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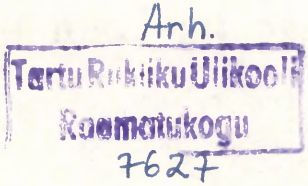

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC DATA IN THE GAS PHASE HOMOLYSIS

3. Calculation of Conventional Formation Enthalpies of Free Radicals in the Approximation of Constant Effective Mean Value of log A_o=14.64.

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Conventional formation enthalpies of free radicals in the gas phase at 0°K have been calculated, proceeding from the formal isoentropic approximation (log A_o = 14.64) for the unimolecular gas phase homolysis and the model expressed by equation (3).

In our previous paper[1] for the gas phase homolysis reaction:

$$R_i - R_j \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_i^{\cdot} + R_j^{\cdot} \qquad (1)$$

the mutual independence of structural effects, influencing the values of the preexponential factor logarithm (log A) and activation energy (E), was concluded. Besides, the dependence of log k_1 on the structure is mainly determined by the corresponding changes in E values. Formally, one can interpret this result as an example of the isoentropic series in which the variation of log A values is considered as a random distribution among the mean value.

There are also indications of relatively high and nearly constant log A values for reactions of type (1) in literature. So, Tsang[2,3] considers in essence the gas phase homo-

lysis of hydrocarbons as an isoentropic reaction with the constant value of log A≈16.2. The kinetic data of the unimolecular gas phase reactions including the gas phase homolysis (simple bond fission) prior to 1967 have been collected and evaluated by Benson and O'Neal[4]. Beside experimental data the preferred values of the Arrhenius parameters are listed as well. The recommended values frequently differ from the experimental ones and the preferred log A values lie generally in the range 14 - 17. In fact, the principal criterion used to evaluate the reported reaction rate data has been the estimated thermochemistry of the transition state. Observed activation energies were compared with the estimated reaction enthalpies at the mean reaction temperature. This procedure was followed for all the reactions for which the formation enthalpies of free radicals were reasonably well known from the work of the indicated authors. The majority of those formation enthalpies used in the given case have been determined by bromination and iodination experiments. The errors associated with the estimated activation energies (reaction enthalpies) do not exceed 2 or 3 kcal/mole. For the majority of reactions considered the estimated value of activation energy was higher than the experimental one. Preferred Arrhenius parameters were calculated by scaling the low parameters to the corrected activation energy if the rate constants were thought to be reliable. In all reactions, rate constants for radical-radical recombinations have been calculated from the estimated reaction entropies and the preferred A-factors. This was done to study what correlations exist between the recombination rates and the geometry, size, and mutual resonance interaction of recombining radicals. The obtained recombination rate constants served also as a criterion of the reliability of the existing kinetic data for homolysis reactions. The general conclusion was drawn[4] that the higher log A values would be preferred. This is in accordance with the activation entropies estimated in the framework of the transition state theory. For example, one can consider all

Arrhenius parameters leading to the negative value of activation entropy as incorrect ones since it is hard to imagine the transition state tighter than the initial one if the homolysis reaction is considered.

Interest in the simple bond fission reactions stems principally from the relations presumed to be valid between the Arrhenius parameters for dissociation and the thermodynamic properties of the free radical products. There is a paper[5] devoted specially to the thermochemistry of free radicals covering the literature prior to May 1971. No doubt kinetic data are regarded as the most reliable ones for the calculation of the formation enthalpies of free radicals. There are three most important kinetic methods[5] which can be applied: iodination and inverse iodination, bromination, and pyrolysis. The initial stage of pyrolysis is reaction (1). In principle, the data of reaction (1) should be excellent sources of reliable formation enthalpies of free radicals. This is so because radical-radical recombination activation energy E_{-1} is probably indistinguishable from zero. Thus, the enthalpy of reaction (1) at the mean reaction temperature T_{mean} equals:

$$\Delta H^{\circ}_{T_{mean}} = E_1 - E_{-1}$$

Taking $E_{-1} \simeq 0$ we set:

$$\Delta H^{\circ}_{T_{mean}} = E_1$$

With heat capacity data, the standard reaction enthalpy (ideal gas, pressure 1 atom, temperature 298.15°K) can be obtained:

$$\Delta H^{\circ}_{298} = \Delta H^{\circ}_{T_{mean}} - \int_{298}^{T_{mean}} \Delta c_p dT$$

Often an approximate formula is used:

$$\Delta H^{\circ}_{298} = \Delta H^{\circ}_{T_{mean}} - \Delta \bar{c}_p \, (T_{mean} - 298)$$

where $\Delta \bar{c}_p$ is the mean value of the heat capacity change

at constant pressure and temperatures from 298 to T_{mean}. Thus, if one has the enthalpy of the homolysis reaction at 298°K, the experimental or calculated formation enthalpy of reactant $\Delta H^{o}_{f\ 298}$ and one radical, new values of free radical formation enthalpies could be estimated from the relation:

$$\Delta H^{o}_{298} = \Delta H^{o}_{f298}\ (R_i^{\cdot}) + \Delta H^{o}_{f298}\ (R_j^{\cdot}) - \Delta H^{o}_{f298}\ (R_iR_j)$$

In practice, the determination of formation enthalpies of free radicals from bond fission reactions has not been very successful. Difficulties arise already with the assumption that the activation energy for radical-radical recombination reaction is equal to zero. In general, two main approaches for the calculation of formation enthalpies of free radicals from kinetic data are employed. The first usual assumption is that the activation energy of the recombination of free radicals equals zero at the temperature T for the rate constants expressed in pressure units[2-4].
In this case

$$\Delta H_T = E_T \quad ,$$

where ΔH_T is the enthalpy change of the bond fission reaction and E_T is the experimental activation energy of bond fission. In earlier studies the usual procedure was to suppose $\Delta H_{298} = \Delta H_T = E_T$, i.e. heat capacity changes was ignored. Assuming that the activation energy of the radical-radical recombination has zero value at the temperature T for the rate constants expressed in concentration units, it follows that

$$\Delta H_T = E_T + RT,$$

since the difference between the activation energies of a bimolecular reaction for rate constants measured in concentration units as opposed to pressure units is equal to RT (i.e. $E_c - E_p = RT$). The latter procedure is more favorable[5]. However, there may be some positive values of activation energies for radical-radical recombinations[5,6]. In general, much remains to be done in radical recombination reactions[6]. The reliability of the assumed definite values of radical

recombination rate constants tabulated in Refs. 4,5 is considered to be critical in the estimation of the gas phase homolysis kinetic parameters[5]. Assuming that $E_{-1}=0$, the main problem is the experimental measurement of rate constants k_1 and activation energies E_1. These values must be extracted from the overall decomposition kinetics of extremely complex reactions. Difficulties often arise in surface catalysis and in the stimulated free radical chain decomposition of R_iR_j . Surface effects can, and usually are, studied or avoided experimentally. Chain decompositions appear to be a more difficult problem. To identify the experimental activation energy of pyrolysis with that of the bond-fission reaction, the latter must be the rate--determining step. This will be the case for all nonchain pyrolytical reactions. Some classes of compounds (e.g., alkyl azo compounds and peroxides) are thought to decompose in this way. However, small amounts of chain decomposition probably do occur even in these reactions. Most decomposition reactions, however, no doubt involve complex free--radical chain processes. The most common procedure used to study these reactions has been to add free-radical scavengers (inhibitors) in the hope to suppress the chain decompositions. It is assumed that free radicals formed in reaction (1), react exclusively with the inhibitors to produce stabilized inert radicals which are unable to stimulate chain decomposition and their principal fate is radical-radical termination. This procedure has been subject to just criticisms[4,5].

Another difficulty in the experimental determination of the rate constants and Arrhenius parameters of reaction (1) is their pressure dependence. There are two limited cases: the ranges of low and high pressure limits. Between them the falloff region exists where the reaction order is changing from the second to the first. The boundary between the ranges of low and high pressures may be characterized by the pressure $p_{1/2}$ at which the effective rate constant

equals half of the rate constant limiting value k_∞ for the high pressure region. The value $p_{1/2}$ strongly depends on the size of the molecule. $P_{1/2}$ is shifting to lower pressures with an increase in the number of atoms and the thermal decomposition of two-atomic molecules always follows the second order law. The $p_{1/2}$ value depends also on temperature: $p_{1/2}$ is moving to higher pressures with an increasing in temperature. The decomposition of all molecules must follow the second order law at high enough temperatures[7]. The majority of reactions belonging to type (1) have been studied in the high pressure region. However, it is considered[8] that the limiting rate constant values of reaction (1) k_∞ are in the majority of cases not accessible and may be estimated only by extrapolation. In practice experimental data are often incomplete, for the determination of reliable k_∞ values because the rate constants cannot be measured at pressures high enough[8].

Taking into account these experimental complications resulting in the considerable uncertainties of the homolysis rate constants, the statistical treatment of a possibly large set of data in the framework of some possible hypotheses about the quantitative representation of structural effects which exert influencing on the log A and E values could be regarded as an alternative approach. The exclusion of significantly deviating points has to be applied as an obligatory procedure. To obtain sufficiently reliable results, it is necessary to have parallel independent data and those should include a set of reliable enough data.

For the true activation energy or enthalpy D the dependence on the nature of radicals $R_i^\bullet$ and $R_j^\bullet$ can be represented as follows:

$$D_{ij} = \Delta H^{\neq}_{R_i^\bullet} + \Delta H^{\neq}_{R_j^\bullet} - \Delta H^{o}_{OR_iR_j} \qquad (3)$$

This relationship assumes the absence of interaction between free radicals formed in the transition state (the additivity rule). $\Delta H^{\neq}_{R^\bullet}$ denotes the conventional formation

enthalpy of the respective free radicals in the transition state at $0^{o}K$, by $\Delta H^{o}_{OR_iR_j}$ the standard formation enthalpy of the compound R_iR_j at $0^{o}K$. It means that the additivity of temperature-contributions of enthalpies during the transition state is also supposed:

$$(H^{o}_{T} - H^{o}_{O})^{\neq}_{R_i} + (H^{o}_{T} - H^{o}_{O})^{\neq}_{R_j} = (H^{o}_{T} - H^{o}_{O})_{R_iR_j}$$

Equation (3) reflects the dependence of D_{ij} value on the nature of radicals-substituents and makes it possible to calculate the $\Delta H^{\neq}_{R}$. values for free radicals in the transition state. If the number of different combinations of radicals with the known values of D_{ij} considerably exceeds the number of different radicals involved in these combinations and the $\Delta H^{o}_{OR_iR_j}$ values are either available or could be calculated, the consistency of eq. (3) can be proved and the values of $\Delta H^{\neq}_{R}$. and their standard deviations could be calculated using the technique of multilinear regression analysis (MLRA) in the coordinates of eq. (3). The calculation of the formation enthalpies of compounds in the gas phase at $0^{o}K$ was discussed in our first paper[9] of this series. To specify the relationships valid for D and log A values, one can check several different hypotheses[1,10]. The present study is concerned with the formal isoentropic model. We have demonstrated[1] that all reactions of type (1) are characterized by an effective mean value of log A which is equal to $\log A_o = 14.64$. For the fission of the aliphatic nitro compounds the significantly different value $\log A_o = 16.0$ was obtained.[1]

Taking into account the formal isoentropic behavior the recalculation of experimental activation energies is possible according to the formula:

$$D = E + 2.3\ RT_{mean}\ (\log A_o - \log A + \log n), \qquad (4)$$

where R is the gas constant, T_{mean} represents the mean temperature for the temperature range studied to calculate the log A and E values, n denotes the statistical factor

(the number of equivalent bonds undergoing the homolysis).

The D values calculated according to eq. (4) (log A_o = =14.64) are presented in the ninth column of Table 2. One can see that the scatter of D values is considerably lower than for the original E values if the respective parallel independent data for the same reaction are available. Thus, the reaction of ethane decomposition forming two methyl free radicals is characterized by 11 independent E estimates in the range of 12.4 kcal/mole from 79.3 to 91.7 kcal/mole ((mean value 85.8, standard deviation 3.4, kcal/mole). The respective D values cover the range 7.0 kcal/mole from 78.4 to 85.2 kcal/mole (mean value 80.0, standard deviation 2.5, kcal/mole).

There are 7 independent estimates of E for nitromethane bond fission ($\bar{E}$ = 51.9±5.1, kcal/mole). From the corresponding D values based on the value of log A_o = 14.64, $\bar{D}$=53.3± ±2.4 kcal/mole and for log A_o = 16.0, $\bar{D}$ = 59.8±1.9 kcal/mole. The extreme log A and E values reported for nitro benzene bond fission differ enormously: 17.32 and 12.63 for log A, and 69.7 and 53.4 kcal/mole for E, respectively. The corresponding D values are 60.9 and 59.7 kcal/mole.

One can see from these examples that a general increase in parallel data self-consistency can be observed. Therefore, even purely formal acceptance of the isoentropic model may appear to be useful for calculation purposes.

Conventional formation enthalpies at 0°K $\Delta H^{\neq}_{R_i}$. could be estimated by the use of the combinations of equations (3) and (4) as a result of multilinear regression analysis in the coordinates of the equation:

$$\Delta H^{\neq}_{R_i} + \Delta H^{\neq}_{R_j} = D_{ij} + \Delta H^{o}_{OR_iR_j} \qquad (5)$$

where D_{ij} is the value recalculated according to eq. (4).

The use of eq. (5) requires known formation enthalpies of the compounds which are homolyzing. The corresponding experimental values are available by no means in all cases. Besides, some of them include significant uncertainties

leading to the respective increase of uncertainties in calculated $\Delta H^{\neq}_{R\cdot}$ values. Therefore, one can use not only experimental but also calculated values of formation enthalpies for R_iR_j compounds.

According to the formal calculation scheme of formation enthalpies for organic compounds R_iR_j, $\Delta H^{\circ}_{OR_iR_j}$ can be represented as a sum of the group additive terms ΔH°_{OR-} and the interaction term $I_{R_iR_j}$:

$$\Delta H^{\circ}_{OR_iR_j} = \Delta H^{\circ}_{OR_i-} + \Delta H^{\circ}_{OR_j-} + I_{R_iR_j}$$

The value of $I_{R_iR_j}$ (in kcal/mol) can be calculated as a sum of φ-and inductive interactions:

$$I_{R_iR_j} = \varphi_{R_i}\,\varphi_{R_j} + \alpha^{*}\,\sigma^{*}_{R_i}\,\sigma^{*}_{R_j}$$

where φ_{R_i}, φ_{R_j} are substituent "φ"-constants, $\sigma^{*}_{R_i}$, $\sigma^{*}_{R_j}$ represent their inductive constants and α^{*} is the inductive scaling factor. Generally speaking, the $I_{R_iR_j}$ value contains also sterical and resonance terms.

The $I_{R_iR_j}$ value can be calculated also as a difference:

$$I_{R_iR_j} = \Delta H^{\circ}_{OR_iR_j} - \Delta H^{\circ}_{OR_iH} - \Delta H^{\circ}_{OR_jH}$$

Therefore, instead of $\Delta H^{\neq}_{R\cdot}$ the $\Delta\Delta H^{\neq}_{R\cdot}$ values could be estimated and used for calculations as follows:

$$\Delta\Delta H^{\neq}_{R\cdot} = \Delta H^{\neq}_{R\cdot} - \Delta H^{\circ}_{OR-}$$

i.e. one can introduce the differences between the formation enthalpy of the free radical and the additive enthalpy term for corresponding substituent.

Then eq.(5) can be rewritten:

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} = D_{ij} + I_{R_iR_j} \qquad (6)$$

The $\Delta\Delta H^{\neq}_{R\cdot}$ values are convenient for the treatment of structural effects for radicals R. because the additive increments for the substituents at the free radical centre drop out.

Initial data for the treatment in accordance with equations (4) - (6) and also employed by us[1] are listed in Table 2. The values of i and j correspond to the sequence numbers of radicals-substituents R from Table 1. The data of log A and E included in the tables of Vedeneev and Kibkalo[11] are quoted according to this source. The date of log A and E data publication is also indicated (the last but one column). The first 307 lines of Table 2 represent the reactions for which the experimental formation enthalpies of reactions are available. Then the reactions for which we were not able to find $\Delta H^{o}_{fR_iR_j}$ values in literature are listed. The final lines (417 ÷ 432) represent the data excluded in the course of the treatment[1] of the complete data set in the coordinates of log k_{T_2} and log k_{T_1}. The Arrhenius parameters for these reactions are obviously unreliable. If it is not otherwise indicated the ΔH^{o}_{0} or ΔH^{o}_{f298} values are extracted from references 56-58 with the exception of lower alkanes for which the data from papers[97,98] are used. The ΔH^{o}_{0} values are estimated from the ΔH^{o}_{f298} values using the technique described by us earlier[9].

Technique of Data Treatment

The statistical treatment of data in the coordinates of equations(5) and (6) was carried out using the programs of multilinear regression analysis (MLRA). It can be done in several ways. Firstly, for the radicals constituted from a single atom (hydrogen and halogen atoms) the $\Delta H^{\neq}_{R\cdot}$ values could be fixed equalling them to the values calcu-

lated from the dissociation energies[99] for H_2 and molecular halogens at $0^{o}K$. However, it must be considered that these values are the standard formation enthalpies for isolated particles.

Another reason for the existence of several versions for the data treatment is caused by the great differences in the degree of representation of various R in the available data set. Although some radicals are represented abundantly (methyl,nitro group etc.) the majority of them occur only in a single combination and the data are reported in a single source. The inclusion of those data into the set for the primary statistical treatment leads to only apparent increase in the statistical representativity of this set since the number of statistical degrees of freedom is not increased. Therefore, side by side with the simultaneous treatment of the complete data set, the data for the most represented radicals were processed separately in other cases.

Further, from such $\Delta H_{R\cdot}^{\neq}$ or $\Delta\Delta H_{R\cdot}^{\neq}$ and D values we calculated the corresponding $\Delta H_{R\cdot}^{\neq}$ or $\Delta\Delta H_{R\cdot}^{\neq}$ for the combinations of radicals represented only in a single or very few combinationa.

Besides, one can prove a version with the special value $\log A_o=16.0$[1] for the reactions of $C-NO_2$ bond fission.

The alternative values of $\sigma^{*}_{NO_2}$ and α^{*} can be used for eq. (6) although we have preferred $\sigma^{*}_{NO_2}=4.48$ and $\alpha^{*}=$ = 1.35 kcal/mole in ref. 9.

