}}{f_{B^*H^+}} = M_c \tag{2}$$

and called $M_c$ "activity coefficient function." R.A. Cox and K. Yates wrote [3]

$$\log \frac{f_{H^+} \cdot f_{B^*}}{f_{B^*H^+}} = X \tag{3}$$

and named it "excess acidity". It is obvious from Table 1 that $-M_c \neq X$. Nevertheless, if Eq. I is valid, the $pK_{BH^+}$ for a weak base B can be estimated as a regression coefficient: [2,3]

$$\log \frac{[B]}{[BH^+]} + \log C_{acid} = n_B M_c - pK_{BH^+} \tag{4}$$

$$- \log \frac{[B]}{[BH^+]} - \log C_{H^+} = m^* X + pK_{BH^+} \tag{5}$$

where $C_{acid}$ is the total concentration of strong acid (mole/dm$^3$), $C_{H^+}$ is the concentration of hydrated protons obtained from Raman spectroscopic measurements (Table 1)

Table 1

Values for $M_c$, $X$ and $\log C_{H^+}$
in Aqueous Sulfuric Acid Solutions

$(25°C)$.

| % $H_2SO_4$ wt / wt | $-M_c$ [2] | $X$ [3] | $\log C_{H^+}$ [3] |
|---|---|---|---|
| 5 | 0.0172 | 0.103 | −0.205 |
| 10 | 0.0354 | 0.231 | 0.117 |
| 15 | 0.0555 | 0.387 | 0.315 |
| 20 | 0.0785 | 0.573 · | 0.461 |
| 25 | 0.1053 | 0.790 | 0.577 |
| 30 | 0.1358 | 1.038 | 0.674 |
| 35 | 0.1706 | 1.317 | 0.757 |
| 40 | 0.2096 | 1.628 | 0.828 |
| 45 | 0.2526 | 1.969 | 0.891 |
| 50 | 0.2999 | 2.345 | 0.945 |
| 55 | 0.3514 | 2.763 | 0.992 |
| 60 | 0.4075 | 3.238 | 1.033 |
| 65 | 0.4682 | 3.795 | 1.069 |
| 70 | 0.5338 | 4.459 | 1.097 |
| 74 | 0.5896 | 5.080 | 1.118 |
| 80 | 0.6786 | 6.150 | 1.143 |
| 84 | 0.7427 | 6.906 | 1.133 |
| 90 | 0.8547 | 7.985 | 0.996 |
| 95 | 0.9809 | 8.989 | 0.654 |
| 99 | − | 10.754 | −0.153 |

and $n_B$, $m*$ are the multipliers for $M_c$ and $X_1$, respectively.

A question of general interest is how close to each other are the $pK_{BH^+}$ – values obtained by Eq. 4 (N.C. Marziano et al[2]) and by Eq. 5 (R.A. Cox and K. Yates [3]). The purpose of this paper is to answer that question. The comparison of $pK_{BH^+}$– values calculated by Eqs. 4 and 5 may be carried out for aqueous $H_2SO_4$ solutions only because the $M_c$ values for $H_2O$ – $HClO_4$ mixtures are not available[2].

It should be noted that the $M_c$ values are given with respective confidence intervals but the X values do not have these intervals.[3] For aqueous sulfuric acid solutions a direct proportionality between $M_c$ and X is not anticipated because the $M_c$ values have been calculated using $C_{acid}$ instead of $C_{H^+}$[2].However, there exists a rather good linearity between $M_c$ and X in aqueous sulfuric acid solutions (see Fig. 1).

In order to estimate the magnitude of differences between $pK_{BH^+}$ (Eq. 4) and $pK_{BH^+}$ (Eq. 5.) we chose a set of hypothetical weak bases which would be half-protonated in 20%, 40%, 60% and 80% $H_2SO_4$ (wt/wt), respectively. In addition to this we took into account the second variable denoted in Cox-Yates treatment as $m*$. Usually $0.4 \le m* \le 1.6$[3] . Therefore the following $m*$-values have been used: 0.4, 0.6, 0.8, 1.0, 1.2, 1.6. The $pK_{BH^+}$ –s for the basis chosen were calculated from the version of Eq. 5

$$pK_{BH^+} (Eq. 5) = -m*X - logC_{H^+} \qquad (6)$$

which is obtained from Eq. 5, taking $[B] = [BH^+]$ . The $pK_{BH^+}$ –s obtained by Eq. 6 are listed in Table 2. The next step was to estimate the interval of sulfuric acid concentrations where the $log( [B] / [BH^+] ) = log I$ varies from $-1$ to $+1$ as it is usually observed in an experimental study[3] :

$$log I = -m*X - log C_{H^+} - pK_{BH^+} (Eq. 5) \qquad (7)$$

where $pK_{BH^+}$ (Eq. 5) is given by Eq. 6. The estimated interval of sulfuric acid concentrations was divided into 10 equal

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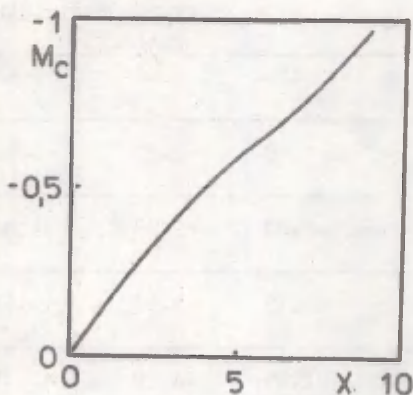
Fig. 1    Plot of $M_c^2$ vs. $X^3$ for aqueous sulfuric acid solutions.

parts which gives us 11 acid concentrations $c_1, c_2, \ldots, c_{II}$ .
For each of these $c_j$ the following parameters were calculated:
(i)   log I by Eq. 7 using respective X and $C_{H+}$ values at the concentrations $c_j$;
(ii)  the $M_c$ - value corresponding to the $c_j$ (see the Experimental Section) and
(iii) the relative confidence interval $E(M_c)$ in % -s for the respective $M_c$ - value (see the Experimental Section).

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Table 2

The $pK_{BH^+}$ (Eq.5) Values for the Bases Chosen[*)]

| m* | $pK_{BH^+}$ (Eq. 5) for bases half-protonated in $H_2O$ – $-H_2SO_4$ mixtures containing $H_2SO_4$ (wt/wt) | | | |
|------|---------|--------|--------|---------|
|      | 20%     | 40%    | 60%    | 80%     |
| 0.40 | –.0.69  | –1.48  | –2.33  | –3.61   |
| 0.60 | – 0.81  | –1.80  | –2.98  | –4.84   |
| 0.80 | – 0.92  | –2.13  | –3.63  | –6.07   |
| 1.00 | – 1.04  | –2.45  | –4.28  | –7.30   |
| 1.20 | – 1.15  | –2.78  | –4.92  | –8.53   |
| 1.40 | – 1.26  | –3.10  | –5.57  | –9.76   |
| 1.60 | – 1.38  | –3.43  | –6.22  | –10.99  |

* obtained by Eq. 6.

The obtained in this way log I – values were weighted, using an error function given by Kresge and Chen [8]. At least according to the N.C.Marziano et al. treatment [2]. $pK_{BH^+}$ (Eq. 4) was estimated by a standard regression analysis using the log I and $M_c$ values obtained at $c_1$, $c_2$, ..., $c_{11}$. (see Table 3). In order to show the influence of $E(M_c)$ on the $pK_{BH^+}$ (Eq. 4) following three $pK_{BH^+}$ (Eq.4) – values were calculated: the first with $M_c$, the second with $M_c(1+ 0.01E(M_c))$ and the third with $M_c(1-0.01 E(M_c))$.

The half of the difference between the second and the third $pK_{BH^+}$-values is denonted as $E(\Delta)$ and in some approximation it can be used as an estimate of probable errors in $pK_{BH^+}$ (Eq. 4) - values due to the errors in the $M_c$ (see Table 3):

$$\Delta = pK_{BH^+} \text{ (Eq. 4)} - pK_{BH^+} \text{ (Eq. 5)} \tag{8}$$

are given in Table 4. This Table shows that for the bases not weak enough (log I = 0 in $\leqslant 60\%$ $H_2SO_4$, wt/wt) the differences (8) are reasonably small.

Table 3

The $pK_{BH^+}$(Eq. 4) Values for the Bases Chosen[*]

| $m^x$ | $pK_{BH^+}$(Eq. 4)$\pm E(\Delta)$ for the bases half-protonated in $H_2O$ – $H_2SO_4$ mixtures containing $H_2SO_4$ (wt/wt) | | | |
|---|---|---|---|---|
| | 20% | 40% | 60% | 80% |
| 0.40 | $-0.63\pm0.01$ | $-1.40\pm0.01$ | $-2.25\pm0.02$ | $-3.80\pm0.06$ |
| 0.60 | $-0.75\pm0.01$ | $-1.74\pm0.02$ | $-2.93\pm0.02$ | $-5.63\pm0.11$ |
| 0.80 | $-0.87\pm0.01$ | $-2.07\pm0.02$ | $-3.61\pm0.03$ | $-7.35\pm0.15$ |
| 1.00 | $-1.00\pm0.02$ | $-2.41\pm0.03$ | $-4.31\pm0.04$ | $-9.00\pm0.20$ |
| 1.20 | $-1.12\pm0.02$ | $-2.74\pm0.04$ | $-5.02\pm0.05$ | $-10.67\pm0.24$ |
| 1.40 | $-1.24\pm0.02$ | $-3.08\pm0.04$ | $-5.72\pm0.06$ | $-12.31\pm0.29$ |
| 1.60 | $-1.36\pm0.03$ | $-3.42\pm0.05$ | $-6.43\pm0.08$ | $-13.95\pm0.34$ |

[*] with respective $E(\Delta)$- values due to the errors in $M_c$.

For weaker bases which are half-protonated in more concentrated $H_2SO_4$ solutions ( $> 60\%$ $H_2SO_4$, wt/wt) Eqs. 4 and 5 yield markedly different $pK_{HH^+}$ - values. In this case the $\Delta$-values are greatly influenced by $m^*$ - values (see Table 4). It should be mentioned here that the probable errors in $pK_{BH^+}$ (Eq. 4) (E ($\Delta$)) due to errors in the $M_c$- function do not play an important role at any $H_2SO_4$ concentrations (see Table 4).

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Table 4

The Differences $\Delta$ Between $pK_{BH^+}$(Eq. 4) and $pK_{BH^+}$
(Eq. 5) for the Bases Chosen.

| $m^x$ | $\Delta \pm E(\Delta)$ at $H_2SO_4$ concentrations (wt/wt) | | | |
|-------|-------|-------|-------|-------|
|       | 20%   | 40%   | 60%   | 80%   |
| 0.4 | $0.06\pm0.01$ | $0.08\pm0.01$ | $0.08\pm0.02$ | $-0.19\pm0.06$ |
| 0.6 | $0.06\pm0.01$ | $0.06\pm0.02$ | $0.05\pm0.02$ | $-0.79\pm0.11$ |
| 0.8 | $0.05\pm0.01$ | $0.06\pm0.02$ | $0.02\pm0.03$ | $-1.28\pm0.15$ |
| 1.0 | $0.04\pm0.02$ | $0.04\pm0.03$ | $-0.03\pm0.04$ | $-1.70\pm0.20$ |
| 1.2 | $0.03\pm0.02$ | $0.04\pm0.04$ | $-0.10\pm0.05$ | $-2.14\pm0.24$ |
| 1.4 | $0.02\pm0.02$ | $0.02\pm0.04$ | $-0.15\pm0.06$ | $-2.55\pm0.29$ |
| 1.6 | $0.02\pm0.03$ | $0.01\pm0.05$ | $-0.21+0.08$ | $-2.96\pm0.34$ |

It is important to realize that the coincidence of $pH_{BH^+}$ values calculated by the Marziano et al and Cox-Yates methods for bases with $\log I = 0$ in $\leqslant 60\%$ $H_2SO_4$, (wt/wt) serves as a proof of reliability of these methods derived both from the same free energy linear relationship (1). On the other hand, the discrepancies in $pK_{BH^+}$ - values for the bases having $\log I = 0$ in $> 60\%$ $H_2SO_4$ (wt/wt) imply that at least one of the functions $M_c$ and X needs to be corrected in the range from 60 to 95% $H_2SO_4$ (wt/wt).

Due to different scaling of $M_c$ and X- functions respective solvation parameters ($n_B$ and $m^*$) are different. However, their ratio ($n_B/m^*$) is mostly about 8, reaching the value 11,8 for very weak bases (see Table 5).

Table 5

The Ratio of Solvation Parameters ($n_B/m^*$) Used
in Eqs. 4 and 5.

| $m^x$ | $n_B/m^*$ at $H_2SO_4$ concentrations (wt/wt) | | | |
|---|---|---|---|---|
| | 20% | 40% | 60% | 80% |
| 0.40 | $8.38 \pm 0.25$ | $8.08 \pm 0.13$ | $7.95 \pm 0.08$ | $9.50 \pm 0.13$ |
| 0.60 | $8.18 \pm 0.27$ | $8.05 \pm 0.12$ | $8.05 \pm 0.07$ | $10.95 \pm 0.13$ |
| 0.80 | $8.06 \pm 0.28$ | $8.04 \pm 0.13$ | $8.15 \pm 0.08$ | $11.40 \pm 0.14$ |
| 1.00 | $8.00 \pm 0.27$ | $8.04 \pm 0.12$ | $8.22 \pm 0.07$ | $11.57 \pm 0.15$ |
| 1.20 | $7.97 \pm 0.27$ | $8.03 \pm 0.12$ | $8.30 \pm 0.07$ | $11.69 \pm 0.16$ |
| 1.40 | $7.94 \pm 0.26$ | $8.03 \pm 0.11$ | $8.34 \pm 0.07$ | $11.75 \pm 0.16$ |
| 1.60 | $7.92 \pm 0.26$ | $8.03 \pm 0.11$ | $8.39 \pm 0.07$ | $11.79 \pm 0.17$ |

## Experimental

The X- values were calculated by the corresponding
empirical equation given in the R.A. Cox paper [3]:

$$X = -1.2192(Z-1) + 1.74213(Z^2-1) - 0.629724(Z^3-1) + 0.116376(Z^4-1) - 0.0104567(Z^5-1) + 0.00036118(Z^6-1)$$

where $Z = 10^{0.01 p}$ and p is $H_2SO_4$ % (wt/wt).
A similar equation has been found to hold for $M_c$:

$$M_c = 0.860976(Z-1) + 0.335635(Z^2-1) - 0.0950794(Z^3-1) + 0.0132739(Z^4-1) - 0.00103897(Z^5-1) + 0.000037054(Z^6-1)$$

where $Z = 10^{0.01p}$ and p is $H_2SO_4$% (nt/wt).

Sulfuric acid concentrations expressed on % (wt/wt) were
converted into acid molarity (mole $H_2SO_4/dm^3$) by

$$C = 0.101752\ p + 1.57523 \cdot 10^{-4} p \cosh (p \cdot 10^{-2}) +$$
$$+ 4.85216 \cdot 10^{-4}\ p^2 + 2.8528 \cdot 10^{-6}\ p^3$$

where p is $H_2SO_4\%$ (wt/wt).

The confidence intervals $E(M_c)$ for $M_c$ in %-s from the corresponding $M_c$ value are given by

$$E(M_c) = 6.7769 - 12.1946\ c - 0.128184(1 + \sqrt{c})/\ c^2$$
$$- 13.5534\ \log(1+c) + 6.07738/\ \sqrt{c}\ -$$
$$- 2651\ (1 - \sqrt{(1 + 0.01c)})$$

where c is $H_2SO_4$ concentration (mole/$dm^3$).

The concentrations of hydrated protons $C_{H^+}$ can be calculated by

$$C_{H^+} = p\ (0.119016 + 0.0169089\ Z + 0.020324\ Z^2 -$$
$$- 0.0141916\ Z^3 + 0.00314939\ Z^4 - 0.000059195\ Z^6)$$

if $p > 65$ and by

$$C_{H^+} = p\ (\ 9.44835 - 6.2132\ Z + 0.517897\ Z^2 +$$
$$+ 0.420937\ Z^3 - 0.0881593\ Z^4 + 0.000713638\ Z^6)$$

if $5 \leq p \leq 65$ . In the last two equations $Z = 0.05\ p$ and p is $H_2SO_4\%$ (wt/wt).

All calculations were carried out on a "Nairi - 2" computer.

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# DIFFERENTIAL CONDUCTOMETRIC EFFECT AND STRUCTURE OF STRONG BASES. VI PROPYL- AND BUTYLAMMONIUM IONS IN AQUEOUS PERCHLORIC ACID

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The differential conductometric effect $y = \Delta \mathscr{A}/c$ has been determined when $n\text{-}C_3H_7NH_2$, $(n\text{-}C_3H_7)_2NH$, $(n\text{-}C_3H_7)_3N$, $n\text{-}C_4H_9NH_2$, $tert\text{-}C_4H_9NH_2$, and $(n\text{-}C_4H_9)_2NH$ were added to the aqueous perchloric acid solutions. For the interpretation of data obtained the model of restructured solvent shell suggested by M. Karelson has been used. The molar volumes of restructured water shell ($V_s$) around the ions studied have been estimated. The $V_s$ values are found to be in the sequence: $Bu_nNH_{4-n}^+ > Pr_nNH_{4-n}^+ > Et_nNH_{4-n}^+ > Me_nNH_{4-n}^+$.

In our previous communications[1-3] the differential conductometric effect $y = \Delta \mathscr{A}/c$ for ammonium ions containing different number of methyl and ethyl groups in aqueous $HClO_4$ solutions has been reported. In this paper $y = \Delta \mathscr{A}/c$ for propyl and butyl substituted ammonium ions in $H_2O - HClO_4$ mixtures is studied (see Table 1). As it has been shown in our previous reports of this series[1-3] the differential conductometric effect has the same value whether free bases or respective perchlorates were added. In this paper the differential conductometric effect was obtained by adding free strong bases $n\text{-}C_3H_7NH_2$, $(n\text{-}C_3H_7)_2NH$,

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The Differential Conductometric Effect of the Bases
Added to Aqueous Solutions of $HClO_4$

| % $HClO_4$ | $y \cdot 10^3$ | % $HClO_4$ | $y \cdot 10^3$ | % $HClO_4$ | $y \cdot 10^3$ |
|---|---|---|---|---|---|
| $n\text{-}C_3H_7NH_2$ | | $(n\text{-}C_3H_7)_2NH$ | | $(n\text{-}C_3H_7)_3N$ | |
| 4.4 | 266 | 2.3 | 311 | 2.2 | 319 |
| 8.8 | 256 | 8.1 | 320 | 6.2 | 368 |
| 14.8 | 225 | 15.6 | 323 | 14.6 | 347 |
| 20.5 | 219 | 21.8 | 314 | 20.8 | 379 |
| 27.5 | 207 | 28.0 | 323 | 29.2 | 421 |
| 32.8 | 193 | 32.4 | 335 | 31.6 | 451 |
| 40.5 | 159 | 40.6 | 288 | 37.2 | 475 |
| 46.0 | 162 | 45.4 | 300 | 42.4 | 520 |
| 52.5 | 150 | 52.0 | 260 | 49.4 | 550 |
| 58.4 | 141 | 58.2 | 243 | 57.4 | 555 |
| $n\text{-}C_4H_9NH_2$ | | $tert\text{-}C_4H_9NH_2$ | | $(n\text{-}C_4H_9)_2NH$ | |
| 1.2 | 243 | 1.1 | 282 | 2.5 | 324 |
| 5.2 | 234 | 5.1 | 275 | 7.3 | 369 |
| 10.4 | 293 | 10.2 | 270 | 14.7 | 373 |
| 15.4 | 283 | 13.9 | 267 | 19.5 | 347 |
| 20.2 | 243 | 21.7 | 244 | 32.3 | 453 |
| 26.3 | 252 | 28.0 | 233 | 37.5 | 430 |
| 29.9 | 243 | 32.4 | 224 | 42.2 | 467 |
| 35.2 | 233 | 41.4 | 227 | | |
| 40.8 | 226 | 54.1 | 183 | | |
| 47.6 | 206 | 50.2 | 195 | | |
| 52.7 | 182 | 58.2 | 178 | | |
| 58.2 | 179 | | | | |

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$(n-C_3H_7)_3N$, $n-C_4H_9NH_2$, $tert-C_4H_9NH_2$ and $(n-C_4H_9)_2NH$ to the aqueous solutions of perchloric acid. The methods used for calculations of $y = \triangle\varkappa/c$ are described in the preceding papers[1,4,5]. Attempts were made to obtain the $y = \triangle\varkappa/c$ for $(n-C_3H_7)_4NOH$, $(n-C_4H_9)_3N$, and $(n-C_4H_9)_4NOH$ also. But they failured because respective perchlorates were found to be quite insoluble in aqueous perchloric acid solutions.

The dependence of differential conductometric effect on the number and size of the alkyl groups is shown in Figs.1 and 2 , where $y = \triangle\varkappa/c$ is plotted as a function of perchloric acid concentration. These Figures show that at any given perchloric acid concentration the y value is larger for ions containing more alkyl groups of the same size.
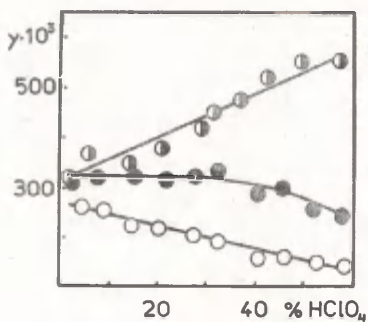


Fig.1. Dependence of differential conductometric effect (y) on the number of propyl groups:

○ – $n-C_3H_7NH_2$

◉ – $(n-C_3H_7)_2NH$

◑ – $(n-C_3H_7)_3N$
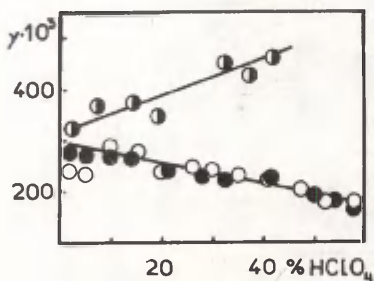


Fig.2. Dependence of differential conductometric effect (y) on the number of butyl groups:

○ – $n-C_4H_9NH_2$

● – $tert-C_4H_9NH_2$

◑ – $(n-C_4H_9)_2NH$

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This is obviously due to the increase in molar volume of restructured water shells ($V_s$, $cm^3$/mole) caused by a larger number of alkyl groups. Provided that ions migrated into the restructured water shells have zero equivalent conductances[6,7] the increase in $V_s$ values results in larger $y$ values[2]:

$$10^3 y = \mathcal{H} V_s + \lambda_{H^+} - \lambda_{BH^+} \qquad (1)$$

where $\lambda_{H^+}$ and $\lambda_{BH^+}$ are the equivalent conductances for $H^+$ - and $BH^+$ - ions, respectively; $\mathcal{H}$ is the specific conductivity of the solution.

The volumes of the hydration shell around the ions studied were calculated by

$$V_s = \frac{1}{\mathcal{H}} (\ 10^3 y - \lambda_{H^+} + \lambda_{BH^+}\ ) \qquad (2)$$

The $\lambda_{H^+}$ values used were obtained from Ref.8. For the interval $40 - 55\ \%$ (w/w) $HClO_4$ the $\lambda_{H^+}$ values were
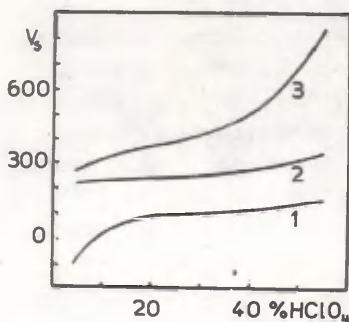


Fig.3. Dependence of $V_s$ on the number of propyl groups:

1 - $n-C_3H_7NH_2$
2 - $(n-C_3H_7)_2NH$
3 - $(n-C_3H_7)_3N$

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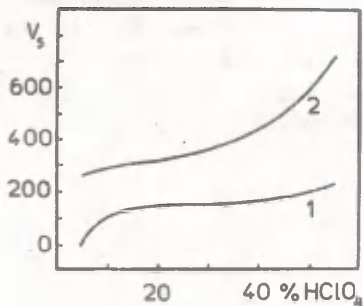
Fig.4. Dependence of $V_s$ on the number of butyl groups:

1 - $n-C_4H_9NH_2$

2 - $(n-C_4H_9)_2NH$

determined by the method used in Ref.2. The $\lambda_{BH^+}$ values of ions studied are not available for concentrated aqueous perchloric acid solutions. Therefore they were calculated by the equation presented in our previous paper[2]. For this procedure the following values of $\lambda_{BH^+,\infty}$ were used[9]: 30.6 for $n-C_3H_7NH_2$, 27.0 for $(n-C_3H_7)_2NH$, 24.6 for $(n-C_3H_7)_3N$, 25.4 for $n-C_4H_9NH_2$ and for $tert-C_4H_9NH_2$ too, 22.4 for $(n-C_4H_9)_2NH$.

From Figs. 3 and 4 it can be seen that all propyl and butyl substituted ammonium ions have $V_s > 0$. The positive $V_s$ values indicate that the solute particles are surrounded by restructured water shells where the conductivities ($\lambda$) of hydrated protons and perchlorate ions are decreased (or even zero) over those in bulk water. An explanation for this phenomenon is suggested in Ref.2.

A comparison of $V_s$ values for propyl and butyl substituted ammonium ions shows that $V_s(Bu_nNH_{4-n}^+) > V_s(Pr_nNH_{4-n}^+)$. That is just the order anticipated because a larger alkyl group should be surrounded by a larger volume of restructured water. This is also illustrated by Figs. 5-7, using the respective data for ethyl

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and methyl groups[1-3].

It should be noted that values of differential conductometric effect for $n-C_4H_9NH_2$ and $tert-C_4H_9NH_2$ are the same. Consequently, the values of $V_s$ for those amines are equal too. In this case the branching of carbon skeleton has no effect on the respective $V_s$ values.
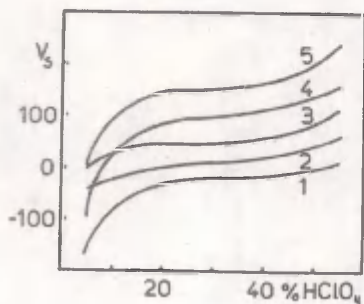


Fig.5. Dependence of $V_s$ on the size of monosubstituted alkyl-ammonia:

1 - $NH_3$
2 - $CH_3NH_2$
3 - $C_2H_5NH_2$
4 - $n-C_3H_7NH_2$
5 - $n-C_4H_9NH_2$
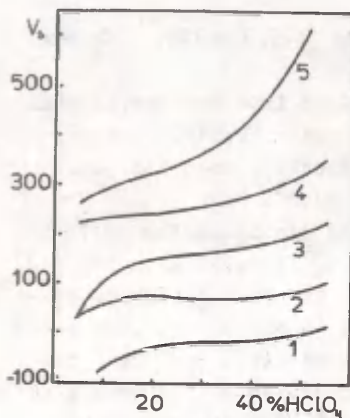


Fig.6. Dependence of $V_s$ on the size of disubstituted alkyl-ammonia:

1 - $NH_3$
2 - $(CH_3)_2NH$
3 - $(C_2H_5)_2NH$
4 - $(n-C_3H_7)_2NH$
5 - $(n-C_4H_9)_2NH$

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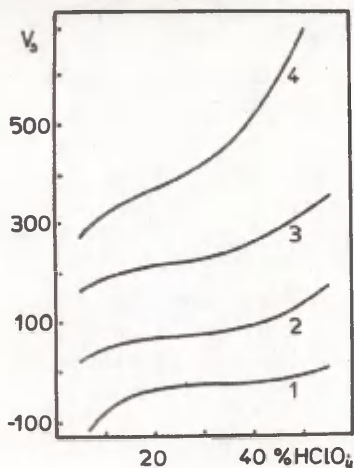
Fig.7. Dependence of $V_s$ on the size of trisubstituted alkyl-ammonia:

1 – $NH_3$

2 – $(CH_3)_3N$

3 – $(C_2H_5)_3N$

4 – $(n-C_3H_7)_3N$

## Experimental

n-Propylamine used had bp. 47.0 – 49.0 °C and $d_4^{25} = 0.712$ g/cm$^3$.

Di-n-propylamine used had bp. 109,0 – 110,0 °C and $d_4^{25} = 0.736$ g/cm$^3$.

Tri-n-propylamine was synthesized from n-propylbromide (grade "Pure") and liquid ammonia (grade "Pure"). The product was distilled. The collected fraction used had bp. 154.0 – 156.0 °C and $d_4^{25} = 0.751$ g/cm$^3$.

n-Butylamine (grade "Pure") was distilled. The collected fraction had bp. 78.0 °C and $d_4^{25} = 0.739$ g/cm$^3$.

tert-Butylamine (grade "Pure") was distilled. The collected fraction had bp. 44.5 – 45.2 °C and $d_4^{25} = 0.693$ g/cm$^3$.

Di-n-butylamine (grade "Pure") was distilled. The collected fraction had bp. 158.0 – 159.5 °C and $d_4^{25} = 0.756$ g/cm$^3$.

The concentration of $HClO_4$ stock solution was determined by titration (w/w) against borax. All $HClO_4$ solutions

for conductivity studies were prepared from $HClO_4$ stock solution by dilution with redistilled water (w/w).

The apparatus and methods used have been described in previous papers[1,5].

We thank H.Kuura for synthesis of dipropylamine and V.Ostrovski for propylamine.