All the main manipulations with data and their statistical treatment were performed using computers and programs written by us. Problems confined to the possibilities of a small universal computer Nairi-2 were solved using this one.

The MLRA program used in the simultaneous calculation of the $\Delta H_{R\cdot}^{\neq}$ values for 98 radicals was composed in FORTRAN for the computer "Minsk-32" *

* Authors are indebted to T. Júriado for the representation of the program written by him which was used in the present study in a somewhat modified form.

The exclusion of significantly deviating points was applied according to Student's criterion on the confidence level of 0.95 during the MLRA programs processing.

Results and Discussion

The data processing according to eq. (5) was performed for the complete data set and also for 15 most represented free radicals. Versions were checked either without previous fixing of $\Delta H^{\neq}_{R\cdot}$ values for any radicals or with fixing this value only for H· or also fixing for Cl·, Br· and I· atoms (there are no data available for F·). Alongside with using the universal value $\log A_o = 14.64$ for all the reactions the special value $\log A_o = 16.0$ for C - NO_2 bond fission was tested as well.

Two main criteria were considered when estimating the results of the data treatment: the reliability of description at the comparable size of data sets involved, and statistical self-consistency or "reasonableness" of the obtained $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values set in the framework of the formal theory of intramolecular interactions. It was sufficient to use the criterion of "reasonableness" only in the case of methyl, ethyl, isopropyl and tert-butyl radicals. These ones are well represented in the initial data set.

Let us assume the simplest hypothesis within the formal theory of intramolecular interactions. This is the additivity of φ interaction for the free-radical centre C· related to substituents. Consequently, the $\Delta H^{\neq}_{R\cdot}$ values for the indicated alkyl free radicals are expressed as follows:

$$\Delta H^{\neq}_{(CH_3)_n H_{3-n} C\cdot} - n\,\Delta H^{o}_{CH_4} = \Delta H^{\neq}_{CH_3\cdot} + n\,\varphi_{C\cdot}\,\varphi_{CH_3}$$

$\varphi_{C\cdot}$ denotes φ constant for the free-radical centre C·.

This equation introduces two new empirical parameters at four possible values of n (from 0 to 3) and its validity can be checked by using the data only for four indicated radicals. If there are interactions between the considered substituents analogously with the alkanes of the general

structure $R_1R_2R_3R_4C$, these interactions must be taken into account by introducing another two additional empirical constants analogous to the constants A and B for alkanes. In this case the data of the considered four radicals are not sufficient for checking the resulting relationship. Nevertheless there remains the "reasonableness" criterion represented by the convergence requirement for the used row. The absolute value of the contribution proportional to the sum φ_{CH_3} (generally the sum of double products for the φ constants of substituents) must be essentially lower than the value of $n\varphi_C.\varphi_{CH_3}$, and the absolute value of the term proportional to $\varphi^3_{CH_3}$ must be by far lower still. Besides, the values of the parameters calculated from the data of the considered four radicals are to describe the terms of φ interaction in the $\Delta H^{\neq}_{R.}$ and $\Delta\Delta H^{\neq}_{R.}$ values for all other substituted methyls.

The $\Delta H^{\neq}_{R.}$ values obtained for the four above radicals, especially for ethyl, appear to be distorted if the $\Delta H^{\neq}_{R.}$ values were considered as unknown for H° and Cl°, Br°, and I° or if all these $\Delta H^{\neq}_{R.}$ values were previously fixed according to the dissociation energies of the respective two-atomic molecules. When doing so the $\Delta H^{\neq}_{H.}$ value is essentially enhanced (approximately by 5 kcal/mole) if compared with the estimate from the H_2 dissociation energy. This is to a large extent conditioned by the use of parallel data which were excluded as the significantly deviating ones in the case of the preliminarly fixed $\Delta H^{\neq}_{H.}$ value. Therefore, later the $\Delta H^{\neq}_{H.}$ and $\Delta\Delta H^{\neq}_{H.}$ values were fixed and the respective values for halogens were considered as the values to be determined.

The results of the treatment of the complete data set according to eq. (5) are presented in Tables 1 and 3. The initial data set contained 297 independent points for 137 reactions. The presence of several parallel points for a single reaction is caused in most cases by the fact that several parallel D values exist. In some cases two or more parallel different $\Delta H^{\circ}_{OR_1R_j}$ values are responsible for it.

The number of radicals with unknown $\Delta H^{\neq}_{R}$. values is equal to 97.

Altogether 65 points were excluded in the course of the data processing. Out of these 38 are alternative to values included into the set defining final result. 12 points for 5 reactions were excluded as a consequence of large discrepancies between the alternative $\Delta H^{o}_{OR_iR_j}$ values. In the final set the data for these compounds and the corresponding five radicals were not used so far as these radicals ($i\text{-}C_3H_7NN^{\cdot}$, $C_6H_5O^{\cdot}$, $Cl_2CH^{\cdot}$, $3,5\text{-}(NO_2)_2\text{-}C_6H_3^{\cdot}$ and $^{\cdot}Pb(CH_3)_3$) are presented in the initial set only in single combinations with other radicals. The remaining 15 points for 9 reactions were excluded owing to the lack of statistical consistency of the corresponding data with the rest of the data. In all these cases it is hard to say if this is caused by the corresponding D_{ij} or $\Delta H^{o}_{OR_iR_j}$ values.

The standard deviation at the end of the data processing is equal to 1.1 kcal/mole. The inital data set is characterized by the value of 3.1 kcal/mole. As a result the conventional values of $\Delta H^{\neq}_{R}$. for 93 free radicals are obtained. Out of this set 17 are represented in five or even more independent combinations of radicals (this number of combinations is equal to 69 for methyl and 45 for NO_2). 45 radicals are represented only in a single combination each, and 23 in couple ones. In the case of all the radicals represented in the final set at least by three points the standard deviations of $\Delta H^{\neq}_{R}$. are below 0.7 kcal/mole. One can hardly ascribe any real significance to the obtained values of those standard deviations for these radicals have a lower degree of representation.

It is of interest to compare the results for the described treatment version when the universal value $\log A_o = 14.64$ is assumed with the ones for the same data set but using D values for nitrocompounds relevant to $\log A_o = 16.0$. In the first case 66 points are excluded before the standard deviation 1.1 kcal/mole is achieved while five of them correspond to $C\text{-}NO_2$ bond fission. In the latter case the

same level of standard deviation is achieved after the exclusion of 71 points while 11 of them correspond to the formation of the NO_2. radical. Therefore the application of the special log A_o value for the reactions of C-NO_2 bond fission does not improve the general statistical indices of the data treatment within the used simplified model.

The comparison of the results obtained according to eq. (5) for the complete data set and those for the 15 most represented radicals shows that they are practically identical. Therefore further statistical data processing according to eq. (6) was performed only for the most represented radicals.

Processing the data according to eq. (6) one can include into the initial data set additionally some reactions which are not characterized by experimental $\Delta H^{o}_{OR_iR_j}$ values. At the same time one can not calculate the $I_{R_iR_j}$ values for other reactions, and the points with alternative $\Delta H^{o}_{OR_iR_j}$ values vanish as well. The resulting initial data set includes only 175 independent points for 111 reactions and 83 radicals. In the present case the data were processed in the framework of MLRA for 15 radicals with the highest degrees of representation in the initial data set. The $\Delta\Delta H^{\neq}_{R\cdot}$ values of other radicals were calculated starting from $\Delta\Delta H^{\neq}_{R\cdot}$ values for H· and these 15 radicals. The initial data set for these radicals includes 81 independent points for 34 reactions. The standard deviation is equal to 1.4 kcal/mole after the exclusion of 16 points while 13 from them represent parallel data for reactions in the final data set. The standard deviations for $\Delta\Delta H^{\neq}_{R\cdot}$ are in the range from 0.20 kcal/mole for CH_3. represented by 36 points to 1.05 kcal/mole for Cl· represented by two points. These results are also listed in Tables 1 and 3.

One can estimate the D_{ij} values by using the $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values obtained as a result of the described procedures. Consequently, one can estimate also the corresponding rate constants for all combinations if the experimental values of $\Delta H^{o}_{OR_iR_j}$ or the calculated values of $I_{R_iR_j}$ are

known.

The model reflected by equations (5) and (6) is more appropriate than one could expect taking into account the general reliability of the initial data. This is due to the exclusion of less reliable or rough erroneous data and the statistical self-consistency of the remaining sets.

Certainly it should be unreasonable to take this statistical conclusion too literally.

The results of the data treatment in the coordinates of eq. (5) indicate that the adoption of $\log A_o = 16.0$ value for the bond-fission reaction of nitrocompounds is statistically groundless. Nevertheless a $\log A_o$ value higher than 14.64 for this reaction was obtained from the results of the data treatment in the coordinates of the isokinetic relationship.

In the previous paper[1] of this series we have estimated the maximum value SMX = 6 kcal/mole for the contribution to the standard deviation which could be caused by neglecting the real variation of log A values. In this study the standard deviations obtained for the final data sets (1.1 and 1.4 kcal/moles using experimental and calculated $\Delta H^o_{OR_iR_j}$ values, respectively) are significantly less in magnitude. One can conclude that the true variation of log A values is essentially lower than it can be estimated from the results of the data processing in the coordinates of the isokinetic relationship. This estimate was obtained assuming that the observed standard deviation is wholly caused by disregarding the real log A variation.

Let us assume that the upper limit of the standard deviation estimate for the data treatment in the coordinates of equations (5) and (6) is equal to 1.5 kcal/mole. If now one assumes that this value reflects the consequence of the disregard the real log A variation, the standard deviation for the real log A difference from the effective mean value at 750°K is estimated as $\Delta_{mean} = 0.4$. This means that the log A value for 2/3 cases of the total number of treated reactions varies in the range from 14.2 to 15.0 and in 95% cases from 13.8 to 15.5.

We are tempted to draw the conclusion that the variation of the supposed "real" log A values lies in even narrower statistical limits taking into account the significant contribution of experimental errors.

We shall remind once more that the present approach does not take into account the heat capacity changes during the activation leading to the formation of free radicals. A number of reactions are characterized possibly by much lower experimental Arrhenius parameters[4,5]. This conclusion is followed from the comparison of experimental activation energies and the independent experimental (iodination and bromination) estimates of the formation enthalpies of free radicals. Too low Arrhenius parameters may be caused also by the fact that the kinetic data listed in Table 2 are in many cases probably not related to the high pressure limit. Therefore, the real mean effective log A_o value should be probably higher than the one obtained from the treatment in the coordinates of the isokinetic dependence. Finally, we should note that the present approach is founded on the model with temperature independent Arrhenius parameters. Significant log A and E temperature dependence is observed in large temperature ranges[100,8,101]. It is clear that within the present approach extrapolation to high or low temperatures in these cases may bring about respective additional uncertainties.

Table 1

List and Enumeration of Departing Groups, and the Values of $\Delta H^{\neq}_{R\cdot}$ and $\Delta\Delta H^{\neq}_{R\cdot}$ for Respective Free Radicals.

$\Delta H^{\neq}_{R\cdot}(98)$ - the result of the data treatment in the coordinates of eq. (5) for 98 radicals R·.

$\Delta H^{\neq}_{R\cdot}(15)$ - the result obtained by solving the MLRA problem for 15 radicals followed by the calculation of these values for other radicals according to eq. (5).

$\Delta\Delta H^{\neq}_{R\cdot}(15)$ - the result of analogous data treatment according to eq. (6).

$^{s}\Delta H^{\neq}_{R\cdot}$ and $^{s}\Delta\Delta H^{\neq}_{R\cdot}$ - standard deviations in kcal/mole.

No	R	$\Delta H^{\neq}_{R\cdot}(98)$	$^{s}\Delta H^{\neq}_{R\cdot}$	$\Delta H^{\neq}_{R\cdot}(15)$	$^{s}\Delta H^{\neq}_{R\cdot}$	$\Delta\Delta H^{\neq}_{R\cdot}(15)$	$^{s}\Delta\Delta H^{\neq}_{R\cdot}$
0	1	2	3	4	5	6	7
0.	H	51.6	0.0	51.6	0.0	51.6	0.0
1.	F	-	-	-	-	-	-
2.	Cl	27.5	1.19	28.1	1.4	50.6	1.05
3.	Br	30.0	0.7	30.2	0.8	38.7	0.89
4.	I	29.3	0.49	31.5	0.48	24.8	0.66
5.	O	-	-	-	-	-	-
6.	OH	10.5	0.79	10.6	2.2	-	-
7.	OF	28.2	0.8	28.3	0.1	-	-

Table 1 continued

0	1	2	3	4	5	6	7
8.	OCl	-	-	-	-	-	-
9.	$OClF$	-	-	-	-	-	-
10.	ClO_2F	-	-	-	-	-	-
11.	ClO_3	-	-	-	-	-	-
12.	ClO_4	-	-	-	-	-	-
13.	N_2	-	-	-	-	-	-
14.	NH_2	44.8	0.3	44.9	0.3	53.1	0.2
15.	NF_2	8.6	0.4	8.6	0.0	-	-
16.	NO	21.2	0.38	24.3	1.49	-	-
17.	NO_2	7.2	0.25	7.1	0.3	29.2	0.5
18.	ONO_2	20.9	0.8	20.9	0.25	-	-
19.	CO	-	-	-	-	-	-
20.	CO_2	-	-	-	-	-	-
21.	SH	18.7	0.68	19.9	0.68	39.3	0.8
22.	SF_5	-	-	-	-	-	-
23.	SO_3F	-	-	-	-	-	-
24.	OCH_3	4.2	0.25	4.0	0.3	51.6	1.0
25.	OCF_3	-	-	-	-	-	-
26.	OC_2H_5	-2.2	0.18	-1.3	2.5	60.4	1.49
27.	OC_3H_7	-8.0	0.7	-10.9	0.1	-	-

Table 1 continued

0	1	2	3	4	5	6	7
28.	$OCH(CH_3)_2$	-	-	-	-	-	-
29.	OC_4H_9	-	-	-	-	-	-
30.	$OC(CH_3)_3$	-15.9	0.16	-15.9	0.19	-	-
31.	$OC(CH_3)_2C_2H_5$	-	-	-	-	-	-
32.	$OCH = CH_2$	12.6	1.15	14.2	-	-	-
33.	$OCH(CH_2ONO_2)_2$	-	-	-	-	-	-
34.	$OCOCH_3$	-	-	-	-	-	-
35.	$OCOC_2H_5$	-	-	-	-	-	-
36.	$OCOC_3H_7$	-	-	-	-	-	-
37.	$OCOC_6H_5$	-	-	-	-	-	-
38.	OC_6H_5	-	-	20.1	4.5	-	-
39.	$NHCH_3$	39.2	1.1	39.2	-	51.1	1.1
40.	NHC_6H_5	60.0	0.6	59.8	1.4	-	-
41.	$N(CH_3)_2$	36.0	1.1	35.9	-	44.0	-
42.	$N(C_2H_5)_2$	-	-	-	-	-	-
43.	$N(CH_3)C_6H_5$	63.0	0.7	62.9	1.9	-	-
44.	$N = CHCH_3$	-	-	-	-	-	-
45.	$NNCH_3$	-	-	-	-	-	-
46.	$NNCD_3$	-	-	-	-	-	-
47.	$NNCF_3$	-	-	-	-	-	-

Table 1 continued

0	1	2	3	4	5	6	7
48.	NNC_2H_5	-	-	-	-	-	-
49.	NNC_3H_7	48.3	1.2	49.5	-	-	-
50.	$NNCH(CH_3)_2$	-	-	51.4	6.2	-	-
51.	NNC_4H_9	-	-	-	-	-	-
52.	$NNCH(CH_3)C_2H_5$	-	-	-	-	-	-
53.	$NNC(CH_3)_3$	31.3	0.8	31.1	1.4	-	-
54.	$NNCH_2CH{=}CH_2$	-	-	-	-	-	-
55.	$NNN(CH_3)_2$	-	-	-	-	-	-
56.	$NNN(C_2H_5)_2$	-	-	-	-	-	-
57.	$NOCH_3$	-	-	-	-	-	-
58.	$NOCH_2CH(CH_3)_2$	-	-	-	-	-	-
59.	SCH_3	14.7	1.1	14.8	-	36.1	-
60.	SC_6H_5	42.8	1.1	42.7	-	-	-
61.	SO_2CH_3	-74.5	0.8	-72.5	3.1	-	-
62.	$Si(CH_3)_3$	-1.2	0.3	-1.2	0.2	-	-
63.	$ZnCH_3$	48.9	1.1	48.7	-	-	-
64.	$CdCH_3$	53.8	0.6	53.7	1.3	-	-
65.	HgCl	22.7	0.9	22.0	1.9	-	-
66.	HgBr	29.1	1.2	28.5	-	-	-

Table 1 continued

0	1	2	3	4	5	6	7
67.	$HgCH_3$	51.1	0.3	51.2	0.9	-	-
68.	HgC_2H_5	47.8	0.8	50.5	5.9	-	-
69.	$HgCH(CH_3)_2$	35.4	0.8	35.2	0.7	-	-
70.	$HgCH = CH_2$	-	-	-	-	-	-
71.	$Ga(CH_3)_2$	-	-	-	-	-	-
72.	$In(CH_3)_2$	-	-	-	-	-	-
73.	$Tl(CH_3)_2$	-	-	-	-	-	-
74.	$SnCl_2CH_3$	-8.2	1.1	-8.3	-	-	-
75.	$Sn(CH_3)_3$	33.9	0.79	29.8	4.7	-	-
76.	$Pb(CH_3)_3$	-	-	54.5	6.6	-	-
77.	$Pb(C_2H_5)_3$	57.6	0.85	59.1	0.8	-	-
78.	$Sb(CH_3)_2$	-	-	-	-	-	-
79.	$Bi(CH_3)_2$	-	-	-	-	-	-
80.	CH_3	31.9	0.15	32.1	0.18	48.0	0.2
81.	CD_3	-	-	-	-	-	-
82.	C_2H_5	25.2	0.36	23.7	0.4	41.9	0.48
83.	C_3H_7	20.7	0.68	19.5	2.66	41.3	3.4
84.	$CH(CH_3)_2$	17.1	0.3	17.4	0.4	37.3	0.5
85.	C_4H_9	-	-	-	-	-	-
86.	$CH(CH_3)C_2H_5$	14.0	0.49	13.9	0.27	35.9	1.8

Table 1 continued

0	1	2	3	4	5	6	7
87.	$C(CH_3)_3$	10.4	0.3	10.5	0.36	35.9	0.48
88.	$CH(CH_3)CH(CH_3)_2$	9.7	1.1	9.6	-	37.4	-
89.	$C(CH_3)_2C_2H_5$	7.0	0.8	7.7	0.39	33.7	0.88
90.	$CH_2CH = CH_2$	40.9	0.45	40.3	0.56	31.9	0.45
91.	$CH_2C(CH_3)=CH_2$	31.9	1.09	31.9	-	30.9	-
92.	$CH(CH_3)CH=CH_2$	33.1	1.1	33.0	-	28.9	0.75
93.	$C(CH_3)_2CH=CH_2$	25.3	1.1	25.2	-	24.4	-
94.	$CH_2C\equiv CH$	-	-	-	-	36.0	-
95.	CH_2Cl	28.3	1.3	28.0	-	45.9	-
96.	CH_2Br	45.9	1.3	45.7	-	48.8	-
97.	CH_2OCH_3	-	-	-	-	32.3	8.5
98.	CH_2COOH	-	-	-	-	-	-
99.	CH_2CN	58.7	0.6	59.3	1.8	38.5	0.26
100.	$CH_2C_6H_5$	51.8	0.4	51.8	0.4	34.6	0.5
101.	$CH_2(2\text{-}CH_3\text{-}C_6H_4)$	41.1	1.1	41.1	-	30.1	-
102.	$CH_2(3\text{-}CH_3\text{-}C_6H_4)$	43.9	1.1	43.9	-	33.0	-
103.	$CH_2(4\text{-}CH_3\text{-}C_6H_4)$	42.0	0.6	42.0	0.6	31.0	0.6
104.	$CH_2(1\text{-}C_{10}H_7)$	65.5	1.1	65.6	-	-	-
105.	$CH_2(2\text{-}C_{10}H_7)$	65.4	1.1	65.5	-	-	-

Table 1 continued

0	1	2	3	4	5	6	7
106.	$2\text{-}CH_2\text{-}C_5H_4N$	61.9	1.1	61.9	-	32.9	-
107.	$3\text{-}CH_2\text{-}C_5H_4N$	64.6	1.1	64.6	-	33.9	-
108.	$4\text{-}CH_2\text{-}C_5H_4N$	-	-	-	-	-	-
109.	$CHCl_2$	18.5	1.3	18.3	-	37.7	-
110.	$CHBr_2$	-	-	45.5	4.2	41.5	-
111.	$CHFNO_2$	-	-	-	-	49.3	-
112.	$CH(NO_2)_2$	36.8	0.8	36.9	2.1	46.7	-
113.	$CH(C_6H_5)_2$	-	-	-	-	25.8	-
114.	CF_3	-122.7	0.5	-121.4	7.4	32.4	4.0
115.	CCl_3	15.3	1.0	15.1	0.4	32.8	0.2
116.	CBr_3	52.2	1.0	52.0	0.7	34.6	-
117.	CF_2NF_2	-63.0	1.2	-63.0	-	-	-
118.	CF_2NO_2	-54.5	1.1	-54.4	-	50.1	-
119.	$CF(NF_2)_2$	-6.9	1.2	-6.9	-	-	-
120.	$CFClNO_2$	-	-	-	-	48.4	-
121.	$CFBrNO_2$	-	-	-	-	47.3	-
122.	$CFINO_2$	-	-	-	-	46.6	-
123.	$CF(NO_2)_2$	1.1	1.1	1.2	-	55.5	-
124.	CCl_2NO_2	-	-	-	-	42.2	-
125.	$CCl(NF_2)_2$	-	-	-	-	-	-

Table 1 continued

0	1	2	3	4	5	6	7
126.	$CCl(NO_2)_2$	38.3	1.1	38.4	-	48.3	-
127.	$CBr(NO_2)_2$	47.6	1.1	47.7	-	47.3	-
128.	$Cl(NO_2)_2$	-	-	-	-	46.6	-
129.	$C(NF_2)_3$	36.4	1.2	36.4	-	-	-
130.	$C(NO_2)_3$	53.2	0.8	53.3	0.8	51.5	0.8
131.	$COOH$	-	-	-	-	44.7	3.5
132.	$COCH_3$	-5.8	0.4	-7.7	-3.5	39.9	4.2
133.	$COCF_3$	-	-	-	-	-	-
134.	COC_6H_5	-	-	-	-	-	-
135.	$C(C_6H_5)_3$	102.0	1.1	102.0	-	23.4	-
136.	CH_2CH_2Cl	26.3	1.6	25.7	-	44.6	-
137.	$CH(OH)CH_3$	-	-	-	-	35.9	-
138.	$CH(CH_3)NO_2$	17.0	1.6	17.1	-	39.3	-
139.	$CH(CH_3)C_6H_5$	46.1	1.1	46.0	-	31.7	-
140.	CCl_2CH_3	-	-	-	-	39.1	-
141.	$C(NO_2)_2CH_3$	25.6	1.1	25.7	-	44.1	-
142.	$CF(NO_2)CH_3$	-	-	-	-	46.7	-
143.	$CCl(NO_2)CH_3$	-	-	-	-	40.7	-
144.	$CBr(NO_2)CH_3$	-	-	-	-	40.8	-
145.	$C(CN)(CH_3)C_6H_5$	-	-	-	-	25.4	-

Table 1 continued

0	1	2	3	4	5	6	7
146.	$CF(NO_2)CF(NO_2)_2$	-	-	-	-	53.4	-
147.	$C(NO_2)_2CF(NO_2)_2$	12.5	1.1	12.6	-	50.4	-
148.	$C(NO_2)_2C(NO_2)_3$	71.3	1.1	71.4	-	50.7	-
149.	$CH(NO_2)C_2H_5$	15.4	1.1	15.5	1.3	40.0	-
150.	$C(CH_3)_2OH$	-	-	-	-	34.3	-
151.	$C(CH_3)_2CN$	41.8	1.1	41.6	-	28.9	-
152.	$C(CH_3)_2NO_2$	11.7	1.1	11.8	-	37.9	-
153.	$CCl_2C_2H_5$	-	-	-	-	39.0	-
154.	$C(NO_2)_2C_2H_5$	20.9	1.1	21.0	-	44.0	-
155.	$CH(NO_2)C_3H_7$	10.2	1.1	10.3	-	39.9	-
156.	$C(NO_2)_2C_3H_7$	-	-	-	-	43.5	-
157.	$CH = CH_2$	55.5	0.8	55.4	2.9	45.0	2.9
158.	$C(CH_3) = CH_2$	40.5	1.1	40.3	-	34.8	-
159.	$C(CF_3) = CF_2$	-	-	-	-	-	-
160.	C_6H_5	73.4	0.6	74.1	0.6	55.2	0.8
161.	$2\text{-}Cl\text{-}C_6H_4$	-	-	-	-	-	-
162.	$3\text{-}Cl\text{-}C_6H_4$	-	-	-	-	-	-
163.	$4\text{-}Cl\text{-}C_6H_4$	-	-	-	-	-	-
164.	$2\text{-}NO_2\text{-}C_6H_4$	75.1	1.1	75.2	-	-	-
165.	$3\text{-}NO_2\text{-}C_6H_4$	71.7	0.8	71.9	1.6	53.3	-

Table 1 continued

0	1	2	3	4	5	6	7
166.	4-NO_2-C_6H_4	68.7	1.1	68.8	-	52.3	-
167.	2-CH_3-C_6H_4	-	-	-	-	-	-
168.	3-CH_3-C_6H_4	-	-	-	-	-	-
169.	4-CH_3-C_6H_4	62.2	0.6	61.0	2.3	47.0	3.1
170.	2,5-$(NO_2)_2$-C_6H_3	-	-	-	-	-	-
171.	2,6-$(NO_2)_2$-C_6H_3	-	-	-	-	-	-
172.	3,5-$(NO_2)_2$-C_6H_3	-	-	78.9	5.7	50.7	-
173.	2-CH_3-5-NO_2-C_6H_3	-	-	-	-	-	-
174.	3-CH_3-5-NO_2-C_6H_3	-	-	-	-	-	-
175.	4-Cl-3,5-$(NO_2)_2$-C_6H_2	-	-	-	-	-	-
176.	4-NH_2-3,5-$(NO_2)_2$-C_6H_2	-	-	-	-	-	-
177.	4-CH_3-3,5-$(NO_2)_2$-C_6H_2	-	-	-	-	-	-
178.	I-$C_{10}H_7$	74.1	1.2	75.7	-	-	-
179.	2-$C_{10}H_7$	-	-	-	-	-	-
180.	9- Anthracenyl	-	-	-	-	-	-
181.	9- Phenanthrenyl	-	-	-	-	-	-
182.	CH_2F	-	-	-	-	-	-
183.	CH_2I	-	-	-	-	-	-
184.	CHF_2	-	-	-	-	-	-
185.	CN	-	-	-	-	-	-

Table 1 continued

0	1	2	3	4	5	6	7
186.	CHFCl	-	-	-	-	-	-
187.	CHFBr	-	-	-	-	-	-
188.	CHFI	-	-	-	-	-	-
189.	C_6H_{11} (cyclo-hexyl)	-	-	-	-	36.1	-

Note. Lack of $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values in the table indicates the following possibilities: 1) the given radical is in combination with only one other radical and it is impossible to calculate the $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values for either of them; 2) the combinations with the given radical have neither $\Delta H^{o}_{OR_iR_j}$ nor $I_{R_iR_j}$ values; 3) radicals 182-188 which have no Arrhenius parameters are included due to the fact that later on they will take into account their substituent effects. There are log A and E values for cases 1) and 2) in Table 2 and these data were used in the data treatment of the coordinates of log k_{T_2} - log k_{T_1} from ref. 1.

Table 2

Initial Experimental Data for Homolyzing Compounds R_iR_j.

i and j correspond to the enumeration of R from Table 1.

T_{mean} and ΔT - mean temperature and the value of temperature range in ^oK.

n - statistical factor.

$\Delta H^o_{OR_iR_j}$, E_{ij} and D_{ij} are in kcal/mole.

References of $\Delta H^o_{OR_iR_j}$ sources are listed if this value has not been taken from ref. 56-58.

No	i	j	T_{mean}	ΔT	n	$\Delta H^o_{OR_iR_j}$	log A_{ij}	E_{ij}	D_{ij}	Source of log A_{ij} and E_{ij} values	Date	Source of $\Delta H^o_{OR_iR_j}$ values
1	2	3	4	5	6	7	8	9	10	11	12	13
1	80	0	1500	(600)	4	-15.9	14.71	101.0	104.72	(11, P. 72)	1959	
2	80	0	1670	(160)	4	-15.9	15.00	103.0	104.84	(11, P. 72)	1965	
3	80	0	1225	(150)	4	-15.9	14.10	101.0	107.45	(11, P. 72)	1963	
4	80	0	1475	(650)	4	-15.9	14.58	103.0	107.47	(11, P. 72)	1963	
5	80	0	1050	(108)	4	-15.9	16.45	107.6	101.83	(12)	1975	
6	91	0	1000	(150)	3	0.98	13.7	76.0	82.53	(11, P. 72)	1949	
7	99	0	1200	(80)	3	22.7	11.8	72.0	90.26	(13)	1969	
8	100	0	999	(-)	3	17.5	13.3	77.5	85.85	(11, P. 72)	1947	
9	100	0	1050	(230)	3	17.5	14.8	85.5	87.07	(11, P. 72)	1962	
10	101	0	1050	(107)	3	11.1	13.7	74.8	81.64	(11, P. 72)	1948	
11	102	0	1070	(127)	3	10.9	13.6	77.1	84.56	(11, P. 72)	1948	
12	103	0	1080	(115)	3	11.06	13.7	76.2	83.24	(11, P. 72)	1948	
13	103	0	1200	(300)	3	11.06	13.97	76.0	82.35	(11, P. 72)	1962	
14	103	0	850	(125)	3	11.06	14.43	79.5	82.21	(11, P. 72)	1955	
15	106	0	1075	(43)	3	29.03	13.3	75.5	84.48	(11, P. 73)	1948	
16	107	0	1075	(43)	3	30.75	13.3	76.5	85.48	(11, P. 73)	1948	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
17	80	80	899	(-)	1	-16.3	17.0	85.0	75.29	(11, P. 74)	1955	
18	80	80	1075	(70)	1	-16.3	15.0	87.0	85.22	(11, P. 74)	1955	
19	80	80	1230	(361)	1	-16.3	14.7	79.3	79.00	(11, P. 74)	1960	
20	80	80	1000	(95)	1	-16.3	16.3	86.0	78.44	(11, P. 74)	1959	
21	80	80	899	(-)	1	-16.3	16.5	85.0	77.35	(11, P. 74)	1961	
22	80	80	860	(44)	1	-16.3	17.45	91.74	80.71	(11, P. 74)	1963	
23	80	80	810	(125)	1	-16.3	14.5	81.0	81.51	(11, P. 74)	1964	
24	80	80	858	(70)	1	-16.3	16.00	86.00	80.66	(11, P. 74)	1966	
25	80	80	980	(120)	1	-16.3	16.8	88.4	78.74	(14)	1972	
26	80	80	860	(37)	1	-16.3	16.3	88.0	81.50	(11, P. 74)	1966	
27	80	80	830	(100)	1	-16.3	16.0	86.3	81.12	(15)	1976	
28	82	80	899	(-)	2	-19.7	17.6	82.0	71.10	(11, P. 74)	1955	
29	83	80	899	(-)	2	-23.6	18.58	86.3	71.36	(11, P. 75)	1962	
30	84	80	350	(100)	3	-25.2	18.5	80.9	75.47	(11, P. 75)	1966	
31	84	80	840	(30)	3	-25.2	18.9	80.0	65.49	(11, P. 75)	1966	
32	84	80	800	(0)	3	-25.2	18.4	83.1	71.10	(11, P. 75)	1967	
33	84	80	760	(101)	3	-25.2	17.8	82.5	73.20	(11, P. 75)	1968	
34	87	80	810	(70)	4	-31.8	17.4	83.0	75.03	(11, P. 75)	1957	
35	87	80	899	(-)	4	-31.8	16.1	78.2	74.70	(11, P. 75)	1966	
36	87	80	1000	(150)	4	-31.8	16.9	80.5	72.95	(11, P. 75)	1969	
37	87	80	800	(89)	4	-31.8	16.1	78.9	75.78	(16)	1976	
38	87	80	760	(80)	4	-31.8	16.8	82.0	76.61	(17)	1971	
39	87	80	770	(110)	4	-31.8	18.05	85.6	75.73	(18)	1969	
40	87	80	870	(160)	4	-31.8	17.7	85.0	75.25	(19)	1973	
41	87	80	1150	(170)	4	-31.8	16.2	77.8	72.80	(20)	1973	
42	157	80	1375	(550)	1	8.5	16.07	85.84	76.89	(11, P. 74)	1968	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
43	157	80	899	(-)	1	8.5	17.8	94.0	81.04	(11, P. 74)	1966	
44	90	80	945	(90)	1	4.96	12.71	59.1	67.47	(11, P. 75)	1965	
45	90	80	850	(106)	1	4.96	13.9	69.5	72.41	(11, P. 75)	1968	
46	90	80	990	(106)	1	4.96	13.0	62.2	69.61	(11, P. 75)	1950	
47	90	80	730	(77)	1	4.96	16.3	71.5	65.98	(21)	1970	
48	88	80	1100	(200)	4	-32.7	16.6	81.1	74.30	(11, P. 75)	1965	
49	92	80	710	(55)	2	-0.68	15.9	68.8	65.70	(21)	1970	
50	93	80	685	(53)	3	-5.82	16.9	68.6	63.03	(21)	1970	
51	158	80	1200	(270)	2	0.98	18.26	89.6	71.41	(22)	1976	
52	100	80	900	(150)	1	13.9	13.0	63.2	69.94	(11, P. 76)	1949	
53	100	80	899	(-)	1	13.9	14.9	70.5	69.47	(11, P. 76)	1967	
54	100	80	940	(124)	1	13.9	14.6	70.1	70.30	(11, P.76)	1963	
55	100	80	960	(104)	1	13.9	14.7	69.2	68.97	(11, P. 76)	1969	
56	139	80	940	(97)	2	9.26	14.3	66.0	68.80	(11, P. 76)	1964	
57	169	80	860	(125)	2	11.06	14.67	81.8	82.89	(11, P. 77)	1955	
58	169	80	1220	(300)	2	11.06	12.97	72.0	83.05	(11, P. 77)	1955	
59	169	80	950	(61)	2	11.06	12.3	67.0	78.52	(11, P. 77)	1964	
60	24	80	860	(154)	2	-40.1	15.0	76.0	75.76	(48)	1975	
61	24	80	785	(154)	2	-40.1	17.5	81.0	71.80	(11, P. 89)	1963	
62	132	80	750	(300)	2	-47.7	15.0	68.0	67.79	(11, P. 77)	1946	
63	132	80	1050	(100)	2	-47.7	14.15	70.9	74.73	(11, P. 77)	1956	
64	132	80	1050	(108)	2	-47.7	14.38	72.0	74.74	(11, P. 77)	1955	
65	132	80	1020	(150)	2	-47.7	15.43	69.5	67.26	(11, P. 77)	1966	
66	17	80	650	(130)	1	-14.55	11.4	42.8	52.45	(11, P. 85)	1950	
67	17	80	683	(60)	1	-14.55	14.6	53.6	53.74	(11, P. 85)	1950	
68	17	80	623	(60)	1	-14.55	13.43	50.0	53.47	(11, P. 85)	1953	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
69	17	80	600	(27)	1	-14.55	13.73	49.2	51.71	(11, P. 85)	1959	
70	17	80	675	(100)	1	-14.55	14.1	55.2	56.88	(11, P. 85)	1969	
71	17	80	650	(30)	1	-14.55	14.35	54.3	55.18	(11, P. 85)	1971	
72	17	80	1200	(600)	1	-14.55	16.25	58.5	49.65	(34)	1972	
73	21	80	1050	(97)	1	-18.4	13.48	67.0	72.62	(11, P. 89)	1954	
74	61	80	800	(30)	2	-99.9	14.33	60.6	62.86	(11, P. 90)	1961	
75	4	80	800	(0)	1	5.4	13.41	54.7	59.19	(11, P. 83)	1951	
76	4	80	800	(0)	1	6.4	13.41	54.7	59.19	(11, P. 83)	1951	
77	82	82	899	(-)	1	-23.6	18.58	86.3	70.12	(11, P. 75)	1962	
78	82	82	940	(86)	1	-23.6	15.3	77.2	74.39	(23)	1974	
79	89	82	1150	(154)	2	36.9	16.57	77.1	68.57	(2)	1969	
80	100	82	950	(149)	1	9.8	12.48	57.5	66.93	(11, P. 76)	1952	
81	100	82	940	(161)	1	9.8	14.9	68.5	67.42	(11, P. 76)	1963	
82	21	82	860	(153)	1	-22.4	13.48	63.0	67.60	(11, P. 89)	1954	
83	84	84	1100	(200)	1	-32.7	16.1	76.0	68.70	(11, P. 75)	1965	
84	87	84	1140	(130)	1	-37.7	16.2	73.0	64.91	(11, P. 76)	1967	
85	89	84	1090	(127)	1	-39.0	16.15	71.3	63.80	(2)	1969	
86	87	87	1060	(155)	1	-41.2	16.3	68.5	60.49	(11, P. 76)	1966	
87	136	2	673	(40)	2	-22.2	13.0	70.0	75.97	(11, P. 79)	1952	
88	96	3	970	(100)	2	6.1	13.3	62.5	69.82	(11, P. 79)	1951	
89	110	3	840	(112)	3	10.2	13.3	55.5	62.52	(11, P. 79)	1951	
90	110	3	840	(112)	3	16.2	13.3	55.5	62.52	(11, P. 79)	1951	
91	116	3	740	(105)	4	19.1	13.3	49.0	55.61	(11, P. 79)	1951	
92	116	3	740	(105)	4	26.1	13.3	49.0	55.61	(11, P. 79)	1951	
93	116	3	740	(105)	4	27.1	13.3	49.0	55.61	(11, P. 79)	1951	
94	114	3	1055	(70)	1	-151.2	13.3	64.5	71.01	(11, P. 79)	1951	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
95	114	3	1055	(70)	1	-155.1	13.3	64.5	71.01	(11, P. 79)	1951	
96	95	3	955	(91)	1	-8.64	13.3	61.0	66.89	(11, P. 79)	1951	
97	109	3	850	(91)	1	-10.2	13.3	53.5	58.75	(11, P. 80)	1951	
98	115	3	775	(109)	1	-8.8	13.3	49.0	53.78	(11, P. 80)	1950	
99	115	3	775	(109)	1	-8.2	13.3	49.0	53.78	(11, P. 80)	1950	
100	160	3	1090	(113)	1	21.6	13.3	70.9	77.62	(11, P. 80)	1952	
101	114	4	675	(100)	1	-142.6	15.4	47.2	44.87	(27)	1975	
102	114	4	675	(100)	1	-138.0	15.4	47.2	44.87	(27)	1975	[59]
103	14	14	1000	(120)	1	26.15	12.6	60.0	69.38	(11, P. 98)	1949	
104	14	14	960	(147)	1	26.15	11.7	54.15	67.09	(11, P. 98)	1963	
105	14	14	1350	(500)	1	26.15	12.8	52.0	63.42	(11, P. 98)	1965	
106	14	14	1350	(500)	1	26.15	12.0	48.0	64.30	(11, P. 98)	1965	
107	14	14	1250	(580)	1	26.15	13.0	54.0	63.38	(11, P. 98)	1965	
108	39	14	700	(316)	1	27.5	13.19	51.9	56.56	(11, P. 98)	1963	
109	17	17	275	(48)	1	4.64	16.0	13.0	11.28	(11, P. 103)	1953	
110	17	17	275	(48)	1	4.47	16.0	13.0	11.28	(11, P.103)	1953	
111	18	17	298	(10)	2	5.7	13.1	20.0	22.52	(11, P.103)	1957	
112	18	17	298	(10)	2	5.7	14.1	21.0	22.16	(11, P.103)	1957	
113	7	17	383	(40)	1	4.3	15.39	32.3	30.99	(11, P.103)	1962	
114	7	17	373	(20)	1	4.3	14.96	31.75	31.20	(11, P.103)	1961	
115	15	15	650	(67)	1	-1.23	14.98	19.4	18.40	(11, P. 98)	1965	
116	15	15	400	(102)	1	-1.23	15.37	19.8	18.47	(30)	1973	
117	83	100	925	(100)	1	5.93	14.48	65.0	65.71	(11, P. 77)	1952	
118	83	100	900	(145)	1	5.93	14.50	67.2	67.76	(11, P. 77)	1963	
119	13	5	1899	(-)	1	20.4	11.66	60.6	86.57	(11, P.102)	1951	
120	13	5	1899	(-)	1	20.4	11.70	60.0	85.63	(11, P.102)	1955	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
121	13	5	1850	(700)	1	20.4	10.36	55.7	92.00	(11, P.102)	1964	
122	13	5	1950	(900)	1	20.4	11.40	59.5	88.50	(11, P.102)	1966	
123	10	5	753	(30)	3	-3.03	13.59	58.4	63.68	(11, P.104)	1960	
124	10	5	753	(30)	3	-3.60	13.59	58.4	63.68	(11, P.104)	1960	
125	22	1	1850	(400)	6	-285.7	12.95	75.92	96.88	(11, P.104)	1969	
126	22	1	1850	(400)	6	-285.2	12.95	75.92	96.88	(11, P.104)	1969	
127	22	1	1850	(400)	6	-288.2	12.95	75.92	96.88	(11, P.104)	1969	
128	135	0	970	(100)	1	78.6	16.45	83.0	75.01	(11, P. 73)	1960	
129	104	0	999	(-)	3	34.8	13.18	73.5	82.40	(11, P. 73)	1950	
130	105	0	999	(-)	3	34.7	13.18	73.5	82.40	(11, P. 73)	1950	
131	38	80	760	(75)	1	-12.4	13.7	58.0	61.3	(49)	1975	[60]
132	38	80	760	(75)	1	-6.0	13.7	58.0	61.3	(49)	1975	[61]
133	40	80	880	(136)	1	28.2	13.4	60.0	65.03	(11, P. 84)	1963	
134	40	80	880	(136)	1	27.0	13.4	60.0	65.03	(11, P. 84)	1963	[62]
135	43	80	890	(129)	2	30.9	12.9	57.0	65.35	(11, P. 84)	1964	
136	43	80	890	(129)	2	28.2	12.9	57.0	65.35	(11, P. 84)	1964	[62]
137	60	80	900	(154)	1	14.0	14.48	60.0	60.70	(11, P. 89)	1960	
138	63	80	970	(254)	2	17.2	11.25	47.2	63.57	(11, P. 90)	1957	
139	64	80	800	(102)	2	30.3	11.9	45.8	56.95	(11, P. 90)	1957	
140	64	80	770	(57)	2	30.3	12.3	45.8	55.13	(11, P. 90)	1965	
141	64	80	770	(57)	2	30.3	13.4	48.8	54.25	(11, P. 90)	1965	
142	67	80	800	(63)	2	27.0	13.5	51.5	56.77	(11, P. 90)	1953	[63]
143	67	80	590	(39)	2	27.0	14.28	51.3	53.10	(11, P. 90)	1955	[63]
144	67	80	810	(143)	2	27.0	13.1	50.1	56.95	(11, P. 90)	1957	[63]
145	67	80	750	(103)	2	27.0	13.6	51.0	55.63	(11, P. 91)	1963	[63]
146	67	80	700	(185)	2	27.0	15.7	57.9	55.49	(11, P. 91)	1959	[63]