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The Joint Influence of Structural Factors, Solvent
and Temperature on Solvolysis of Substituted Benzene-
sulphonates. Part I. Solvolysis in Alcohols

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Regression analysis of the kinetic data for solvoly-
sis (I) of $m,p-XC_6H_4SO_2OCH_2R_I$ with varied substitu-
ents X and $R_I$ in some alcohols $R_2OH$ and at some tem-
peratures confirms the efficiency of the experimen-
tal plans $3^n$ for constructing, within the correla-
tion analysis axiomatics,the models describing com-
bined effects of different factors on organic reac-
tivities.The 'inner' scales of the effects of factors
are shown to be very effective also for this pur-
pose. It is found that the effects of substituents
X, $R_I$ and $R_2$, and of temperature on the solvolysis
of benzenesulphonates are described accurately by
the equation (7) with statistically significant coef-
ficients $a_0 + a_4$, $a_6$, $a_8$ and $a_{10}$. The regression
analyses of the matrix formed of 6I2 log $k_2$-values
for process (I) and of I35 log $k_2$-values selected
from the matrix lead to the same multiple regression
models for the process. Those I35 values are five
united samples $3^3$ from the experimental data ana-
lyzed for five groups $R_I$.

Non-additivities in the effects of various factors on organic
reactivities are observed experimentally in many reactions[1-3].
For this reason, searching    new criteria for mechanisms
of reactions is now the acute problem in formal way to quan-
titative describing   organic reactions. A possible way to
solve[1] that problem is, in our view, a construction of mul-

tiple regression models for different reactions. These models should describe adequately organic reactivities as a function of all those factors that are available to vary in real experiments. That way requires, however, special multifactorial experiments. We have proposed[1] to use plans $3^n$ for these purposes; n is a number of factors varied (i.e. controlled) experimentally.

To test the effectiveness of these plans again we try here to describe (by means of a single multiple regression) the influences of structural factors, temperature and solvent on solvolyses (I) of m,p-substituted benzenesulphonates

$$m,p\text{-}XC_6H_4SO_2CH_2R_I + R_2OH \longrightarrow R_2OCH_2R_I + m,p\text{-}XC_6H_4SO_2OH \ (I)$$

For that reaction of nucleophilic substitution at $C_{sp}3$ -atom, there is a great body of selfconsistent and reliable kinetic data of Sendega and coworkers[4]. Under the same conditions these authors studied kinetically the effects of both temperature $(30 - 70^\circ)$ and structure of sulphonates (X= p-OMe, p-Me, H, p-Cl, p-Br, m-Cl, p-NO$_2$, m-NO$_2$; $R_I$ = p-CH=CH$_2$, -C(CH$_3$)=CH$_2$, -C=CH, Et, i-Pr) in 29 solvents (alcohols MeOH, EtOH, n-PrOH, n-BuOH, i-PrOH, t-BuOH as well as binary mixtures with compositions varied) on solvolysis (I). The authors[4] did no attempts to describe their data by means of a single multiple correlation. We have recently showed[5] however, that this is possible. The present paper deals with the process (I) in the alcohols (612 rate constants from Refs. 4) only. A special attention is paid here to check usefulness of "inner" scales[2,5-7] for describing the effects of different factors. We attempt also to describe the solvent effect on the process by means of a single parameter.

The free energy change in the process (I) should follow, in accordance with PPL[2,5-8], the equation

$$\log k = a_0 + a_IX + a_2t + a_3S + a_4Xt + a_5XS + a_6tS + a_7tSX$$

$$(2)$$

when a formal mechanism[2] of the effect of one of three fac-

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tors, which are varied and are related with a leaving group
m,p-$XC_6H_4SO_2O$ structure (X), with a reaction temperature (t)
and with a solvent (S), i.e. with a substituent $R_2$ in alcohol
$R_2OH$,is the same for all levels of two other factors and when
combined influence of these factors is completely non-ad-
ditive. In that equation, X,S and t denote the general mea -
sures or scales of the effects of the corresponding factors.
Having accepted arbitrary log k($C_6H_5SO_2OCH_2CH=CH_2$, $40^{\circ}C$, MeOH)=
-4.028 as the standard or "zero" point[5] log k(0,0,0), we de-
fine then the "inner" scales of the factors varied as the dif-
ferences[5]

$X_i$ = log k($X_iC_6H_4SO_2OCH_2CH=CH_2$; $40^{\circ}C$, MeOH) -
$\quad$ - log k(0,0,0) $\hspace{4cm}$ (3)

$t_j$ = log k($PhSO_2OCH_2CH=CH_2$, $t_j{}^{\circ}C$, MeOH) - log k(0,0,0) (4)

$S_k$ = log k($PhSO_2OCH_2CH=CH_2$, $40^{\circ}C$, $R_kOH$) - log k(0,0,0) (5)

respectively. PPL imposes[2,5-8] the following conditions on
the equation (2) coefficients: $a_0$ = log k(0,0,0) and $a_I = a_2 = a_7 = I$. Consequently, it is impossible to judge strictly ap-
plicability of the equation (2) with "inner" scales (3) - (5)
for adequate describing the experimental data[4] only on the
basis of good statistical indices (R, $S_0$,etc.) of the corres-
ponding regression. Another strong and necessary criterion
of this applicability should be adherence of the correspond-
ing coefficients, within their uncertainties, to the above
requirements. As it is, however, seen from these equations,
those conditions are valid only for m,p-substituted allyl
benzenesulphonates,since numerical magnitudes of the equation
(2) coefficients may, in principle, depend on nature of ali-
phatic group $CH_2R_I$; see equation (7).

$\quad$ The results of multiple regression analysis,within a
framework of equation (2), of the experimental data[4] for
different aliphatic groups $CH_2R_I$ are summurized in Table I.
Having considered those results one should do some conclu-
sions.

I. Equation (2) describes rather satisfactorily the complete
sets[4] of the rate constants measured for sulphonates with

each substituent $CH_2R_I$ and with all leaving groups studied at all temperatures and in all alcohols investigated. The smallest regression standard is found for allyl sulphonates. A certain increase in that standard observed for other aliphatic groups is apparently a result of unhappy choise of the "zero" point.

2. The estimates of $a_0 + a_2$ in the regression for allyl sulphonates obey well the PPL conditions. Some biasing observed for its coefficient $a_3$ seems to be a response on insignificant terms included.

3. In all regressions there are no terms related with $a_4$ and $a_6$ whereas all coefficients $a_0$ agree well with experimental values of log k for the corresponding compounds. All other coefficients of the regressions do not vary much with variations in the aliphatic group $CH_2R_I$ structure.

4. For each group $CH_2R_I$, the regression found on the basis of the sample $3^n$ from the data[4] does not differ significantly from that found from the parent experimental matrix for that group. There are no differences in the estimates for the coefficients of two regressions as well as in their indices R and $S_0$ for all groups $CH_2R_I$, but one[+]. However, the coefficients of the former regression generally have larger uncertainties. Hence, such samples are well-representative. One can, thence, use plans $3^n$ successfully to uncover, within correlation analysis axiomatics, the quantitative relations between organic reactivities and the factors governing them.

5. The effects of factors related with leaving group structure and temperature on reactivities of sulphonates in process (I) are well described by means of "inner" scales X and t respectively. It is a direct result of their accurate representations by Hammett and Arrhenius equations. Having described the solvent effect on that process by means of single scale S, one should then conclude that the effect of alcohols studied is qualitatively independent of temperature and of leaving group structure. That is, ratio of differ- .

[+]When $R_I = -C(CH_3)=CH_2$; see Table I.

Table I

Coefficients and Statistics of Eq. (2) for Solvolysis[4] (I)

| Coeffs.and Statistics | $R_I = -CH=CH_2$ | | $R_I = -CH_2-CH_3$ | | $R_I = -C\equiv CH$ | |
|---|---|---|---|---|---|---|
| | A[a] | B[b] | A | B | A | B |
| $a_0$ | -4.035±0.005 | -4.025±0.009 | -5.680±0.047 | -5.661±0.062 | -5.208±0.040 | -5.187±0.067 |
| $a_I$ | 0.990±0.009 | 0.999±0.013 | 0.890±0.074 | 0.980±0.098 | 0.896±0.068 | 0.896±0.107 |
| $a_2$ | 1.050±0.013 | 1.037±0.024 | 1.041±0.081 | 1.042±0.106 | 1.086±0.069 | 1.044±0.115 |
| $a_3$ | 0.959±0.008 | 0.952±0.014 | 0.980±0.076 | 1.090±0.090 | 1.065±0.064 | 1.113±0.098 |
| $a_4$ | -0.051±0.023 | -0.044±0.034 | -0.012±0.127 | -0.025±0.169 | -0.025±0.116 | -0.035±0.183 |
| $a_5$ | -0.247±0.014 | -0.254±0.196 | -0.192±0.120 | -0.235±0.144 | -0.343±0.109 | -0.366±0.156 |
| $a_6$ | 0.183±0.021 | 0.199±0.035 | 0.163±0.131 | 0.140±0.155 | 0.201±0.111 | 0.178±0.168 |
| $a_7$ | 0.039±0.036 | 0.020±0.050 | -0.013±0.206 | -0.015±0.247 | 0.064±0.188 | 0.059±0.268 |
| n | 142[c] | 27 | 105[d] | 27 | 144[e] | 27 |
| R | 0.9993 | 0.9997 | 0.9826 | 0.9935 | 0.9838 | 0.9924 |
| $s_0$ | 0.028 | 0.028 | 0.147 | 0.114 | 0.136 | 0.124 |
| $\Delta\log k$ | 3.477 | | 3.431 | | 3.441 | |

[a]The results of the analyses of the total bodies of the data for each substituent $R_I$. [b]The results of the analyses of the samples $3^n$ from the total bodies of the data for each $R_I$: X = p-OMe, p-Cl, m-$NO_2$ for each $R_I$ except $R_I$ = -CH=$CH_2$. In the last case X = p-OMe, p-Cl, and p-$NO_2$. The temperatures chosen are as follows: 30°, 40° and 50°C for $R_I$ = -CH=$CH_2$ and -C($CH_3$)=$CH_2$, 40, 50 and 60°C for $R_I$ = Et, and -C≡CH, 50°, 60° and 70°C for $R_I$ = i-Pr. The alcohols chosen are as follows: MeOH, n-BuOH and t-BuOH in all cases. [c]The initial number of the log k-values analyzed is 144. The k-values for X = p-Br and m-$NO_2$ in i-PrOH at 30° and in MeOH at 40°C are excluded as significant outliers. [d]The initial number of k-values is 108.

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Table I (continued)

| Coeffs. and Statistics | $R_I = -C(CH_2)=CH_2$ | | $R_I = -CH(CH_3)_2$ | |
|---|---|---|---|---|
| | A | B | A | B |
| $a_0$ | -3.598± 0.016 | -3.645± 0.054 | -6.854± 0.051 | -6.807± 0.098 |
| $a_1$ | 1.047± 0.033 | 1.074± 0.087 | 0.889± 0.099 | 0.829± 0.156 |
| $a_2$ | 0.953± 0.042 | 0.996± 0.140 | 1.110± 0.053 | 1.104± 0.103 |
| $a_3$ | 1.391± 0.028 | 1.257± 0.079 | 0.987± 0.090 | 1.057± 0.143 |
| $a_4$ | -0.104± 0.086 | -0.193± 0.223 | 0.016± 0.104 | 0.014± 0.164 |
| $a_5$ | -0.208± 0.056 | -0.001± 0.127 | -0.190± 0.164 | -0.255± 0.229 |
| $a_6$ | 0.237± 0.074 | 0.673± 0.204 | 0.066± 0.094 | 0.090± 0.150 |
| $a_7$ | -0.172± 0.149 | -0.752± 0.325 | 0.038± 0.172 | 0.028± 0.240 |
| n | 123[f] | 27 | 83[g] | 27 |
| R | 0.9935 | 0.9881 | 0.9927 | 0.9941 |
| $S_0$ | 0.085 | 0.160 | 0.086 | 0.105 |
| $\triangle \log k$ | 3.614 | | 3.362 | |

The points for X = $m-NO_2$ in i-PrOH at $40^0$, $50^0$ and $60^0C$ are excluded because of their significant deviations from the regression surface. [e]There are no excluded points at the risk level accepted. [f]The initial number of points is 126. The points for X = p-OMe at $40^0$ and $50^0$ and X = H at $40^0$ in t-BuOH are excluded as significant outliers. [g]The initial number of log k-values is 90. Those for X = p-Me and H in t-BuOH at $30^0$, $40^0$ and $50^0$ are excluded because of their significant deviations.

ent  solvation mechanisms in the total solvent effect on the process (I) appears to be the same for all those alcohols.

Treating  the total matrices of k-values obtained[4] for each aliphatic group $CH_2R_I$ by the method[I] of consecutive one-variable correlations leads in all cases to the multiple equations  whose coefficients $a_0 \div a_7$ and standards do not differ significantly from those listed in Table I.

In Table I it is also noteworthy that the estimates for the coefficients $a_I \div a_7$ are nearly the same for different groups $CH_2R_I$, i.e. the effect of structure of that group on the re-activities of sulphonates is practically independent of both the leaving group structure and temperature. One can thence assume that all data[4] for process (I) should obey a single multiple regression equation when scale R for the effect of $CH_2R_I$ is defined,by analogy with (3)-(5), as follows:

$$R_1 = \log k(PhSO_2OCH_2R_I,\ 40^0O,\ MeOH) - \log k(0,0,0) \qquad (6)$$

In the case of complete non-additivity of the effects of four factors considered this equation should have a form:

$$\log k = a_0 + a_1X + a_2t + a_3S + a_4R + a_5Xt + a_6XS + a_7XR +$$
$$a_8tS + a_9Rt + a_{10}RS + a_{11}XtS + a_{12}XRS + a_{13}XRt +$$
$$a_{14}RtS + a_{15}XRtS \qquad (7)$$

In accordance with Table I, most of its coefficients $a_5 \div a_{15}$ would be statistically insignificant whereas the co-efficients $a_0 \div a_4$ should obey the PPL conditions: $a_0 = \log k(0,0,0)$ and $a_1 = a_2 = a_3 = a_4 = I$.

Collecting together five samples $3^n$ from the parent data matrices for sulphonates with five groups $CH_2R_I$ leads to the new matrix of I35 (27 x 5) values of log k. Its multiple regression analysis within the framework of Eq.(7) gives the results listed in Table 2. Having searched that Table one should draw the following conclusions.
I. That matrix is well described by means of equation (7); see Reg.I in Table 2. In Reg.I coefficients $a_0 \div a_4$ actually

Table 2

Coefficients and Statistics of Eq.(7) for the Matrix Formed from Five Samples $3^n$ of the Data[4] for Different Groups $R_I$

| Coeffs.and Statistics | Reg.1 | Reg.2 | Reg.3 | Reg.4 | Reg.5 |
|---|---|---|---|---|---|
| $a_0$ | -3.970∓0.030 | -3.987∓0.027 | -3.955∓0.024 | -3.976∓0.028 | -3.943∓0.027 |
| $a_1$ | 1.007∓0.046 | 1.045∓0.024 | 0.925∓0.032 | 0.931∓0.034 | 0.925∓0.031 |
| $a_2$ | 1.028∓0.072 | 0.888∓0.037 | 0.905∓0.032 | 0.954∓0.046 | 1.014∓0.049 |
| $a_3$ | 1.105∓0.044 | 1.059∓0.031 | 1.148∓0.031 | 1.078∓0.039 | 1.171∓0.041 |
| $a_4$ | 0.950∓0.029 | 0.912∓0.016 | 0.911∓0.013 | 0.912∓0.014 | 0.955∓0.020 |
| $a_5$ | -0.136∓0.107 | | | | |
| $a_6$ | -0.152∓0.066 | | -0.248∓0.047 | -0.214∓0.050 | -0.247∓0.046 |
| $a_7$ | 0.069∓0.046 | | | | |
| $a_8$ | 0.385∓0.105 | | | 0.126∓0.059 | 0.208∓0.072 |
| $a_9$ | -0.015∓0.039 | | | | |
| $a_{10}$ | 0.044∓0.043 | | | | 0.084∓0.030 |
| $a_{11}$ | -0.300∓0.157 | | | | |
| $a_{12}$ | -0.061∓0.060 | | | | |
| $a_{13}$ | 0.074∓0.068 | | | | |
| $a_{14}$ | 0.084∓0.057 | | | | |
| $a_{15}$ | 0.160∓0.088 | | | | |
| $n$ | 135 | 135 | 135 | 135 | 135 |
| $R$ | 0.9935 | 0.9908 | 0.9933 | 0.9922 | 0.9938 |
| $S_0$ | 0.142 | 0.161 | 0.138 | 0.149 | 0.134 |
| $\Delta \log k$ | 5.654 | 5.654 | 5.654 | 5.654 | 5.654 |

Table 2 (continued)

| Coeffs, and Statistics | Reg.6 | Reg.7 | Reg.8 | Reg.9 |
|---|---|---|---|---|
| $a_0$ | -3.953∓ 0.027 | -3.946∓ 0.029 | -3.960∓ 0.027 | -3.957∓ 0.027 |
| $a_1$ | 0.961∓ 0.033 | 0.931∓ 0.033 | 0.984∓ 0.035 | 0.985∓ 0.035 |
| $a_2$ | 1.045∓ 0.049 | 0.965∓ 0.058 | 1.014∓ 0.047 | 0.985∓ 0.054+ |
| $a_3$ | 1.175∓ 0.040 | 1.127∓ 0.042 | 1.174∓ 0.039 | 1.173∓ 0.039 |
| $a_4$ | 0.956∓ 0.020 | 0.978∓ 0.024 | 0.940∓ 0.020 | 0.959∓ 0.022 |
| $a_5$ | -0.106∓ 0.039 | | | -0.039∓ 0.051 |
| $a_6$ | -0.250∓ 0.045 | -0.215∓ 0.049 | -0.250∓ 0.044 | -0.249∓ 0.044 |
| $a_7$ | | | 0.053∓ 0.016 | 0.042∓ 0.021 |
| $a_8$ | 0.203∓ 0.070 | 0.254∓ 0.076 | 0.204∓ 0.069 | 0.205∓ 0.069 |
| $a_9$ | | -0.052∓ 0.023 | | -0.035∓ 0.020 |
| $a_{10}$ | 0.084∓ 0.029 | 0.082∓ 0.032 | 0.084∓ 0.029 | 0.084∓ 0.029 |
| $a_{11}$ | | | | |
| $a_{12}$ | | | | |
| $a_{13}$ | | | | |
| $a_{14}$ | | | | |
| $a_{15}$ | | | | |
| $n$ | 135 | 135 | 135 | 135 |
| $R$ | 0.9941 | 0.9929 | 0.9943 | 0.9945 |
| $S_0$ | 0.131 | 0.144 | 0.129 | 0.129 |
| $\triangle \log k$ | 5.654 | 5.654 | 5.654 | 5.654 |

obey the PPL restrictions; coefficients at the highest order
interaction term as well as those at all triple terms and some
double ones are statistically insignificant whereas signifi-
cance of $a_8$ agrees with the results of Table I. The standard
deviations for all regressions of Table 2 are as large as
those for most of the regressions of Table I.

2. Excluding all cross-terms from Eq. (7) worsens slight-
ly the regression standard (see Reg.2),but leads to large
biasings in the estimates for $a_2$ and $a_4$. Those biasings
prove that there are some "non-zero" cross-terms in the mul-
tiple regression of equation (7) type for the process (I).

3. Addition of the terms $a_6 XS$ and $a_8 St$ (see Regs. 3 and 4),
that are found to be significant in Reg.I, to the additive
model raises the estimate of $a_2$ up to the theoretical value
whereas $a_4$ remains smaller than that. One can then assume
that the true regression equation would have one cross-term,
at any rate, related with factor $R_1$.

4. When term $a_{10} RS$ is included into the multiple regression
(see Reg.5) it is found to be significant and $a_4$ becomes equal
to its theoretical value as well. Addition of one of the terms
$a_5 Xt$ (see Reg.6), $a_7 XR$ (see Reg.8) or $a_9 Rt$ (see Reg.7) to the
last regression has no effect on its indices R and $S_0$ and
leads to significant but small estimates for the correspond-
ing coefficients. When one includes all these terms or a
pair of them in Reg.5, the corresponding coefficients are insig-
nificant statistically whereas all the other coefficients of
the regressions resulted are rather the same as those in Reg.5.

   In Regs.5 ÷ 9 it is noteworthy (i) that their estimates
for $a_0$ ÷ $a_4$ are equal and agree well with the PPL requirements
and (ii) that the estimates found for $a_6$, $a_8$, and $a_{10}$ are
stable. The latter fact appears to reflect reality of the cor-
responding cross-terms in the true regression equation. Hav-
ing included into these regression equations[+] other double

[+]Besides, the regressions listed in Table 2 we have also consi-
dered 22 other versions of Eq. (7) for the process of in-
terest.

and triple cross-terms as well as the highest interaction term $a_{15}$XRtS we found their insignificant effect on the property decribed. In Table 2, Reg.7 obeys in the best way all conditions of PPL, from statistical point of view. These conclusions agree with the generally accepted models[9,10] of the mechanism of the substitution reactions at $C_{sp}3$ -atom and with the results[4] of various one-factorial correlations[+]. It is possible also that an activation energy of the solvolysis (I) depends slightly on the leaving group structure (see significant term $a_5$Xt in Reg.6) or on the structure of substituent $R_I$ (see significant term $a_9$tR in Reg.9). It is also possible that there is some non-additivity in the effects of leaving group and substituent $R_I$ in sulphonates on that process (see significant term $a_7$XR in Reg.8). We are cannot draw any final conclusion on the basis of the experimental data analyzed because of their low sensitivity to the corresponding interactions if those really take place.

In Table 3 there are the results of analyses, within the framework of Eq. (7), of the complete matrix (i.e. 612 values of k) of the data measured in Ref.4. It is evident (Cf. the corresponding regressions in Tables 2 and 3) that the regressions found by means of analysis of the matrix formed from the samples $3^n$ (i.e. 135 values of k) are comparable, in the indices R and $S_0$ as well as in the estimates of the equation coefficients, with those found on the basis of the total body of the data. That confirms a good representativeness of the matrix formed from the samples $3^n$ and proves the efficiency of that way for design of the multifactorial experiments when their aim is to construct, within the correlation

[+]The constant $\rho$ in the Hammett equations for leaving group effect on the process (I) for each substituent $R_I$ was found[4] to depend on the alcohol used. The constant $\rho^*$ in the Taft equations for solvent effect on the process (I) was also found[4] to depend on the substituent in the leaving group. These facts prove non-additivity in the effects of these two factors on the process under investigation.

Table 3. Coefficients[a] and Statistics of Eq.(7) for Total Body of the Data[4]

| Coeffs.and Statistics | Reg. 2 | Reg. 3 | Reg. 4 | Reg. 5 | Reg. 6 | Reg. 7 |
|---|---|---|---|---|---|---|
| $a_0$ | -3.991∓0.011 | -3.953∓0.011 | -3.966∓0.012 | -3.947∓0.013 | -3.947∓0.013 | -3.940∓0.013 |
| $a_1$ | 1.073∓0.011 | 0.924∓0.020 | 0.925∓0.020 | 0.922∓0.020 | 0.951∓0.020 | 0.924∓0.020 |
| $a_2$ | 0.933∓0.015 | 0.933∓0.014 | 0.973∓0.022 | 1.040∓0.026 | 1.062∓0.026 | 1.021∓0.027 |
| $a_3$ | 1.074∓0.017 | 1.148∓0.018 | 1.124∓0.021 | 1.172∓0.023 | 1.173∓0.023 | 1.171∓0.023 |
| $a_4$ | 0.919∓0.007 | 0.919∓0.006 | 0.919∓0.006 | 0.964∓0.011 | 0.966∓0.011 | 0.973∓0.012 |
| $a_5$ | | | | | | |
| $a_6$ | | -0.285∓0.032 | -0.282∓0.032 | -0.287∓0.032 | -0.288∓0.031 | -0.287∓0.031 |
| $a_7$ | | | | | -0.086∓0.021 | |
| $a_8$ | | | 0.076∓0.032 | 0.203∓0.042 | 0.202∓0.041 | 0.203∓0.042 |
| $a_9$ | | | | | | -0.020∓0.010 |
| $a_{10}$ | | | | 0.087∓0.018 | 0.087∓0.018 | 0.086∓0.018 |
| n | 612 | 612 | 612 | 612 | 612 | 612 |
| R | 0.9916 | 0.9926 | 0.9927 | 0.9930 | 0.9931 | 0.9930 |
| $S_0$ | 0.139 | 0.131 | 0.131 | 0.128 | 0.127 | 0.128 |

[a] The regressions listed are found at Student test value t=3. Using Reg.3 as an example, we find that at $t_{0.05}$= 1.96 exclusion of 48 values of k is observed. The points excluded have small statistically significant deviations from the surface found. That exclusion requires another 40 min. of machine time of computer "Odra-1304". In the final regression there are some improvements in R (up to o.997) and $S_0$ (up to 0.081). The estimates of the regression coefficients and their standards remain practically the same. The numbers of the regressions in this table are the same as those in Table 2.

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analysis axiomatics, the multiple mathematical models described the effects of different factors on organic reactivities. On the other hand, the fact of good representation by means of a single regression equation of the large body of the experimental data for solvolysis (I) proves that this process appears to be, in accordance with the correlation analysis formalism and within the explored variations in the factors considered, a general reaction series with the same detailed reaction mechanism.

The computers "BESM-4", "M-222" and "Odra-I304" as well as the corresponding programs based on the algorythms of Ref. II with some our modifications[1,8] have been used for the reggression analyses of the data[4].These programs accurately reproduce the tests of Ref.II.

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# IR SPECTRA OF AMIDES AND HYDRAZIDES
## OF OXALIC ACID

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Substituted amides and hydrazides of oxalic acid
which IR spectra had been taken and interpreted
were synthesized. The stretching frequencies
of CO, $SO_2$ groups were calculated.

Earlier [1-4] we obtained a number of derivatives of
oxalic acid which acidic and basic properties as well
as spectral ones were studied and correlation of the latter
with Hammett $\sigma$-constants was carried out.

Continuing the study of reactivity of derivatives
of oxalic acid we synthesized hydrazides of substituted
arylamides of oxalic acid $RC_6H_4NHCOCONHNH_2$ (I), phenyl-
amides of arylsulfohydrazides of oxalic acid $p-RC_6H_4SO_2-$
$NHNHCOCONHC_6H_5$ (II), aroylhydrazides of benzosulfohydra-
zides of oxalic acid $C_6H_5SO_2NHNHCOCONHNHCOC_6H_4R-p$ (III)
and substituted aroylhydrazides of p-toluenesulfohydra-
zides of oxalic acid $p-CH_3C_6H_4SO_2NHNHCOCONHNHCOC_6H_4R-p$ (IV).

Synthesis of hydrazides (I) was carried out as a
result of hydrazinolysis of ethers of aryloxamin acid.
Compounds (II) were synthesized by the reaction
of amiding the ethers of arylsulfohydrazides of oxalic
acid with the primary aromatic amines, and acylhydra-
zides (III) and (IV) were obtained with the help of acyla-
tion of hydrazides of arylsulfohydrazides of oxalic acid
with chloranhydrides of carbonic acid.

The synthesized compounds are colorless crystaline
matters, soluble in aqueous alkalies and organic solvents.

Identification of the obtained compounds was carried
out by means of IR spectroscopy (see the Table). IR spectro-
grams were taken making use of UR-20 spectrometer in the
region of 800-3600 cm$^{-1}$ with prizms of NaCl and LiF in KBr
pellets, the concentration was 0.5%.

Table

IR SPECTRA OF COMPOUNDS (I-IV)

| Nos. of comp. | R | $\nu_{NH}$ | | | $\nu_{CO}$ | | $\nu^{as}_{SO_2}$ | $\nu^{s}_{SO_2}$ |
|---|---|---|---|---|---|---|---|---|
| I-1 | p-CH$_3$ | 3300 | | | 1680 | | | |
| I-2 | m-CH$_3$ | 3335 | | | 1690 | | | |
| I-3 | H | 3336, | 3300 | | 1676 | | | |
| I-4 | p-OCH$_3$ | 3330, | 3292 | | 1685 | | | |
| I-5 | p-Cl | 3350, | 3300 | | 1670 | | | |
| I-6 | m-Cl | 3340, | 3300 | | 1680 | | | |
| I-7 | p-Br | 3350, | 3300 | | 1670 | | | |
| I-8 | p-NO$_2$ | 3345, | 3285 | | 1665 | | | |
| II-1 | H | 3350, | 3320, | 3270 | 1712, | 1690 | 1355 | 1174 |
| II-2 | CH$_3$ | 3310, | 3190 | | 1705, | 1690 | 1360 | 1170 |
| II-3 | OCH$_3$ | 3360, | 3305, | 3270 | 1712, | 1690 | 1362 | 1165 |
| II-4 | Br | 3360, | 3325, | 3275 | 1718, | 1692 | 1355 | 1175 |
| II-5 | NO$_2$ | 3365, | 3310, | 3275 | 1710, | 1690 | 1350 | 1178 |
| III-1 | H | 3362, | 3268, | 3218 | 1690 | | 1355 | 1180 |
| III-2 | Br | 3370, | 3288, | 3218 | 1695 | | 1358 | 1180 |
| III-3 | NO$_2$ | 3190, | 3130 | | 1710, | 1680 | 1358 | 1182 |
| IV-1 | H | 3350, | 3268, | 3212 | 1695 | | 1355 | 1178 |
| IV-2 | Br | 3358, | 3285, | 3212 | 1690 | | 1360 | 1178 |
| IV-3 | NO$_2$ | 3180, | 3128 | | 1708 | | 1355 | 1178 |

The IR spectra of all the groups of compounds contain
the absorption bands characterizing the valence oscilla-
tions of the NH group (3130-3370 cm$^{-1}$) as well as those of
carbonyl groups in the region of 1700 cm$^{-1}$. Besides,
the absorption bands of symmetric (1165-1182 cm$^{-1}$) and asym-

metric ($1355$–$1362$ cm$^{-1}$) valence oscillations of the sulfonyl
group are characteristic of compounds (II-IV). For hydra-
zides (II-5), (III-3), and (IV-3) with $NO_2$ group the stretch-
ing frequencies of this group are present in the range   of
$1540$ cm$^{-1}$ ($\nu^{as}_{NO_2}$) and $1330$ cm$^{-1}$ ($\nu^{s}_{NO_2}$).