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
147	67	80	750	(99)	2	27.0	14.8	53.7	54.20	(11, P. 91)	1963	[63]
148	67	80	650	(116)	2	27.0	15.02	58.0	57.79	(11, P. 91)	1964	[63]
149	67	80	800	(63)	2	26.4	13.5	51.5	56.77	(11, P. 90)	1953	[64]
150	67	80	590	(39)	2	26.4	14.28	51.3	53.10	(11, P. 90)	1955	[64]
151	67	80	810	(143)	2	26.4	13.1	50.1	56.95	(11, P. 90)	1957	[64]
152	67	80	750	(103)	2	26.4	13.6	51.0	55.63	(11, P. 91)	1963	[64]
153	67	80	700	(185)	2	26.4	15.7	57.9	55.49	(11, P. 91)	1959	[64]
154	67	80	750	(99)	2	26.4	14.8	53.7	54.20	(11, P. 91)	1963	[64]
155	67	80	650	(116)	2	26.4	15.02	58.0	57.79	(11, P. 91)	1964	[64]
156	75	80	870	(138)	4	2.9	15.7	64.5	62.71	(52)	1972	[64]
157	75	80	870	(138)	4	3.4	15.7	64.5	62.71	(52)	1972	[65]
158	75	80	870	(138)	4	-6.1	15.7	64.5	62.71	(52)	1972	[66]
159	75	80	870	(138)	4	-3.5	15.7	64.5	62.71	(52)	1972	[67]
160	74	80	890	(134)	2	-38.2	13.52	56.1	61.91	(11, P. 93)	1958	
161	76	80	710	(82)	4	40.1	14.7	49.4	51.18	(53)	1972	[64]
162	76	80	710	(82)	4	30.7	14.7	49.4	51.18	(53)	1972	[66]
163	99	80	1000	(79)	1	15.7	14.1	72.7	75.20	(11, P. 78)	1965	[69]
164	99	80	1000	(79)	1	14.5	14.1	72.7	75.20	(11, P. 78)	1965	[71]
165	151	80	900	(50)	3	5.6	15.16	70.2	70.02	(11, P. 78)	1965	
166	178	82	980	(122)	1	31.2	13.9	64.8	68.15	(11, P. 77)	1955	
167	4	82	710	(40)	1	0.43	14.33	51.6	52.62	(11, P.83)	1964	[72]
168	4	82	730	(140)	1	0.43	11.9	45.0	54.18	(11, P. 83)	1965	[72]
169	4	82	730	(140)	1	0.43	13.65	50.0	53.34	(11, P. 83)	1965	[72]
170	4	82	710	(40)	1	1.9	14.33	51.6	52.62	(11, P. 83)	1964	[73]
171	4	82	730	(140)	1	1.9	11.9	45.0	54.18	(11, P. 83)	1965	[73]
172	4	82	730	(140)	1	1.9	13.65	50.0	53.34	(11, P. 83)	1965	[73]

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
173	26	82	860	(70)	2	-53.2	14.0	78.0	81.70	(11, P. 89)	1964	[74]
174	26	82	860	(70)	2	-53.7	14.0	78.0	81.70	(11, P. 89)	1964	[76]
175	32	82	640	(0)	1	-28.5	15.9	70.0	66.33	(11, P. 89)	1967	
176	68	82	620	(50)	2	28.4	13.0	49.5	55.00	(11, P. 91)	1953	[63]
177	68	82	640	(100)	2	28.4	14.1	42.5	44.99	(11, P. 91)	1956	[63]
178	68	82	640	(72)	2	28.4	15.4	45.7	44.37	(50)	1971	[63]
179	68	82	620	(50)	2	23.7	13.0	49.5	55.00	(11, P. 91)	1953	[64]
180	68	82	640	(100)	2	23.7	14.1	42.5	44.99	(11, P. 91)	1956	[64]
181	68	82	640	(72)	2	23.7	15.4	45.7	44.37	(50)	1971	[64]
182	77	82	530	(30)	4	38.8	12.08	36.9	44.58	(11, P. 93)	1933	
183	77	82	530	(42)	4	38.8	12.6	37.0	43.43	(11, P. 93)	1964	
184	69	84	375	(60)	2	19.3	11.0	27.0	33.76	(11, P. 91)	1963	[77]
185	69	84	375	(60)	2	18.3	11.0	27.0	33.76	(11, P. 91)	1963	[64]
186	100	84	1100	(0)	1	4.4	15.23	69.1	66.17	(2)	1969	
187	17	84	1050	(285)	1	-27.5	15.38	54.0	50.49	(36)	1973	[78]
188	17	84	1050	(285)	1	-27.1	15.38	54.0	50.49	(36)	1973	[79]
189	90	87	1070	(130)	1	-8.9	15.78	65.53	59.59	(11, P. 76)	1967	
190	16	87	700	(300)	1	3.8	15.6	36.0	32.95	(55)	1974	
191	90	90	910	(93)	1	25.7	13.4	56.0	61.20	(11, P. 76)	1967	
192	90	90	1020	(93)	1	25.7	13.3	45.6	51.58	(11, P. 76)	1966	
193	2	90	921	(119)	1	2.9	13.17	59.3	65.48	(11, P. 79)	1954	
194	3	90	800	(133)	1	16.6	12.7	47.5	54.63	(11, P. 80)	1950	
195	4	90	900	(326)	1	26.3	14.45	42.8	43.61	(29)	1972	
196	61	90	690	(100)	1	-82.2	14.1	47.7	49.42	(11, P. 90)	1961	
197	100	3	820	(104)	1	21.8	13.3	50.5	55.56	(11, P. 81)	1949	
198	100	3	820	(104)	1	25.5	13.3	50.5	55.56	(11, P. 81)	1949	[81]

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
199	100	3	820	(104)	1	26.7	13.3	50.5	55.56	(11, P. 81)	1949	[82]
200	160	4	910	(94)	1	44.6	15.0	64.4	62.89	(28)	1976	[83]
201	160	4	910	(94)	1	43,0	15.0	64.4	62.89	(28)	1976	[84]
202	40	14	650	(112)	1	54.8	11.8	39.99	48.46	(11, P. 98)	1964	
203	41	14	770	(122)	1	26.2	13.22	49.6	54.62	(11, P. 98)	1963	
204	118	17	535	(35)	2	-92.5	15.83	47.4	45.23	(11, P. 85)	1968	
205	112	17	463	(20)	3	4.8	15.94	42.4	40.66	(11, P. 85)	1969	[85]
206	112	17	463	(20)	3	1.9	15.94	42.4	40.66	(11, P. 85)	1969	[86]
207	123	17	480	(58)	3	-33.0	15.4	41.9	41.29	(11, P. 85)	1968	
208	126	17	415	(45)	3	10.29	15.75	36.4	35.17	(11, P. 86)	1967	
209	127	17	408	(50)	3	20.4	16.1	36.2	34.37	(11, P. 86)	1967	
210	130	17	520	(153)	4	24.4	17.53	40.9	35.46	(11, P. 86)	1966	
211	130	17	405	(91)	4	24.4	16.3	38.6	36.64	(11, P. 86)	1967	
212	138	17	500	(69)	2	-18.8	16.74	47.1	43.00	(11, P. 86)	1968	
213	141	17	460	(50)	3	-6.1	17,18	43.2	38.87	(11, P. 86)	1968	
214	147	17	387	(52)	3	-12.9	17.3	36.5	32.63	(11, P. 86)	1968	
215	148	17	383	(40)	6	46.0	17.3	35.8	32.49	(11, P. 86)	1967	
216	149	17	515	(50)	2	-21.7	16.91	48.0	43.38	(11, P. 87)	1968	[79]
217	149	17	515	(50)	2	-19.9	16.91	48.0	43.38	(11, P. 87)	1968	[79]
218	152	17	465	(35)	2	-24.0	18.5	50.5	42.92	(11, P. 87)	1962	
219	154	17	453	(40)	3	-10.6	16.86	42.3	38.69	(11, P. 87)	1968	
220	155	17	515	(48)	2	-25.9	17.0	48.2	43.33	(11, P. 87)	1968	
221	160	17	720	(70)	1	20.7	17.32	69.7	60.89	(38)	1975	[87]
222	160	17	690	(50)	1	20.7	12.65	53.4	59.70	(43)	1963	[87]
223	160	17	720	(70)	1	20.0	17.32	69.7	60.89	(38)	1975	[79]
224	160	17	690	(50)	1	20.0	12.65	53.4	59.70	(43)	1963	[79]

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
225	164	17	600	(50)	2	26.3	14.6	55.1	56.05	(40)	1972	
226	165	17	650	(65)	2	19.2	13.0	52.9	58.66	(41)	1966	[79]
227	165	17	650	(65)	2	21.4	13.0	52.9	58.66	(41)	1966	[79]
228	166	17	600	(50)	2	18.3	13.5	53.7	57.64	(41)	1966	
229	169	17	600	(50)	1	13.7	16.73	61.5	55.78	(42)	1969	
230	172	17	590	(85)	3	34.0	13.6	51.9	56.01	(43)	1963	[79]
231	172	17	590	(85)	3	25.9	13.6	51.9	56.01	(43)	1963	[79]
232	83	17	1060	(285)	1	-24.0	15.36	55.0	51.55	(36)	1973	
233	26	17	470	(25)	1	-31.9	15.8	39.9	37.41	(11, P. 98)	1949	
234	26	17	444	(20)	1	-31.9	16.85	41.23	36.75	(11, P. 98)	1954	
235	26	17	465	(34)	1	-31.9	14.74	38.0	37.80	(11, P. 98)	1956	
236	24	17	500	(30)	1	-25.1	14.4	39.5	40.07	(11, P. 97)	1936	
237	83	49	590	(170)	2	22.4	14.6	45.7	46.63	(11, P. 88)	1968	
238	84	50	543	(40)	2	19.3	13.75	40.9	43.84	(11, P. 88)	1928	[88]
239	84	50	590	(170)	2	19.3	13.68	40.75	44.18	(11, P. 88)	1968	[88]
240	84	50	543	(40)	2	30.2	13.75	40.9	43.84	(11, P. 88)	1928	[89]
241	84	50	590	(170)	2	30.2	13.68	40.75	44.18	(11, P. 88)	1968	[89]
242	87	53	473	(40)	2	2.9	16.34	42.8	39.78	(11, P. 88)	1960	
243	87	53	530	(66)	2	2.9	17.15	43.0	37.66	(11, P. 88)	1962	
244	24	6	610	(90)	1	-29.1	11.0	32.0	42.16	(11, P. 94)	1965	
245	30	6	600	(100)	1	-44.1	13.7	37.8	40.39	(11, P. 94)	1960	
246	24	24	440	(25)	1	-25.5	15.6	36.89	34.94	(11, P. 95)	1954	[90]
247	24	24	415	(43)	1	-25.5	15.2	35.3	34.23	(11, P. 95)	1959	[90]
248	24	24	440	(25)	1	-27.5	15.6	36.89	34.94	(11, P. 95)	1954	[91]
249	24	24	415	(43)	1	-27.5	15.2	35.3	34.23	(11, P. 95)	1959	[91]
250	16	24	490	(50)	1	-12.4	13.26	36.4	39.47	(11, P. 96)	1934	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
251	16	24	900	(220)	1	-12.4	12.9	34.0	41.19	(11, P. 96)	1970	
252	16	24	500	(30)	1	-12.4	13.1	36.1	39.62	(11, P. 97)	1936	
253	26	16	490	(50)	1	-20.0	14.13	37.7	38.82	(11, P. 97)	1934	[92]
254	26	16	495	(21)	1	-20.0	14.13	37.3	38.43	(11. P. 97)	1936	[92]
255	26	16	455	(40)	1	-20.0	13.78	37.5	39.28	(11, P. 97)	1956	[92]
256	26	16	498	(30)	1	-20.0	13.65	36.68	38.92	(11, P. 97)	1966	[92]
257	26	16	490	(50)	1	-20.6	14.13	37.7	38.82	(11, P. 97)	1934	[93]
258	26	16	495	(21)	1	-20.6	14.13	37.3	38.43	(11, P. 97)	1936	[93]
259	26	16	455	(40)	1	-20.6	13.78	37.5	39.28	(11, P. 97)	1956	[93]
260	26	16	498	(30)	1	-20.6	13.65	36.68	38.92	(11, P. 97)	1966	[93]
261	27	16	463	(40)	1	-24.6	14.43	37.64	38.07	(11, P. 97)	1935	
262	27	16	500	(0)	1	-24.6	14.43	37.0	37.47	(11, P. 97)	1936	
263	27	16	488	(30)	1	-24.6	13.2	34.7	37.91	(11, P. 97)	1956	
264	129	15	495	(64)	4	6.6	16.13	40.4	38.36	(32)	1970	
265	119	15	590	(124)	3	-43.0	16.44	48.3	44.70	(32)	1970	
266	117	15	690	(85)	2	-105.4	15.75	53.6	51.02	(32)	1970	
267	114	114	1720	(300)	1	-320.1	18.22	94.4	66.20	(11, P. 74)	1965	
268	114	114	1450	(285)	1	-320.1	17.62	94.4	74.60	(11, P. 74)	1965	
269	132	132	899	(-)	1	-74.4	15.7	66.0	61.67	(11, P. 77)	1953	
270	132	132	725	(99)	1	-74.4	16.0	67.2	62.66	(11, P. 77)	1969	
271	26	26	430	(60)	1	-38.6	14.7	31.5	31.39	(11, P. 95)	1938	[60]
272	26	26	473	(80)	1	-38.6	12.03	29.9	35.52	(11, P. 95)	1946	[60]
273	26	26	495	(45)	1	-38.6	13.3	31.7	34.73	(11, P. 95)	1952	[60]
274	26	26	420	(40)	1	-38.6	12.67	30.4	34.16	(11, P. 95)	1952	[60]
275	26	26	425	(34)	1	-38.6	16.1	37.3	34.46	(11, P. 95)	1967	[60]
276	26	26	430	(60)	1	-39.1	14.7	31.5	31.39	(11, P. 95)	1938	[90]

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
277	26	26	473	(80)	1	-39.1	12.03	29.9	35.52	(11, P. 95)	1946	[90]
278	26	26	495	(45)	1	-39.1	13.3	31.7	34.73	(11, P. 95)	1952	[90]
279	26	26	420	(40)	1	-39.1	12.67	30.4	34.16	(11, P. 95)	1952	[90]
280	26	26	425	(34)	1	-39.1	16.1	37.3	34.46	(11, P. 95)	1967	[90]
281	30	30	423	(20)	1	-67.3	16.5	39.1	35.47	(11, P. 95)	1948	
282	30	30	413	(40)	1	-67.3	13.3	34.0	36.54	(11, P. 95)	1950	
283	30	30	500	(108)	1	-67.3	14.72	36.0	35.80	(11, P. 95)	1951	
284	30	30	415	(25)	1	-67.3	16.0	38.0	35.40	(11, P. 95)	1952	
285	30	30	510	(210)	1	-67.3	15.84	38.0	35.18	(11, P. 95)	1952	
286	30	30	415	(25)	1	-67.3	16.6	39.0	35.28	(11, P. 95)	1954	
287	30	30	400	(44)	1	-67.3	16.4	38.7	35.47	(11, P. 96)	1959	
288	30	30	490	(118)	1	-67.3	16.07	38.3	35.07	(11, P. 96)	1961	
289	30	30	418	(30)	1	-67.3	15.6	37.4	35.56	(11, P. 96)	1962	
290	30	30	435	(35)	1	-67.3	16.12	38.1	35.13	(11, P. 96)	1962	
291	30	30	383	(40)	1	-67.3	15.8	37.8	35.76	(11, P. 96)	1968	
292	30	30	500	(260)	1	-67.3	15.8	37.9	35.22	(11, P. 96)	1968	
293	21	100	830	(175)	1	12.5	13.47	53.0	57.43	(11, P. 89)	1954	[94]
294	21	100	830	(175)	1	12.2	13.47	53.0	57.43	(11, P. 89)	1954	[95]
295	61	100	710	(90)	1	-75.1	14.51	51.2	51.60	(11, P. 90)	1961	
296	65	160	1010	(80)	1	28.1	13.0	59.0	66.56	(11, P. 91)	1956	[64]
297	65	160	1010	(80)	1	30.9	13.0	59.0	66.56	(11, P. 91)	1956	[96]
298	66	160	980	(80)	1	38.0	14.3	63.0	64.55	(11, P. 92)	1956	
299	62	62	980	(80)	1	-73.6	12.2	49.5	60.47	(11, P. 94)	1967	
300	62	62	812	(82)	1	-73.6	13.5	67.3	71.51	(11, P. 94)	1968	
301	62	62	820	(102)	1	-73.6	17.2	80.5	70.92	(54)	1975	
302	11	12	383	(20)	2	70.0	15.64	32.9	31.65	(11, P.104)	1956	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
303	11	12	383	(20)	2	66.4	15.64	32.9	31.65	(11, P.104)	1956	
304	82	17	1100	(450)	1	-19.4	15.9	57.0	50.69	(35)	1973	
305	86	86	1100	(109)	1	-38.6	16.33	75.3	66.77	(3)	1972	
306	86	87	1100	(129)	1	-39.8	16.3	72.3	63.97	(3)	1972	
307	100	59	830	(175)	1	10.6	13.47	51.5	55.93	(11, P. 89)	1955	
308	100	2	970	(98)	1	-	15.35	70.0	66.83	(11, P. 79)	1954	
309	100	14	990	(120)	1	-	12.77	59.0	67.46	(11, P. 84)	1949	
310	100	14	950	(252)	1	-	13,0	59.8	66.90	(11, P. 84)	1963	
311	100	14	1150	(210)	1	-	15.2	71.9	68.98	(24)	1972	
312	133	80	950	(100)	1	-	13.47	67.8	72.86	(11, P. 77)	1956	
313	145	80	850	(104)	2	-	12.3	54.1	64.39	(11, P. 78)	1965	
314	92	84	1070	(93)	1	-	15.7	64.6	59.43	(2)	1969	
315	94	84	1100	(165)	1	-	15.55	69.4	64.80	(26)	1970	
316	137	87	1080	(135)	1	-	16.32	74.5	66.18	(25)	1976	
317	97	2	653	(40)	1	-	18.62	69.3	57.38	(11, P. 79)	1967	
318	115	17	427	(32)	1	-	15.68	37.66	35.61	(11, P. 85)	1938	
319	115	17	428	(30)	1	-	15.34	37.4	36.00	(11, P. 85)	1971	
320	124	17	403	(40)	2	-	15.25	34.3	33.71	(11, P. 85)	1967	
321	111	17	527	(20)	2	-	16.67	48.5	44.32	(11, P. 85)	1969	
322	120	17	465	(44)	2	-	15.7	41.5	39.89	(11, P. 85)	1968	
323	121	17	463	(40)	2	-	15.3	39.5	38.75	(11, P. 85)	1968	
324	122	17	452	(37)	2	-	15.7	39.7	38.13	(11, P. 85)	1968	
325	128	17	405	(37)	3	-	15.25	34.4	34.13	(11, P. 86)	1967	
326	142	17	510	(48)	2	-	17.0	47.7	42.87	(11, P. 86)	1968	
327	143	17	443	(40)	2	-	14.72	37.4	37.82	(37)	1971	
328	144	17	448	(30)	2	-	16.13	40.5	38.05	(11, P. 86)	1971	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
329	140	17	485	(45)	1	-	15.21	42.6	41.31	(11, P. 86)	1971	
330	146	17	415	(73)	4	-	18.02	42.2	36.90	(11, P. 86)	1968	
331	153	17	500	(58)	1	-	15.14	42.7	41.53	(11, P. 87)	1971	
332	156	17	453	(40)	3	-	17.7	43.6	38.25	(11, P. 87)	1968	
333	97	97	760	(45)	1	-	15.35	71.3	68.81	(11, P. 77)	1967	
334	100	131	899	(-)	1	-	14.3	66.0	67.42	(11, P. 78)	1955	
335	100	131	930	(135)	1	-	12.9	55.0	62.43	(11, P. 78)	1960	
336	113	131	800	(21)	1	-	12.9	52.0	58.39	(11, P. 78)	1960	
337	100	39	870	(117)	1	-	12.85	57.7	64.80	(11, P. 84)	1963	
338	150	84	1170	(85)	1	-	16.23	74.3	65.76	(25)	1976	
339	87	189	1100	(139)	1	-	16.3	74.1	65.72	(3)	1972	
340	100	39	1100	(179)	1	-	15.1	68.7	66.41	(24)	1972	
341	100	41	950	(225)	1	-	15.2	60.9	58.48	(24)	1972	
342	43	90	620	(90)	1	-	13.75	48.5	51.01	(33)	1974	
343	134	2	1020	(109)	1	-	15.37	73.6	70.17	(11, P. 79)	1954	
344	33	17	428	(10)	1	-	15.5	36.0	34.30	(46)	1970	
345	26	6	600	(100)	1	-	13.4	37.7	41.11	(11, P. 94)	1960	
346	41	16	560	(70)	1	-	15.3	50.2	48.51	(11, P. 99)	1967	
347	108	0	1075	(43)	1	-	13.3	77.5	86.47	(11, P. 73)	1948	
348	71	80	850	(297)	3	-	15.53	59.5	57.88	(11, P. 92)	1963	
349	72	80	670	(231)	3	-	15.7	47.2	45.42	(11, P. 92)	1965	
350	78	80	850	(189)	3	-	15.2	57.0	56.70	(11, P. 93)	1958	
351	79	80	740	(238)	3	-	14.01	44.3	47.75	(11, P. 93)	1958	
352	73	80	500	(84)	3	-	15.1	36.4	36.44	(51)	1973	
353	134	3	880	(132)	1	-	13.7	57.0	60.81	(11, P. 82)	1952	
354	178	3	1075	(119)	1	-	13.54	70.9	76.29	(11, P. 82)	1952	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
355	179	3	1075	(111)	1	-	13.17	70.0	77.22	(11, P. 82)	1952	
356	180	3	1010	(98)	1	-	13.17	65.6	72.37	(11, P. 82)	1952	
357	181	3	1060	(123)	1	-	13.0	67.7	75.63	(11, P. 82)	1952	
358	157	4	870	(118)	1	-	15.61	66.5	62.62	(11, P. 83)	1964	
359	161	17	620	(70)	1	-	12.82	51.1	56.25	(39)	1973	
360	162	17	623	(60)	1	-	12.21	49.8	56.70	(39)	1973	
361	163	17	630	(50)	1	-	13.72	54.4	57.03	(39)	1973	
362	168	17	598	(50)	1	-	17.88	65.0	56.13	(42)	1969	
363	173	17	573	(60)	1	-	13.34	49.1	52.48	(41)	1966	
364	174	17	600	(50)	2	-	12.4	48.2	55.18	(40)	1972	
365	170	17	593	(40)	1	-	12.3	46.2	52.55	(40)	1972	
366	8	17	383	(40)	1	-	14.17	30.0	30.81	(11, P.104)	1961	
367	45	80	750	(137)	2	-	14.5	49.6	51.09	(44)	1975	
368	45	80	575	(50)	2	-	16.47	52.4	48.35	(11, P. 87)	1932	
369	45	80	543	(140)	2	-	15.9	50.2	47.82	(11, P. 87)	1936	
370	45	80	548	(92)	2	-	15.7	51.2	49.30	(11, P. 87)	1959	
371	45	80	587	(44)	2	-	16.54	52.5	48.19	(11, P. 87)	1939	
372	45	80	693	(60)	2	-	14.0	46.0	48.97	(11, P. 87)	1953	
373	45	80	599	(-)	2	-	17.3	55.4	48.94	(11, P. 87)	1961	
374	45	80	1050	(500)	2	-	17.0	53.0	43.09	(11, P. 87)	1966	
375	46	81	550	(41)	2	-	15.48	50.7	49.32	(11, P. 87)	1969	
376	114	47	725	(70)	2	-	13.95	48.5	51.77	(11, P. 87)	1956	
377	114	47	600	(62)	2	-	15.1	52.7	52.27	(11, P. 88)	1962	
378	114	47	625	(50)	2	-	15.31	52.8	51.72	(11, P. 88)	1969	
379	114	47	600	(62)	2	-	16.16	55.2	51.83	(11, P. 88)	1962	
380	48	82	599	(-)	2	-	15.7	48.5	46.43	(11, P. 88)	1959	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
381	48	82	599	(-)	2	-	14.76	48.5	48.98	(11, P. 88)	1960	
382	51	85	630	(57)	2	-	17.7	53.2	45.22	(11, P. 88)	1962	
383	41	55	425	(48)	2	-	13.82	34.58	36.75	(11, P. 98)	1967	
384	41	55	500	(73)	2	-	14.4	36.1	37.34	(11, P. 99)	1963	
385	41	55	410	(22)	2	-	11.4	31.9	38.54	(11, P. 99)	1960	
386	42	56	490	(37)	2	-	13.7	33.0	35.79	(11, P. 99)	1963	
387	45	90	445	(19)	2	-	14.5	35.4	36.27	(45)	1972	
388	28	6	600	(100)	1	-	15.2	40.0	38.47	(11, P. 94)	1960	
389	34	6	500	(129)	1	-	14.0	32.0	33.45	(11, P. 96)	1962	
390	44	6	650	(110)	1	-	12.82	47.0	52.40	(11, P. 98)	1962	
391	28	16	463	(40)	1	-	14.43	37.64	38.07	(11, P. 97)	1935	
392	28	16	500	(0)	1	-	14.1	37.0	38.25	(11, P. 97)	1936	
393	29	16	500	(0)	1	-	14.47	37.0	37.37	(11, P. 97)	1936	
394	29	16	495	(37)	1	-	13.65	36.2	38.42	(11, P. 97)	1936	
395	125	15	493	(21)	3	-	13.23	36.04	40.28	(31)	1974	
396	159	114	1000	(50)	2	-	14.03	82.7	86.84	(11, P. 75)	1957	
397	30	26	430	(40)	1	-	14.4	34.5	34.98	(11, P. 95)	1952	
398	27	27	400	(50)	1	-	14.95	35.0	34.42	(11, P. 95)	1970	
399	28	28	440	(37)	1	-	15.4	37.1	35.56	(11, P. 95)	1967	
400	28	28	400	(44)	1	-	15.14	36.8	35.86	(11, P. 95)	1967	
401	31	31	413	(20)	1	-	16.71	38.7	34.76	(11, P. 96)	1966	
402	34	34	413	(100)	1	-	14.25	29.5	30.22	(11, P. 96)	1954	
403	35	35	420	(91)	1	-	14.4	30.0	30.47	(11, P. 96)	1955	
404	36	36	410	(82)	1	-	14.27	29.6	30.27	(11, P. 96)	1955	
405	25	25	495	(47)	1	-	15.93	46.2	43.25	(47)	1975	
406	34	100	799	(-)	1	-	14.5	67.0	67.50	(11, P. 89)	1955	

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
407	37	100	955	(42)	1	-	15.3	69.0	66.14	(11, P. 89)	1953	
408	60	98	800	(75)	1	-	15.0	58.0	56.67	(11, P. 90)	1968	
409	70	157	850	(140)	2	-	11.9	48.3	60.14	(11, P. 91)	1961	
410	57	57	385	(30)	1	-	11.8	21.7	26.70	(11, P. 99)	1960	
411	57	57	385	(30)	1	-	13.4	23.0	25.19	(11, P. 99)	1960	
412	58	58	385	(30)	1	-	14.4	25.6	26.02	(11, P. 99)	1960	
413	9	5	593	(40)	2	-	13.4	45.0	49.19	(11, P.104)	1959	
414	23	1	380	(30)	2	-	15.12	33.0	32.67	(11, P.104)	1968	
415	19	20	960	(125)	1	-	14.1	54.0	56.40	(11, P.104)	1962	
416	52	86	580	(79)	2	-	17.27	48.4	42.19	(11, P. 88)	1962	
417	167	17	598	(50)	1	-	10.21	42.5	54.61	(42)	1969	
418	171	17	548	(50)	1	-	4.8	23.4	48.08	(40)	1972	
419	176	17	595	(42)	1	-	8.8	38.5	54.41	(40)	1972	
420	177	17	573	(40)	1	13.4	8.45	34.5	50.75	(40)	1972	
421	177	17	573	(40)	1	13.4	7.4	31.5	50.50	(40)	1972	
422	175	17	583	(40)	1	-	8.45	37.0	53.53	(40)	1972	
423	26	17	585	(430)	1	-31.9	20.7	38.0	21.80	(11, P. 98)	1962	
424	41	17	456	(35)	1	-	20.0	53.0	41.80	(11, P. 99)	1962	
425	13	5	1850	(700)	1	20.4	9.1	49.5	96.38	(11, P.102)	1964	
426	13	5	1850	(700)	1	20.4	9.4	51.4	95.65	(11, P.102)	1964	
427	13	5	1850	(700)	1	20.4	9.6	52.4	95.13	(11, P.102)	1964	
428	13	5	1850	(700)	1	20.4	10.1	55.0	93.50	(11, P. 102)	1964	
429	13	5	1850	(700)	1	20.4	8.95	48.2	96.34	(11, P.102)	1964	
430	13	5	1899	(-)	1	20.4	9.3	50.0	96.48	(11, P.102)	1964	
431	76	80	785	(70)	4	40.1	10.17	28.2	46.39	(11, P. 93)	1947	[64]
432	76	80	785	(70)	4	30.7	10.17	28.2	46.39	(11, P. 93)	1947	[66]

Table 3

Results of the Statistical Treatment in the Coordinates of Equations (5) and (6).