The compounds studied have two carbonyl groups which
are bound with each other by a simple bond. As is mentioned
in Ref.5 one band of valence oscillations of the CO groups
in the range of $1700$ cm$^{-1}$ should be observed for such  com-
pounds, if the compounds have translocation of the carbonyl
groups and two bands in this range in the case of cisloca-
tion of the carbonyl groups. Dublet character of the carbo-
nyl bands in the IR spectrograms of compounds (II) indicates
the presence of symmetric oscillations of the CO group,which
may be due to their cis-location. For hydrazides (I,III,IV)
translocation of carbonyl groups is,probably, characteris-
tic.

The presence of NH, CO, and $SO_2$ groups in the   com-
pounds under investigation creates favorable conditions for
the formation of both inter-and intramolecular hydrogen
bonds.

Such an assumption is confirmed by the IR spectrograms
of hydrazides (I-IV). The absorption caused by the   NH
groups is of the same order that the one usually occured
during formation of the hydrogen bonds of the NH...O type.

IR analysis of the compounds studied provides a means
for detecting the substituent effects in the benzene  ring
of the arylsulfohydrazide moiety upon the characteristic
oscillations of the CO and $SO_2$ groups. For hydrazides (II)
a correlation equation between $\nu^{s}_{SO_2}$ and Hammett $\sigma$ constants
was obtained: $\nu^{s}_{SO_2}$ = $1171+22.3 \cdot \sigma$ ($r$ = $0.971$, $S_\rho$ = $5.3$).

The point corresponding to R = NO falls out of the
general correlation.   The stretching frequencies of the
CO group of compound (I) correlate with Hammett $\sigma$ constant:

$\nu_{CO} = 1679 - 16.8 \cdot \sigma$ (r = 0.968, $S_\rho$ = 6.1). $\nu_{CO}$ of the meta substituents were not included into the general correlation.

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# ALKYLATION KINETICS OF BENZENESUFONIC ACID
## IN THE $H_2SO_4$-i-PrOH-$H_2O$ SYSTEM. EVIDENCE FOR
## ASSOCIATION OF SULFONATE ANION

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With the purpose to investigate acid catalyzed C-alkyl-ation of aromatic compounds [1,2] medium effect on the iso-propylation rate of benzenesulfonic acid in the $H_2SO_4$-i-PrOH-$H_2O$ system is studied. The range of composition of this system is chosen to obtain information about reactivity of both non-dissociated sulfonic acid and sulfonate anion.

## Results and Discussion

The reaction was studied under pseudofirst order conditions on substrate and at the constant ratio of benzene-sulfonic acid (sodium salt):isopropanol:sulfuric acid equalled 1:100:300. Amount of water in the system was varied from 0.18 to 1.35 moles per a mole of sulfuric acid providing thus a means for covering the range of the system acidity function[3], $H_o$, from -8.8 to -6.14. Table I lists first order rate constants and isomeric composition of cumene-sulfuric acids for various media.

Benzenesulfonic acid is known to be half dissociated in aqueous sulfuric acid solutions at $H_o = -7.9$[4].In the $H_2SO_4$-i-PrOH-$H_2O$ system (Fig. 1) there are also changes in the benzenesulfonic acid spectrum which can occur due to ion-ization (indicator ratio $a_{BH}/a_B = 1$ at $H_o = -7.1$).

Table 1

Isopropylation of Benzenesulfonic Acid in the
$H_2SO_4$-i-PrOH-$H_2O$ System at 25°C

| Acid conc. (w/w) | Medium acidity, $H_o$ | $k \cdot 10^5, min^{-1}$ | Composition of cumenesulfonic acids | | |
|---|---|---|---|---|---|
| | | | ortho | meta | para |
| 96.85 | 8.82 | 140 | 1.1 | 88.6 | 10.3 |
| 95.67 | 8.64 | 78 | 1.4 | 89.9 | 8.6 |
| 94.50 | 8.45 | 62 | 1.5 | 88.6 | 10.0 |
| 92.95 | 8.20 | 33 | 1.5 | 88.4 | 10.1 |
| 92.00 | 8.05 | 26 | 1.8 | 88.6 | 9.6 |
| 90.90 | 7.87 | 23 | 1.6 | 88.1 | 10.3 |
| 89.91 | 7.72 | 15 | 2.3 | 87.4 | 10.3 |
| 88.79 | 7.54 | 10 | 2.3 | 86.5 | 11.2 |
| 87.05 | 7.26 | 5.6 | 2.9 | 86.1 | 11.1 |
| 85.03 | 6.93 | 3.0 | 3.9 | 84.7 | 11.4 |
| 83.07 | 6.62 | 1.9 | 4.8 | 82.1 | 13.0 |
| 80.12 | 6.14 | 0.81 | 5.6 | 81.7 | 12.8 |

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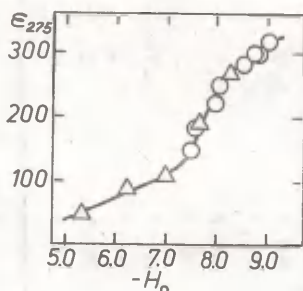
Fig. 1. Plot of molar extinction coefficient of benzenesulfonic acid in the $H_2SO_4$-i-PrOH(n-PrOH)-$H_2O$ system vs. medium acidity at 25°C.
$C_{PhSO_3H} = 4.5 \cdot 10^{-3}$ mol/l, the cell length is 0.200 cm.
$\triangle$ - Data for i-PrOH;
0 - for n-PrOH

Thus, the alkylation kinetics of benzenesulfonic acid was studied over the acidity range including that of substrate ionization.
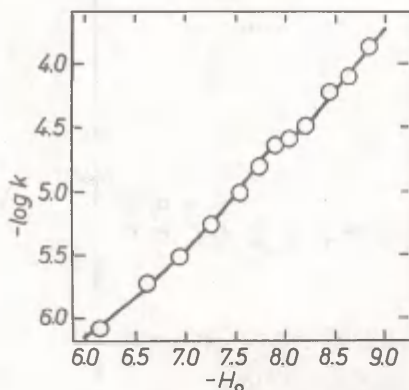


Fig. 2. Plot of isopropylation rate constant logarithm (benzenesulfonic acid)vs. medium acidity $H_o$.

Fig. 2 illustrates the plot of alkylation rate constant of benzenesulfonic acid vs. medium acidity function. As one can see in the range $7.8 \leqslant -Ho \leqslant 8.4$ the plot gives a sigmoid curve. Therefore, and also taking into account that in the same acidity range changes in the spectrum of benzenesulfonic acid occur (see Fig. 1), the discontinuity in the

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plot of lgk vs. Ho can be related to the substrate ioniza-
tion. Attention is, however, attracted by extremely small
differences in the reactivity of non-dissociated sulfonic
aoid and the assumed sulfonate ion: mutual vertical biasing
of the curve areas corresponding to the two forms is
just 0.12 of log unit (about 30% on a constant value). At the
same time the appearence of a unit charge on a substituent
changes usually its $\bar{\sigma}$ constant by $0.5 \div 1.3$ units which
should be manifested in the changes in alkylation rate
constant not less than by an order of magnitude. Let us
use the known values of $\sigma_{mSO_3^-} = 0.05$[5] and $\bar{\sigma}_{mSO_3H} = 0.56$[6]
for estimation. The absent in literature value of reaction
constant $\rho$ can be calculated on the basis of data [7-13] on
isopropylation of toluene under various conditions. The
obtained mean value of $\rho$ is $-2.5$. Taking into account
that the main reaction product at the monosubstitution step
is meta isomer and its amount over the acidity range
$7.5 < -Ho < 8.5$ changes negligibly (see Table 1), one would
obtain:

$$ \lg \frac{k^{SO_3^-}}{k^{SO_3H}} \approx \lg \frac{f_m^{SO_3^-}}{f_m^{SO_3H}} = -2.5 \cdot (0.05 - 0.56) = 1.28 $$

Striking discrepancy between experimental and calculated
dissociation effects of $SO_3H$ group in the reaction rates
are, probably, due to the nature of a reaction medium.
According to the literature date such discrepancies take
no place in aqueous sulfuric acid system. As an example let
the data on sulfonation of 2-phenyl ethane [14] and 3-phenyl
propane-1-sulfonic acids [15] be considered. These sulfonic
acids are half ionized in 82-84% sulfuric acid [16] and near
this range of medium compositions the plot of rate profile
vs. $H_2S_2O_7$ activity also gives a sigmoid curve (see Fig. 3).
The differences of constant logarithms corresponding to
sulfonic acid and sulfonate anion (interpolated to the point
of curve bend) can be calculated by the data for 3-phenyl

propane-I-sulfonic acid [15] and roughly calculated for 2-phenyl ethane-I-sulfonic acid[14]. In the latter case the data available do not cover the range of acid ionization completely. The corresponding experimental values are 0.30 and $> 0.70$. The values which are in satisfactory agreement with experimental ones, viz. 0.22 and 0.57, can be calculated similarly, but with consideration of attenuation factor of the methylene group, Z=0.39, and the value of $\rho$ sulfonation.*
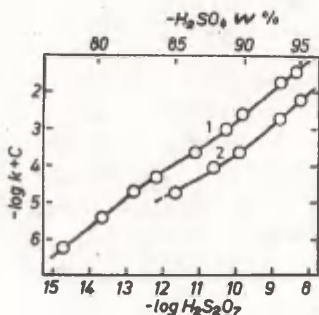


Fig. 3. Plot of the logarithm of sulfonation rate constant of 3-phenyl-propane-I-sulfonic acid(I) and 2-phenyl ethane-I-sulfonic acid (2) vs. $H_2S_2O_7$ activity[15,14].

(I) – C=0;

(2) – C=2.

Different behavior of sulfonic acid in the $H_2SO_4$-$H_2O$ system and in the triple system with isopropanol (1/3 of mole per a mole of $H_2SO_4$) is, probably, accounted for by the high trend of sulfonate anions to association [18,19] which should be favored by decrease in the medium permittivity.

This explanation is in complete agreement with different UV spectral behavior of benzenesulfonic acid in the system studied and in aqueous sulfuric acid[4]. The position and intensity of absorption band of the non-ionized form of benzenesulfonic acid in the range of forbidden transition $^1L_b \leftarrow {}^1A$ are essentially the same in both systems. Molar

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* Calculated by the interpolated (83% $H_2SO_4$) value of the selectivity factor $S_f$, of toluene sulfonation[17].

extinction coefficients in the band maximum are:

$\mathcal{E}_{BH}^{263} = 1110$ for the $H_2SO_4$-i-PrOH-$H_2O$ system and

$\mathcal{E}_{BH}^{263} = 1140$ for aqueous solutions of sulfuric acid.
At the same time maximum differences between absorption
coefficients of sulfonic acid and its anion are much less
in the system with isopropanol. The values of $\Delta\mathcal{E} = \mathcal{E}_{BH}^{\lambda} -$
$- \mathcal{E}_B^{\lambda}$ are 90 and 600, respectively. Taking into account
that substituent effect perturbing nucleous $\pi$-electronic
system increases in the order: free sulfonate anion ($\sigma_{pSO_3^-} =$
$= 0.09^5$) < ion pair ( $\sigma_{pSO_3^-X^+}^{\circ} = 0.35^{18}$) non-ionized
sulfonic group $\sigma_{mSO_3H} = 0.56^6$), the observed in the triple
system decrease in the differences between $\mathcal{E}_{BH}$ and $\mathcal{E}_B$ -
should be considered quite natural.

A significant difference between the systems studied
is manifested also in the values of angular coefficients in
the plot of indicator ratio logarithm vs. medium acidity.

$$H_2SO_4-H_2O^4 : \lg I = -(0.73^{\pm}0.03) \cdot Ho-(7.9^{\pm}0.1)$$

$$H_2SO_4-i-PrOH-H_2O : \lg I = -(2.0^{\pm}0.2) \cdot Ho-(15.4^{\pm}1.5)$$

Since transition from one system to another influences the
$\mathcal{E}_{BH}$ value negligibly, these differences should, probably,
be ascribed to different behavior of the charged
form of sulfonic acid. In the first case it is
similar to that of protonated primary amides ( lgI follows
the $H_A^4$ function), in the second case to that of ionized
triphenylmethanols (lgI follows the $H_R$ function). According
to Bunnett[20] the two classes of bases are characterized by
significantly different values of a solvation constant :
$f \simeq 0.5$ for primary amides and $-1.5 \leqslant f \leqslant -1.0$ for triphenyl-
methanols. Assuming that in the $H_2SO_4$-i-PrOH-$H_2O$ system
sulfonate anion is associated, the above similarity of its
behavior with that of triphenylmethanol ions is unexpected.

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Solvation requirements of ion pair should be undoubtedly
much less than those of a free sulfonate anion.

It is significant that changes in the composition of
monoalkylation products observed over the range of the
kinetic curve bend and at lower medium acidities (Fig. 4)
are the most profound for ortho isomer, i.e. in the position
nearest to the arising charged center.
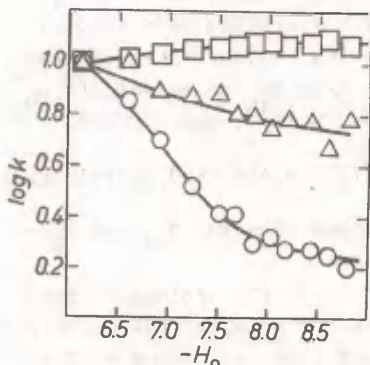


Fig. 4. Medium acidity
effect on the isomeric
composition of monoalkyl-
ation products of benzene-
sulfonic acid. $\square$ , $\triangle$ , 0
denote relative changes
in the amounts of meta,
para and orthocumene-
sulfonic acids. For each
isomer its content in the
medium with Ho= -6.14 is
taken as a unit.

It is interesting that the amount of this isomer continues
increasing beyond the ionization range. Simultaneously devia-
tions from the linear plot of lgk vs. $H_o$ (see below) to
the increase in the rate constants are observed. These facts
may indicate that as the system is diluted with water, -
changes in the structure or partial dissociation of reacting
ion pairs occur. Within the range of about $\pm 0.8$ $H_o$ un. from
the region of bend both regions can be approximated with
straight lines with a unit slope.

$$lgk = -1.00 \cdot H_o - 12.5 \quad S_o = 0.02 \quad \text{(lower region)}$$
$$lgk = -0.96 \cdot H_o - 12.3 \quad S_o = 0.04 \quad \text{(upper region)}$$

Close values of the angular coefficients were obtained

earlier on isopropylation of aryl ammonium ions: -0.92 for phenyl ammonium[1] and -1.22 for benzyl ammonium [2]. This result may be considered as an indication that in the reaction transition state not a free carbenium ion but a species of oxonium-like structure with considerably loosed but still present alkyl group-oxygen bond participates[21].

## Experimental

### Experimental technique and product analysis.

The solution of Na salt of benzenesulfonic acid in sulfuric acid cooled in the glacial bath was mixed with isopropanol at $t°$ 25°C and thermostated at 25°C during the time needed for 15-20% conversion degree. The reaction course was monitored by the method of GLC analysis of sulfonyl fluorides synthesized by a modification of the ordinary technique[22]. The latters are volatile derivatives of the corresponding alkylsulfonic acids formed during the reaction.

Reaction mass samples were diluted with glacial water, neutralized with NaOH solution, thickened by boiling, and dried. From the mixture obtained the salts of sulfonic acid were extracted with boiling 90% aqueous ethanol. The solvent was removed then and the salts were converted into sulfonyl chlorides ($POCl_3$, 110°C, 30 min) and further into sulfonyl fluorides (KF, $CCl_4$, 150°C, 1 hour in the ampule. Analysis of the obtained mixture of sulfonyl fluorides was carried out on an LKhM-8MD apparatus with flame-ionization detector under the following conditions: column 3 m/3mm with 5% of silicone KhE -60 on Chromatone N-AW-DMCS fr. 0.160-0.200 mm, $t°$ = 150°C, helimm rate was 25ml/min. The complete separation of isomeric cumenesulfonic fluorides was observed. The isomeric ratio is established by the data on the products with the known structure. The conversion degree is determined on the basis of calculation of chromatograms by the method of internal standard. For the reaction products correction for molar sensitivity coefficients was introduced. The latters were determined with

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the help of benzenesulfonic fluoride on artificial mixtures.
**Spectral measurements.** Intrinsic absorption of the $H_2SO_4$- -i-PrOH-$H_2O$ system is in the near UV region and increases with decrease in the amount of water and with time. In this connection the differential scheme of measurements was used, i.e. the substrate extinction was determined as difference between the total solution absorption at the given wave-length and the intrinsic system absorption. In each case to prepare the substrate solution and fill the reference cell in the same freshly prepared mixture of alcohol and sulfuric acid was used. The length of cells (0.200 cm) and concentration of benzenesulfonic acid ($4.5.10^{-3}$ mol/l) were chosen to provide reliability of measurements over the whole range of the medium compositions. In the range with small amount of water in the system isopropanol was replaced by equimolar amount of alcohol with normal structure (see Fig. 1)more stable under these conditions. The correctness of this substitution was shown elsewhere[3]. Observance of the Lambert-Bouguer-Behr law was checked for some wave-lengths in the region of co-existence of neutral and charged substrate forms. In the range of benzenesulfonic acid concentration from $2.5.10^{-4}$ to $5.10^{-3}$ mol/l between the D and $C_{PhSO_3H}$ values distinct linear dependences are observed.

Measurements of optical density were carried out on a SF-4A spectrophotometer with relatively higher sensitivity than recording devices. This is very important because of considerable background absorption of the system studied. Fig. 5 illustrates the scale of changes in the absorption intensity in the range of $^1L_b \leftarrow {}^1A$ benzene nucleous transition, accompanying the substrate ionization ($6.16 \leqslant -Ho \leqslant 8.93$). One can see that maximum differences, just as in the case with aqueous sufuric acid solutions of benzenesulfonic acid[4], are observed on the band "tail". Table 2 lists molar extinction coefficients at wave-length 275 nm.As can be seen from Fig. 1 both magnitudes $\mathcal{E}_B$- and $\mathcal{E}_{BH}$, suffer "the

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medium effect" and their values are linear functions of the system composition. In this connection indicator ratio for various media were calculated on the basis of $\varepsilon_B$- and $\varepsilon_{BH}$ values extrapolated to the ionization range. It was assumed [4] that these values should preserve the linear nature of their changes also in this range.
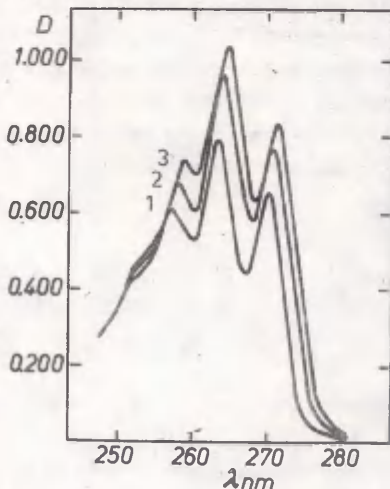


Fig.5. Absorption curves of benzenesulfonic acid in the media with various acidity. $H_o$ values for 1,2,and 3 equal −6.16, −7.96, and −8.93, respectively.

Table 2

Molar Extinction Coefficients of Benzenesulfonic Acid in the Media with Various Acidity at $\lambda$ =275 nm

| $\lambda 275$ | $-Ho$ | $\lambda 275$ | $-Ho$ | $\lambda 275$ | $-Ho$ |
|---|---|---|---|---|---|
| 49 | 5,3 | 190 | 7,7 | 300 | 8.8 |
| 87 | 6,2 | 220 | 8.0 | 300 | 8.9 |
| 110 | 7.0 | 250 | 8.1 | 320 | 9.1 |
| 150 | 7.5 | 270 | 8.3 | | |
| 180 | 7.6 | 280 | 8.6 | | |

Reagents. For kinetic experiments the following compounds were used: isopropanol ("Pure" grade), sulfuric acid ("Pure" grade), monohydrate of Na-salt of benzenesulfonic acid

("Pure for analysis" grade). Spectral measurements were
done with isopropanol ("For UV-spectroscopy" grade) and
n-propanol ("Pure" grade ); sulfuric acid was distilled
two times (the first time over $K_2Cr_2O_7$). Sulfuric acid so-
lutions of the needed concentration were prepared from three
stock solutions with concentrations 40, 95, and 100%. The
exact concentration of these solutions was established on
the basis of pycnometric measurements of specific gravities.
The concentration for the first solution was established
directly. The more concentrated solutions were diluted with
the known amount of the first one up to concentration
55-60%. Mean error of determination is $\pm$ 0.03%.

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# KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLORO-CYCLOPENTADIENE WITH CYCLIC DIENOPHILES.

## XVII. Effect of Substituents on Reactivity of N-Aryl Imides of Endo- Bicyclo/2.2.1/ -Heptene-5-Dicarboxylic-2,3 Acid.

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Substituent and temperature effects on the reaction rate of diene condensation of hexachlorocyclopentadiene (HCP) with N-(p- and m-aryl) imides of endo-bicyclo/2.2.1/-heptene-5-dicarboxylic-2,3 acid (BHDA) in nitrobenzene is studied. Kinetic and thermodynamic parameters of reaction activation are determined. The linear correlation between logarithms of rate constants and Hammett $\acute{e}$-constants of substituents is found. The observance of isokinetic relationship is examined and the value of isokinetic temperature for the reaction series is determined.It is shown that the reaction rate increases with increasing electron-donating activity of substituents.

We have recently[1-3] reported the results of kinetic studies of diene condensation of hexachlorocyclopentadiene (HCP) with anhydrides of cis-4-cyclohexene-1,2-dicarboxylic acid (4-CHDA) and endo-bicyclo/2.2.1/-heptene-5-dicarboxylic-2,3 acid (endo-BHDA). We have shown that anhydride of endo-BHDA is 1.5-1.8 times as active as anhydride of cis-4-CHDA. Further comparison of these data with those for anhydrides of cia,cia- and cis,trans-3-methyl-4-CHDA has shown that the dienophilic activity of anhydride of endo-BHDA is higher than that of the given anhydrides (by a factor of 2--3).On the basis of these data it has been concluded that

endo-methylene bridge makes a significant positive contribution into the activation of double bond of endo-BHDA.

It is an object of this paper to compare the dienophilic activity of N-aryl imides of endo-BHDA with that of similar imides of cis-4-CHDA[4] in the course of reaction with HCP. N-(p- and m-aryl)imides of endo-BHDA with the general formula:
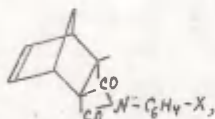


I-VII

where X is p-OH(I); p-OCH$_3$ (II); p-CH$_3$(III); H(IV); m-OCH$_3$(V); p-Br(VI); p-NO$_2$ (VII).

were used as dienophiles.

The obtained values of the rate constants together with the known ones[4-6] can be used for establishing the quantitative relationship between the reactivity and structure of the compounds studied.

### R E S U L T S   A N D   D I S C U S S I O N

Reaction kinetics of imides (I-VII) of endo-BHDA with HCP is studied polarographically in nitrobenzene as described in our previous papers. The dienophile to diene ratio is 2:1, temperature range is 110-150°C, duration is 6 hours.

The rate constants are estimated as mean values of 2 - 3 parallel runs, using the methods of mathematical statistics (reliability is 0.95[7]). These constants are given in Table 1.

As can be seen from this Table the reaction rate regularly decreases with a decrease in degree of electron-donating ability of substituents; for p-OH and p-NO$_2$ substituents the reaction rate decreasing by a factor of 3-4 depending on temperature (with increase in the temperature the difference was observed to decrease).

Data of Table 1 show that the reactivity of dienophiles studied changes with substituent nature in the following order: p-OH  p-OCH$_3$  p-CH$_3$  H  m-OCH$_3$  p-Br  p-NO$_2$

Table 1.

Rate Constants of Diene Condensation of HCD with N-(p- and m-Aryl)Imides of Endo-Bicyclo/2.2.1/-5-Heptene-2,3-Dicarboxylic Acid in Nitrobenzene.

| X | $k^2 \cdot 10^6$, l/mol·sec, at T, °C | | | | |
|---|---|---|---|---|---|
| | 110 | 120 | 130 | 140 | 150 |
| p-OH | $13.24 \pm 0.13$ | $23.56 \pm 0.10$ | $39.40 \pm 0.22$ | $71.33 \pm 0.22$ | $130.63 \pm 0.78$ |
| p-OCH$_3$ | $10.47 \pm 0.15$ | $19.02 \pm 0.26$ | $33.99 \pm 0.26$ | $61.19 \pm 0.25$ | $111.11 \pm 0.46$ |
| p-CH$_3$ | $8.70 \pm 0.11$ | $16.22 \pm 0.13$ | $30.33 \pm 0.26$ | $56.07 \pm 0.25$ | $102.19 \pm 0.54$ |
| H | $6.48 \pm 0.08$ | $12.49 \pm 0.17$ | $19.52 \pm 0.22$ | $41.57 \pm 0.31$ | $77.39 \pm 0.21$ |
| m-OCH$_3$ | $5.55 \pm 0.09$ | $10.59 \pm 0.16$ | $19.35 \pm 0.39$ | $36.25 \pm 0.19$ | $69.19 \pm 0.34$ |
| p-Br | $4.21 \pm 0.07$ | $8.53 \pm 0.09$ | $16.58 \pm 0.12$ | $32.05 \pm 0.38$ | $61.65 \pm 0.71$ |
| p-NO$_2$ | $1.70 \pm 0.06$ | $3.28 \pm 0.11$ | $7.06 \pm 0.25$ | $14.65 \pm 0.20$ | $31.93 \pm 0.36$ |

The comparison of obtained results with our previous data concerning reactivity of N(p-aryl)imides of cis-4-CHDA[4] indicates the higher reactivity of N(p-aryl)imides of BHDA (see Table 2).

Rate Constants of Diene Condensation of HCP with N(p-Aryl) Imides of Endo-BHDA and Cis-4-CHDA in Nitrobenzene.

| X | T, °C | | | |
|------|------|------|------|------|
|      | 120  | 130  | 140  | 150  |
| OH   | 1,60 | 1,80 | 2,05 | 1,89 |
| OCH₃ | 1,55 | 1,66 | 1,89 | 1,70 |
| CH₃  | 1,69 | 2,29 | 2,11 | 1,82 |
| H    | 1,89 | 1,88 | 1,98 | 1,88 |
| Br   | 1,71 | 1,89 | 2,02 | 1,98 |
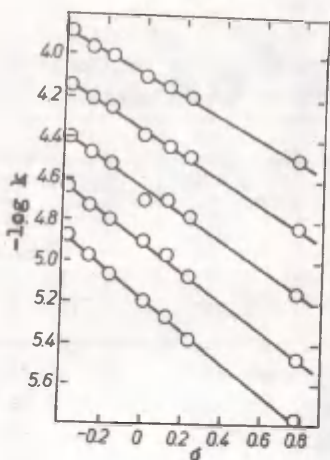


Fig.1 Logarithms of rate constants vs. $\sigma$-constants of substituents.

Figure 1 shows a dependence of logarithms of rate constants upon Hammett $\sigma$-constants of substituents. The linear nature of this dependence is indicative of induction effect of substituent exerting an influence upon the reactivity of compounds (I-VII).

To check this assumption we have carried out correlation analysis of values of logarithms of rate constants (lgk) with $\sigma$-constants of substituents. It was established that lgk of compounds (I-VII) in the reaction with HCP are well correlated with Hammett $\sigma$ constants which is in agreement with our

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previous results[4-6].

Table 3 lists correlation equations describing the linear dependence of lgk upon substituents.

It is interesting to note that these correlation dependences (Table 3) combined with those established previously[4-6] for reaction with HCP describe correctly the behavior of varied X substituent in N-aryl fragment of imides of the corresponding acids. Electron-donating substituents within the range of reaction series studied increase the rate constant and electron-seeking ones decrease it. This is also confirmed by the negative values of the reaction constant (Table 3).

The obtained values of reaction constant are close to similar constant given in our previous papers[4-6] for N-aryl imides of cis-4-CHDA and cis,cis-3-Me-4-CHDA. Hence, transition states in the diene synthesis with participation of imides of these series have similar structure.

Table 3.

Correlation Dependences of Logarithms of Rate Constants upon Hammett $\sigma$ Constants of Substituents.

| T,°C | Correlation Equations | r | s |
|------|----------------------|------|------|
| 110 | lgk = -5,183 - 0,764 $\sigma$ | 0,998 | 0,016 |
| 120 | lgk = -4,908 - 0,724 $\sigma$ | 0,998 | 0,014 |
| 130 | lgk = - 4,647 - 0,645 $\sigma$ | 0,995 | 0,028 |
| 140 | lgk = -4,393 - 0,590 $\sigma$ | 0,998 | 0,015 |
| 150 | lgk = -4,089 - 0,524 $\sigma$ | 0,997 | 0,015 |

Table 4 lists activation parameters of reaction studied estimated from lgk=f(1/T)(fig.2). It was found that the changes in the activation enthalpy ( $\Delta H^{\neq}$ ) and entropy ($\Delta S^{\neq}$) are similar to those found in the previously studied reaction series[4-6].

In spite of relatively small discrepancy in numerical values of activation energy ($E_a$) and preexponential (lgA) the regular increase in these parameters with decrease in electron-donating properties of substituents (Fig.2) is observed.

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Table 4.

Kinetic and Thermodynamic Parameters for Activation of Diene Condensation of HCP with
N(p- and m-Aryl)Imides of Endo-BHDA in Nitrobenzene.(T,110-150°C; $\alpha$=0.95; n=6; $t_\alpha$=2.57)

| Cpd. | X | $E_a$,kcal/mol | lgA | $\Delta H^{\neq}$,kcal/mol | $-\Delta S^{\neq}$,eu | $\Delta P^{\neq}$(403°K), kcal/mol |
|------|-----|-----|-----|-----|-----|-----|
| I | p-OH | 18.17±0.12 r=0.998 | 5.48±0.31 S=0.024 | 17.42±0.46 r=0.998 | 35.96±1.16 S=0.991 | 31.92 |
| II | p-OCH$_3$ | 18.07±0.09 r=0.999 | 5.76±0.22 S=0.017 | 18.07±0.36 r=0.999 | 34.71±0.89 S=0.070 | 32.06 |
| III | p-CH$_3$ | 19.71±0.11 r=0.999 | 6.18±0.27 S=0.022 | 18.95±0.28 r=0.999 | 32.79±0.70 S=0.055 | 32.16 |
| IV | H | 20.38±0.23 r=0.996 | 6.40±0.55 S=0.043 | 19.65±0.84 r=0.997 | 31.72±2.03 S=0.159 | 32.43 |
| V | m-OCH$_3$ | 20.11±0.10 r=0.999 | 6.21±0.25 S=0.020 | 19.30±0.42 r=0.999 | 32.77±1.04 S=0.082 | 32.50 |
| VI | p-Br | 21.39±0.13 r=0.998 | 6.88±0.32 S=0.025 | 20.64±0.26 r=0.999 | 29.80±0.65 S=0.051 | 32.64 |
| VII | p-NO$_2$ | 23.49±0.23 r=0.997 | 7.61±0.56 S=0.045 | 22.76±0.81 r=0.998 | 26.19±1.99 S=0.153 | 33.31 |

The values of free activation energy ($\Delta F^{\neq}$) within limits of the reaction series studied change slightly due to the presence of a compensation effect.

The examination of the observance of isokinetic relationship is effected by some procedures.

A common point of intersection of extrapolated Arrhenius straight lines (Fig.2), a compensation nature of changes in the activation enthalpy and entropy at relatively small changes in free activation energy in N-aryl imide fragment (Fig.3a) indicate that the reactions studied belong to the same isokinetic series. This is also confirmed by the linearity of Exner dependences[8] /$\lg k_{T_2}$ =f($\lg k_{T_2}$)/ where $T_2 > T_1$ (Fig.3b), reaction constant on temperature (Fig. 3c), activation energy on preexponential (Fig.3d), activation enthalpy on free activation energy (Fig.3e). The presence of these relationships enables to estimate the values of isokinetic temperature with enough reliability.

From the data of Table 5 one can see that the mean value of isokinetic temperature ($554 \pm 5$°K) is markedly higher than experimental ones; this suggests that the substituent effects on the entropy component of free activation energy should be basic[9].

These results led us to the conclusion that the reaction mechanism of cycloaddition of reaction series studied is similar to that proposed previously involving a pre-reaction complex with electron transfer from dienophile to diene. The only difference is that due to the rigid structure of imides of endo-BHDA (as compared with imides of cis-4-CHDA) the pre-reaction complex has a more organized structure.

## E X P E R I M E N T A L

Synthesis of initial N-aryl imides of endo-BHDA (I-VII), their purification, yields, and physico-chemical characteristics are given in Ref.10.

The procedure of polarographic determination of the reaction rates is described in Refs,1,4-6.
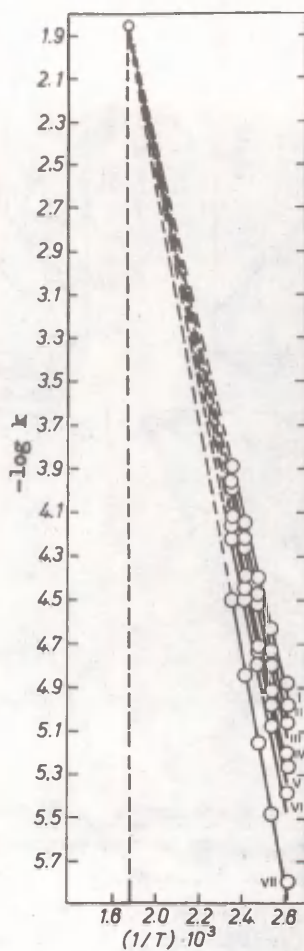
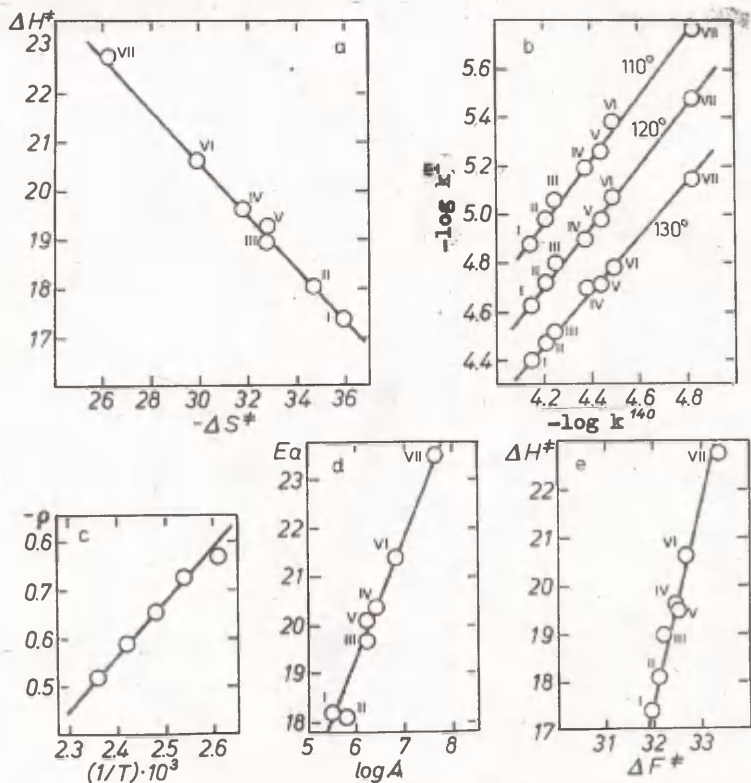Fig.2. Logarithms of rate constants vs. reciprocal
temperature

Fig.3(a-e). Activation enthalpy vs. activation entropy(a); logarithms of rate constants at two temperatures (b); reaction rate constant vs. tepmerature (c); activation energy vs. activation preexponential (d); activation . enthalpy vs. free activation energy (e) in the diene condensation of HCP with imides (I-VII).

Table 5.

Correlation Parameters of y=ax+b Equations, Dependences of Kinetic and Activation Parameters of N-Aryl Imides of Endo-BHDA and Isokinetic Temperature

| Eqn. | X | Y | a | b | r | S | $\beta$, K° |
|---|---|---|---|---|---|---|---|
| 1a | | | $-3.976 \pm 0.125$ | $5.48 \pm 0.31$ | 0.998 | 0.024 | |
| 1b | | | $-4.122 \pm 0.088$ | $5.76 \pm 0.22$ | 0.999 | 0.017 | |
| 1c | | | $-4.314 \pm 0.110$ | $6.18 \pm 0.27$ | 0.998 | 0.021 | |
| 1d | $\frac{1}{T} \cdot 10^3$ | $lgk^T$ | $-4.399 \pm 0.102$ | $6.21 \pm 0.25$ | 0.999 | 0.020 | 555 |
| 1e | | | $-4.466 \pm 0.229$ | $6.40 \pm 0.56$ | 0.996 | 0.043 | |
| 1f | | | $-4.680 \pm 0.127$ | $6.83 \pm 0.32$ | 0.998 | 0.025 | |
| 1g | | | $-5.140 \pm 0.231$ | $7.61 \pm 0.56$ | 0.997 | 0.045 | |
| 2a | | $lgk_{110}$ | $1.291 \pm 0.045$ | $0.453 \pm 0.014$ | 0.997 | 0.025 | 564 |
| 2b | $lgk_{140}$ | $lgk_{120}$ | $1.224 \pm 0.039$ | $0.537 \pm 0.012$ | 0.997 | 0.022 | 534 |
| 2c | | $lgk_{180}$ | $1.094 \pm 0.035$ | $0.132 \pm 0.011$ | 0.997 | 0.020 | 560 |
| 3 | $\frac{1}{T} \cdot 10^3$ | $\rho$ | $-0.982 \pm 0.083$ | $1.788 \pm 0.084$ | 0.990 | 0.016 | 549 |
| 4 | $\Delta S^{\neq}$ | $\Delta H^{\neq}$ | $.543 \pm 15.40$ | $36912 \pm 962$ | 0.998 | 0.121 | 543 |
| 5 | $\Delta P^{\neq}$ | $\Delta H^{\neq}$ | $3.736 \pm 0.304$ | $-101.62 \pm 0.393$ | 0.979 | 0.345 | 550 |
| 6 | IgA | $E_a$ | $2.637 \pm 0.188$ | $3.432 \pm 0.516$ | 0.988 | 0.311 | 576 |

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KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLORO-
CYCLOPENTADIENE WITH CYCLIC DIENOPHILES.
XVIII. Interrelation of Reactivity and Configuration of
N(p- and m-Aryl)Imidee of endo- and exo-Bicyclo/2.2.1/-5-
heptene-2,3-dicarboxylic Acid.

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Kinetics of diene condensation of N-aryl imides of
exo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid
(BHDA) with hexachlorocyclopentadiene (HCP) in nit-
robenzene at different temperatures is studied. Ki-
netic and thermodynamic parameters of the process
activation are determined.An excellent correlation
between logarithms of rate constants and Hammett -
induction $\sigma$ -constants is found. The higher reac-
tivity of dienophiles with   exo-configuration
over   the   corresponding endo-compounds is es-
tablished. The values of isokinetic temperature
are estimated. On this basis the conclusion has
been made that reactions of dienophiles of the
series studied have a common mechanism.

In one of our previous papers of this series[1], using
as an example endo- and exo-anhydrides and phenyl imides of
bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid (BHDA),  we
showed that the reactivity of dienophiles with endo-confi-
guration in the reaction with hexachlorocyclopentadiene (HCP)
is higher than that of the   corresponding  endo-compounds.
To   further  investigate  this   problem   we   have
studied the reaction kinetics of diene condensation of N-
aryl imides of exo-BHDA[2] (I-VII) with  the general struc-
ture:



I-VII

where X is p-OH(I);
p-OCH$_3$(II); p-CH$_3$(III);
H(IV); m-OCH$_3$(V); p-Br(VI);
p-NO$_2$(VII).

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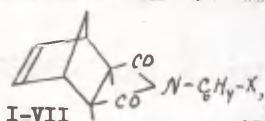
with HCP under conditions similar to those given in our pre-
vious work[3]. Kinetic regularities obtained for the process
are used for description of exo-configuration contribution
into their reactivity.

## RESULTS AND DISCUSSION

Kinetics of the reaction studied is described by the
overall second order equation: the first on diene and the
first on dienophile. The rate constants obtained from
this equation based on a decrease in HCP con-
centration measured polarographically from 2-3 parallel runs
are presented in Table 1.

It is apparent from the data in this Table that rate
constant in this series of compounds increases
with an increase in the temperature and electron-donating
properties of substituents. Similar regularities were es-
tablished for diene condensation of N-aryl imides of endo-
BHDA with HCP[3],i.e. the electron-donating substituents
cause an increase in the reaction rate,and the reaction is
hindered by electron-seeking ones.

An examination of the activation parameters of the pro-
cess (Table 2) shows that the values of activation energy
and lgA increase mainly with a decrease in electron-donat-
ing properties of a substituent in N-aryl imide fragment,
the common point of intersection of straight lines within
temperature range of $532 \pm 5\,°K$ being found in coordinates of
$lgA-T^{-1}$. This indicates that there may be an isokinetic re-
lationship in the reaction series studied (Fig.1).

The obtained values of enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$)
of activation are well consistent, assuming the par-
ticipation of donor-acceptor complexes with charge transfer[4];
strongly negative values of activation entropy can be ex-
plained by formation of a highly organized transition state.
The $\Delta F^{\neq}$ value decreases with an increase in electron-do-
nating nature of substituents.
It should be noted that reactivity of the series studied of
N-aryl imidee of exo-BHDA (I-VII) is well correlated with

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Table 1.

Rate Constants ($k_2 \cdot 10^{-6}$ l/mol·sec) for Diene Condensation of N-aryl Imides of Exo-BHDA (I-VII) with HCP in Nitrobenzene at Different Temperatures

| X | 110 | 120 | 130 | 140 | 150 |
|---|---|---|---|---|---|
| p-OH | $23.67 \pm 0.16$ | $41.45 \pm 0.06$ | $68.77 \pm 0.46$ | $119.73 \pm 0.41$ | $213.06 \pm 2.45$ |
| p-OCH$_3$ | $18.50 \pm 0.64$ | $32.61 \pm 0.31$ | $57.04 \pm 0.23$ | $100.69 \pm 0.20$ | $175.35 \pm 1.17$ |
| p-CH$_3$ | $15.41 \pm 0.23$ | $27.95 \pm 0.26$ | $50.22 \pm 1.09$ | $92.70 \pm 1.06$ | $165.45 \pm 1.43$ |
| H | $11.45 \pm 0.15$ | $22.40 \pm 0.28$ | $35.16 \pm 0.34$ | $69.01 \pm 1.72$ | $126.97 \pm 1.00$ |
| m-CCH$_3$ | $10.06 \pm 0.23$ | $18.62 \pm 0.20$ | $33.16 \pm 0.33$ | $61.22 \pm 0.55$ | $116.02 \pm 0.27$ |
| p-Br | $7.45 \pm 0.14$ | $14.85 \pm 0.08$ | $28.81 \pm 0.20$ | $54.75 \pm 0.31$ | $101.99 \pm 0.63$ |
| p-NO$_2$ | $3.11 \pm 0.17$ | $5.83 \pm 0.23$ | $12.48 \pm 0.18$ | $25.59 \pm 0.40$ | $54.73 \pm 0.26$ |

Table 2.

Kinetic and Thermodynamic Activation Parameters for Diene Condensation of HCP with N(p-and m-Aryl)Imides of exo-Bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic Acid in Nitrobenzene.

| No | X | Ea kcal/mol | lgA | r | S | $\Delta H^{\neq}$, kcal/mol | $-\Delta S^{\neq}$, eu | r | S | $\Delta F^{\neq}$ (403°K), kcal/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| I | p-OH | $17.41^{\pm}0.137$ | $5.30^{\pm}0.34$ | 0.9980 | 0.0270 | $16.67^{\pm}0.44$ | $36.76^{\pm}1.10$ | 0.9989 | 0.0866 | 31.48 |
| II | p-OCH$_3$ | $17.99^{\pm}0.110$ | $5.53^{\pm}0.273$ | 0.9989 | 0.0216 | $17.22^{\pm}0.29$ | $35.80^{\pm}0.73$ | 0.9995 | 0.0578 | 31.65 |
| III | p-CH$_3$ | $19.01^{\pm}0.078$ | $6.03^{\pm}0.193$ | 0.9995 | 0.0152 | $18.24^{\pm}0.41$ | $33.50^{\pm}1.03$ | 0.9992 | 0.0812 | 31.74 |
| IV | H | $19.14^{\pm}0.82$ | $5.90^{\pm}1.98$ | 0.9460 | 0.1564 | $18.38^{\pm}0.68$ | $33.75^{\pm}1.64$ | 0.9970 | 0.1236 | 31.99 |
| V | m-OCH$_3$ | $19.45^{\pm}0.16$ | $6.09^{\pm}0.370$ | 0.9979 | 0.0305 | $18.67^{\pm}0.47$ | $33.25^{\pm}1.16$ | 0.9990 | 0.0914 | 32.07 |
| VI | p-Br | $20.91^{\pm}0.078$ | $6.80^{\pm}0.193$ | 0.9995 | 0.0152 | $20.15^{\pm}0.25$ | $29.94^{\pm}0.62$ | 0.9998 | 0.0493 | 32.21 |
| VII | p-NO$_2$ | $23.06^{\pm}0.192$ | $7.59^{\pm}0.48$ | 0.9978 | 0.0378 | $22.28^{\pm}0.81$ | $26.25^{\pm}2.02$ | 0.9980 | 0.1599 | 32.86 |

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the Hammett $\sigma$ constants (Fig.2). This indicates that both in endo- and exo-series of N-substituted imides[3] of BHDA in this reaction the free energy changes linearly.

Relatively small negative values of reaction constant (Table 3) for exo-compounds both refer to the lower sensitivity of reaction towards electron effects of substituents (as with endo-isomers[3]) and indicate negligible separation of charges in the transition state as confirmed by molecular mechanism of diene synthesis.

Table 3,

Parameters of the Correlation Dependence of lgk on $\sigma$-
-Constants of Substituents for Compounds (I-VII).

| T,°C | $\rho$ | $lgk_o$ | r | S |
|------|--------|---------|---|---|
| 110 | $-0.753 \pm 0.042$ | $-4.926 \pm 0.055$ | 0.992 | 0.040 |
| 120 | $-0.723 \pm 0.018$ | $-4.660 \pm 0.024$ | 0.998 | 0.017 |
| 130 | $-0.641 \pm 0.019$ | $-4.410 \pm 0.031$ | 0.997 | 0.018 |
| 140 | $-0.575 \pm 0.016$ | $-4.140 \pm 0.027$ | 0.998 | 0.015 |
| 150 | $-0.502 \pm 0.015$ | $-3.873 \pm 0.029$ | 0.998 | 0.014 |

To quantitatively estimate the configuration contribution into reactivity we have carried out (Table 4) comparative analysis for rate constants of N-aryl imides of endo- and exo-BHDA.

As can be seen from the data in Table 4 the reaction rate of diene condensation with HCP markedly depends on endo- and exo-configuration of imide ring of initial N-aryl imides of BHDA. The effect of substituents in the case of exo-configuration is more profound (by a factor of 1.6-1.8) than in the case of dienophiles of endo-series[3]. The $k_{exo}/k_{endo}$ ratio for every temperature does not depend practically on electron-donating and electron-seeking nature of substituents on phenyl ring. This fact indicates that induction effect of aromatic ring substituents on the reaction center is of a common nature in the series of N-aryl imides of endo- and exo-BHDA.
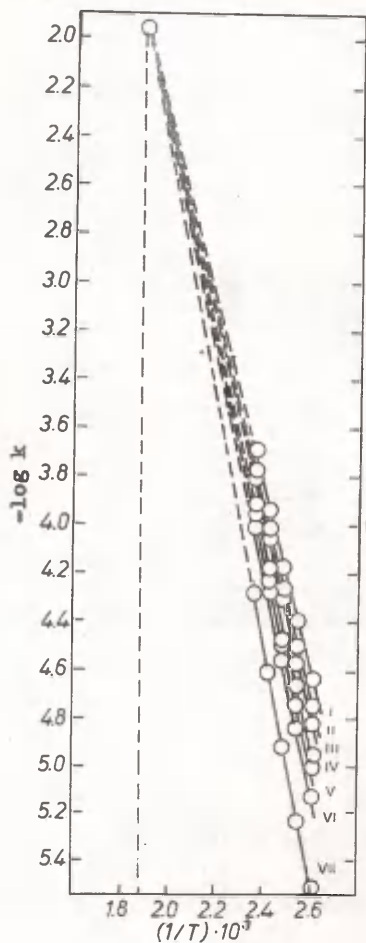
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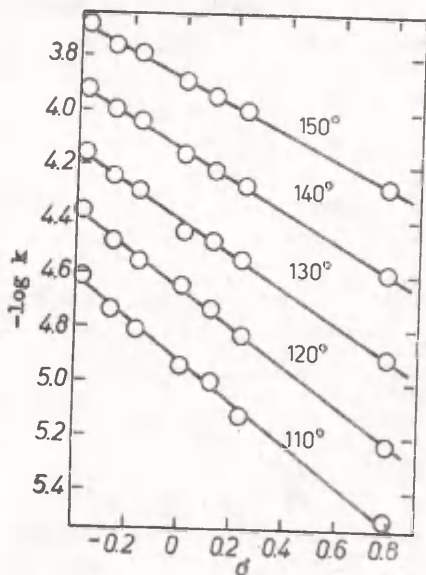Fig.1 Logarithms of rate
constants vs. reciprocal
temperature.

Fig.2 Logarithms of rate con-
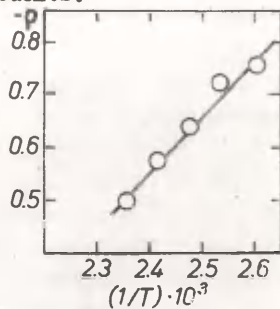stants vs. $\sigma$ constants of sub-
stituents.

Fig.3 Reaction constant $\rho$ vs.
temperature.

Table 4.

Relative Values of Rate Constants of N-aryl Imides of BHDA
with exo- and endo-Configuration in the Reaction with HCP

| X | $k_{exo}/k_{endo}$, at T,°C | | | | | Mean |
|---|---|---|---|---|---|---|
| | 110 | 120 | 130 | 140 | 150 | |
| p-OH | 1,78 | 1,76 | 1,74 | 1,68 | 1,65 | $1,71\pm0,03$ |
| p-OCH$_3$ | 1,76 | 1,71 | 1,68 | 1,64 | 1,58 | $1,67\pm0,03$ |
| p-CH$_3$ | 1,77 | 1,72 | 1,66 | 1,65 | 1,62 | $1,68\pm0,02$ |
| H | 1,76 | 1,79 | 1,80 | 1,66 | 1,64 | $1,73\pm0,03$ |
| m-OCH$_3$ | 1,81 | 1,74 | 1,71 | 1,69 | 1,67 | $1,73\pm0,02$ |
| p-Br | 1,76 | 1,74 | 1,73 | 1,70 | 1,68 | $1,72\pm0,01$ |
| p-NO$_2$ | 1,82 | 1,79 | 1,76 | 1,74 | 1,71 | $1,76\pm0,01$ |

Relatively lower value of the reaction rate for endo-die-
nophiles can be associated with a decrease in electron den-
sity at double bond of bicyclcheptene ring due to its conju-
gation with $\pi$ -electrons of carbon atoms of carboxyl groups
through the space and thus leading to the decrease in stabi-
lization of oriented complex.

It is interesting to note that the $k_{exo}/k_{endo}$ ratio for
all substituents decreases linearly with the temperature
rise (Table) and has a common point of intersection (Fig.4)
corresponding to isokinetic temperature (434+4°K).A regular
decrease in $k_{exo}/k_{endo}$ ratio with an increase in the tempe-
rature of the process is well correlated with existence of
isokinetic relationship in the series of identical compounds.
Thus, in previous works from this laboratory concerning
with diene condensation of N-substituted aryl imides of cis-
4-CHDA[5,6], cis,cis-3-methyl-4-CHDA[4,6], and endo-BHDA[3] the
existence of isokinetic relationship was found with tempe-
rature equal to 499, 578, and 554°K, respectively. Isoki-
netic temperature ($\beta$) for this reaction series was deter-
mined by quite a number of methods recommended by theory[7],
and also by us on the basis of varying the relative values
of rate constants of N-aryl imides of BHDA with exo and endo-

Table 5.

Correlation Parameters of Equations y=ax+b, of Relationships for Kinetic and Activation Parameters of Diene Condensation of N(p- and m-aryl)Imidee of exo-BHDA and Isokinetic Temperature.

| Eqn. | $x$ | $y$ | $a$ | $b$ | $r$ | $S$ | $\beta$, °K |
|------|-----|-----|-----|-----|-----|-----|------|
| 1a | | | $-3.812 \pm 0.137$ | $5.30 \pm 0.34$ | 0.998 | 0.027 | |
| 1b | | | $-3.937 \pm 0.110$ | $5.53 \pm 0.27$ | 0.998 | 0.022 | |
| 1c | | | $-4.161 \pm 0.079$ | $6.03 \pm 0.19$ | 0.999 | 0.015 | |
| 1d | $\frac{1}{T} \cdot 10^3$ | lgk | $-4.256 \pm 0.155$ | $6.09 \pm 0.37$ | 0.997 | 0.030 | 532 |
| 1e | | | $-4.187 \pm 0.82$ | $5.90 \pm 1.98$ | 0.946 | 0.156 | |
| 1f | | | $-4.576 \pm 0.079$ | $6.81 \pm 0.19$ | 0.999 | 0.015 | |
| 1g | | | $-5.046 \pm 0.191$ | $7.59 \pm 0.48$ | 0.997 | 0.038 | |
| 2a | | $lgk_{110}$ | $1.313 \pm 0.044$ | $0.507 \pm 0.013$ | 0.997 | 0.024 | 551 |
| 2b | $lgk_{140}$ | $lgk_{120}$ | $1.252 \pm 0.044$ | $0.523 \pm 0.013$ | 0.997 | 0.024 | 518 |
| 2c | | $lgk_{130}$ | $1.1141 \pm 0.016$ | $0.2025 \pm 0.05$ | 0.999 | 0.009 | 528 |
| 3 | $\frac{1}{T} \cdot 10^3$ | $\beta$ | $-1.042 \pm 0.092$ | $1.947 \pm 0.230$ | 0.987 | 0.018 | 535 |
| 4 | $\Delta S^{\neq}$ | $\Delta H^{\neq}$ | $526 \pm 14.10$ | $36028 \pm 1090$ | 0.981 | 0.124 | 526 |
| 5 | $\Delta F^{\neq}$ | $\Delta H^{\neq}$ | $4.065 \pm 0.365$ | $-111.26 \pm 0.456$ | 0.980 | 0.480 | 534 |
| 6 | lgA | Ea | $2.418 \pm 0.088$ | $4.630 \pm 0.324$ | 0.997 | 0.169 | 528 |
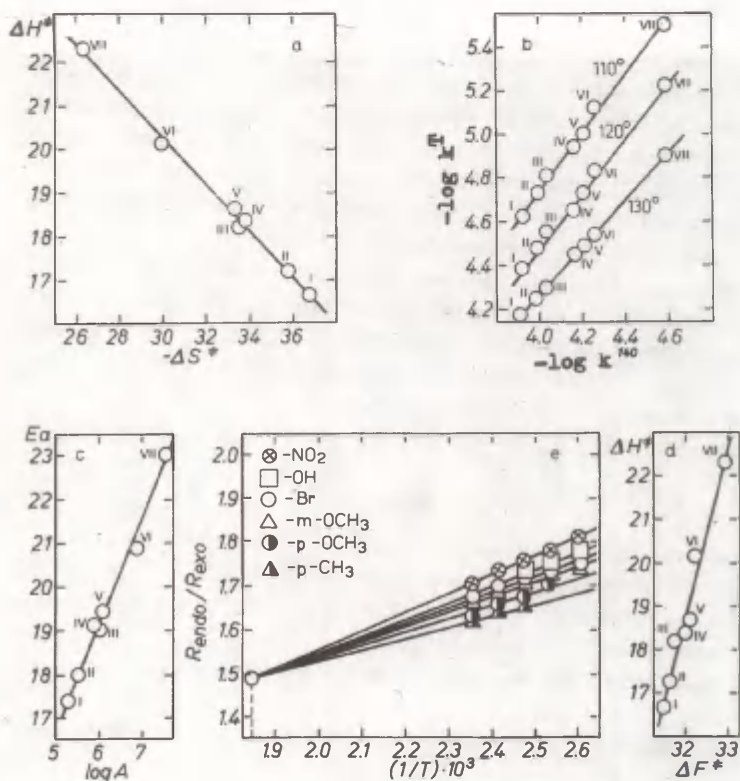
Fig.4(a-e) Activation enthalpy vs. activation entropy (a);
logarithms of rate constants at two temperatures (b); acti-
vation energy vs. preexponential (c); activation enthalpy vs.
free activation energy (d); rate constants of exo- and
endo-N-aryl imides vs. reciprocal temperature (e) of diene
condensation of HCP with imides (I-VII).

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configuration depending on temperature, its values were obtained (Table 5) from the following relationships: $lgk-1/T$ (Fig. 1), $\rho-1/T$ (fig.3), $\Delta H^{\neq}-\Delta S^{\neq}$, $lgk_{T_2}-lgk_{T_1}$, $Ea-lgA$, $\Delta H^{\neq}-\Delta F^{\neq}$, $k_{endo}/k_{exo}-1/T$ (fig.4a-d) on an average ($532\pm3^\circ K$).

Compounds of the reaction series studied do not change the general direction of reaction course of diene condensation of HCP with N-substituted aryl imides of series studied as confirmed by the existence of isokinetic relationship and similarity of the values of isokinetic temperature with those given in the previous works.

Thus the data represented in this work are well correlated with those on substituent effects on the reaction rate of diene condensation of HCP with N-aryl imides of different cyclic dienophiles and confirm completely the earlier conclusion about formation of donor-acceptor complexes with charge transfer in the transition state.

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KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLORO-
CYCLOPENTADIENE WITH CYCLIC DIENOPHILES.

XIX. PMR-Spectra and Reactivity of N(P-aryl)Imides of Endo-
and Exo-Bicyclo/2.2.1/-5-Heptene-2,3-Dicarboxylic Acid.

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The PMR-spectra of N-substituted phenyl imides of
endo- and exo-bicyclo/2.2.1/-5-heptene-2,3-dicar-
boxylic acid are investigated.

The linear dependence of chemical shifts of double
bond protons upon Hammett $\delta$ constants of substit-
uents and also upon their logarithms of rate con-
stants for the reaction of studied imides with he-
xachlorocyclopentadiene is established.