NE - the number of independent equations (points)

NRN - the number of different reactions (combinations of R_i and R_j).

NRD - the number of different radicals-substituents with unknown $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ values.

s - standard deviation in kcal/mole.

Variants:

1) Eq. (5). MLRA treatment of data for 98 radicals. The value $\Delta H^{\neq}_{H\cdot}$ = 51.63 kcal/mole is fixed prior data processing.

2) The D_{ij} values for the reactions of C-NO_2 bond fission are calculated assuming log A_o = 16.00

3) Eq. (5) for 15 the most represented radicals.

4) Eq. (6) MLRA treatment of data for the most represented 15 radicals. $\sigma^{*}_{NO_2}$ = 3.55 and α^{*}=2.2 kcal/mole

The results for the final data set after the exclusion of significantly deviating points are listed. The figures for the initial data set are given in parenthesis.

Variant	NE	NRN	NRD	s
1)	231(297)	125(138)	93(97)	1.1(3.1)
2)	213(297)	117(138)	95(97)	0.9(3.2)
3)	107(134)	35(41)	15(15)	1.3(2.6)
4)	65(81)	31(34)	15(15)	1.4(3.0)

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A MODEL FOR INTERPRETATION OF ACTIVITY COEFFICIENT BEHAVIOR OF WEAK BASES IN AQUEOUS ACID SOLUTIONS

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The activity coefficient (f_B) of a weak base in aqueous acid solution determined by the distribution method reflects the changes in solvation energy of an unhydrated base (B). The activity coefficient of the hydrated base ($B.bH_2O$) really existing in aqueous solutions may be calculated by the equation $f_{B.bH_2O} = f_B \cdot a_{H_2O}^{-b}$. It has been assumed that in distribution equilibria the relative changes in weak base concentrations in the aqueous phase are due to changes in the molar concentrations of all ionic and nonionic components present in aqueous acid solutions. This assumption leads to an extended form of the Sechenov equation which is now suggested for the interpretation of activity coefficient behavior in aqueous acid solutions.

The activity coefficient behavior of weak bases plays an important role in their basicity studies [1-3]. The respective papers have been reviewed by K.Yates and R.McClelland [1]. Since only the activity coefficient of the unionized weak base can be determined without using some additional assumptions, most of the work done deals with this activity coefficient (f_B). It has been found that organic compounds of different structure exhibit rather a different f_B behavior in aqueous strong acid solutions [1]. To the best of our knowledge till now no attempts have been made to derive an equation describing the f_B behavior in terms of concentrations (or activities) of ionic and nonionic components present in aqueous strong acid solutions.

Our objective is to derive such an equation.

First, it is reasonable to suppose that all organic compounds remarkably soluble in water and in aqueous strong acid solutions are hydrated. In the case of weak bases the electrophilic hydration predominates [4]. The activity coefficient of an unionized base determined by the distribution method [1] is calculated by the equation

$$f_B = D \cdot D_o^{-1} \qquad (1)$$

where D_o and D are the distribution coefficients in standard state (in water) and in aqueous strong acid solution, respectively. Assuming that in the organic phase only the non-hydrated base (B) is dissolved [5] we can write

$$D_o = [B]_{org} \cdot [B]_o^{-1} \qquad (2)$$

and

$$D = [B]_{org} \cdot [B]^{-1} \qquad (3)$$

where $[B]_{org}$ is the B concentration in the organic phase, $[B]_o$ and $[B]$ are the B concentrations in water and in aqueous strong acid solution, respectively.

It is evident from Fig. 1 that the $[B]_{org}$ has the same value in Eqns. (2) and (3). Equation (1) then becomes

$$f_B = [B]_o \cdot [B]^{-1} \qquad (4)$$

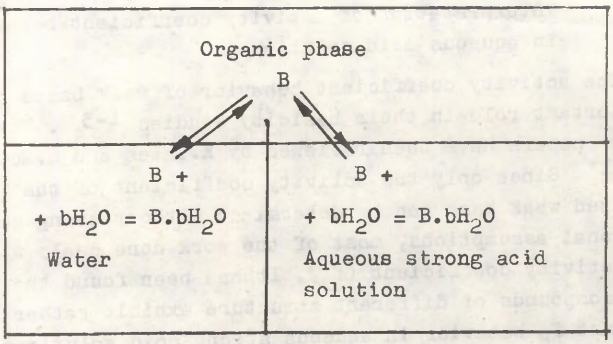

Fig. 1 The scheme for a distribution experiment

Thus the distribution method yields the activity coefficient of the unhydrated and unionized base (B) which is not the hydrated species really existing in aqueous solutions ($B.bH_2O$). It remains to mention that in case the remarkable protonization of the base B occurs, the respective correction must be used [1]:

$$f_B = \frac{[B]_o}{[B]} \left(1 + \frac{h}{K_{BH^+}}\right) \qquad (5)$$

where h is the appropriate acidity scale for the base B and K_{BH^+} is the basicity constant of the base B.

In order to obtain the activity coefficient for the species $B.bH_2O$ we have to account for the equilibrium taking place in the aqueous phase:

$$B.bH_2O \rightleftharpoons B + bH_2O \qquad (6)$$

with the constant

$$K = \frac{[B] \cdot a_{H_2O}^{b}}{[B.bH_2O]} \qquad (7)$$

Combining Eqns. (4) and (7), the latter being written twice - for water and for aqueous strong acid solution, we obtain

$$f_B = \frac{[B.bH_2O]_o \cdot a_{H_2O}^{b}}{[B.bH_2O]} \qquad (8)$$

where $[B.bH_2O]_o$ and $[B.bH_2O]$ are the $B.bH_2O$ concentrations in water and in aqueous strong acid solution, respectively. Then

$$f_{B.bH_2O} = \frac{[B.bH_2O]_o}{[B.bH_2O]} = f_B \cdot a_{H_2O}^{-b} \qquad (9)$$

In aqueous solutions of strong acids the water activity (a_{H_2O}) decreases with increasing acid concentration so that $a_{H_2O} < 1$. Consequently, $f_{B.bH_2O} > f_B$. The ratio $f_{B.bH_2O} \cdot f_B^{-1} = a_{H_2O}^{-b}$ should be larger for more heavily hydrated bases, i.e. for those having more lone pairs of

electrons.

The second point to be discussed here is how the f_B and/or $f_{B.bH_2O}$ values depend on the total concentration of strong acid in its aqueous solution. For instance, if the sulfuric acid total concentration increases, the molar concentrations of SO_4^{2-}, HSO_4^-, $HSO_4^-.H_3O^+$, etc., vary over a wide range [6,7]. In order to set up a quantitative relationship between the f_B ($f_{B.bH_2O}$) and the molar concentrations of different species present in the aqueous acid solutions considered, let us have a hypothetical model consisting of a very large volume of organic phase and a small volume of aqueous strong acid solution. The compound studied (B) is distributed between these two phases and the equilibrium is reached. Following the suggestion of A.Zdanovsky [8] proposed for the case when the considered compound is an electrolyte, we assumed that the relative changes in the weak base concentration in the aqueous phase follow a linear relationship

$$-\frac{d[B]}{[B]} = A_1 dc_1 + A_2 dc_2 + \ldots + A_n dc_n \qquad (10)$$

where A_1, A_2, ... A_n are constants and c_1, c_2, ... c_n are the molar concentrations of species present in aqueous strong acid solution.

If integrated from water to the given solution, the Eq. (10) yields

$$\ln \frac{[B]_o}{[B]} = A_1 c_1 + A_2 c_2 + \ldots + A_n c_n \qquad (11)$$

Taking into account Eqns.(4) and (9) we obtain

$$\log f_B = A_1' c_1 + A_2' c_2 + \ldots + A_n' c_n \qquad (12)$$

and

$$\log f_{B.bH_2O} = A'' c_1 + A' c_2 + \ldots + A' c_n - b \cdot \log a_{H_2O} \qquad (13)$$

The derived expression Eqn.(11) seems to be reasonable because this is an extended form of the Secnenov equation[1,8-11] whose applicability to a number of cases is well known [8-11]. In confirmity with general views on the

nature of hydration numbers [9] we should expect that the hydration parameter b in Eqn.(13) will probably be not a constant if the strong acid concentration increases to a large extent.

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PHOTOELECTRON SPECTRA OF MOLECULES
2. ETHERS

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Photoelectron spectra (PES) of 9 aliphatic ethers and 3 O-and N-methyl-substituted hydroxylamines have been recorded. The substituent effects on PES of the ethers have been analyzed. The performance of the semiempirical CNDO/2 method for the analysis of the PES has been discussed.

In the previous paper[1] of this series the PES of some aliphatic alcohols were analyzed on the basis of empirical relationships between IP and energetic characteristics (proton affinity (PA), core level ionization energies, etc.) as well as from the viewpoint of some semiempirical and nonempirical quantum chemical methods.

In the present work primarily the effects of the halogen substitutions on the PES of the aliphatic ethers have been studied. Also, some other ($SiMe_3$, $CNCH_2$, NH_2, etc.) substituents were involved.

It should be mentioned that while the PES of the alkylsubstituted ethers have been thoroughly studied[2,3,4] the PES of ethers with the electronegative substituents have received much less attention. So, PES of a few perfluorinated ethers were analyzed in Ref. 5. Halogen-substituted propylene oxides[6], ICH_2CH_2OMe[7], F_2O and Cl_2O[8], and CF_3OF[9] were also studied. PES of silicon-containing

ethers were reported in Refs. 10 and 11.

Experimental

The procedure of determination of ionization potentials and the instrumentation used were described in detail in the 1st communication[1] of this series. The argon gas was used for the calibration of spectra. The vertical ionization potentials (IP_v) were determined at the location of the maximum of the corresponding bond in PES, whereas the adiabatic ones (IP_a) refer to the beginning of the PES band (the half-width of the argon line was added to the corresponding ionization energy value).

The PES measured* are shown in Fig. I. The IP values determined** from PES are given in Table 1 alongside with some literature data. A few values of 1st adiabatic ionization potentials were determined by the photoionization (IP) technique.

As a rule, the commercial samples were used. CF_3CH_2OMe and CF_3CH_2OEt were synthesized by standard techniques. H_2NOMe, MeNHOMe and $MeONMe_2$ were liberated from their hydrochlorides by the treatment with the aqueous KOH. The purity of compounds was checked by g.l.c. Each sample was subjected to several freeze-pump-thaw cycles to remove entrapped gaseous impurities.

For the most compounds measured in this study as well as for the reference compounds the semiempirical CNDO/2 calculations were performed using the original[12] parametrization of Pople and Beveridge. Mostly, the "optimum" bond lengths (CO=1.367, CC=1.457, CH=1.119, CF=1.343) from Ref. 13 were used. Some other values (CCl=1.67, S_iO=1.63, and SiC=1.87) were accepted on the basis of the calculations by the present authors. All valence angles were considered tetrahedral.

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* As a matter of fact the averaged spectra from several (3-5) scans are reported in Fig.1.

** Analogously to Ref.1, part of this data was already reported and used while discussing various aspects of the dependence of IP on the structure and proton affinities of molecules (See Ref. 1 for further references).

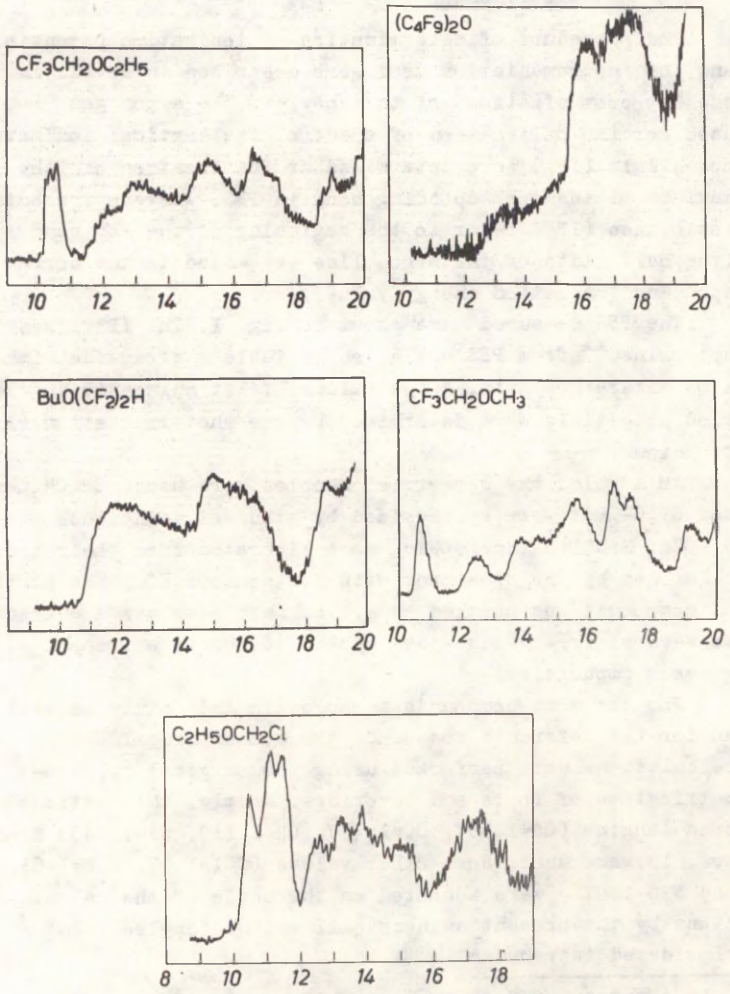

Fig. 1. PES of some compounds of general formula X_1OX_2

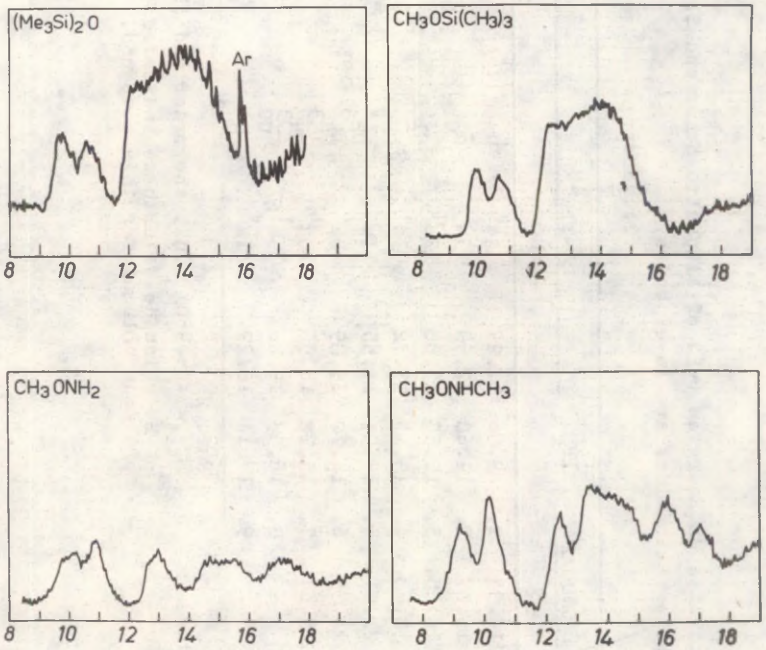

Fig. 1 (continuation).

The results of our calculations alongside with some literature data are included in Table 1. Generally accepted notations for the symmetry type and characters of localization of MO-s were used (for example, n_O, σ_{CC}, σ_{SiC}, pseudo-π_{CH_3}, etc.).

Table 1

Ionization Potentials and Calculated MO Energies (-ε) of Aliphatic Ethers and Some Other Oxygen-containing Compounds. All Values are In eV Units.

1. Me_2O

	IP_v[a]	4-31G[a] -ε	MO		CNDO/2[b] -ε
1.	10.04	11.36	$2b_2$	n_O	14.33
2.	11.91	12.76	$6a_1$	$\bar{n}_O$	16.07
3.	13.43	14.33	$4b_1$	π_{CH_3}	16.25
4.	14.20	15.04	$1a_2$	π_{CH_3}	18.63
5.	16.0	17.20	$3b_1$	σ_{CO}	21.91
6.		17.67	$5a_1$	π_{CH_3}	24.25
7.	16.5	17.97	$1b_2$	π_{CH_3}	25.57

a - Ref. 2

b - E_{tot} = -37.2601 a.u., the order and characters of MO coincide with those indicated in the previous columns for this compound.