In one of our previous works[1] we attempted to carry out
the investigation of the dependence of reactivity of N-sub-
stituted phenyl imides of cis-4-cyclohexane-1,2-dicarboxylic
acid (cis-4-CHDA) in the reaction course with hexachlorocyclo-
pentadiene (HCP) upon chemical shifts ($\delta$) of double bond
protons of cyclohexene ring. An approximate correlation be-
tween logarithms of rate constants of these reactions and
chemical shifts of double bond protons is observed.

Continuing this investigation we have examined
the correlation dependences of chemical shifts
in PMR-spectra of N(p-aryl)imides of endo-(I-VI) and
exo-(VII-XII) bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic
acids (endo- and exo-BHDA) on Hammett $\delta$-constants of sub-
stituents and also upon their reactivity in the course of
Diels-Alder reaction with HCP.

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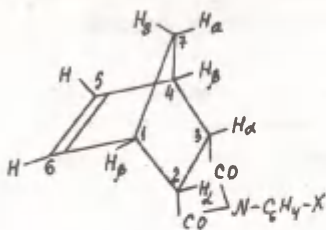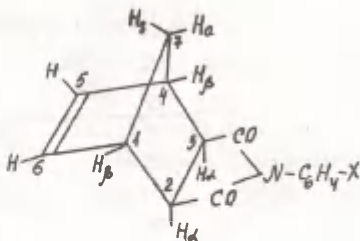
I÷VI                    VII-XII

where X is p-OH(I,VII); p-OCH$_3$(II,VIII); p-CH$_3$(III,IX);
        H(IV,X); p-Br(V,XI); NO$_2$(VI,XII).

# RESULTS AND DISCUSSION

The data of PMR-spectra for N(p-aryl)imides of endo-
and exo-BHDA measured for the first time during the present
study are summarized in Table 1. Endo- and exo-confi-
guration for the imides was assumed on the basis of pre-
paration methods and identification of their structures by
chemical and PMR-speotroscopical means described elsewhere[2].

The data in Table 1 indicate that the chemical shifts
of protons are markedly varied with the nature of sub-
stituents in phenyl ring. Thus rather appreciable shifts
of protons are observed when passing from N-phenyl imides
to N(p-aryl)substituted imides. For example, the chemical
shifts of H$^7_{syn}$- and H$^7_{anti}$-protons are substantially depen-
dent on the substituent nature in aromatic ring and differ
from those of compounds unsubstituted in phenyl ring.
As earlier[1] in the case of imides of BHDA an increase in the
values of chemical shifts is observed with strengthening elec-
trophilic activity of substituents in aromatic ring, this im-
plies a decrease in electron density at multiple bond[3]. At the
present the mechanism of such transfer of induction effect
of N-substituent has remained unclarified, although in our
early works[4,5] the variation in reactivity of such dieno-
philes in the reaction with HCP was interpreted as a result
of electron interaction of imide ring with a reaction center

through the space.

Starting from these results the dependence of chemical shifts of protons on $\sigma$ -constants of substituents could be expected to have different character for N-aryl imides of BHDA of endo- and exo-series. Table 1.

Effect of Substituents on Chemical Shifts of Protons in PMR-spectra of N(p-Aryl)Imides of Endo(I-VI) and Exo-(VII-XII) Bicyclo/2.2.1/-5-Heptene-2,3-Dicarboxylic Acid.

| Cpd.* | Subst. | Chemical shifts of protons, ppm | | | | |
|-------|--------|-------------------|-------------------|--------------|--------------|---------|
| | | $H^7_{anti}$ | $H^7_{syn}$ | $H_\alpha$ | $H_\beta$ | CH=CH |
| I | OH | 1.40 | 1.60 | | 3.20 | 6.01 |
| II | CH$_3$O | 1.43 | 1.62 | | 3.23 | 6.08 |
| III | CH$_3$ | 1.47 | 1.65 | | 3.27 | 6.10 |
| IV | H | 1.49 | 1.68 | | 3.30 | 6.15 |
| V | Br | 1.57 | 1.75 | | 3.45 | 6.18 |
| VI | NO$_2$ | 1.70 | 1.85 | | 3.55 | 6.21 |
| VII | OH | 1.27 | 1.43 | 2.69 | 3.15 | 6.12 |
| VIII | CH$_3$O | 1.29 | 1.48 | 2.67 | 3.16 | 6.15 |
| IX | CH$_3$ | 1.35 | 1.54 | 2.72 | 3.22 | 6.20 |
| X | H | 1.37 | 1.56 | 2.78 | 3.28 | 6.25 |
| XI | Br | 1.38 | 1.58 | 2.80 | 3.30 | 6.27 |
| XII | NO$_2$ | 1.40 | 1.68 | 2.87 | 3.32 | 6.32 |

*For numbering see the text.

With this end in view the correlation analysis of values of $\delta$ protons of bicycloheptene ring with Hammett $\sigma$ constants of substituents (Table 2) was carried out according to the equation:

$$\delta = a + b\sigma$$

where b is a parameter estimating the sensitivity of chemical shifts of protons with respect to the variation of substituent nature characterized by the Hammett $\sigma$ constants; and a is a free term.

It is apparent from    equations (1) and (5) in Table 2 that the sensitivity of double bond protons towards the substituent effects increase insignificantly with transition from

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Table 2.

Correlation Relationships between Chemical Shifts of Protons in N(p-aryl) Imides of Endo- and Exc-BHDA and the Hammett $\sigma$ Constants of Substituents.

| Eqn. | Compound | Correlation Equation | r | S |
|------|----------|----------------------|-----|-----|
| 1 | N(p-aryl) | $\delta_{CH=CH} = (6.155 \pm 0.214) + (0.155 \pm 0.036)\sigma$ | 0.900 | 0.035 |
| 2 | imides of endo- BHDA | $\delta_{H_{anti}} = (1.501 \pm 0.020) + (0.259 \pm 0.005)\sigma$ | 0.999 | 0.005 |
| 3 | | $\delta_{H^7_{syn}} = (1.683 \pm 0.040) + (0.220 \pm 0.008)\sigma$ | 0.998 | 0.008 |
| 4 | | $\delta_{H_{\alpha,\beta}} = (3.319 \pm 0.100) + (0.317 \pm 0.032)\sigma$ | 0.979 | 0.031 |
| 5 | | $\delta_{CH=CH} = (6.20 \pm 0.160) + (0.167 \pm 0.028)$ | 0.946 | 0.027 |
| 6 | N(p-aryl) | $\delta_{H^7_{anti}} = (1.337 \pm 0.103) + (0.119 \pm 0.013)$ | 0.977 | 0.012 |
| 7 | imides of exo- BHDA | $\delta_{H^7_{syn}} = (1.538 \pm 0.134) + (0.195 \pm 0.027)$ | 0.959 | 0.026 |
| 8 | | $\delta_{H_{\alpha}} = (2.749 \pm 0.142) + (0.171 \pm 0.025)$ | 0.959 | 0.024 |
| 9 | | $\delta_{H_{\beta}} = (3.235 \pm 0.233) + (0.151 \pm 0.040)$ | 0.878 | 0.038 |

N(p-aryl)imides of endo-BHDA to those of exo-BHDA, the me-
thylene group protons in the compounds of endo-BHDA being
more sensitive (by a factor of 1.5-1.7) to the ef-
fects of substituents over the double bond protons
(eqns.2 and 3, Table 2), and also over the corresponding
protons in exo-compounds (eqns.6 and 7, Table 2).

It appears possible, therefore, that transfer of in-
duction effect of substituents to the reaction center(CH=CH)
may occur through the skeleton of bicyclic structure
with participation of bridge bonds. In this case the decrease
in the charged density at bridged carbon will favor the dis-
placement of double bond electrons towards this carbon atom
and thereby will hinder the charge transfer from dienophile
to diene,i.e.,will lead to the decrease in the reactivity of
endo-dienophile in the reaction with HCP, which is,in fact,
observed.
However,it should be noted that such an induction effect on
the reaction center in the case of endo-imides will be much
weaker than induction transfer through overlaps of $\mathcal{K}$-orbi-
tals of carbonyl groups effected by $\mathcal{K}$-orbitals of $sp^2$ car-
bon atom of the reaction center (field effect) due to the
frontal approach of these orbitals.

It is clear that in the case of exo-imides, on the
contrary, the transfer of induction effect is performed
only via the skeleton of a molecule due to exo-direction of
carbonyl groups (absence of field effect). The correlations
(eqns.6 and 7, Table 2) between $\overset{2}{\phantom{o}}$-substituents of phenyl
ring and chemical shifts of $H_{syn}^7$- and $H_{anti}^7$-protons are in-
dicative of possibility for transfer of induction effect of
substituents through bridged carbon atom. In the case of
$H_{syn}^7$-protons the sensitivity is approximately two times as
high as that of $H_{anti}^7$-protons. This can be explained by the
presence of "W"-intercation[2,6] between these and $H_\alpha$-protons
For that possible reason the reactivity of exo-imides in
the reaction with HCP increases[7,8].

Further, from analysis of the data in Table 3 one can
find the approximate correlation between chemical shifts of

$H_\alpha$-and $H_\beta$-protons of bicycloheptene ring and $\acute{o}$-constants of substituents (eqns.4,8,9), the sensitivity of $H_{\alpha,\beta}$-protons in N(p-aryl)imides of endo-BHDA (presented by one singlet in PMR-spectra[2]) towards substituent effect being approximately equal to the sum of sensitivities of chemical shifts of $H_\alpha$-and $H_\beta$-protons in imides of exo-BHDA.

Table 3.

Logarithms of Rate Constants* for Diene Condensation of N(p-aryl)Imides (I-XII) of Endo- and Exo-BHDA with HCP at Different Temperatures in Nitrobenzene.

| Cpd. | $-\lg k$ , at T.$^\circ$C. | | | | |
|------|------|------|------|------|------|
|      | 110  | 120  | 130  | 140  | 150  |
| I    | 4.88 | 4.63 | 4.40 | 4.15 | 3.88 |
| II   | 4.98 | 4.72 | 4.47 | 4.21 | 3.95 |
| III  | 5.06 | 4.79 | 4.52 | 4.25 | 3.99 |
| IV   | 5.19 | 4.90 | 4.70 | 4.38 | 4.11 |
| V    | 5.37 | 5.07 | 4.78 | 4.49 | 4.21 |
| VI   | 5.76 | 5.48 | 5.15 | 4.83 | 4.49 |
| VII  | 4.63 | 4.38 | 4.16 | 3.92 | 3.67 |
| VIII | 4.73 | 4.49 | 4.24 | 3.99 | 3.76 |
| IX   | 4.81 | 4.55 | 4.29 | 4.03 | 3.78 |
| X    | 4.94 | 4.65 | 4.45 | 4.16 | 3.89 |
| XI   | 5.13 | 4.82 | 4.54 | 4.26 | 3.99 |
| XII  | 5.51 | 5.23 | 4.90 | 4.59 | 4.26 |

* Rate constants are determined from three parallel runs to within 4-6%.

It is noteworthy that equations (1-9) can be used to predict(on the basis of the estimated data) the $\sigma$ constants of such substituents in the reaction series, whose experimental determination involves certain difficulties.

Then, it has been found that logarithms of rate constants for the reaction between dienophiles studied and HCP are in the correlation relationships with chemical shifts of double bond protons of bicycloheptene fragment. The values of rate constants for imides(I-XII) in the reaction with HCP were taken from our previous works[7,8] and are presented

in Table 3.

Correlations of double bond protons and lgk are useful for obtaining linear relationships presented in Table 4. It should be pointed out that the obtained correlation relationships between chemical shifts and $\mathcal{C}$-constants of substituents and also between the former and lgk combined with similar relationships determined elsewhere for raection of HCP with N(p-aryl)imides of cis-4-CHDA[1], describe well the substituent behavior in N-aryl fragment of the dienophiles studied.

Table 4.
Correlation Relationships between Logarithms of Rate Constants and Chemical Shifts of Double Bond Protons in N(p-aryl)Imides of Endo- and Exo-BHDA.

| Compound | Correlation Relationship | r | s |
|----------|--------------------------|-----|-----|
| N(p-aryl) imides of endo-BHDA | $lgk_{110} = 19.316 - 4.007\, \delta_{CH=CH}$ | 0.915 | 0.144 |
| | $lgk_{120} = 18.263 - 3.790\, \delta_{CH=CH}$ | 0.897 | 0.152 |
| | $lgk_{130} = 16.278 - 3.423\, \delta_{CH=CH}$ | 0.908 | 0.128 |
| | $lgk_{140} = 14.341 - 3.059\, \delta_{CH=CH}$ | 0.893 | 0.126 |
| | $lgk_{150} = 12.948 - 2.786\, \delta_{CH=CH}$ | 0.915 | 0.099 |
| N(p-aryl) imides of exo-BHDA | $lgk_{110} = 20.673 - 4.122\, \delta_{CH=CH}$ | 0.958 | 0.102 |
| | $lgk_{120} = 19.184 - 3.839\, \delta_{CH=CH}$ | 0.931 | 0.125 |
| | $lgk_{130} = 17.009 - 3.448\, \delta_{CH=CH}$ | 0.957 | 0.088 |
| | $lgk_{140} = 15.118 - 3.100\, \delta_{CH=CH}$ | 0.948 | 0.086 |
| | $lgk_{150} = 12.884 - 2.698\, \delta_{CH=CH}$ | 0.952 | 0.073 |

In terms of these considerations the signals of double bond protons in PMR-spectra of imides with electron-donating and electron-seeking dienophiles are to be expected to occur in relatively strong and weak fields, respectively, and in fact have been observed (Table 1).

Besides, the correlation relationships (Table 4) between logarithms of rate constants and chemical shifts can be used for approximate estimation of reaction rates of die-

nophiles with HCP whose experimental determination is somewhat difficult ( poor solubility in common solvents, isomerization at high temperatures, etc).

To check this suggestion we have calculated the corresponding rate constants by substituting the $\delta_{CH=CH}$ values for N(p-aryl)imides of endo- and exo-BHDA into the correlation equations in Table 4.

As can be seen from the data in Table 5 the values estimated for rate constants are in agreement with those determined from the experimental data within errors.

Table 5.

Values of Rate Constants (Experimental and Calculated on the Basis of Correlation Relationships) for Reaction of Imides of BHDA Series with HCP at Different Temperatures in Nitrobenzene.

| Cpd. | X | T,°C | $k_2 \cdot 10^6$, 1/mol·sec. | |
|------|------|------|------------|------------|
| | | | Experimental | Calculated |
| II | OCH$_3$ | 140 150 | 61.19 111.11 | 58.85 103.60 |
| V | Br | 140 150 | 32.05 61.65 | 33.93 64.72 |
| VIII | OCH$_3$ | 130 140 | 57.04 100.69 | 62.90 110.25 |
| XI | Br | 110 150 | 7.45 101.99 | 6.99 95.37 |

EXPERIMENTAL

The syntheses and properties of N(p-aryl)imides of endo- and exo-BHDA (I-XII) are described elsewhere[2].

PMR-spectra were obtained with a "TESLA" BS 4878B radiospectrometer, 80mc, at room temperature. All spectra were determined in the CCl$_4$ solutions with HMDS as an internal standard.

Parameters of correlation equations were calculated by the least-squares method. Their confidence was checked by means of Student t-criterion, with reliability of 0.95.

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SOLVENT EFFECTS ON THE DISTRIBUTION COEFFICIENTS

IV.    DISTRIBUTION OF PHENOLS BETWEEN WATER

AND ORGANIC SOLVENTS

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The mathematical treatment of literature data
on the phenol distributions between water and organ-
ic solvents confirms the applicability of the previ-
ously suggested equation for the extraction process
treatment which correlates the distribution constant
with solvent parameters: $lgK = A_0 + A_1 f(n) + A_2 f(\varepsilon) + A_3 \delta^2 + A_4 B + A_5 E$. A satisfactory correlation is ob-
tained for 26 phenols ($R \geqslant 0.95$) and only strongly
ionized picric and picramic acids do not    obey
the proposed equation. In the most cases the five-
parameter equation  can be satisfactorily substitut-
ed by a simplier equation which takes into account
solvent  polarity, polarizability,  and  basicity
only. The first of these parameters reduces the val-
ue  of lgK, while the other two parameters raise
it.

In the previous papers[1,2] we showed that the distribution
process of substances   between two  liquid phases, aqueous
and organic, can be described by a linear five-parameter
equation which takes into account polarizability, polarity,
cohesion energy density, basicity and electrophilicity of
solvents: $lgK = A_0 + A_1 \frac{n^2-1}{n^2+2} + A_2 \frac{\varepsilon-1}{2\varepsilon+1} + A_3 \delta^2 + A_4 B + A_5 E$

To confirm the general applicability of this equation
it is desirable to check it with a greater number of cases.

In the present paper we treat the results of Ref[3-17] on the distribution of phenols between water and organic phases. In Table I the logarithms of distribution constants for 28 phenols between water and 12-22 organic solvents $K = (C_{org})^n / C_{aq}$ are listed. As shown in Ref.[3-17] phenols do not associate in the organic phase, i. e. $n = 1$ and therefore there is no necessity to use the distribution constants only at infinite dilution. The solvent parameters are listed in communication II of this series[2].

In Table I the correlation coefficients R and mean errors s are also given. As one can see in the majority of cases a good or satisfactory correlation $(R \geqslant 0.95)$ is immediately achieved. Yet to achieve satisfactory correlation for some phenols it is necessary to exclude the data for 1-3 solvents; these values of lgK are marked in TableI by an asterisk (*). In the majority of cases the excluded solvent is n-heptane; it is, probably, due to a systematical error in the phenol determination in this solvent. The new values of R and s after the exclusion of "doubtful" points are also listed in Table I.

Thus on 26 examples the applicability of a linear poly-parameter equation for describing the distribution process of phenols between two immiscible phases is confirmed. One does not obtain a satisfactory correlation for picric acid $N°24$ and only after excluding the data for five solvents from the consideration one obtains the correlation for picramic acid N°23.

Since the values of pair correlation coefficients do not reflect satisfactorily the significance of separate parameters, to estimate the latter we excluded these by turn and determined the values of R and s each time as described in Ref.18.We found that for a majority of phenols the extraction process may be satisfactorily described by two- or three-parameter equations. The elimination of the cohesion energy density $\delta^2$ and the electrophilicity E from the equation do

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Table I

## lg K  FOR PHENOL DISTRIBUTIONS

| N° | Solvent | Phenols | | | |
|---|---|---|---|---|---|
| | | Diphenylol-propane[3] | Phenol [4] | o-Cresol [4] | m-Cresol [5] |
| 1. | n-Pentanol | 3,543 | 1,565 | 2,235 | – |
| 2. | n-Hexanol | 3,415 | 1,499 | 2,176 | 2,176 |
| 3. | n-Octanol | 3,322 | 1,495 | 2,045 | 2,017 |
| 4. | Butylacetate | 3,579 | 1,685 | – | – |
| 5. | Amylacetate | 3,322 | 1,642 | 2,309 | – |
| 6. | Nitrobenzene | 2,352 | 0,897 | 1,676 | 1,322 |
| 7. | Dichloroethane | 1,558 | 0,602 | 1,361 | 1,042 |
| 8. | Dichloromethane | 1,303 | 0,690 | – | – |
| 9. | Chloroform | 1,161 | 0,267 | 1,230 | 0,886 |
| 10. | Benzene | 1.187 | 0.322 | 1.140 | 0.785 |
| 11. | Toluene | 1.075 | 0.217 | 1.079 | 0.699 |
| 12. | Chlorobenzene | 0.924 | 0.255 | 1.072 | 0.770 |
| 13. | Bromobenzene | 0.918 | 0.176 | 1.021 | 0.612 |
| 14. | Iodobenzene | 0.880 | 0.096 | 0.934 | 0.398 |
| 15. | o-Xylene | 0.908 | 0.274 | 1.009* | 0.643 |
| 16. | m-Xylene | 0.844 | 0.209 | 1.004 | 0.653 |
| 17. | p-Xylene | 0.812 | 0.187 | 1.009 | 0.612 |
| 18. | o-Dichlorobenzene | 0.568 | 0.130 | – | – |
| 19. | CCl$_4$ | 0.000 | –0.260 | 0.672 | 0.230 |
| 20. | Cyclohexane | –0.824 | –0.658 | 0.176 | –0.155 |
| 21. | n-Heptane | –1.047 | –0.825 | 0.245* | –0.200 |
| 22. | Ethylacetate | – | – | – | – |
| | R | 0.959 | 0.957 | 0.926 | 0.965 |
| | s | 0.443 | 0.243 | 0.281 | 0.173 |
| | R' | | | 0.958 | |
| | s' | | | 0.214 | |

Table I (continued)

lg K FOR PHENOL DISTRIBUTIONS

| N° | p-Cresol [5] | Ethyl-phenol [6] | 2,4-Xylenol [7] | 3,5-Xylenol [7] | Thymol [8] | o-Chlorophenol [9] | m-Chlorophenol [9] |
|---|---|---|---|---|---|---|---|
| I. | 2.284 | 2.389 | 2.389 | 2.398 | 3.04I | 2.955 | - |
| 2. | 2.245 | 2.352 | 2.352 | 2.373 | 3.033 | 2.I46 | 2.602 |
| 3. | 2.I67 | 2.255 | 2.30I | 2.3II | 3.0I3 | 2.I20 | 2.522 |
| 4. | 2.3I4 | 2.447 | 2.5I2 | 2.5I0 | 3.I07 | 2.24I | 2.68I |
| 5. | 2.I96 | 2.389 | 2.462 | 2.456 | 3.097 | 2.I96 | 2.633 |
| 6. | I.462 | I.857 | I.886 | I.902 | - | I.774 | I.809 |
| 7. | I.I76 | I.672 | I.658 | I.672 | 2.8I2 | I.59I | I.348 |
| 8. | ⊄ | - | - | - | - | - | - |
| 9. | I.064 | I.475 | I.498 | I.580 | 2.799 | I.362 | I.020 |
| I0. | 0.892 | I.380 | I.336 | I.330 | 2.638 | I.455 | I.I20 |
| II. | 0.832 | I.279 | I.255 | I.292 | 2.602 | I.369 | I.048 |
| I2. | 0.799 | I.30I | I.246 | I.265 | 2.748 | I.365 | I.000 |
| I3. | 0.77I | I.243 | I.I55 | I.I70 | 2.667 | I.352 | 0.929 |
| I4. | 0.68I | - | - | - | - | I.320 | 0.857 |
| I5. | 0.732 | I.272 | I.2I5 | I.30I | 2.544 | I.352 | I.068 |
| I6. | 0.778 | I.243 | I.204 | I.274 | 2.5I2 | I.369 | I.049 |
| I7. | 0.755 | I.255 | I.I6I | I.262 | 2.544 | I.328 | 0.996 |
| I8. | - | - | - | - | - | - | - |
| I9. | 0.462 | 0.832 | 0.778 | 0.8I9 | 2.388* | I.I90 | 0.490 |
| 20. | -0.I55 | 0.332 | 0.342 | 0.380 | I.748 | 0.863 | 0.078 |
| 2I. | -0.056 | 0.290* | 0.342* | 0.322* | I.690* | 0.844 | -0.076 |
| 22. | - | - | 2.574 | 2.577 | - | 2.30I | - |
| R | 0.965 | 0.943 | 0.950 | 0.946 | 0.842 | 0.964 | 0.966 |
| s | 0.240 | 0.264 | 0.263 | 0.267 | 0.270 | 0.I4I | 0.257 |
| R' | | 0.968 | 0.97I | 0.972 | 0.978 | | |
| s' | | 0.I85 | 0.I9I | 0.I82 | 0.090 | | |

Table I (continued)

lg K FOR PHENOL DISTRIBUTIONS

| N° | Phenols | | | | | |
|---|---|---|---|---|---|---|
| | p-Chloro-phenol [9] | 2,4-Di-chlorophe-nol [9] | o-Fluoro-phenol [10] | o-Bromo-phenol [10] | p-Bromo-phenol [11] | o-Iodo-phenol [10] |
| I. | 2.5I2 | - | I.728 | 2.369 | 2.555 | 2.670 |
| 2. | 2.476 | - | I.7I0 | 2.356 | 2.476 | 2.668 |
| 3. | 2.398 | - | I.638 | 2.334 | 2.43I | 2.644 |
| 4. | 2.5I0 | - | I.9I3 | 2.464 | 2.52I | 2.78I |
| 5. | 2.469 | - | I.880 | 2.44I | 2.498 | 2.738 |
| 6. | I.863 | 2.I99 | I.I30 | 2.02I | I.929 | 2.275 |
| 7. | I.332 | 2.II4 | 0.839 | I.85I | I.405 | 2.02I |
| 8. | - | - | - | - | - | - |
| 9. | I.0I2 | - | 0.568 | I.643 | I.068 | I.967 |
| I0. | I.I34 | I.9I6 | 0.55I | I.682 | I.230 | I.906 |
| II. | I.079 | I.872 | 0.456 | I.6I2 | I.I46 | I.850 |
| I2. | I.042 | I.943 | 0.502 | I.688 | I.030 | I.888 |
| I3. | 0.964 | I.902 | 0.447 | I.656 | I.000 | I.872 |
| I4. | 0.902 | I.832 | 0.398 | I.640 | 0.968 | I.838 |
| I5. | I.052 | I.950 | 0.490 | I.579 | I.I76 | I.86I |
| I6. | 0.99I | I.890 | 0.438 | I.620 | I.I43 | I.849 |
| I7. | 0.9I9 | I.904 | 0.4I4 | I.556 | I.II4 | I.846 |
| I8. | - | - | - | - | - | - |
| I9. | 0.486 | I.652 | -0.046 | I.49I | 0.556 | I.568 |
| 20. | 0.079 | I.385 | -0.30I | I.I64 | 0.I46 | I.255 |
| 2I. | -0.I08 | I.269 | -0.432 | I.045* | -0.076* | I.000* |
| 22. | - | - | 2.000 | 2.520 | - | 2.838 |
| R | 0.965 | 0.973 | 0.963 | 0.955 | 0.959 | 0.944 |
| s | 0.252 | 0.079 | 0.236 | 0.25I | 0.267 | 0.I98 |
| R' | | | | 0.977 | 0.975 | 0.976 |
| s' | | | | 0.I02 | 0.I95 | 0.II8 |

Table I (continued)

Ig K  FOR  PHENOL DISTRIBUTIONS!

| N⁰ | Phenols | | | | | |
|---|---|---|---|---|---|---|
| | p-Iodo-phenol [11] | Guaja-col [12] | o-Nitro-phenol [13] | m-Nitro-phenol [13] | p-Nitro-phenol [13] | Picramic acid [14] |
| I. | - | 1.463 | - | - | - | - |
| 2. | - | 1.428 | 1.972 | 2.114 | 2.037 | 1.132 |
| 3. | 2.929 | 1.352 | 1.785 | 2.000 | 1.954 | 0.924 |
| 4. | 3.118 | - | 2.301 | 2.422 | 2.322 | 2.086 |
| 5. | 3.061 | - | 2.190 | 2.322 | 2.220 | 2.029 |
| 6. | 2.401 | 1.628 | 2.704 | 1.623 | 1.455 | 2.060* |
| 7. | 2.883* | 1.622 | 2.596 | 0.944 | 0.732 | 1.522 |
| 8. | - | - | - | - | - | - |
| 9. | 1.562 | 1.699* | 2.348* | 0.602 | 0.204 | 0.990 |
| 10. | 1.653 | 1.322 | 2.322* | 0.342 | -0.061 | 1.152* |
| 11. | 1.602 | 1.255 | 2.260 | 0.204 | -0.187 | 1.060* |
| 12. | 1.562 | 1.188 | - | - | - | - |
| 13. | 1.552 | - | - | - | - | 0.949 |
| 14. | 1.502 | - | - | - | - | 0.838 |
| 15. | 1.606 | 1.207 | - | - | - | 1.143 |
| 16. | 1.556 | 1.147 | - | - | - | 1.086 |
| 17. | 1.544 | 1.230 | - | - | - | 1.117 |
| 18. | - | - | - | - | - | - |
| 19. | 1.049 | 0.978 | 1.913 | -0.638 | -0.921 | 0.064* |
| 20. | 0.568 | 0.476 | 1.447 | -1.220 | -1.699 | -0.854* |
| 21. | 0.342* | 0.362 | 1.401 | -1.398 | -2.000 | -1.000* |
| 22. | - | - | - | - | - | - |
| R | 0.925 | 0.813 | 0.711 | 0.961 | 0.964 | 0.793 |
| s | 0.376 | 0.277 | 0.391 | 0.512 | 0.546 | 0.543 |
| R' | 0.973 | 0.963 | 0.945 | | | 0.963 |
| s' | 0.212 | 0.113 | 0.216 | | | 0.140 |

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Table I (continued)

lg K FOR PHENOL DISTRIBUTIONS

| N° | Picric acid [I4] | Hydro-quinone [I5] | α-Naphtol [I6] | α-Nitroso-β-naphtol [I7] | β-Nitroso α-naphtol [I7] |
|---|---|---|---|---|---|
| | | | Phenols | | |
| I. | - | 0.799 | 2.353 | 2.I30 | 2.397 |
| 2. | I.626 | 0.735 | 2.754 | - | - |
| 3. | I.444 | 0.6I2 | 2.370 | 2.278 | 2.567 |
| 4. | 2.I00 | 0.672 | - | 2.504 | 2.254 |
| 5. | I.979 | 0.602 | - | 2.49I | 2.I76 |
| 6. | I.900 | 0.43I | - | - | - |
| 7. | I.759 | 0.322 | I.882 | 3.267* | 2.204 |
| 8. | - | - | - | - | - |
| 9. | I.228 | 0.230 | I.8I6 | 3.04I | 2.04I |
| I0. | I.643 | 0.I46 | I.854 | 2.633 | I.447 |
| II. | I.556 | - | I.8I3 | 2,602 | I.43I |
| I2. | - | - | I.8I6 | 2.806 | I.662 |
| I3. | I.272* | - | I.839 | 2.857 | I.690 |
| I4. | I.I64 | - | - | - | - |
| I5. | I.798* | - | I.68I | 2.623* | I.447 |
| I6. | I.782 | - | I.709 | 2.590 | I.424 |
| I7. | I.786 | - | I.708 | 2.568 | I.388 |
| I8. | - | - | - | - | - |
| I9. | I.49I* | 0.04I | I.233 | 2.I30* | 0.954* |
| 20. | I.322 | - | 0.580* | I.380 | 0.30I |
| 2I. | -0.785* | 0.053 | 0.5I8 | I.278 | 0.204* |
| 22. | - | 0.792 | - | - | - |
| R | 0.600 | 0.982 | 0.882 | 0.628 | 0.902 |
| s | 0.620 | 0.072 | 0.337 | 0.503 | 0.305 |
| R' | 0.820 | | 0.98I | 0.970 | 0.972 |
| s' | 0.I89 | | 0.I23 | 0.I40 | 0.I76 |

not reduce the value of R or reduces it negligibly only,i.e.
do not reduce the correlation. The exceptions are m-cresol,
thymol, 2,4-dichlorophenol, guajacol and naphtols. The moat
affecting  parameter on the distribution  constant values
is basicity,B,but the correlation is improved remarkably,
when one takes into account the nonspecific solvation,i.e.
the polarity and polarizability parameters.The former de-
creases and the latter increases the value of lgK.These de-
pendences are natural. Phenols  are weak acids and are
extracted from water the better the stronger is their
interaction with the extragent determined by basicity. On
the contrary the increase in electrophilicity of the extra-
gent should decrease its interaction with acidic phenol.The
solvent polarity favors the acid-base interaction.  How-
ever,there are many exceptions: for example,  for nitro-
phenols  the  solvent  polarity  plays  a  key  role
and the influence of the basicity on the lg K value is neg-
ligible. It is possible that  as  a  result  of  a higher
acidity of nitrophenols  the acid-base interaction in
this case has a negative influence as in this case it leads
to  the partial extraction of basic solvents by nitro-
phenols in water.

Below we list the multiparameter equations for the ex-
traction process from which the insignificant parameters
are excluded, and corresponding values of R and s and of
the pair correlation coefficients $r_{OB}$ for basicity or,in
some cases, electrophilicity $r_{OE}$ parameters. The phenols
for which other parameters, besides polarity, polarizability,
and basicity  are significant, are underlined.

I.Diphenylolpropane: lgK= -I.365+5.568f(n) +0.0II2 B

R=0.959; s=0.420; $r_{OB}$=0.904

2.Phenol:          lgK= -0.607-I.32If(n)+3.055f($\varepsilon$) +
+0.00559 b; R=0.955;s=0.233;$r_{OB}$=0.896

3.o-Cresol: lgK=I.74I-5.279f(n)+2.546f($\varepsilon$)+0.00272 B

R=0.948; s=0.2I7; $r_{OB}$=0.80I

4.m-Cresol: lgK=-I.459+22.764$b^2$ +0.00336 B;

R=0.967; s=0.I83; $r_{OB}$=0.866

5.p-Cresol: $\lg K = 0.442 - 2.683f(n) + 2.812f(\varepsilon) + 0.00582$ B

R=0.964; s=0.225; $r_{OB}$=0.924

6.Ethylphenol: $\lg K = I.967 - 5.345f(n) + 2.378f(\varepsilon) + 0.00334$ B

R=0.960; s=0.I88; $r_{OB}$=0.890

7.2,4-Xylenol: $\lg K = 2.329 - 6.753f(n) + 2.462f(\varepsilon) + 0.0034I$ B

R=0.96I; s=0.202; $r_{OB}$=0.892

8.3,5-Xylenol: $\lg K = 2.4I7 - 6.824f(n) + 2.394f(\varepsilon) + 0.00326$ B

R=0.964; s=0.I9I; $r_{OB}$=0.892

9.Thymol: $\lg K = 6.52I - I7.535f(n) + I8.080 \, \delta^2 - 0.I85$ B

R=0.974; s=0.092; $r_{OB}$=0.89I

I0.o-Chlorophenol: $\lg K = 0.742 + I.44If(\varepsilon) + 0.00459$ B $- 0.0339$ E

R=0.957; s=0.I44; $r_{OB}$=0.924

II.m-Chlorophenol: $\lg K = 0.0I2 - 0.857f(n) + 2.795f(\varepsilon) + 0.00768$ B

R=0.965; s=0.244; $r_{OB}$=0.930

I2.p-Chlorophenol: $\lg K = -0.263 + 2.973f(n) + 0.0068I$ B

R=0.963; s=0.24I; $r_{OB}$=0.923

I3.2,4-Dichlorophenol: $\lg K = 0.699 + II.034 \, \delta^2 + 0.00502$ B

R=0.970; s=0.073; $r_{OB}$0.80I

I4.o-Fluorophenol: $\lg K = -0.6I2 + 2.523f(\varepsilon) + 0.00633$ B

R=0.950; a=0.255; $r_{OB}$=0.9I7

I5.o-Bromophenol: $\lg K = I.98I - 2.877f(n) + I.3I3f(\varepsilon) + 0.00270$ B

R=0.958; s=0.I28; $r_{OB}$=0.9I4

16.p-Bromophenol: $\lg K = I.oI6 - 3.089f(n) + 2.345f(\varepsilon) + 0.00584$ B

R=0.968; s=0.206; $r_{OB}$=0.933

I7.o-Iodophenol: $\lg K = 2.229 - 3.22If(n) + l.474f(\varepsilon) + 0.003I0$ B

R=0.962; s=0.I38; $r_{OB}$=0.9I9

I8.p-Iodophenol: $\lg K = I.4I4 - 3.33If(n) + 2.757f(\varepsilon) + 0.00646$ B

R=0.965; s=0.2I8; $r_{OB}$=0.922

I9.Guajacol: $\lg K = -2.284 + 8.8I0f(n) + I0.079 \delta^2 - 0.00I35 B + 0.0974 E$

R=0.962; s=0.I09; $r_{OB}$=0.425

2o.o-Nitrophenol: $\lg K = I.I65 - 2.I37f(n) + 5.I25f(\varepsilon) - 0.002I6$ B $- 0.0696$ E; R=0.943; s=0.I96; $r_{OB}$=0.I42

2I.m-Nitrophenol: $\lg K = -I.780 + 7.795f(\varepsilon) - 8.6I9 \, \delta^2 + 0.00674$ B

R=0.960; s=0.450; $r_{OB}$=0.862

22.p-Nitrophenol: $\lg K = -2.748 + 7.457f(\varepsilon) + 0.00824$ B

R=0.958; s=0.5II; $r_{OB}$=0.867

23. <u>Picramic acid</u>: $\lg K = 4.332 - 12.139f(n) + 1.809f(\varepsilon) + 0.0013B +$
$+ 0.050E;$ $R = 0.963;$ $s = 0.140;$ $r_{OB} = 0.426$

24. <u>Picric acid</u>: One do not obtain a satisfactory correlation.
For the five parameters $R = 0.600$.

25. <u>Hydroquinone</u>: $\lg K = 0.253 - 1.609f(n) + 1.086f(\varepsilon) + 0.00182\ B$
$R = 0.973;$ $s = 0.077;$ $r_{OB} = 0.938$

26. $\alpha$-<u>Naphtol</u>: $\lg K = -2.927 + 14.987f(n) + 0.245\ E$
$R = 0.977;$ $s = 0.121;$ $r_{OB} = 0.766$

27. $\alpha$-<u>Nitroso</u>-  $\lg K = -3.49o + 27.446f(n) + 4.908f(\varepsilon) - 41.378\delta^2$
$\beta$-<u>naphtol</u>: $-0.00397B + 0.368E;$ $R = 0.970;$ $s = 0.140;$ $r_{OB} = 0.57$

28. $\beta$-<u>Nitroso</u>-  $\lg K = 6.446 - 22.248f(n) + 22.377\delta^2 - 0.161\ E$
$\alpha$-<u>naphtol</u>: $R = 0.960;$ $s = 0.186;$ $r_{OE} = 0.694$

Hence, the distribution of phenols also may be satisfactori-
ly described by the linear five-parameter equation of free
energies with the exception of strongly dissociated picric
and picramic acids. The analysis of the significance of se-
parate parameters allows to make some conclusions about the
extraction mechanism of phenols.

For the purpose of verification of the significance
of acid-base interaction for the extraction process we
studied a possible correlation between the values of loga-
rithms of distribution constants $\lg K$ and the $pK$ of phenols
in water. One finds a linearity neither between these val-
ues nor between the values of $\lg K$ and $A_4$ (the coefficients
at the basicity parameter) or Hammett $\sigma$ constants. This
failure confirms again the complicated nature of the
extracted phenol interaction with the organic solvent and
the necessity of considering both specific and nonspecific
solvation.

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# HYDROLYSIS KINETICS OF ALKYL HALIDES (MeI, EtBr, EtI, i-PrCl, i-PrBr, and i-PrI) UNDER THE INFLUENCE OF AQUA-PALLADIUM(II)

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Hydrolysis kinetics of MeI, EtBr, EtI, i-PrCl, i-PrBr, and i-PrI in aqueous solutions of palladium(II) perchlorate is studied.The kinetic equation takes into account the contribution of the reaction with a solvent ($k_o$) and palladium ions: $-d[RX]/d\mathcal{C} = k_o[RX] + k_I[RX][Pd^{2+}]$. Reaction rates of RBr and RI with palladium $d^8$-complexes are considerably higher than those expected on the basis of the correlation equation suggested elsewhere for $M^+$-$S_N2$ reactions of alkyl halides with non-transition metal complexes such as $Hg^{2+}$ and $Ag^+$. This indicates that there may be some additional interactions between RX and $Pd^{2+}$ not taken into account by an ordinary $M^+$-$S_N2$ model of transition states.

The interaction kinetics of primary and secondary alkyl halides RX (R=Me, Et, i-Bu, i-Pr, X=Cl, Br, I) with aqua-complexes of $Ag^+$, $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$, and $Tl^{3+}$ was studied in detail elsewhere[1-4]. These ions with filled d-shells accelerate the hydrolysis of RX via the electrophilic contribution into the carbon-halogen bond heterolysis (mechanism $M^+$-$S_N2$). $M^+$ effect increases in proportion to the stability constant ($K_{MX}$) of the MX complex formed at the limiting reaction step:

$$lg(k_I^o / k_o) = lgK_{MX} - P_RP_XP_M \tag{1}$$

where $k_I^o$ and $k_o$ are reaction rate constants of RX with $M^+$

and a solvent at zero ionic strength and at 25°; $P_R$, $P_X$, and $P_M$ are parameters depending on R, X, and $M^+$ properties, respectively.

It was of interest to study the hydrolysis kinetics of alkyl halides under the influence of $d^S$-complexes, such as $Pd(H_2O)_4^{2+}$. Since a d-shell is unoccupied and also due to coordination unsaturation of palladium (II), some additional interactions between $Pd^{2+}$ and RX, not taken into account by Eq. (1), may occur. In fact, we have established that regularities of the RX interaction with metal ions change with transition from $Hg^{2+}$ (and other similar ions) to $Pd^{2+}$ and that Eq. (1) does not work with palladium (II).

## Results and Discussion

The interaction rate of alkyl halides with aqueous solutions of $Pd^{2+}$ perchlorate obeys the kinetic equation:

$$-\frac{d[RX]}{d\tau} = k_o [RX] + k_I [RX] [Pd^{2+}] \qquad (2)$$

The first term describes the reaction with a solvent, the second takes into account the induced hydrolysis. Table 1 lists the second order rate constants.

Table 1

The Second Order Rate Constants of the Reactions of Alkyl Halides with Palladium (II)

| RX | t, °C | $[Pd^{2+}] \cdot 10^3$, M | $[HClO_4]$, M | $k_I^a \cdot 10^2$, $M^{-1}sec^{-1}$ |
|---|---|---|---|---|
| I | 2 | 3 | 4 | 5 |
| | 73.0 | 7.35 | 0.69 | 5.59 |
| | 73.0 | 7.35 | 0.69 | 5.46 |
| | 73.0 | 9.80 | 0.92 | 5.81 |
| | 73.0 | 9.80 | 0.92 | 5.83 |
| | 73.0 | 14.7 | 1.38 | 6.14 |
| MeI | 80.0 | 2.45 | 0.23 | 8.29 |
| | 80.0 | 4.90 | 0.46 | 9.76 |
| | 80.0 | 7.35 | 0.69 | 9.18 |

Table 1 (continued)

|  | | | | |
|---|---|---|---|---|
| Mel | 80.0 | 9.80 | 0.92 | 10.7 |
|  | 80.0 | 14.7 | 1.38 | 11.8 |
|  | 80.0 | 7.35 | 1.58 | 11.9 |
|  | 96.3 | 14.7 | 1.38 | 34.5 |
| EtBr | 73.0 | 14.7 | 1.38 | 0.91 |
|  | 80.0 | 14.7 | 1.38 | 1.73 |
|  | 96.3 | 7.35 | 0.69 | 7.29 |
| EtI | 73.0 | 4.90 | 0.46 | 22.0 |
|  | 73.0 | 7.35 | 0.69 | 24.2 |
|  | 73.0 | 9.80 | 0.92 | 24.6 |
|  | 73.0 | 9.80 | 0.92 | 23.1 |
|  | 80.0 | 14.7 | 1.38 | 51.1 |
|  | 80.0 | 14.7 | 1.38 | 53.5 |
|  | 96.3 | 7.35 | 1.38 | 144 |
| i-PrCl | 73.0 | 7.35 | 0.69 | 7.71 |
|  | 73.0 | 9.80 | 0.92 | 8.06 |
|  | 73.0 | 14.7 | 1.38 | 9.59 |
|  | 80.0 | 7.35 | 0.69 | 18.2 |
|  | 80.0 | 10.8 | 1.01 | 18.3 |
|  | 80.0 | 14.7 | 1.38 | 22.0 |
|  | 80.0 | 7.35 | 1.58 | 21.1 |
|  | 96.3 | 7.35 | 0.69 | 137 |
| i-PrBr | 25.0 | 14.7 | 1.38 | 1.28 |
| i-PrI | 25.0 | 7.35 | 0.69 | 103 |

$^a$ slow increase in $k_I$ with increase in $[HClO_4]$ corresponds to the perchloric acid effect (see Eq.3). The $k^o_I$ values for i-PrBr and i-PrI were obtained by Eq.3, using the values $(B-B^{\neq}) = 0.4$ from Ref. 12

The direct measurements of the hydrolysis rate at $25^o$ and low concentrations of palladium ( $[Pd^{2+}] \leq 0.02$ M) were possible only with the fastest reactions of i-PrBr and

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i-PrI (Table 1). The increase in $Pd^{2+}$ concentration leads to the formation of polynuclear complexes[5]. Therefore $k_I$ for i-PrCl, EtBr, EtI, and MeI were determined by extrapolating the values of rate constants measured at higher temperatures to $25^o$ (Table 1)

On calculation the contribution of the RX reaction with a solvent into the rate observed was taken into account. The procedure of calculation involved also the extrapolation of $k_I$ to zero ionic strength by the linear relationship between $lgk_I$ and the $HClO_4$ concentration[1,6]:

$$lgk_I = lgk_I^o + (B-B^{\neq}) \left[HClO_4\right] \qquad (3)$$

where B and $B^{\neq}$ are salting out coefficients for ground and transition states. It should be noted that the $k_I^o$ values failed to be established for MeCl, MeBr, and EtCl, since with these substrates at high temperatures the reaction rate with a solvent exceeds much that with palladium (II).

The $k_I^o$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ values for the RX reactions with aqua-complexes of palladium (II) at $25^o$ are represented in Table 2. The last two columns list the reaction rate constants of RX with a solvent (taken from Refs. 8 and 9) and the stability constants of monohalide $PdX^+$ complexes. The $lgK_{PdCl^+}$ and $lgK_{PdBr^+}$ values are obtained by extrapolating the data from Ref.11 to zero ionic strength by the Vasiliev equation[10]; the $lgK_{PdI^+}$ value is estimated by the linear correlation between $lgK_{PdX^+}$ and $lgK_{HgX^+}$.

When varying RX, the $k_I$ values increase in the order Me < Et < i-Pr. Activation enthalpy and entropy change into opposite direction. Comparison of the $lgk_I^o$, $lgk_o$, and $lgk_{PdX^+}$ values indicates that the rate behavior, when varying halogen, is unusual for the induced hydrolysis: with transition from isopropyl chloride to isopropyl iodide the $k_I^o/k_o$ ratio increases more than by 3 orders of magnitude, whereas the stability constants of the $PdX^+$ complexes increase by 2 orders of magnitude only. For ions of a non-transition metal, mercury (II), this increase is, for example, 5 and 6 orders of magnitude, respectively.[1] The $RX-Pd^{2+}$ and $RX-Hg^{2+}$

systems manifest their differences more distinctly when
treating the results in the coordinates of Eq.(1):

$$\lg(k_I^o/k_o K_{mx}) - P_R^P X$$

Data for reactions of the substrates studied (R = Me, Et,
and i-Pr; X = Cl, Br, and I) with mercury (II) yield to the
straight line with the slope $P_{Hg}2+$ (see the Fig.). On the
basis of closeness of electron affinity values of the $Pd^{2+}$
and $Hg^{2+}$ ions in the gas phase and presence of the corre-
lation between this affinity and $P_m$ values[12] one could ex-
pect that $P_{Pd}2+ \simeq P_{Hg}2+ = 12.8$ and the data for the reac-
tions

Table 2

The Values of Rate Constants and Activation Parameters
of the Reactions of RX with Aqua-Complexes of Palla-
dium (II) at Zero Ionic Strength and 25°C

| RX | $-\lg k_I^o$ | $\Delta H\neq$ kJ/mol | $\Delta S\neq$ J/mol·degr | $-\lg k_o^a$ | $\lg K_{PdX}{}^b$ |
|---|---|---|---|---|---|
| MeI | 3.56 | 87 | −20 | 7.13 | 7.0[c] |
| EtBr | 4.20 | 88 | −22 | 6.42 | 5.8 |
| EtI | 2.68 | 81 | −21 | 6.82 | 7.0[o] |
| i-PrCl | 4.68 | 82 | 140 | 6.68 | 5.1 |
| i-PrBr | 2.40 | − | − | 5.42 | 5.8 |
| i-PrI | 0.28 | − | − | 5.56 | 7.0[c] |

[a] acc. to Refs. 8,9

[b] acc. to Ref. 11

[c] estimated by the linear correlation between
$\lg K_{PdX}+$ and $\lg K_{HgX}+$

of RX with $Pd^{2+}$ should yield to the same straight line.
However, the reaction rates of RBr and RI with palladium
(II) exceed much those expected from Eq.(1) and the values
$P_{Pd}2+ = 12.8$. Data for the RX-$Pd^{2+}$ system form three lines
whose slope decreases with the transition from chlorides
to bromides and iodides (12.8:10:6.5, respectively).

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Assuming that characteristics of the i-PrCl-Pd$^{2+}$ system correspond to the normal ones for M$^+$-S$_{N}$2 interactions, deviations from this interaction (leading to the observed increase in the rate) should be considered to increase in the order Cl < Br < I.

It is of interest that the data for various R at X = Br or I yield to the same straight lines (the Fig.). Thus, formally Eq.(1) works, but one should assume that either the $P_{Pd^{2+}}$ parameter depends on the halogen nature, or the $P_X$ parameters in the case of interaction of RX with palladium complexes differ from those in the case of interaction of alkyl halides with complexes of non-transition metals. It is difficult to say whether these deviations result from the manifestation of new RX activation mechanisms (the possibility of their realization was assumed in Refs. 13 and 12), or Eq. (1) does not describe all the interaction peculiarities corresponding to the M$^+$-S$_{N}$2 model of the transition state: H$_2$O... R  ...  X ... M$^+$ and this incomplete description manifested itself with



Fig. Correlation between $\lg(k_I^o/k_o K_{mx})$ values and the product of the $P_R P_X$ parameters for the RX-Hg$^{2+}$(● - data from Ref. 12) and RX-Pd$^{2+}$(○) systems.

transition to palladium d$^8$-complexes. Further study of these problems is called for.

### Experimental

The kinetics was studied by the GLC method[1] by decrease in RX under conditions of substrate equilibrium distribution between the gas and the solution. The values of distribution coefficients $\alpha = [RX]^g / [RX]^s$, needed to calculate true rate constants (see Ref. 16) were measured directly by

the method[17] and are in satisfactory agreement (Table 3)
with the data obtained kinetically[16]. The mean solvation
heat of alkyl halides estimated by the data obtained is
25 kJ/mol.

The $Pd^{2+}$ solutions were prepared by dissolving freshly
prepared palladium (II) hydroxide in $HClO_4$ ("Pure" grade).
Spectrum of the solutions corresponded to that of aqua-
palladium (II)[11].

Table 3

Values of Distribution Coefficients of RX
($\alpha = [RX]^g / [RX]^s$) in Water

| RX | t, $^oC$ | $[HClO_4]$, M | $\alpha$ |
|---|---|---|---|
| MeI | 25.0 | 0.00 | 0.23[a] |
| MeI | 73,0 | 0.69 | 0.89 |
| MeI | 73.0 | 1.38 | 0.83 |
| MeI | 80.0 | 0.69 | 1.10 |
| MeI | 80.0 | 1.00 | 0.68[b] |
| EtBr | 25.0 | 0.00 | 0.32[a] |
| EtBr | 73.0 | 1.38 | 1.14 |
| EtBr | 80.0 | 1.38 | 1.60 |
| EtBr | 80.0 | 0.50 | 1.66[b] |
| EtI | 25.0 | 0.00 | 0.32[a] |
| EtI | 73.0 | 0.69 | 0.91 |
| EtI | 73.0 | 1.38 | 0.86 |
| EtI | 80.0 | 1.78 | 1.38 |
| i-PrCl | 25.0 | 0.00 | 0.69 |
| i-PrCl | 73.0 | 0.69 | 3.16 |
| i-PrCl | 73.0 | 0.92 | 3.03 |
| i-PrCl | 73.0 | 1.38 | 2.77 |
| i-PrCl | 80.0 | 0.00 | 4.60 |
| i-PrCl | 80.0 | 0.69 | 4.36 |
| i-PrCl | 80.0 | 1.01 | 3.94 |
| i-PrCl | 80.0 | 1.38 | 3.47 |
| i-PrBr | 25.0 | 1.38 | 0.30 |
| i-PrI | 25.0 | 0.00 | 0.47[a] |

[a] Taken from Ref. 12

[b] Calculated on the basis of kinetic runs at various gas and liquid ratios (v/v) in the reactor (see Ref.1).

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# COMPARISON OF THE SCALES OF BASICITIES $B_{PhOH}$ AND DONOR NUMBERS DN

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The calorimetric basicity scale of Gutmann do-
nor numbers and spectral basicity of Koppel–Palm,
$B_{PhOH}$, are shown to be interconnected by the equa-
tion: $DN = 8.200 + 0.0876B - 35.734 \dfrac{n^2-I}{n^2+2}$ ;
$R = 0.974$; $s = 3.32$.

When considering the solvation effects, the basicity of
solvents is one of the most important characteristics. The
scale widely used in the literature is that of Gutmann do-
nor number DN[I] based on estimating mixing heats of solvents
with the strong acceptor $SbCl_5$. However, this scale involves
a small number of substances only. The Koppel–Paju scale of
basicities, $B_{PhOH}$[2], based on the optical shift of phenol OH
in its IR-spectrum in the presence of the corresponding sol-
vents contains much more substances (about 200). In the same
paper the authors show the equivalence of the above scale
with a number of other scales based on optical measurements,
in particular with the scale based on the shift of OD band
of deuteromethanole $CH_3OD$[3].

In the recent paper[4] we showed that the Gutmann calori-
metric scale of basicities and the Koppel–Palm spectral
scale are equivalent and there is a linear dependence with
$R = 0.857$ between them and between the DN and $B_{OH_3OD}$ values
($R = 0.959$).

In the past years new data on DN values including the
values for such strong bases as amines have appeared. There-
fore it is expedient to recalculate the correlation between

the DN and $B_{PhOH}$ values, using the new data. Since the non-specific solvation influences the kinetic and spectral phenomena which occur in the solution, it was interesting to compare the above scales including the possible influence of the nonspecific solvation, using the linear polyparameter equation.

Table I lists the donor numbers, DN, of solvents according to Gutmann[I] and other supplementary sources, the basicities according to Koppel-Palm-Paju[2] and the parameters of nonspecific solvation: polarity (acc. to Kirkwood) $\frac{\delta-I}{2\delta+I}$, polarizability $\frac{n^2-I}{n^2+2}$, and cohesion energy density $\delta^2 = \frac{\Delta H_{vap}-RT}{V}$. The calculation were carried out on a "Mir-2" computer.

There is a satisfactory linear dependence (R=0.958) between DN and B. Further the worst data for ammonia (point N°40) are excluded from the consideration. For remained 40 solvents the following dependence has been obtained:

$$DN = -0.687 + 0.0877B; \quad R=0.970; \quad s=3.48$$

With the use of the four-parameter equation the correlation coefficient R increases insignificantly:

$$DN = 7.377 + 0.0879B - 1.701 \frac{n^2-1}{n^2+2} - 32.840 \frac{\delta-1}{2\delta+1} + 5.976 \delta^2; \quad R=0.974; \quad s=3.384.$$

The influence of the polarity and cohesion energy density parameters is negligible. When excluding these parameters the correlation does not become worse and, as a result, the dependence between DN and B may be well described by the two-parameter equation:

$$DN = 8.200 + 0.0876B - 35.734 \frac{n^2-1}{n^2+2}; \quad R=0.973; \quad s=3.32$$

Hence, the calorimetric (DN) and spectral (B) basicity scales are equivalent. The polarizability term which corresponds to the nonspecific solvation of substances is of relatively little importance. The proposed correlation may

Table I
## SOLVENT DONOR NUMBERS AND CHARACTERISTICS

| $N^{o}$ | Solvent | DN | B | $\dfrac{\varepsilon - 1}{2\varepsilon + 1}$ | $\dfrac{n^2 - 1}{n^2 + 2}$ | $\delta^2$ |
|---|---|---|---|---|---|---|
| 1. | n-Hexane | 0 | 0 | 0.185 | 0.2289 | 0.054 |
| 2. | CCl$_4$ | 0 | 0 | 0.225 | 0.2742 | 0.076 |
| 3. | Dichloroethane | 0.1 | 40 | 0.431 | 0.2661 | 0.108 |
| 4. | Benzene | 0.1[5] | 48 | 0.231 | 0.2947 | 0.085 |
| 5. | Nitromethane | 2.7 | 63 | 0.481 | 0.2386 | 0.167 |
| 6. | Nitrobenzene | 4.4 | 67 | 0.479 | 0.3215 | 0.113 |
| 7. | Acetic anhydride | 10.5[5] | 100 | 0.465 | 0.2371 | 0.141 |
| 8. | Benzonitrile | 11.9 | 155 | 0.471 | 0.3084 | 0.123 |
| 9. | Ethylchloroacetate | 12.8[7] | 125 | 0.463 | 0.2545 | 0.096 |
| 10. | Acetonitrile | 14.1 | 160 | 0.480 | 0.2106 | 0.140 |
| 11. | Sulfolane | 14.8 | 157 | 0.483 | 0.2849 | 0.133 |
| 12. | Dioxane | 14.8[5] | 237 | 0.223 | 0.2543 | 0.110 |
| 13. | Butyronitrile | 15.4 | 166 | 0.464 | 0.2339 | 0.111 |
| 14. | Diethylcarbonate | 16.0 | 145 | 0.274 | 0.2341 | 0.079 |
| 15. | Propionitrile | 16.1 | 162 | 0.474 | 0.2237 | 0.105 |
| 16. | Methylpropionate | 16.2[7] | 174 | 0.376 | 0.2300 | 0.076 |
| 17. | Methylacetate | 16.5 | 170 | 0.395 | 0.2218 | 0.091 |
| 18. | Ethylpropionate | 16.8[3] | 174 | 0.387 | 0.2338 | 0.072 |
| 19. | Acetone | 17.0 | 224 | 0.465 | 0.2201 | 0.095 |
| 20. | Ethylacetate | 17.1 | 181 | 0.374 | 0.2275 | 0.082 |
| 21. | Methylethylketone | 17.4[7] | 209 | 0.461 | 0.2309 | 0.084 |
| 22. | Cyclohexanone | 17.8[7] | 242 | 0.461 | 0.2699 | 0.104 |
| 23. | Diisopropyl ether | 17.8 | 279 | 0.329 | 0.2256 | 0.052 |
| 24. | Water | 18.0 | 156 | 0.494 | 0.2057 | 0.592 |
| 25. | Diethyl ether | 19.2 | 280 | 0.345 | 0.2167 | 0.057 |
| 26. | Methanol | 18.9[8] | 218 | 0.478 | 0.2034 | 0.201 |
| 27. | Ethanol | 19.2[8] | 235 | 0.461 | 0.2214 | 0.167 |
| 28. | Butanol | 19.5[8] | 231 | 0.458 | 0.2421 | 0.108 |
| 29. | Tetrahydrofurane | 20.0 | 287 | 0.404 | 0.2451 | 0.076 |
| 30. | Diglyme | 24.0 | 238 | 0.400 | 0.2315 | 0.091 |
| 31. | Tributylphosphate | 23.7 | 283 | 0.397 | 0.2555 | 0.040 |

Table I (continued)

| $N^o$ | Solvent | DN | B | $\dfrac{\varepsilon-1}{2\varepsilon+1}$ | $\dfrac{n^2-1}{n^2+2}$ | $\delta^2$ |
|---|---|---|---|---|---|---|
| 32. | Dimethylformamide | 26.6 | 291 | 0.488 | 0.2584 | 0.198 |
| 33. | N-methylpyrrolidone | 27.3[5] | 319 | 0.488 | 0.2773 | 0.121 |
| 34. | Dimethylacetamide | 27.8 | 343 | 0.481 | 0.2627 | 0.199 |
| 35. | Dimethylsulfoxide | 29.8 | 362 | 0.485 | 0.2826 | 0.225 |
| 36. | Pyridine | 33.1 | 472 | 0.441 | 0.2989 | 0.104 |
| 37. | $(Me_2N)_3PO$ | 38.8 | 471 | 0.475 | 0.2730 | 0.096 |
| 38. | Ethylamine | 55.5[5] | 667 | 0.388 | 0.2265* | 0.086 |
| 39. | Isobutylamine | 57.0[5] | 537** | 0.347 | 0.2388 | 0.066 |
| 40. | $NH_3$ | 59.0[5] | 473 | 0.457 | 0.2012 | 0.212 |
| 41. | Triethylamine | 61.0 | 650 | 0.243 | 0.2430 | 0.051 |

Notes: All the values of DN are taken from Ref.[1] excluding the data especially remarked.