2. MeOEt

	IP_v[a]	4-31G[a] -ε	MO		CNDO/2[b] -ε
1.	9.86	11.27	4a''	n_O	13.99
2.	11.60	12.59	13a'	$\bar{n}_O$	15.48
3.	12.57	13.60	12a'	σ_{Cl}	15.64
4.	13.13	13.72	3a''	π_{CH_2}	16.31
5.	13.94	14.55	11a'	π_{CH_3}	18.14
6.	14.70	15.89	2a''	π_{CH_3}	21.27
7.	15.72	16.96	10a'	π_{CH_3}	22.55
8.	16.53	17.56	9a'	σ_{CO}, σ_{CC}	23.85
9.	17.14	18.27	1a''	π_{CH_2}	

a - Ref. 2

b - E_{tot} = -45.9601 a.u., the order and characters of MO coincide with those indicated in the previous columns for this compound.

continuation of Table 1

	3. CF_3CH_2OMe				4. CF_3CH_2OEt			
	IP_v^a	CNDO/2[b]			IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO			$-\varepsilon$	MO	
1.	10.69	15.14	8a''	n_O	10.35	14.70	9a''	n_O
2.		15.44	14a'	σ_{CC}	10.38	15.10	16a'	σ_{CC}, σ_{CO}
3.	12.38	16.74	13a'	$\bar{n}_O$, π_{CH_3}	10.56	16.14	15a'	$\bar{n}_O$
4.	13.80	18.62	7a''	π_{CH_2}		16.77	8a''	π_{CH_2}
5.	14.40	19.42	12a'	n_F	12.26	18.06	14a'	π_{CH_3}
6.		19.81	6a''	n_F	13.21	19.33	7a''	n_F
7.	15.49	20.64	11a'	π_{CH_3}		19.40	13a'	n_F
8.		21.08	5a''	n_F		20.26	12a'	σ_{CO}, n_F
9.		21.40	10a'	n_F..		20.98	6a''	n_F
10.	16.70	21.83	4a''	n_F		21.01	5a''	n_F
11.	17.18	22.52	9a'	σ_{CO}		21.69	11a'	n_F
12.	19.14	24.80	3a''	n_O, π_{CH_2}	15.49	22.21	4a''	n_F
13.	20.32	26.36	8a'	σ_{CF}	16.67	23.59	10a'	n_O
					14.(17.5)	25.17	9a'	π_{CH_3}
					15. 19.11	25.85	3a''	π_{CH_2}

a - This work :

$IP_a^{(1)}$ = 10.53,

$IP_a^{(2)}$ = 11.99,

$IP_a^{(3)}$ = 13.19 eV.

b - This work:

E_{tot} = -126.9310 a.u.

a - This work:

$IP_a^{(1)}$ = 10.27 eV

b - This work:

E_{tot} = -135.6315 a.u.

continuation of Table 1

	5. $ClCH_2OEt$			6. HCF_2CF_2OBu	7. $(n\text{-}C_4F_9)_2O$
	IP_v^a	CNDO/2[b]		IP_v^a	IP_v^a
		$-\varepsilon$	MO		
1.	10.50	13.61	$5a''$ n_{Cl}, n_O	1. 11.80	1. 13.30
2.	11.06	13.80	$11a'$ n_{Cl}	2. 15.01	2. 16.11
3.	11.42	14.29	$4a''$ n_O, n_{Cl}	3. 15.86	3. 17.75
4.		15.79	$10a'$ σ_{CCl}, σ_{CO}	4. 18.76	
5.	12.39	16.10	$9a'$ n_O		
6.	13.09	16.92	$3a''$ n_O, π_{CH_2}		
7.	13.70	18.53	$8a'$ π_{CH_3}		
8.	14.88	20.72	$7a'$ n_O, π_{CH_3}		
9.		23.41	$2a''$ π_{CH_2}		
10.	17.06	23.62	$6a'$ σ_{CO}		

a - This work:
$IP_a^{(1)}$ = 10.30 eV
b - This work:
E_{tot} = -61.3801 a.u.

a - This work:
$IP_a^{(1)}$ = 10.78 eV

a - This work:
$IP_a^{(1)}$ = 12.68,
$IP_a^{(2)}$ = 15.60 eV.
Due to the misprint in Ref. 14. incorrect structure $[(CF_3)_3C]_2O$ was ascribed to this compound

Discussion

As in the 1st paper[1] of this series it seems reasonable to accept the idea that it is necessary to use the complex approach to the analysis of the PES of the larger molecules. So along with the quantum chemical methods the use of the relationships[16] between IP-s and several independent energetic characteristics could be very helpful for the interpretation of PES of complex molecules characterized by several broad structureless bands and competing ionization centers.

continuation of Table 1

	8. Cl_2CHOMe				9. $NCCH_2OMe$			
	IP_v^a	CNDO/2[b]			IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO			$-\varepsilon$	MO	
1.	10.98	13.41	$6a''$	n_{Cl}, n_O	10.96	14.36	$4a''$	n_O
2.	11.35	14.10	$10a'$	n_{Cl}	12.62	15.54	$10a'$	π_{CN}, $\bar{n}_O$
3.		14.49	$5a''$	n_{Cl}		16.14	$9a'$	σ_{CO}
4.		14.58	$9a'$	n_{Cl}, $\bar{n}_O$		16.17	$3a''$	π_{CN}, $\bar{n}_O$
5.		15.06	$4a''$	n_O, n_{Cl}		17.57	$8a'$	$\bar{n}_O$, π_{CN}
6.		17.18	$8a'$	π_{CH_3}		19.33	$7a'$	n_N
7.		18.03	$7a'$	n_O, $_{Cl}$		20.82	$2a''$	π_{CH_2}, π_{CN}
8.		18.83	$3a''$	π_{CH_3}		23.60	$6a'$	σ_{CO}, π_{CH_3}
9.		21.82	$6a'$	σ_{CO}		26.00	$5a'$	π_{CH_3}
10.		23.95	$2a''$	n_O, π_{CH_2}		26.95	$1a''$	n_O, π_{CH_2}

a - This work: $IP_a^{(1)}$ = 10.84, $IP_a^{(2)}$ = 11.19 eV

b - This work: E_{tot} = -68.1184 a.u.

a - This work: $IP_a^{(1)}$ = 10.75

b - This work: E_{tot} = -55.0314 a.u.

So, for the ethers the following simple linearity between IP (n_O band) and proton affinity holds[16]:

$$IP_v = -0.057(0.002)PA + 21.33(0.52), \qquad (1)$$

$r = 0.985$; $s = 0.08$ eV; $s\% = 5.0$, $n = 17$

where r - the correlation coefficient;
s - standard deviation;
$s\% = (s/\Delta IP_{max})100$, where ΔIP_{max} is the maximum range of the variation of IP_v;
n - the number of points;
the confidence intervals of regression coefficients are given in parentheses.
Relationship (1) is visualized in Fig. 2.

10. Et_2O

	IP_v[a]	4-31G[a]		CNDO/2[b]	
		$-\varepsilon$	MO	$-\varepsilon$	MO
1.	9.61	11.24	$5a'' n_O$	13.77	$5a'' n_O$
2.	11.68	12.43	$16a' n_O$	15.06	$11a' \sigma_{CO}, \sigma_{CC}$
3.	11.92	13.08	$15a' \sigma_{CC}$	15.18	$10a' n_O$
4.		13.35	$4a'' \pi_{CH_2}, \pi_{CH_3}$	15.30	$4a'' \pi_{CH_2}$
5.		14.13	$14a' \pi_{CH_3}$	16.88	$9a' \pi_{CH_3}$
6.		14.44	$3a'' \pi_{CH_3}$	18.29	$3a'' n_O, \pi_{CH_3}$
7.		14.95	$13a' \pi_{CH_3}$	19.61	$8a' \pi_{CH_3}$
8.		16.04	$12a' \sigma_{CC}$	21.60	$7a' \sigma_{CO}, \sigma_{CC}$
9.	16.23	16.51	$2a'' \pi_{CH_2}, \pi_{CH_3}$	23.41	$2a'' \pi_{CH_2}$
10.		17.87	$11a' \sigma_{CO}$	25.26	$6a' \sigma_{CO}$
11.		18.56	$1a'' \pi_{CH_2}, n_O$	26.73	$5a'$

a - Ref. 2

b - This work: E_{tot} = -55.6598 a.u.

One can see that Me_3SiOMe does not obey Eqn.(1) - its PA value (204.4 kcal/mol) occurs to be cá by 5 kcal/mol too low to fit the linearity (1). $CNCH_2OMe$ probably protonates on the CN-group and the measured PA(189.7 kcal/mol) corresponds to IP_v=13.29 eV for the nitrogen's lone pair (calculation on the basis of Eqn.(11) from Table 2 of Ref.16). Eqn.(1) could be used for the rough prediction of PA values for some compounds with the experimentally unaccessible gas phase basicities.

The approximate linearity between IP values of alcohols and the complex formation shifts $\Delta\nu_{PhOH}$ of the OH-stretching frequency of phenol[17] with these bases in CCl_4 was found to hold. The analogous relationship seemsto be true also for the ethers (see Fig. 3):

$$IP_v = -0.009\ (0.001)\Delta\nu_{PhOH} + 12.13(0.08) \qquad (2)$$

r = 0.988, s = 0.08 eV; s% = 5.2;

continuation of Table 1

11. Me_3SiOMe

	IP_v^a	CNDO/2[b] -ε	MO
1.	9.85	13.61	$7a'' n_O$
2.		13.79	$12a' \sigma_{SiC}$
3.	10.64	14.69	$11a' n_O$
4.		14.95	$6a'' \pi_{SiO}$
5.		17.34	$10a' \pi_{CH_3}$
6.	12.33	17.92	$9a' \sigma_{CO}$
7.		18.09	$5a'' \pi_{CH_3}$
8.		19.09	$4a'' \pi_{CH_3}$
9.	13.82	19.82	$8a' \sigma_{CO}$

a - This work:
$IP_a^{(1)}$ = 9.61,
$IP_a^{(2)}$ = 10.39,
$IP_a^{(3)}$ = 11.96 eV

b - This work:
E_{tot} = -60.1737 a.u.

12. $(Me_3Si)_2O$

	IP_v^a	CNDO/2[b] -ε	MO
1.	9.69	13.61	$17a' \sigma_{SiC}$
2.		13.63	$11a'' n_O$
3.		13.96	$16a' \pi_{CH_3}$
4.		13.99	$10a'' \sigma_{SiC}$
5.	10.54	14.29	$15a' \pi_{CH_3}$
6.		16.12	$9a'' \pi_{CH_3}$
7.	12.21	16.59	$14a' \bar{n}_O$
8.		16.73	$13a' \bar{n}_O$
9.		16.80	$8a'' \bar{n}_O$
10.		18.40	$7a'' \pi_{CH_3}$
11.		18.47	$12a' \pi_{CH_3}$
12.		18.71	$6a'' \pi_{CH_3}$
13.	13.84	19.39	$11a' n_O$

a - This work: $IP_a^{(1)}$ = 9.64±0.01 (PI - technique). See also Ref. 11.

b - This work:
E_{tot} = - 83.1750 a.u.

($\Delta\nu)_{PhOH}$ is given in cm^{-1} units)

As in the case of Eqn. (1), trimethylsilyl-substituted ether do not fit Eqn. (2).

continuation of Table 1

13. t-BuOMe

	IP_v[a]	CNDO/2[b] -ε	MO
1.	9.48	13.12	$7a''$ n_O
2.		13.69	$12a'$ σ_{CC}
3.		15.19	$11a'$ σ_{CO}
4.		15.94	$6a''$ n_O, π_{CH_2}
5.		17.06	$10a'$ π_{CH_3}
6.		17.19	$5a''$ π_{CH_3}
7.		18.18	$9a''$ π_{CH_3}
8.		18.26	$4a''$ π_{CH_3}
9.		20.36	$8a'$ $\bar{n}_O$
10.		22.60	$3a''$ π_{CH_3}
11.		23.73	$7a'$ π_{CH_3}
12.		24.15	$2a''$ $\bar{n}_O$
13.		24.91	$6a'$ π_{CH_3}
14.		26.83	$5a'$ σ_{CO}

a - Ref. 3

b - This work:
E_{tot}= -63.3174 a.u.

14. $t\text{-Bu}_2O$

	IP_v[a]	CNDO/2[b] -ε	MO
1.	9.16	11.66	$17a'$
2.	10.24	12.59	$11a''$
3.	10.95	13.80	$16a'$
4.		14.13	$15a'$
5.		14.30	$10a''$
6.		15.54	$9a''$
7.		15.67	$14a'$
8.		16.93	$13a'$
9.		17.37	$8a''$
10.		17.71	$7a''$
11.		18.29	$6a'$
12.		19.02	$12a'$
13.		19.71	$5a''$
14.		20.83	$11a'$

a - Ref. 15

b - This work:
E_{tot}= -89.2398 a.u.

Due to the existence of the linear relationship between $IP(n_O)$ and the gas phase proton affinity (PA) one might expect also the observance of the linear dependence of the latter quantity on the $\Delta\nu)_{PhOH}$ parameters. As a matter of fact, this kind of relationship means that the changes of the so called general basicity in solution (i.e. formation of hydrogen bonded complexes between acid AH and base B) and of the intrinsic basicity in the gas

continuation of Table 1

15. H_2NOMe[a]	16. MeHNOMe[a]	17. $MeONMe_2$[a]
IP_v[b]	IP_v[c]	IP_a
1. 10.16	1. 9.39	1. 8.78
2. 10.93	2. 10.22	
3. 12.94	3. 12.61	
4. 15.0	4. 13.95	
5. 17.31	5. 16.11	
	6. 17.25	

a - The analysis of the PES will be given in the forthcoming communications of this series.

b - This work: $IP_a^{(1)}$= 9.55, $IP_a^{(2)}$= 10.46 eV; See also Ref. 2.

c - This work: $IP_a^{(1)}$= 8.92, $IP_a^{(2)}$= 9.97, $IP_a^{(3)}$= 12.20 eV

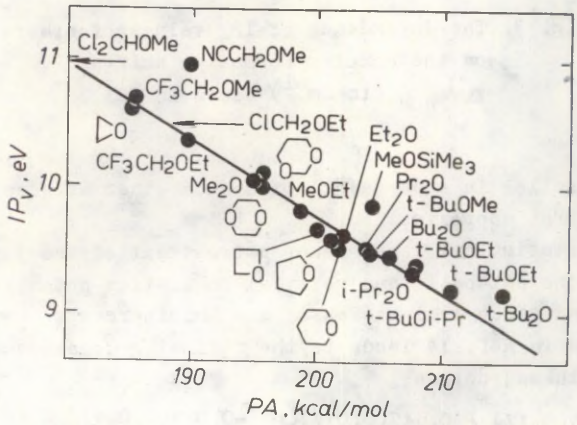

Fig. 2. The relationship between IP_v and PA for ethers.

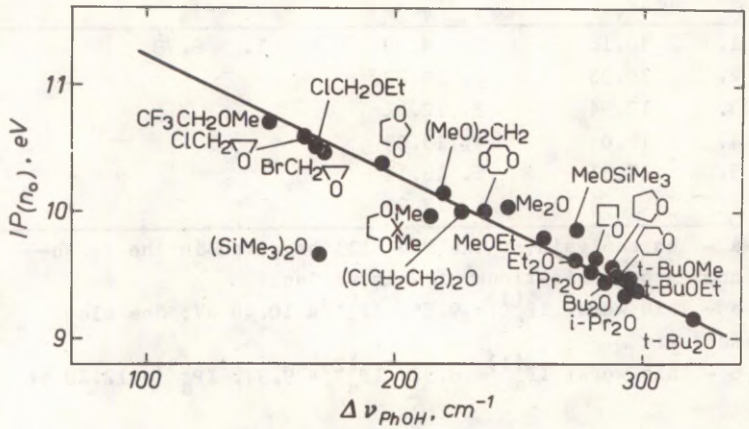

Fig. 3. The dependence of IP_v values of ethers on the complex formation shifts $\Delta\nu_{PhOH}$ (in cm^{-1}) bases in CCl_4.

phase parallel in a certain limits each other at least in the first approximation.

The statistical least squares treatment of the joint data on the adiabatic and vertical ionization potentials of ethers and alcohols in terms of the multiparameter equation suggested in Ref. 14 leads to the following dependences of IP-s on the structure:

$$IP_a = 10.09(0.17) + 0.547(0.017)\Sigma\sigma^* - 0.027(0.004)\Delta R + 0.493(0.169)\Sigma\sigma_R^0 + 0.446(0.087)n_1 + 0.057(0.016)\Delta n_2 \quad (3)$$

$R=0.982$; $s=0.15$ eV; $s\%=3.5$; $n=34$

and

$$IP_v = 10.09(0.21) + 0.670(0.024)\Sigma\sigma^* - 0.012(0.003)\Delta R + \\ +1.028(0.089)n_1 + 0.162(0.031)\Delta n_2 \qquad (4)$$

$R=0.978$; $s=0.17$eV; $s\%=4.1$; $n=40$,

where $-\sigma^*$ and σ_R^0 are Taft's inductive and resonance constants, ΔR - the relative molecular refractivity of the substituent, n_1 and Δn_2 are the numbers of the hydrogen atoms attached immediately and in α-position to the ionization center.

As a rule, the use of Eqns. (3) and (4) for the calculation of $IP(n_O)$ values of these compounds leads to quantities which, within the error limits, coincide with the experimentally determined ionization energies of the first PES bands of these molecules. Trimethyl silyl-substituted ethers does not fit Eqns.(3) and (4).

For the chlorosubstituted ethers the question about the identity of the ionization center needs clarifications. As in the case of the alcohols Eqns.(3) and (4) suggest that the first IP in PES of these compounds corresponds to the ionization of the electrons of the lone pair of the oxygen atom. The use of Eqn. (9) Table 2 from Ref. 14 for the calculation of $IP(n_{Cl})$ for the chlorides XCl predicts for $ClCH_2OEt$ IP=11.37 eV which agrees well with the energy (11.42 eV) of the 3rd band in PES (identified) by CNDO/2 as n_{Cl}) .

In the fluorinated molecules the perfluoroalkyl group could be studied by comparing the PES of the corresponding methyl (alkyl) and perfluoromethyl (perfluoroalkyl) derivatives. In the present paper, by the analogy with the Ref.1, CF_3 substitution is used for the separation of σ-and π-molecular orbitals. As earlier[1], the order of σ-orbitals (σ_{CC}, σ_{CO}) was assumed on the ab anitio calculation of the ethanol molecule.

The σ-orbitals for the two pairs of etners determined according to this principle are listed in Table 2.

Table 2

The energies (in eV) of MO-s of some ethers determined on the basis of perfluoroalkyl effect.

Compound	n_O	σ_{CC}	σ_{CO}	σ_{CO}
EtOMe	9.68	11.60	14.70	16.53
CF_3CH_2OMe	10.69	12.30	15.49	17.18
EtOEt	9.61	11.08		16.23
CF_3CH_2OEt	10.35	12.26		16.67

In the PES of substituted alkyl ethers the presence of the intense and sharp peaks of 2p nonbonding electrons of the oxygen and of the halogen lone pairs as well as bands from the electrons of C-C and C-O bonds. Also the broad overlapping bands characteristic to the alkanes should appear.

As in the case of alcohols the $IP(n_O)$ bands are broader than expected which evidences about the bonding character of these orbitals. The width of these bands increases with the increase of the volume of the alkyl group and is especially significant in the case of the PES of $(n\text{-}C_4F_9)_2O$ (see Fig. 1). Simultaneously with that the intensity of the corresponding band decreases and its structure becomes apparent. Due to the p-d interaction[18] of the orbitals of oxygen and silicon, PES of ethers containing the silicon atom attached immediately to the oxygen atom, are characterized by the decrease of the nonbonding character of the first band in the spectrum. In the PES of alkyl ethers with the normal chains the increase of the volume of the alkyl substituent moves the area of the overlapping bands of the inner MO-s towards $IP(n_O)$. It is noteworthy that in the case of $n\text{-BuO}(CF_2)_2H$ the complete overlapping of this kind takes place and, therefore, it is impossible to identify the $IP(n_O)$ orbital in the usual way. However, the calculations according to Eqn. (3) lead to the IP_a = 11.05 eV which is in a reasonable agreement with the determination of the starting point (10.78 eV) of the PES band.