* ) $n_D$ value was calculated by means of additive refraction scheme

** ) We use the value of B for n-Butylamine

be useful for mutual conversion of both scales and for wider interpretation of the literature data about solvent effects on the kinetic and spectral characteristics of solutes.

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# IR SPECTRA AND ACID-BASE PROPERTIES OF SUBSTITUTED AMIDES OF 2-AMINO-1,3,4-TIADIAZOL-5-SULFONYLOXAMINE ACID

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Synthesis of substituted amides of 2-amino-1, 3,4-tiadiazol-5-sulfonyloxamine acides is carried out. For the obtained compounds IR spectrograms are taken and interpreted, acid-base equilibria in 60% aqueous dioxane and 70% aqueous dimethylsulfoxide being studied by the method of potentiometric titration. Correlation of pKa and stretching frequencies of the CO and $SO_2$ groups with the Hammett $\sigma$ constants is carried out. The mechanism of substituent effect transfer to the reaction center is discussed.

Continuing the study of the relationship between the structure and properties of sulfamide derivatives of oxamine acids [1-4], substituted amides of 2-amino-1,3,4-tiadiazol-5-sulfonyloxamine acid were obtained. Synthesis of the above mentioned compounds was carried out by the reaction of acylation of the sodium salt of 2-amino-1,3,4-tiadiazol-5-sulfamide with ethers of N-R substituted oxamine acid.

The synthesized compounds are colorless substances easily soluble in aqueous solutions of alkali, ammonia and organic solvents. Identification of the obtained compounds was done by the data of elemental analysis and IR spectroscopy (see the Table).

In the IR spectrograms of the obtained sub-

ACID—BASE AND SPECTRAL CHARACTERISTICS OF SUBSTITUTED
AMIDES OF 2-AMINO-1,3,4-TIADIAZOL-5-SULFONYLOXAMINE ACID

$$H_2N \overset{N-N}{\underset{S}{||}} SO_2NHCOCONHR \qquad (I)$$
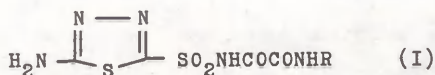
| Nos. of comp. | R | $pKa_1$ in 60% aqueous dioxane | $pKa_2$ in 70% aqueous DMSO | IR spectra, $cm^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | $\nu_{NH}$ | $\nu_{CO}$ | $\nu^{as}_{SO_2}$ | $\nu^{s}_{SO_2}$ |
| 1 | $C_6H_5$ | 6.84 | 3.85 | 3340, 3245 | 1690 | 1368 | 1193 |
| 2 | $C_6H_4CH_3-m$ | 6.56 | 3.90 | 3330, 3265 | 1692 | 1365 | 1180 |
| 3 | $C_6H_4CH_3O-p$ | 7.15 | 3.90 | 3365, 3290 | 1705 | 1372 | 1180 |
| 4 | $C_6H_4OCH_3-m$ | 6.52 | 3.81 | 3325, 3268 | 1690 | 1358 | 1180 |
| 5 | $C_6H_4Cl-m$ | 6.57 | 3.80 | 3330, 3270 | 1690 | 1360 | 1180 |
| 6 | $C_6H_4Br-p$ | 6.56 | 3.78 | 3330, 3265 | 1685 | 1365 | 1180 |
| 7 | $C_6H_4Br-m$ | 6.64 | 3.75 | 3330, 3250 | 1690 | 1365 | 1185 |
| 8 | $C_6H_4J-p$ | 6.63 | 3.72 | 3355, 3275 | 1680 | 1358 | 1179 |
| 9 | $C_6H_4NO_2-p$ | 6.16 | 3.65 | 3315, 3288 | 1668 | 1352 | 1180 |

stances there are bands of valent oscillations of the NH group in the region of 3200-3400 cm$^{-1}$. The valent oscillations of the sulfonyl group are represented by two bands: $V_{SO_2}^{as}$ (1350-1370 cm$^{-1}$) and $V_{SO_2}^{s}$ (1170-1190 cm$^{-1}$). Carbonyl group is characterized by one absorption band (1680-1710 cm$^{-1}$), which indicates the translocation of the CO group [5].

Presence of a protonated hydrogen atom in the salfamide group in heterylsulfonyloxamides (I) and also translocation of the CO group of a sulfamide residue favors the formation of intramolecular hydrogen bonds (IHB), providing thus substituent electron effect transfers in the molecules of amides (I):



(I)
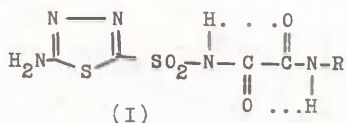
Substituent electron effect transfers to the reaction centers may be effected also through the system of conjugated bonds, which in the structure of oxamides (I) can be presented in the following way:



(II)
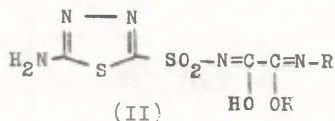
IR analysis of the compounds studied enabled to detect the influence of the substituent nature in the benzene ring of oxamides (I) upon the stretching frequencies of the CO and SO$_2$ groups. The correlation relationships of $V_{CO}$ and $V_{SO_2}^{as}$ with the Hammett $\sigma$ constants are:

$$V_{CO} = 1693 - 35.7 \cdot \sigma \quad (r = 0.986; \quad S_f = 3.3)$$

$$V_{SO_2}^{as} = 1369 - 17.8 \cdot \sigma \quad (r = 0.991; \quad S_p = 1.8)$$

(included into correlation are the values of the stretching frequencies of amides (I) with para substituents in the

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benzene ring).

For the synthesized compounds the acidic and basic equilibria were also studied by the method of potentiometric titration. The process of acidic and basic dissociation of compounds (I) can be presented by the following scheme:

$$H_2N \overset{N-N}{\underset{S}{\bigsqcup}} SO_2NHCOCONHR + H_2O \overset{pKa_1}{\rightleftharpoons} H_2N \overset{N-N}{\underset{S}{\bigsqcup}} SO_2\bar{N}COCONHR + H_3O^+$$

$$H_3\overset{+}{N} \overset{N-N}{\underset{S}{\bigsqcup}} SO_2NHCOCONHR + H_2O \overset{pKa_2}{\rightleftharpoons} H_2N \overset{N-N}{\underset{S}{\bigsqcup}} SO_2NHCOCONHR + H_3O^+$$
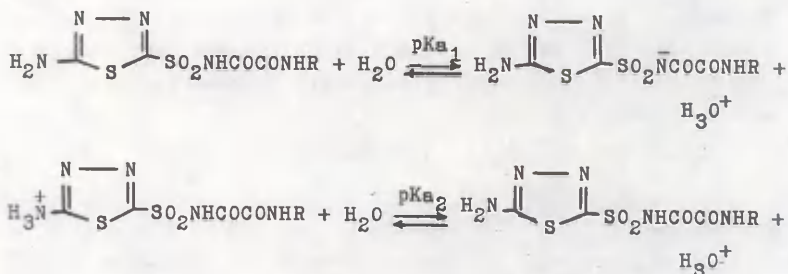
The constants of acidic dissociation ($pKa_1$) determined in 60% aqueous dioxane and those of basic dissociation ($pKa_2$) in 70% aqueous DMSO are presented in the Table.

As seen from the data of the Table, the nature of the radicals bound with amide nitrogen of the oxamoyl residue influences the acceptor properties of both the sulfonyl and carbonyl groups, which manifests itself by changes in the dissociation constants of amides (I) whose acidity increases with introducing electron acceptor and decreases with introducing electron donor substituents. Comparing the acidic properties of substituted aryl amides of benzenesulfonyloxamides [1] and heteryloxamides (I), one can note that the latter have considerably lower acidity, which results from the donor properties of tiadiazol residue.

Oxamides (I) with meta substituents in the benzene ring are characterized by approximately equal acidity (for $pKa_1$ of compounds 2, 4, 5, 7 see the Table). This is due to the fact that in the solutions of heteryloxamides (I) the substituent effect transfer is, probably, effected through the system of conjugated bonds (structure II) and meta substituents which are not included into the conjuga-

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tion system influence insignificantly on the acidity of the sulfamide group.

The basic dissociation constants $(pKa_2)$ of the compounds under study change negligibly, depending on the nature of a radical in the benzene ring, which is accounted for by its remoteness from the reaction center. Quantitative estimation of substituent effects on the acidity of the sulfamide group was carried out by the Hammett equation. The obtained correlation relationship between the $pKa_1$ values and Hammett $\sigma$ is:

$$pKa_1 = 6.79 - 0.79 \cdot \sigma \quad (r = 0.988; \quad s_0 = 0.062).$$

## Experimental

IR spectrograms were taken with UR-20 spectrometer in KBr (concentration of the substance was 0.5%).

The dissociation constants were determined by the method of potentiometric titration with pH meter pH-340 with glass and chlorine-silver electrodes in 60% aqueous dioxane $(pKa_1)$ and 70% aqueous DMSO. The pKa values were calculated as pH in the point of 50% neutralization.

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# STUDY OF $S_N 1$ REACTIONS, USING TRIPHENYLVERDAZYLS.
## I. KINETICS OF DIPHENYLMETHYL BROMIDE IONIZATION IN ACETONITRILE

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Kinetics of $Ph_2CHBr$ ionization in $CH_3CN$ was studied spectrophotometrically by the decrease in triphenylverdazyl ($RN^\cdot$) concentration and the increase in the concentration of triphenylverdazylium bromide ($RN^+Br^-$), $-d[RN^\cdot]/2dt = d[RN^+Br^-]/dt = k_1[Ph_2CHBr]$ . Linear increase in the reaction rate with the increase in water concentration was observed, the reaction order on water being 0.35. The formation of $Ph_2CH^+Br^-$ ion pair was assumed to occur at the rate-determining step followed by further fast reactions with water ($Ph_2CHOH$ and HBr formation) and $RN^\cdot$ (the formation of 1,2,5,6-tetrahydro-1,3,5-triphenyl-2-diphenylmethyl-1,2,4,5-tetrazine and $RN^+Br^-$).HBr formed at this step reacts fast and quantitatively with $RN^\cdot$ to give $RN^+Br^-$ and leucoverdazyl. At the rate-determining step of $Ph_2CHBr$ ionization the more polar transition state over that on t-BuBr ionization is formed. It has been concluded that triphenylverdazyls can be used as an ion pair indicator.

Diphenylmethyl halide alongside with t-butyl halides constitute principal objects in the studies of kinetics and mechanisms of carbon-halogen bond ionization (monomolecular solvolysis, $S_N 1$ and E1 reactions) [1,2] . Data provided by such studies contribute considerably into the theory of organic transformations.Many aspects of monomolecular solvolysis mechanisms were clarified when studying diphenylmethyl

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halide ionization in protic solvents and their mixtures with various aprotic solvents [1-3]. Under such conditions, however, the reaction monomolecularity is of formal character. Thus, it is assumed that $Ph_2CHBr$ solvolysis in alcohols [4] proceeds via the combined mechanism ($S_N1 + S_N2$), whereas in benzene alkohol mixtures [5] it occurs via the trimolecular mechanism ($v=k[Ph_2CHBr]\cdot[ROH]^2$). The study of the first order reactions with no solvolysis involved ($S_N1$) gives a more definite information. Such data are obtained when studying nucleophilic substitutions in aprotic solvents. In the case of diphenylmethyl halides (mainly $Ph_2CHCl$) information is available on the reactions in liquid $SO_2$ [1], DMF and DMSO [6], acetone [7,8] and acetonitrile [8,10]. Basically, the Finkelstein reaction has been studied and, as a rule, a combined mechanism ($S_N1 + S_N2$) has been assumed. The rate of $Ph_2CHCl$ reaction with PhOK in acetonitrile is described by the monomolecular kinetic equation ($v=k_1\cdot[Ph_2CHCl]$), whereas that of the reaction with $Bu_3N$ and 2,6-ditert.butyl-4-methylphenate is expressed by a bimolecular one [9]. In the latter case the electron transfer between a nucleophile and $Ph_2CH^+Cl^-$ ion pair is observed at the rate determining step.

Not without reason it has been suggested in Ref. [10] that "the mechanism of $S_N1$ reaction is very complicated". This can be applied, first of all, to diphenylmethyl halides. Nucleophilic substitution in $Ph_2CHX$ has received little study and the literature data available are of indefinite ($S_N1 + S_N2$ or $S_N1$ + salt effect?) [6,8] and contradicting [1,6,7] nature. Further study of kinetics and mechanism of these reactions is hampered by the lack of effective controlling means for $Ph_2CHX$ ionization rate.

Nucleophilic substitution rate in $Ph_2CHX$ is usually controlled by titrimetric [3], radioisotopic [6,8], spectroscopic (at $\lambda_{max}$ $Ph_2CHX$) [10] and n.m.r. [11] methods. As a rule these methods require greater degrees of substrate conversion ( > 20 %), radioisotopic methods being the only exception (about 4%). Kinetic study of these reactions with

considerable degrees of substrate conversion hinders the investigation of salt effects.

The purpose of the authors was to study diphenylmethyl halides ionization kinetics in aprotic organic solvents using triphenylverdazyl radicals as internal indicators. Recently [12] these radicals were used to control the ionization rate of t-butyl halides (E1 reaction). In this case hydrohalide eliminated at the rate-determining step[*] reacts fast and quantitatively with triphenylverdazyl ($RN^{\cdot}$, in acetonitrile, $\lambda_{max.}$ 720 nm, $\varepsilon = 4330$) forming equal amounts of triphenylverdazylium salt ($RN^{+}X^{-}$, $\lambda_{max.}$ 540 nm, $\varepsilon = 12170$) and leucoverdazyl ($RNH$, $\lambda_{max.}$ 280 nm).

$$(CH_3)_3CX \rightleftharpoons (CH_3)_3C^{+}X^{-} \longrightarrow (CH_3)_2C = CH_2 + HX \qquad (1)$$



$$HX + 2 \qquad \longrightarrow \qquad + \qquad \qquad (2)$$
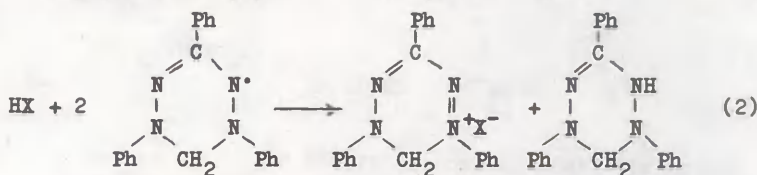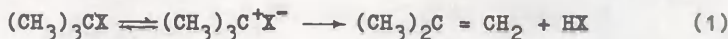
Additions of $RN^{\cdot}$, $RN^{+}X^{-}$ and $RNH$ have no effect on the reaction rate (1). The ionization rate is controlled spectrophotometrically by $RN^{\cdot}$ and $RN^{+}X^{-}$ absorption. Under these conditions

$$- \frac{d[RN^{\cdot}]}{2dt} = \frac{d[RN^{+}X^{-}]}{dt} = k_1 [t\text{-BuX}] \qquad (3)$$

Application of this method provided a means for thorough investigating ionization kinetics of t-BuX in various aprotic solvents [12,13].

This communication represents the information on $Ph_2CHBr$ ionization kinetics in acetonitrile.

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[*] Intimate ion pair formation.

## RESULTS AND DISCUSSION

The product study and kinetic experiments were performed in $CH_3CN$, containing about $4.5 \cdot 10^{-2}$ M or more of water. Some kinetic tests were carried out in anhydrous acetonitrile.

On addition of triphenylverdazyl to $Ph_2CHBr$ solution in moist $CH_3CN$ the following reactions may be expected to occur:

$$\begin{Bmatrix} Ph_2CHBr \\ \updownarrow \\ Ph_2CH^+Br^- \end{Bmatrix}$$

$$\xrightarrow{H_2O} Ph_2CHOH + HBr \xrightarrow{2RN^\cdot} RN^+Br^- + RNH \qquad (4a)$$

$$\xrightarrow{2RN^\cdot} RN^+Br^- + RN - CHPh_2 \qquad (4b)$$

$$\xrightarrow{2RN^\cdot} RN^+Br^- + RNH + Ph_2C: \begin{cases} \xrightarrow{O_2} Ph_2C=O \\ \rightarrow Ph_2C=CPh_2 \end{cases} \qquad (4c)$$

$$\xrightarrow{RN^\cdot} RN^+Br^- + Ph_2CH^\cdot \begin{cases} \rightarrow Ph_2CHCHPh_2 \\ \xrightarrow{RN^\cdot} RN-CHPh_2 \end{cases} \qquad (4d)$$
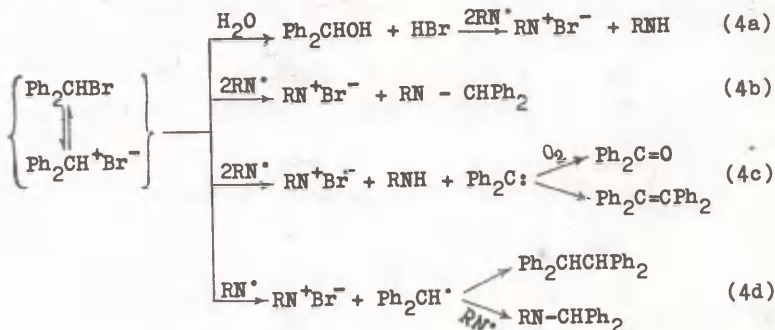
Hydrolysis (4a) may proceed either by the mechanism of $S_N1$ (interaction with $Ph_2CH^+Br^-$) or by that of $S_N2$ (interaction with $Ph_2CHBr$). The literature data available are conflicting [1,14]. HBr formed in this reaction reacts ae shown by Eq. (2).

The interaction of two radical molecules with one $Ph_2CH^+Br^-$ molecule may lead either to the formation of a verdazylium salt and 1,2,5,6-tetrahydro-1,3,5-triphenyl-2-diphenylmethyl-1,2-tetrazine ($RN-CHPh_2$) (reaction 4b) or to the formation of $RN^+Br^-$, RNH and diphenylcarbene (1,1-elimination) (reaction 4c). HBr elimination from a non-ionized $Ph_2CHBr$ molecule is also likely to occur. Diphenylcarben formed in the reaction should convert into $Ph_2C=O$, tetraphenylethylene and tetraphenylethane [15]. During $RN^\cdot$ and $Ph_2CH^+Br^-$ interaction one may also observe the electron transfer from the radical to the ion pair which yields $RN^+Br^-$ and diphenylmethyl radical (reaction 4d), the latter in such a case will either be dimerized up to $Ph_2CHCHPh_2$ or recombine with $RN^\cdot$ to give $RN-CHPh_2$. Ion pair $Ph_2CH^+Cl^-$ ($Br^-$) is known to form $Ph_2CH^\cdot$ in

the reaction with sterically hindered nucleophiles[9]. This comparison is warrantable,since triphenylverdazyl is a strong electron donor with sterically screened reaction center [16].

The authors have found that in all cases 1 mole of tri-phenylverdazyl radical reacting with $Ph_2CHBr$ yields 0.5 mole of $RN^+Br^-$(proved spectroscopically). Other products of this reaction are $RN-CHPh_2$ (shown by spectroscopy, by quantitative conversion to $RN^+$ under the action of a mineral acid and by the melting point of the mixed sample), leucoverdazyl (izolated as hydrobromides) and $Ph_2CHOH$ (IR-spectrum). $Ph_2CO$ (IR-spectrum), $Ph_2C=CPh_2$ and $Ph_2CHCHPh_2$ were not detected in the reaction mixture. This suggests that in the above case reactions 4a and 4b should be observed rather than 4c and 4d. Kinetic data confirm this conclusion.

Fig.1 gives a number of typical kinetic curves. Descending curves show $RN^\cdot$ concentration change in the test, whereas ascending ones indicate the change in $RN^+Br^-$ concentration[*]. With $Ph_2CHBr$ being about 50 times in excess over $RN^\cdot$ the reaction rate in each individual test is satisfactorily described by the kinetic equation of zero order

$$- \frac{d[RN^\cdot]}{2dt} = \frac{d[RN^+Br^-]}{dt} = k_o \qquad (5)$$

Indeed the slope of the curves shown in Fig.1 is independent of $RN^\cdot$ concentration (tests 6,8,9), whereas radical and ver-dazylium salt concentration varies with time linearly until $RN^+Br^-$ concentration reaches app. $2 \cdot 10^{-5}$ M. Further the reaction proceeds with lower rate and the variations in $RN^\cdot$ and $RN^+Br^-$ concentration become curvilinear (test 11).This seems to be a manifestation of $RN^+Br^-$ salt effect[**]. Calculations were performed by the least squares method in the linear sections of the kinetic curves.

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[*] "Jump" of $RN^\cdot(RN^+Br^-)$ concentration at the beginning of the test seems likely to be attributed to the fast reaction of $RN^\cdot$ with $Ph_2CH^+Br^-$ and HBr formed prior to the measurements.

[**] Salt effects in this reaction will be treated separately in the further communication.
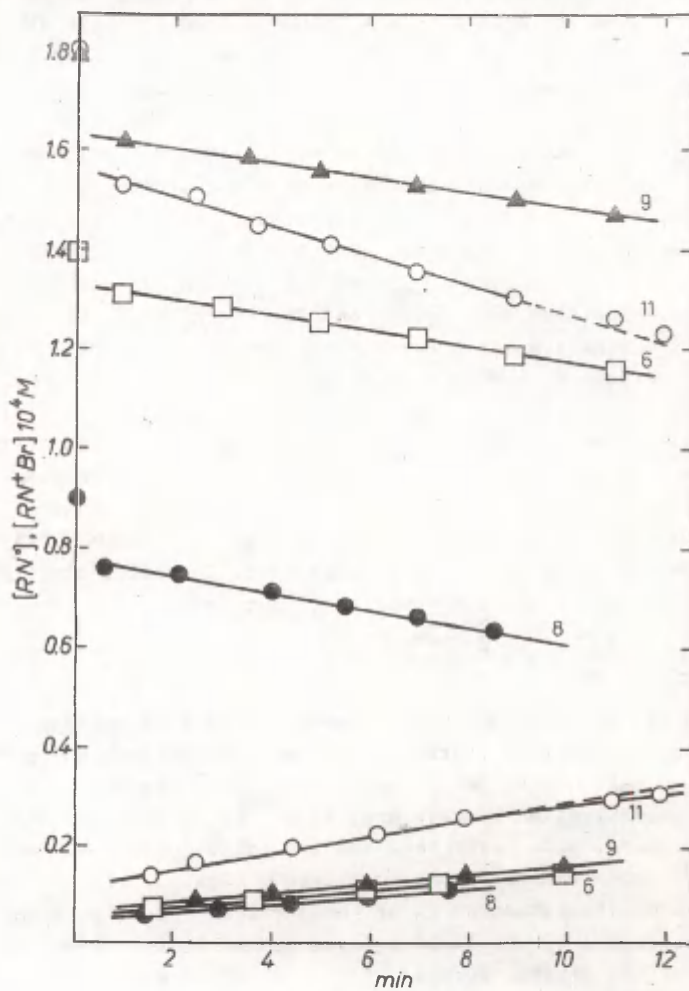
Fig.1. The kinetics of $Ph_2CHBr$ ionization in aceto-nitrile

Tests performed at various concentrations of $Ph_2CHBr$ (Table 1, Fig.1, tests 9,11) show that the reaction rate is described by the first order kinetic equation.

$$-\frac{d[RN^{\cdot}]}{2dt} = \frac{d[RN^+Br^-]}{dt} = k_1[Ph_2CHBr] \qquad (6)$$

Conditions and results of kinetic tests in moist $CH_3CN$ (about $4.5 \cdot 10^{-2}$ M of water) are given in Table 1. The Table shows that the reaction rate control by $RN^{\cdot}$ consumption or $RN^+Br^-$ formation results in satisfactory correlation of $k_1$ values (see columns 5 and 6 of the Table). Parallel tests show good agreement(tests 4 to 7). Reaction rate is satis- factorily described by equation (6) and is independent of the concentration and nature of the radical used (tests 4-11 and 17,18). This suggests that the radical should undergo the reaction after the rate-determining step.

$Ph_2CHBr$ conversion in the above tests was about 0.1 %.

At its rate-determining step the reaction may proceed through the interaction of $Ph_2CHBr$ with water and/or through the formation of $Ph_2CH^+Br^-$ ion pair which then rapidly re- acts with the radical and water.To elucidate this problem the water effect has been studied thoroughly. Linear in- crease in the reaction rate with the increase in water con- centration in the solution was observed (see Fig.2).
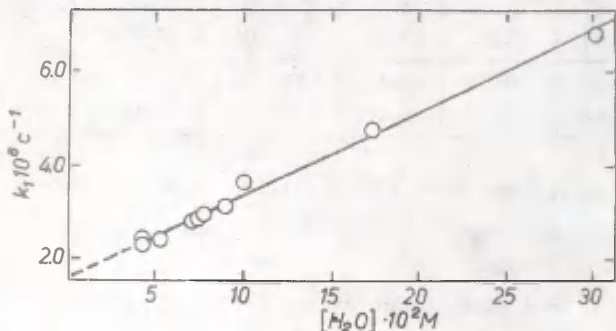


Fig.2. Water effect on the ionization rate of $Ph_2CHBr$ in $CH_3CN$.

Table 1

Kinetics of $Ph_2CHBr$ Ionization in Moist $CH_3CN$[e] in the
Presence of Triphenylverdazyl Radicals

| Nos. | $[RN°]·10^4 M$ | $[Ph_2CHBr]·10^3 M$ | $°C$ | $10^6·k_1$ $s^{-1}$ [d] as RN° | as $RN^+Br^-$ | $10^6 k_{1 aver.}$ $s^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 1.43 | 10.3 | 13.0 | 0.68 | 0.68 | 0.68 |
| 2 | 1.73 | 9.30 | 17.0 | 1.11±0.01 | 1.18±0.02 | 1.10±0.04 |
| 3 | 1.73 | 9.41 | 17.0 | 1.08±0.10 | 1.15±0.04 | |
| 4 | 1.01 | 5.77 | 25.0 | 2.44 | 2.35 | |
| 5 | 1.01 | 5.77 | 25.0 | 2.43 | 2.44 | |
| 6 | 1.34 | 5.07 | 25.0 | 2.49 | 2.51 | |
| 7 | 1.34 | 5.07 | 25.0 | 2.49 | 2.51 | |
| 8 | 0.901 | 5.13 | 25.0 | 2.61±0.01 | 2.64±0.04 | 2.5±0.06 |
| 9 | 1.80 | 5.16 | 25.0 | 2.54±0.04 | 2.63±0.01 | |
| 10 | 1.85 | 5.02 | 25.0 | 2.37±0.02 | 2.49±0.05 | |
| 11 | 1.80 | 10.02 | 25.0 | 2.50±0.02 | 2.59±0.13 | |
| 12 | 1.29 | 3.38 | 30.5 | 3.62±0.02 | 3.80±0.04 | |
| 13 | 1.31 | 3.07 | 30.5 | 3.81±0.06 | 3.90±0.01 | 3.67±0.11 |
| 14 | 1.31 | 3.50 | 30.5 | 3.50±0.02 | 3.79±0.02 | |
| 15 | 1.87 | 4.84 | 33.8 | 5.33±0.05 | 5.40±0.02 | 5.35±0.05 |
| 16 | 1.87 | 4.84 | 33.8 | 5.38±0.01 | 5.33±0.05 | |
| 17[b] | 1.96 | 5.16 | 25.0 | 2.55±0.03 | - | |
| 18[c] | 1.64 | 5.02 | 25.0 | 2.46±0.01 | 2.49±0.01 | |

a) Acetonitrile continued $(4.5±0.5)·10^{-2}$ M of water.

b) The test was carried out with 1,5-diphenyl-3-(4-nitro-phenyl)-verdazyl.

c) The test was carried out with 1,5-diphenyl-3-(4-methoxy-phenyl)-verdazyl.

d) Values of constants were calculated from two parallel tests.

Fig.2 shows also the water content in initial $CH_3CN$. Extrapolation of the straight line in Fig.2 to zero water content gives $k_1 = (1.67 \pm 0.14) \cdot 10^{-6}$ $s^{-1}$ (the least squares method). The reaction order is 0.35 on water.

Table 2 lists the results and conditions for kinetic tests performed in anhydrous acetonitrile ($CaH_2$ treatment[*]). The reaction rate was monitored by the $RN^{\cdot}$ consumption. In all cases the reaction rate is described by Eq.(6) well.

Table 2

Kinetics of $Ph_2CHBr$ Ionization of Anhydrous $CH_3CN$ in the Presence of Triphenylverdazyl.

| $[RN^{\cdot}] \cdot 10^4$ M | $[Ph_2CHBr] \cdot 10^3$ M | $10^6 \cdot k_1$ [*] $s^{-1}$ (on $RN^{\cdot}$) |
|---|---|---|
| 1.25 | 6.32 | $1.98 \pm 0.13$ |
| 1.28 | 6.07 | $1.69 \pm 0.15$ |
| 1.55 | 9.89 | $1.90 \pm 0.1$ |
| 1.55 | 8.42 | $1.88 \pm 0.03$ |
| | | aver. $1.86 \pm 0.1$ |

[*] mean of 2-3 runs.

Satisfactory agreement of $k_1$ values is observed and the the mean $k_1$ value in anhydrous $CH_3CN$ ($1.86 \pm 0.1$) practically coinsides with $k_1$ value found by extrapolation from Fig.2. This indicates that $Ph_2CHBr$ ionization may also occur in the absence of water, the latter gives only small increase in the rate with the reaction order on water being much less than unity. All said above gives evidence to the fact, that at the rate-determining step water is not involved as a nucleophilic reagent. Its role is limited to catalytic effects via the formation of H-complexes $Ph_2CHBr$----HOH [1,2].

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[*] According to [17] residual water content after the treatment is app. $10^{-8}$ M.

Thus we may conclude that under these conditions C–Br bond ionization with the formation of an intimate or solvent-separated ion pair occurs at the rate–determining step. At the next fast steps the ion pair reacts with RN· or water. The latter reaction seems to pass through a bimolecular mechanism. Triphenylverdazyl interaction with $Ph_2CH^+Br^-$ proceeds by the trimolecular mechanism

$$RN\cdot \; + \; Ph_2CH^+Br^- \longrightarrow \underset{Br^-\;\;\;I}{\overset{Ph}{\underset{}{\overset{\underset{Ph}{|}}{CH}}}} \xleftarrow{\quad} \cdot NR \quad \xrightarrow{\;RN\cdot\;} \underset{Br^-\;\;\;II}{RN\overset{\overset{Ph}{|}}{\underset{+}{-CH}}} \xleftarrow{} \cdot NR \longrightarrow$$

$$\longrightarrow \; RN^+Br^- \; + \; RN\text{--}CHPh_2$$
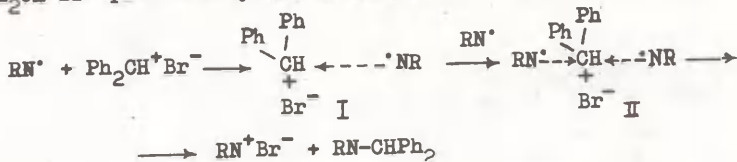
The donor–acceptor complex I is the first to be formed. The complete electron transfer from RN· to $Ph_2CH^+Br^-$ does not occur in it, however, with the influence of $Bu_3N$ and ionole anion [9]. The electron transfer is observed in the cation-diradical complex II which is formed similar to $H_3^+$ [19] due to the three-center molecular orbital including two upper occupied orbitals of RN· and the lower vacant orbital of $Ph_2CH^+$. The reaction rate of triphenylverdazyl with cationoid reagents is indeed known to be related to the square of RN· concentration value [20]. Therefore the alternative mechanism, i.e. the electron transfer from RN· to $Ph_2CH^+$ with further reaction of $Ph_2CH\cdot$ with the second RN· molecule in the cell, is of low probability.

Rates of monomolecular chlorine substitution in $Ph_2CHCl$ under the action of PhOK in $CH_3CN$ are available in the literature [9] ($k_1^{70°} = 2.6\cdot10^{-4}$ $s^{-1}$). Our data show $k_1^{70°}$ for $Ph_2CHBr$ in $CH_3CN$ to be $1.2\cdot10^{-4}$ $s^{-1}$ (calculated from $k_1$ temperature relation (see Table 1). From the comparison of the above values one can see that $Ph_2CHCl$ ionization rate is slightly higher than that of $Ph_2CHBr$. However, the solvolysis rate of $Ph_2CHBr$ is known to be from 5 to 30 times higher than that of $Ph_2CHCl$ [11]. In aprotic solvents this difference should be much greater [1]. The date in Ref. 9 are of preliminary nature. The authors give no procedures of mea-

suring the rate, purifying $CH_3CN$, determining water content in the solvent and show no errors of measurements. The value of $k_1$ for $Ph_2CHCl$ in acetonitrile given in [9] seems to be too high.

Table 3 gives kinetic parametres of the reaction studied in the present paper as well as those for $Ph_2CHBr$ solvolysis in $CH_3OH$ and $CH_3COOH$ [22] in comparison with similar data for t-BuBr [12,22].

Table 3

Kinetic Parameters of $Ph_2CHBr$ and t-BuBr Ionization

| Sub-strate | Solvent | $lg\ k_1^{25}$ | $\Delta H^{\neq}$ kcal/mol | $-\Delta S_{25}^{\neq}$ e.u. | $\Delta G_{25}^{\neq}$ kcal/mol |
|---|---|---|---|---|---|
| $Ph_2CHBr$ | $CH_3CN$ | $-5.6$ | 16.6 | 29.1 | 25.1 |
| | $CH_3CO_2H$ | $-4,8$ | 21.6 | 8.0 | 23.8 |
| | $CH_3OH$ | $-1.8$ | 19.2 | 2.9 | 20.1 |
| t-BuBr | $CH_3CN$ | $-5.9$ | 19.5 | 20.0 | 25.4 |
| | $CH_3CO_2H$ | $-5.5$ | 24.1 | 2.9 | 25.0 |
| | $CH_3OH$ | $-4.5$ | 23.5 | 0 | 23.5 |

Ionization rates of both substrates are increasing with the increase in the solvation power of the solvent in $CH_3CN < CH_3COOH < CH_3OH$ order. In this order of solvents 25-fold and 6000-fold increase in ionization rate was observed for t-BuBr and $Ph_2CHBr$, respectively. This suggests that $Ph_2CHBr$ ionization should proceed through the formation of the transition state with higher polarity over that observed in the transition state during t-BuBr ionization.

It should be noted that steric requirements for the activated complex formation are increasing for both substrates when protic solvents are replaced by $CH_3CN$. This may be due to the fact that in aprotic solvents the number of solvent molecules participating in transition state formation is greater than in protic ones. At any rate differences in the

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solvatatior of initial and transition states in $CH_3CN$ are
more considerable than in protic solvents.

Ionization rate of $Ph_2CHBr$ is app. twice as high as that
of t-BuBr. This is due to the sharp decrease in the acti-
vation enthalpy overlapping the simultaneous decrease in ac-
the activation entropy.

The results obtained show that triphenylverdazyl radicals
are convenient for studying the kinetics of diphenyl-
methyl halide ionization in aprotic organic solvents.
The authors consider triphenylverdazyls to be a potential
indicator for ion pairs (further study is required to es-
tablish the nature of ion pairs capable of reacting with
triphenylverdazyls). It seems reasonable to suggest that
triphenylverdazyls could be used to study the ionization ki-
netics over a broad range of substrates.

## Experimental

Kinetic experiments were performed in the thermostatic
cell of $C\Phi$-4A spectrophotometer. The reaction mixture was
prepared by mixing $Ph_2CHBr$ and $RN^.$ solutions in acetonitrile.
Before mixing the solutions were thermostated in a two-
-branch tube. The mixture was quickly poured into the
cell.

IR-spectra were recorded with UR-20. $CH_3CN$ electric con-
ductivity was measured with a.c. P5010 bridge in the cell
with flat platinum electrodes ($k_{cell} = 2.0 \cdot 10^{-2}$).

Diphenylmethyl bromide was obtained from benzhydrol and
$PBr_3$ [23]. For kinetic tests fresh preparations (m.p. 38-
39°C) recrystallized from pentane were used. Triphenylverda-
zyls were obtained and purified as in [24]. 1,2,5,6-Tetra-
hydro-1,3,5-triphenyl-1,2,4,5-tetrazine (leucoverdazyl)
was prepared as in [25] and its hydrobromide was obtained
according to [26].

Acetonitrile was repeatedly boiled over $P_2O_5$, distilled
over potash and fractionated [27]. The preparation usually
had water content of $4.5 \pm 0.5 \cdot 10^{-2}$ M (determined by Fischer
titration) and electric conductivity of $5.9 \cdot 10^{-8}$ $ohm^{-1} cm^{-1}$

(Lit. 5 to $9 \cdot 10^{-8}$ [27]). $CH_3CN$ with greater water content was re-purified. Anhydrous $CH_3CN$ was obtained by boiling and distillation over $CaH_2$ after treating with $P_2O_5$ [10,17].

1,2,5,6-Tetrahydro-1,3.5-triphenyl-2-diphenylmethyl-1,2,4,5-tetrazine was obtained elsewhere from $Ph_2CHCl$, triphenylverdazyl and silver powder in benzene (m.p. 160°C with decomposition [28] ). Having attempted to reproduce this procedure we obtained almost quantitative yield of 1,1,2,2-tetraphenyl ethane. We obtained $RN-CHPh_2$ from $Ph_2CHBr$, RN˙ and metallic silver and isolated the product in the preparative experiment of the reaction studied.

To 15 ml of benzene 1 g (0.003 mole) of RN˙ and 5.2 g of silver powder were added and the mixture was heated up to boiling.Then 0.9g (0.004 mole) of $Ph_2CHBr$ in 10 ml of benzene was slowly added to the mixture and unreacted silver and AgBr were removed by filtration.After benzene evaporation and residue crystallization from ether-hexane (2:1) mixture 0.6g (40% yield) of white small-size crystalls was obtained, m.p. 160°C with decomposition. The compound obtained was shown to have strong absorption in UV-region (in $CH_3CN$ $\lambda_{max.}$ = 333 nm, $\varepsilon$ = 15650) and to give quantitative conversion into triphenylverdazylium salt after heating with $H_2SO_4$ or other mineral acids. The product is stable in strong alkalies.

Product study tests of $Ph_2CHBr$ reaction with RN˙ in moist $CH_3ON$.

a) 1 g (0.003 mole) of RN˙ and 0.95 g (0.004 mole) of $Ph_2CHBr$ in 35 ml. $CH_3CN$ containing about $4.5 \cdot 10^{-2}$ M $H_2O$ were mixed and stored for two days at the room temperature. The analysis of the reaction mixture by RN˙ and $RN^+Br^-$ absorption showed that the reaction was completed on triphenylverdazyl up to 78%.IR absorption typical for C=O in benzphenone (1680 $cm^{-1}$) was absent. Bands typical for OH group in benzhydrole were observed at app. 3600 $cm^{-1}$.

Verdazylium salt is known to be quantitatively converted into RN˙ in the presence of $CH_2O$ and alkali excess, whereas leucoverdazyl will undergo quantitative oxidation into the

radical under similar conditions[29]. When adding the excess
of formaline and aqueous alkaline solution to some amount of
the reaction mixture,it was shown spectrophotometrically that
app. 10 % of $RN^+Br^-$ formation proceeded via the (4a)mecha-
nism and the rest seemed to occur through (4b).

$CH_3CN$ was distilled in the stream of methane under water-
jet pump vacuum, the residue was ground with ether (app.
50 ml) and the residue was separated (0,9 g) (Evaporation
was accompanied by intensive resin formation). Ether solu-
tion had light-green color suggesting that minor quanti-
ties of RN˙ were present.After the distillation of ether
and the solvation of the residue (0.7g), in ether triphenyl-
verdazyl is again converted into the verdazylium salt (due
to the reaction with HBr formed from $Ph_2CHBr$ left in excess).
Verdazylium salt is readily isolated from the ether solution.
Both triphenylverdazyl and triphenylverdazylium salt are
absent in the ether solution obtained.Spectrophotometrical-
ly, by absorption at $\lambda_{max}$ of $RN-CHPh_2$ and verdazylium salt,
formed under the influence of $H_2SO_4$ on the solution obtained,
it was found that 0.27g of $RN-CHPh_2$ was present in ether so-
lution (47% yield). Alkali does not change the color of the
solution, suggesting that the ether solution is lacking in
leucoverdazyl.

The ether was distilled off and the residue was repeat-
edly washed with methanol and hexane. On crystallization
from ether-hexane mixture (2:1) white small-size crystals
were obtained ($RN-CHPh_2$). Mixed sample with the preparation
obtained in the presense of metallic silver gives no tempe-
rature depression. Both preparations have identical electro-
nic and IR spectra,under the influence of mineral acids they
are quantitatively converted into the verdazylium salt and
are resistant to strong alkalies.

In the residue not dissolved in ether 0.1 g of triphenyl-
verdazyl and 0.22 g of $RN^+Br^-$ (45 % yield) were detected by
spectrophotometry. The availability of $RN^+Br^-$ was also con-
firmed by quantitative conversion into RN˙ (under the influ-
ence of $CH_2O$ and NaOH).

b) <u>Hydrobromic acid salt of 1,2,5,6-tetrahydro-1,3,5-triphenyl-1,2,4,5-tetrazine</u> (RNH·HBr). 1.9 g (0.008 mole) of $Ph_2CHBr$ was dissolved in 20 ml of $CH_3CN$ containing 0.5 M $H_2O$ (ionization rate constant for $Ph_2CHBr$ in this solution ($k_1^{25}$) is $1.1 \cdot 10^{-5}$ $s^{-1}$). 0.55 g of RN° (0.0017 mole) in 50 ml $CH_3CN$ was added and the solution was kept at room temperature for several days. $CH_3CN$ was partially evaporated and RNH.HBr was precipitated with benzene. 0.1 g of white crystalline substance was obtained, m.p. 150–151°C (20% yield). Mixed samples of this preparation and of that obtained according to [26] showed no melting temperature depression. Alkali gives rapid conversion of the salt into the radical.

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Comparison of $pK_{BH^+}$ - Values for Weak Bases
Calculated by the Bunnett-Olsen and Cox-Yates
Methods

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$pK_{BH^+}$ - Values for two sets ot hypothetical
weak bases have been calculated using the methods
of Bunnett-Olsen and excess acidities suggested
by R.A. Cox and K. Yates. In $H_2O - H_2SO_4$ as well
as in $H_2O - HClO_4$ the agreement between the $pK_{BH^+}$
- values obtained by the above methods is rather
good for not too weak bases which are half-proto-
nated in $\leqslant 70\%$ $H_2SO_4$ or in $\leqslant 50\%$ $HClO_4$, respec-
tively. For very weak bases the $pK_{BH^+}$ -s calculat-
ed by the methods studied differ from each other
remarkably, especially in the solvation parameter
$m^* > 1$.

The Bunnett-Olsen method [1] has become a standard one for
estimating $pK_{BH^+}$ - values of weak bases (B):

$$\log \frac{[BH^+]}{[B]} + H_o = \phi (H_o + \log M) + pK_{BH^+} \qquad (1)$$

where $H_o$ is the Hammett acidity function, M is the molarity
of strong acid, and $\phi$ is the solvation parameter.

Recently a new, generalized method for the determination
of basicities in aqueous acid mixtures has been suggested
by R.A. Cox and K. Yates [2] :

$$\log \frac{[BH^+]}{[B]} - \log C_{H^+} = m^*X + pK_{BH^+} \qquad (2)$$

where $C_{H^+}$ is the concentration of hydrated protons in solution, $m^*$ is the solvation parameter, and X is the "excess acidity".

Both these methods are based on the free energy linear relationship discussed in references [1-3].

In this paper we are concerned with the question how close to each other are the $pK_{BH^+}$ – values obtained from Eqs. 1 and 2. The comparison of $pK_{BH^+}$ – values calculated by Eqs. 1 and 2 is carried out for aqueous solutions of $H_2SO_4$ and $HClO_4$. In both cases the $pK_{BH^+}$ –s obtained from a modified Bunnett-Olsen treatment (using $-\log a_{H^+}$ instead of $H_o$) [4] are also considered.

In order to estimate the magnitude of differences between $pK_{BH^+}$ (Eq.1) and $pK_{BH^+}$ (Eq.2) we chose two sets of hypothetical weak bases which would be half-protonated in 20%, 40%, 60%, 80% $H_2SO_4$ (wt/wt) and in 20%, 30%, 50% $HClO_4$ (wt/wt), respectively. Besides, we took into account the solvation parameter denoted in Cox-Yates treatment as $m^*$, using the following values of $m^*$: 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6. The $pK_{BH^+}$ –s for the bases chosen were calculated from relationship [5]

$$pK_{BH^+} \ (Eq.2) = -m^*X - \log C_{H^+} \tag{3}$$

The following mathematical procedures including the calculation of $\log^{[BH^+]}\!/_{[B]}$ – values (in the range of $1 \div -1$) and using them for estimating the $pK_{BH^+}$ –s by Eq. 1 were exactly the same as used in our previous communication [5] where we compared the $pK_{BH^+}$ –s obtained by Eq. 2 and MCP-method.

The differences

$$D_1 = pK_{BH^+} \ (Eq.1) - pK_{BH^+} \ (Eq.2) \tag{4}$$

$$D_2 = pK_{BH^+} \ (Eq.1, \text{replacing } H_o \text{ by } -\log a_{H^+} \text{ from ref.}[6]) -$$
$$- pK_{BH^+} \ (Eq.2) \tag{5}$$

and $D_3 = pK_{BH^+}$ (Eq.1, replacing $H_o$ by $-\log a_{H^+}$ from ref.[7])$-$
$- pK_{BH^+}$ (Eq.2)  (6)

are given in Tables 1-4. The $pK_{BH^+}$ (Eq.2) - values used for
obtaining $D_1$, $D_2$, and $D_3$ are listed  i) for $H_2O-HClO_4$ mix-
tures in Table 5 and  ii) for $H_2O-H_2SO_4$ mixtures in Table
2 in reference[5]

Table 1

The Differences $D_1(4)$ for the Bases Chosen
in $H_2O - H_2SO_4(25°C)$.

| $m^*$ | $D_1$ for the bases half-protonated in aqueous $H_2SO_4$, containing $H_2SO_4$ (wt/wt) | | | |
| --- | --- | --- | --- | --- |
| | 20% | 40% | 60% | 80% |
| 0.4 | 0.07 | 0.09 | 0.09 | 0.08 |
| 0.6 | 0.07 | 0.08 | 0.09 | -0.15 |
| 0.8 | 0.08 | 0.05 | 0.10 | -0.33 |
| 1.0 | 0.10 | 0.02 | 0.11 | -0.52 |
| 1.2 | 0.12 | -0.01 | 0.13 | -0.68 |
| 1.4 | 0.14 | -0.05 | 0.14 | -0.90 |
| 1.6 | 0.16 | -0.08 | 0.16 | -1.10 |

Table 2

The Differences $D_2(5)$ and $D_3(6)$ for the Bases Chosen
in $H_2O-H_2SO_4(25°C)$.

| $m^*$ | $D_2/D_3$ values for the bases half-protonated in aqueous $H_2SO_4$, containing $H_2SO_4$ (wt/wt)[*] | | | |
| --- | --- | --- | --- | --- |
| | 20% | 40% | 60% | 80% |
| 0.4 | 0.06/0.08 | 0.06/0.09 | — /0.07 | -/1.46 |
| 0.6 | 0.05/0.08 | 0.05/0.09 | — /0.03 | -/1.27 |
| 0.8 | 0.05/0.09 | 0.03/0.08 | — /-0.03 | -/0.80 |
| 1.0 | 0.04/0.11 | 0.01/0.07 | — /-0.09 | -/0.95 |
| 1.2 | 0.04/0.12 | 0.00/0.06 | -0.17/-0.17 | -/0.58 |
| 1.4 | 0.04/0.13 | -0.01/0.05 | -0.27/-0.25 | -/0.84 |
| 1.6 | 0.04/0.14 | -0.02/0.03 | -0.39/-0.34 | -/1.00 |

*The $D_2$-values were not calculated with Modro-Yates $a_{H^+}$ - - scale for the bases protonated in concentrated $H_2SO_4$ solutions because the corresponding $a_{H^+}$ - scale is published up to 65% $H_2SO_4$ only.[6]

Table 3

The Differences $D_1(4)$ for the Bases Chosen in $H_2O$ - $HClO_4$ (25°C).

| $m^*$ | $D_1$ for the bases half-protonated in aqueous $HClO_4$, containing $HClO_4$ (wt/wt) | | |
|---|---|---|---|
| | 20% | 40% | 60% |
| 0.4 | -0.11 | -0.05 | 0.17 |
| 0.6 | -0.16 | -0.08 | 0.35 |
| 0.8 | -0.21 | -0.11 | 0.51 |
| 1.0 | -0.23 | -0.14 | 0.67 |
| 1.2 | -0.25 | -0.17 | 0.82 |
| 1.4 | -0.25 | 0.19 | 0.97 |
| 1.6 | -0.28 | -0.22 | 1.11 |

Table 4

The Differences $D_2(5)$ and $D_3(6)$ for the Bases Chosen in $H_2O$ - $HClO_4$ (25°C)

| $m^*$ | The ratio $D_2/D_3$ for the bases half-protonated in aqueous $HClO_4$ containing $HClO_4$ (wt/wt)[*] | | |
|---|---|---|---|
| | 20% | 40% | 60% |
| 0.4 | -0.03/-0.04 | - /-0.14 | - /-0.24 |
| 0.6 | -0.03/-0.04 | - /-0.24 | - /-0.77 |
| 0.8 | -0.02/-0.04 | -0.21/-0.33 | - /-1.71 |
| 1.0 | -0.03/-0.05 | -0.26/-0.41 | - /-3.08 |
| 1.2 | -0.03/-0.06 | -0.31/-0.49 | - /-4.88 |
| 1.4 | -0.04/-0.07 | -0.35/-0.55 | - /-7.91 |
| 1.6 | -0.04/-0.08 | -0.40/-0.63 | -/-10.80 |

*$D_2$- values were not calculated with Modro-Yates $a_{H^+}$ - scale for the bases protonated in concentrated $HClO_4$ solutions because the corresponding $a_{H^+}$ scale is published up to 50% $HClO_4$ only[6].

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Table 5

The p$K_{BH}$+ (Eq.2)- Values for the Bases Chosen
in $H_2O$ - $HClO_4$ (25°C)

| $m^*$ | p$K_{BH}$+ (Eq.2) for the bases half-protonated in aqueous $HClO_4$, containing $HClO_4$ (wt/wt) | | |
|-----|-------|-------|-------|
|       | 20%   | 40%   | 60%   |
| 0.4 | −0.58 | −1.46 | −2.69 |
| 0.6 | −0.69 | −1.84 | −3.56 |
| 0.8 | −0.87 | −2.21 | −4.43 |
| 1.0 | −0.92 | −2.59 | −5.30 |
| 1.2 | −1.04 | −2.97 | −6.16 |
| 1.4 | −1,15 | −3.34 | −7.03 |
| 1.6 | −1.26 | −3.72 | −7.90 |

Table 6

The Ratio of Solvation Parameters 1- $\phi$ (Eq.1) and
$m^*$ (Eq.2) for the Bases Chosen in $H_2O$-$H_2SO_4$ (25°C)[*])

| $m^*$ | $(1-\phi)/m^*$ for the bases half-protonated in aqueous $H_2SO_4$ containing $H_2SO_4$ (wt/wt) | | | |
|-----|-------|-------|-------|-------|
|       | 20%   | 40%   | 60%   | 80%   |
| 0.4 | 0.983 | 0.931 | 0.939 | 0.928 |
| 0.6 | 0.968 | 0.938 | 0.944 | 1.007 |
| 0.8 | 0.948 | 0.953 | 0.943 | 1.034 |
| 1.0 | 0.918 | 0.963 | 0.941 | 1.050 |
| 1.2 | 0.894 | 0.972 | 0.939 | 1.058 |
| 1.4 | 0.873 | 0.979 | 0.939 | 1.069 |
| 1.6 | 0.864 | 0.983 | 0.938 | 1.076 |

[*]) Eq.1 with $H_o$[8] was used

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Table 7

The Ratio of Solvation Parameters
$1-\phi$ (Eq.1) and $m^*$ (Eq.2) for the Bases
Chosen in $H_2O-HClO_4$ (25°C) *)

| $m^*$ | $(1-\phi)/m^*$ for the bases half-protonated in aqueous $HClO_4$, containing $HClO_4$ (wt/wt) | | |
|---|---|---|---|
| | 20% | 40% | 60% |
| 0.4 | 1.330 | 1.172 | 0.938 |
| 0.6 | 1.361 | 1.191 | 0.893 |
| 0.8 | 1.377 | 1.202 | 0.876 |
| 1.0 | 1.366 | 1.207 | 0.869 |
| 1.2 | 1.341 | 1.209 | 0.865 |
| 1.4 | 1.311 | 1.209 | 0.864 |
| 1.6 | 1.300 | 1.210 | 0.862 |

*) Eq.1 with $H_o$ [9] was used

Tables 1-4 show that the differences $D_1$, $D_2$, and $D_3$ all are rather small for the bases half-protonated in not very concentrated $H_2SO_4$ or $HClO_4$ solutions. Only for the bases having $[BH^+] = [B]$ in $\leqslant 70\%$ $H_2SO_4$ or in $\leqslant 50\%$ $HClO_4$ equations 1 and 2 yield remarkably different $pK_{BH^+}$ - values, especially in the case if $m^* > 1$. Replacing $H_o$ in Eq.1 by the $-\log a_{H^+}$, as suggested in reference [4], does not lead to a definitely better agreement between $pK_{BH^+}$ -s calculated by Eqs. 1 and 2 (see Tables 2 and 4).

As pointed out by R.A. Cox and K. Yates [2] the set of $H_o$-indicators is not so "well-behaved" in perchloric as it is in sulfuric acid, because in $H_2O-HClO_4$ the variations in $m^*$ values are larger than $\pm 0.1$. One might thought that this should result in larger $D_1$ values for $H_2O-HClO_4$ over $H_2O-H_2SO_4$. But in fact this turned out to be not the case: the $D_1$ values for both acids have approximately the same order of magnitude (see Tables 1 and 3).

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The last point to be discussed is the relationship between the solvation parameters used in Equations 1 and 2. It should be noted that a lot of work has been done to connect the $\phi$-values from Eq. 1 with solvation phenomena occuring with the protonation of the bases studied. [10] According to reference [2] there should exist a reasonable approximation $m^* = 1 - \phi$ ,at least in aqueous sulfuric acid solutions. Tables 6 and 7 show that the ratio $(1-\phi)/m^*$ is rather close to one in aqueous sulfuric acid solutions but varies more in aqueous perchloric acid solutions.

## Experimental

For $H_2O-H_2SO_4$ mixtures (25°C) the following empirical equations have been used:

$$X = -1.21924(Z-1) + 1.74213 (Z^2-1) - 0.629724(Z^3-1) +$$
$$+ 0.116376(Z^4-1) - 0.0104567(Z^5-1) + 0.00036118(Z^6-1)$$

where $Z = 10^{0.01p}$ and p is $H_2SO_4\%$ $(wt/wt)^2$

$$H_o = 0.458774 - 5.97195(Z-1) + 2.00607(Z^2-1) -$$
$$- 0.382031(Z^3-1) + 0.0286362(Z^4-1) - 0.000061536(Z^6-1)$$

where $Z = 10^{0.01p}$.

$- \log a_H+$ (from reference [6] ) $= 0.589863 - 19.3760(Z-1) +$
$$+ 11.5959(Z^2-1) - 3.72915(Z^3-1) + 0.493575(Z^4-1) -$$
$$- 0.00373866(Z^6-1)$$

where $Z = 10^{0.01\ p}$

$-\log a_H^+$ (from reference [7]) $= 0.567790 - 8.90602(Z-1) +$
$+ 3.43493(Z^2-1) - 0.873866(Z^3-1) + 0.0941722(Z^4-1) -$
$- 0.000456978(Z^6-1)$

where $Z = 10^{0.01p}$

Sulfuric acid concentrations expressed in %(wt/wt) were converted into acid molarity (mole $H_2SO_4$ /$dm^3$) by

$$M = 0.101752 \, p + 1.57523 \cdot 10^{-4} \, p \cosh(p.10^{-2}) +$$
$$+ 4.85216.10^{-4}p^2 + 2.8528.10^{-6}p^3$$

where p is $H_2SO_4$ % (wt/wt) .

For $H_2O-HClO_4$ mixtures (25°C) the following empirical equations have been used:

$X = -0.745077(Z-1) + 1.00915(Z^2-1) - 0.305916(Z^3-1) +$
$+ 0.0497385(Z^4-1) - 0.00405171(Z^5-1) + 0.000128552(Z^6-1)$

where $Z = 10^{0.0125p}$ and p is $HClO_4$% (wt/wt). [2]

$H_o = 0.182329 - 1.41855(Z-1) - 1.06539(Z^2-1) + 0.675690\cdot$
$\cdot(Z^3-1) - 0.133463(Z^4-1) + 0.00153774(Z^6-1)$

where $Z = 10^{0.01p}$ and p is $HClO_4$% (wt/wt).

$-\log a_H^+$ (from reference [6]) $= 0.704273 - 15.7921(Z-1) +$
$+ 7.41985(Z^2-1) - 1.775298(Z^3-1) + 0.125001(Z^4-1) +$
$+ 0.00143836(Z^6-1)$

where $Z = 10^{0.01p}$ and p is $HClO_4$% (wt/wt).

$-\log a_H^+$ (from reference [7]) $= 0.717084 - 15.6461(Z-1) +$
$+ 5.95144(Z^2-1) - 0.719096(Z^3-1) - 0.106362(Z^4-1) +$
$0.00487287(Z^6-1)$

where $Z = 10^{0.01p}$ and p is $HClO_4$% (wt/wt).

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Perchloric acid concentrations expressed in %(wt/wt) were converted into acid molarity (mole $HClO_4$ /$dm^3$ by

$$M = p \cdot (10.066 - 0.059826 \, p + 0.016604 \cdot \sqrt{p})^{-1}$$

where p is $HClO_4$% (wt/wt).

All calculations were carried out on a "Nairi-2" computer.

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