For the more detailed identification of the PES band the semiempirical CNDO/2 calculations were performed.

PES of Me_2O has been interpreted on the different levels of the quantum chemical approach. So, K. Kimura et al.[2] have made the calculations of the energies of the ionic states of this molecules using the method of configurational interactions. The SCF MO calculations on the 6-31G basis set level were also made by the same group using the Koopman's theorem. The calculations on the 4-31G level[2] as well as using the more primitive CNDO/2 method[20] lead to the conclusions regarding the order and character of the localization of MO-s.

For the study of the substituent effects on the spectrum of the MO energies one might start with the analysis of the PE spectrum of the methylethyl ether. The optimized CNDO/2 geometry of this molecule agrees with the data[2] from microwave spectroscopy(trans-$Me\underline{O}CH_2CH_3$, C_s -symmetry). The order of MO-s coincides with that calculated[2] for the same configuration using nonempirical method whereas the charge distribution and MO characters differ only slightly (see Table 1).

As in our earlier papers[1,19,20] the linearity

$$IP_i = -a\varepsilon_i + b , \qquad (5)$$

where a and b are constants between the measured consecutive IP-s of the molecules and the corresponding calculated MO energies ε_i (Koopmans' approach) was used for the identification of the PES bands.

Fig. 4 visualizes the linearity (5) for the MeOEt molecule.

The results of the statistical treatment of the data from Table 1 in terms of Eqn. (5) are given in Table 3.

As one can see from the correlation diagram (see Fig.5), the change of the methyl group for the hydrogen atom in the ethers with the non-branched alkyl groups destabilizes the $n_O(2b_2$ MO in $Me_2O)$ and π ($1a_2$ and $3a_1$) MO-s and stabilizes the $\sigma_{CO}(2b_1)$ and $\pi(1b_2)$ MO-s. Starting with the ethyl substituent the MO with the σ_{CC} character appears.

This orbital is somewhat destabilized by the increase of the length of the chain.

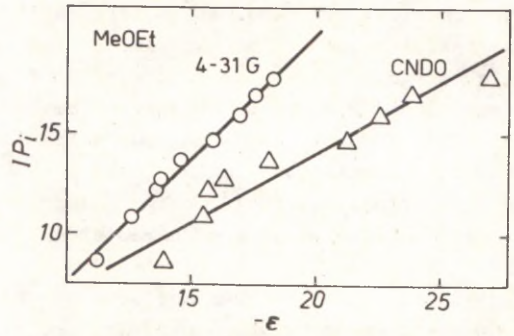

Fig. 4. The linearity between the measured IP-s and calculated MO energies ($-\varepsilon_i$) for the methylethyl ether.

C_{2v} turns out to be the most stable configuration for the diethylether whereas the hydrogens of the methyl group are in the cis-position to the oxygen atom. The corresponding transform is by 5.5 kcal/mol less stable. The results[2] of the more sophisticated quantum chemical calculations agree in general features (the order and character of localization) with the predictions of the CNDO/2 method.

The effect of substitution of the CF_3-group for the methyl-group on the PES could by monitored in the case of CF_3CH_2OMe and CF_3CH_2OEt molecules. The assignment of the geometry of these species could be made by the analogy with the corresponding alkylsubstituted alcohols[1]. As compared with the corresponding alkyl ethers the CNDO/2 MO-s of the CF_3-derivatives with the n_O(8a'' and 9 a''), π_O(13a' and 15a'), and π_{CH_2} (7a'' and 8a'') characters are stabilized whereas σ_{CC} (14 a' and 16a') is almost unsensitive towards that kind of substitution.It means that CNDO/2 calculations are unable to confirm the effect of the stabilization of σ-MO-s (as suggested in Ref. 21.) by the CF_3-substituent.

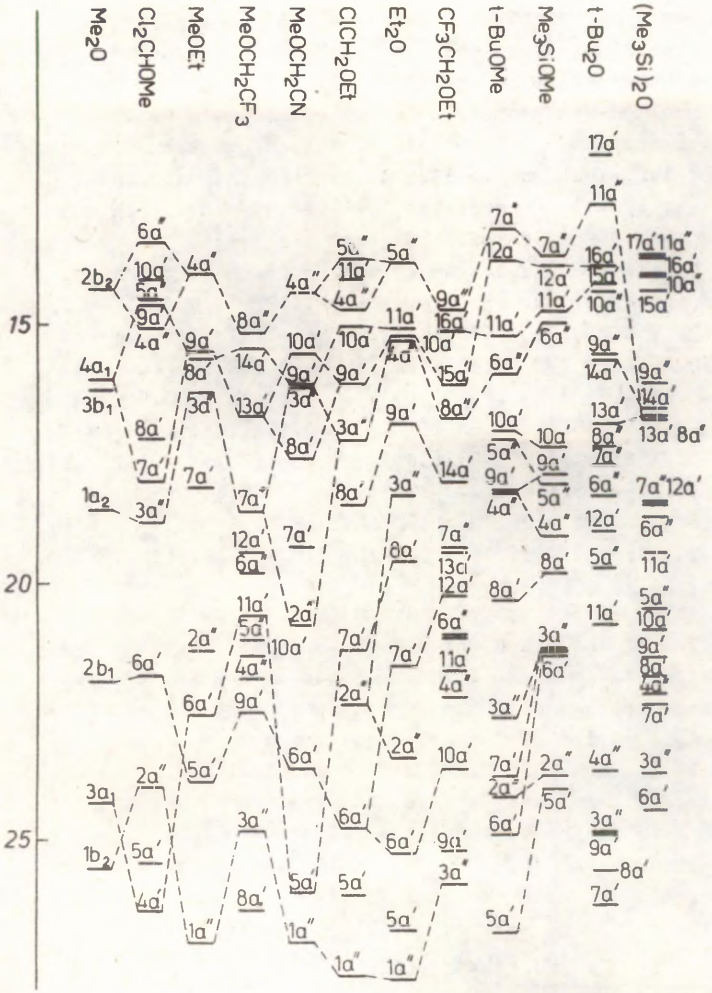

Fig. 5. Correlation diagram of CNDO/2 eigenvalues of some aliphatic ethers.

To our knowledge there is no literature data about the experimental PES of the simplest fully perfluorinated ether $(CF_3)_2O$. That, unfortunately, excludes the possibility to study the perfluoreffect which accompanies the transfer from dimethylether to its perfluorinated analog. One has only to mention that the IP(1) value predicted[16] by us for the latter compound on the basis of the information of its energy of 1s0 electrons is 13.3 eV whereas the calculated (this work, STO-3G basis set; E_{tot}= -736.9396 a.u., d_{CO}= =1.43; d_{CF}= 1.365 Å, formal charge on the oxygen is - 0.276 charges of electron) spectrum of the corresponding orbital energies is as follows (in a.u.): 0.521($12b_1$), 0.464($14a_1$), -0.4463($7b_2$, HOMO), -0.4516($13a_1$), -0.4641($11b_1$), -0.4951 ($6a_2$), -0.4964($10b_1$), -0.5019($6b_2$), -0.5025($12a_1$),-0.5136 ($5a_2$), -0.5172($5b_2$), -0.5340($4a_2$), -0.5417($9b_1$),-0.5455 ($11a_1$), -0.5595($4b_2$), -0.6230($10a_1$), -0.6721($8b_1$), -0.6842 ($3a_2$), -0.7162($3b_2$), -0.7233($9a_1$), -0.7385($7b_1$), -0.8131($8a_1$), -0.9008($6b_1$), -1.3658($7a_1$), -1.5335($2a_2$), -1.5350($5b_1$) , -1.5387($6a_1$),-1.5409($2b_2$), -1.627($4b_1$), -11.35($4a_1$), -11.35 ($3b_1$), -20.35($3a_1$), -26.0($1a_2$), -26.0($1b_2$), -26.0($2b_1$), -26.0($1a_1$), -26.0($1b_1$).

On chloro-substitution, alongside with the appearance in the PES of the lines which correspond to the chlorine lone pairs, the mixing of the orbitals of the latter type with those belonging to the oxygen lone pairs becomes possible. As a matter of fact this situation is characteristic to PES of Cl_2CHOMe and $ClCH_2OEt$* molecules. The pairs of the mixed 6a'', 4a'' and 9a', 7a' MO-s in the former and 5a'' and 4a'' MO-s in the latter molecule.

In the case of $NCCH_2OMe$ the mixing (symmetric combination) of π_{CN} MO with the orbital of the oxygen's lone pair (10a', 8a') as well of the π_{CN} orbital with (asymmetric combination) the pseudo-π_{CH_2} orbital (3a'' and 2a'').

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* Despite the fact that the gauche-form of $\underline{Cl}CH_2\underline{O}CH_2CH_3$ (C_1 symmetry group) is the most stable CNDO/2 conformation of this molecule, Table 1 and the text refer to the symmetry notations of MO-s for the Cis-form (C_s-symmetry).

Table 3.

The Results of the Statistical Analysis of PES in terms of Eqn.(5) for some Alkyl Ethers*

	Compound	Method	a	b	r	s	n
1.	Me_2O	4-31G	0.962 (0.049)	-0.545 (0.738)	0.995	0.28	6
		CNDO/2	0.536 (0.110)	3.606 (2.070)	0.925	1.04	6
2.	MeOEt	4-31G	0.993 (0.043)	-0.922 (0.645)	0.993	0.29	9
		CNDO/2	0.508 (0.057)	4.061 (1.121)	0.957	0.73	9
3.	Et_2O	4-31G	1.242 (0.004)	-4.347 (0.058)	0.999	0.02	4
		CNDO/2	0.630 (0.093)	1.584 (1.580)	0.979	0.72	4
4.	CF_3CH_2OMe	CNDO/2	0.855 (0.011)	-2.120 (0.239)	0.999	0.12	9
5.	CF_3CH_2OEt	CNDO/2	0.767 (0.033)	-1.423 (0.670)	0.993	0.41	9
6.	$ClCH_2OEt$	CNDO/2	0.565 (0.021)	3.090 (0.379)	0.996	0.22	8
7.	Me_3SiOMe	CNDO/2	0.616 (0.036)	1.486 (0.598)	0.997	0.18	4
8.	$(Me_3Si)_2O$	CNDO/2	0.699 (0.056)	0.393 (0.903)	0.994	0.26	4
9.	$(t\text{-}Bu)_2O$	CNDO/2	0.824 (0.162)	-0.336 (2.055)	0.981	0.25	3

* r - correlation coefficient
s - standard deviation
n - the number of points

For the study of the behavior of the orbital energies accompanying the substitution of Me_3Si group for the methyl-substituent one can begin with the Me_3COMe molecule which could be considered as a prototype of Me_3SiOMe. Unfortunately, PES of this reference compound, is with the exception

of the first IP(9.48 eV), unavailable. The same (C_s) symmetry was assigned to Me_3SiOMe molecule. One can see (Table 1) that n_O IP for the trimethylsilyl derivative is evidently lower than that for the corresponding alkyl-substituted compound. Such a change is not fully accounted for by the inductive effect of the substituent.

Most reasonable explanation[18,22] seems to be the connected with the idea about the participation of the d-AO-s of the silicon in the higher occupied MO-s (the so called reversed (p_π - d_π) conjugation).

CNDO/2 reproduces correctly the shift of the intensity of the n_O band. However, it fails to indicate the significant contribution of d-AO-s of the silicon into the HOMO-s.

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PHOTOELECTRON SPECTRA OF MOLECULES
3. Nitriles.

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Photoelectron spectra (PES) of 8 aliphatic nitriles (halogen-substituted acetonitriles, $NCCH_2CN$, Me_2NCH_2CN, Et_2NCN, and $ClCH_2SCN$).

The linear dependences of ionization potentials (IP) on the energetic characteristics (proton affinity, the complex-formation shifts of the OH-group of the phenol, etc.) of the molecule, the quantum chemical SCF calculations (CNDO/2 and Gaussian 70), and the so called method of comparison were used for the interpretation of the spectra.

In the earlier publications of this series PES of some aliphatic alcohols[1] and ethers[2] were reported (see also Ref. 3). The linear relationships established between IP-s of the localized lone pairs and some energetic characteristics (proton affinity, the energy of the core level 1s electrons of the oxygen, complex formation shifts of the stretching frequencies of the phenol OH-group, etc.) of the molecules were shown to serve for the purposes of the identification of the spectral bands.

Already for some time period and partially due to the well resolved spectral bands the PES of the nitriles have received the continuous attentions of several scholars. So, experimental studies of PES of alkylnitriles[4-9], halogen-nitriles[10,11], vinyl-[4], ethynyl-[8], and phenyl[8] nitriles as well as dicyanogen[8] were performed. The analysis of PES

of cyanamide[6] and dimethylcyanamide PES of methyl and halogenthionitriles were also studied[12].

In the present work PES of halogen-substituted acetonitriles $NCCH_2CN$, Me_2NCH_2CN, Et_2NCN, and $ClCH_2SCN$ were recorded and analyzed.

There are theoretical calculations of the relatively simple nitriles on the different levels of theory which can determine the general strategy of analysis of their PES.

From one hand, the semiempirical SCF methods could be formally considered as some algorithms of calculation of IP-s as it was done, e.g., in Ref. 3b. It should be mentioned that corresponding to the highest correlation coefficient slope of the straight line of the plot of the experimental IP-s vs., calculated on the basis of the Koopmans' theorem IP-s is essentially close to the unity.

From the other hand, these semiempirical calculation schemes also could be considered as SCF-methods of the calculation of the charge distribution in the molecule. Meanwhile, the latter approach is being used throughout the present series of papers. It is evident that in this case the ability of the given method to reproduce adequately at least the order of MO-s in one of the key elements of the latter approach. While comparing the calculated orbital energies with the experimental PES values of vertical IP-s on the basis of the Koopmans' theorem one has to keep in mind the shortcomings of the latter (See Ref. 3). So, for the HCN molecule the CNDO/2 order of the higher occupied MO-s (HOMO) is a_1, e_1 which contradicts to the experimentally determined[8,13-15] order of these orbitals (e_1, a_1). Also, in Ref.16 some discrepancies between CNDO/2 and experimental orders of the lower MO-s were noticed for EtCN and $H_2C{=}CHCN$.

However, the order of HOMO-s (π, σ, π, σ) suggested in Refs. 10 and 11 for the halogennitriles is correctly reproduced by the present CNDO/2 calculations.

The $(1\pi g)^4 (5\sigma_g)^2 (4\sigma_u)^2 (1\pi_u)^4 (4\sigma_g)^2$ electronic configuration has been suggested[8,13] for the dicyanogen

molecule. Our SCF MO calculations* on the STO-3G minimum basis as well as CNDO/2 calculations of this molecule reproduce adequately this order of IP-s. However, the earlier nonempirical calculations of Clementi[17] lead to the inverted order of $4\sigma_u$ and $1\pi_u$ MO-s.

It seems clear that the results of the semiempirical calculations of PES using Koopmans' theorem should be taken with the proper caution. Despite that in many cases they lead to the fully reasonable and adequate results.

Experimental

The photoelectron spectrometer used and the technique of experiments were already described elsewhere.[1,2]

Figure 1 shows the typical PES of compounds measured. Table 1 lists the vertical and adiabatic IP-s of these compounds as determined from PES. For comparison, some literature spectra of aliphatic nitriles are also reported in the same Table.

Most of the reagents used are commercical. Their purity was controlled by g.l.c. Monofluoromethyl- and trifluoromethylnitriles were synthesized during the experiment in the PE instrument by dehydration of the corresponding amides by diphosphorpentoxide (P_2O_5) . As far as PES have roughly equal sensitivity towards the components of the mixtures there can be, in the general case, some serious difficulties in measuring the PES of all components. However, in our special cases the situation is less complicated. At the room temperature the PES of the pure amide was monitored**

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* These calculations[32] were made using Gaussian 70 system of programs. The linear geometry was used whereas NC=1.15 Å, CC=1.38 Å and E_{tot}= -182.2178 a.u. The corresponding HOMO are as follows: 11.84, 11.84, 14.40, 15.04, 15.05, 15.05, 24.36.

** PES of $FCONH_2$ includes the following IP_v(eV):10.38;10.68; 12.99;13.91;14.47;15.18;16.39, whereas PES of CF_3CONH_2 is as follows (IP_v,eV): 11.23;14.81;15.42;16.02;16.37;17.30; 18.42. PES of these compounds and their analysis will be given in the forthcoming communications of this series.

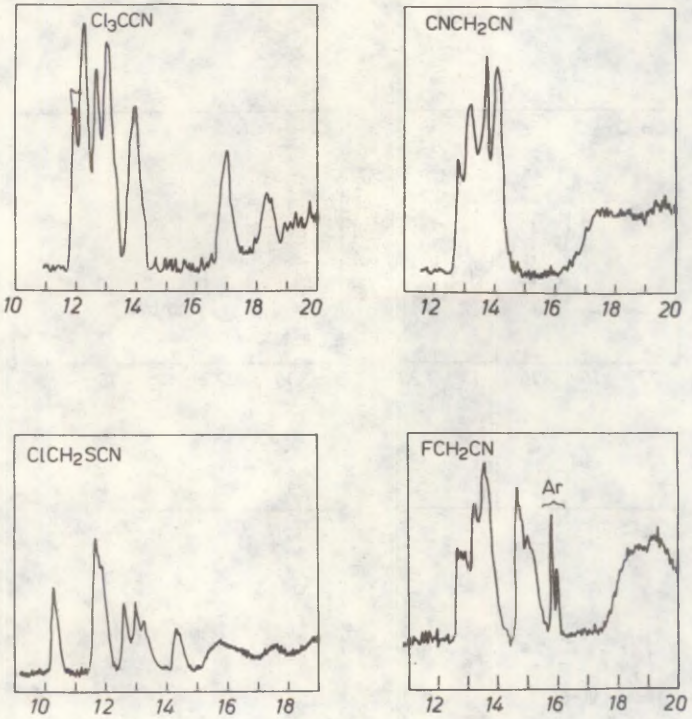

Fig. 1. PES of some nitriles.

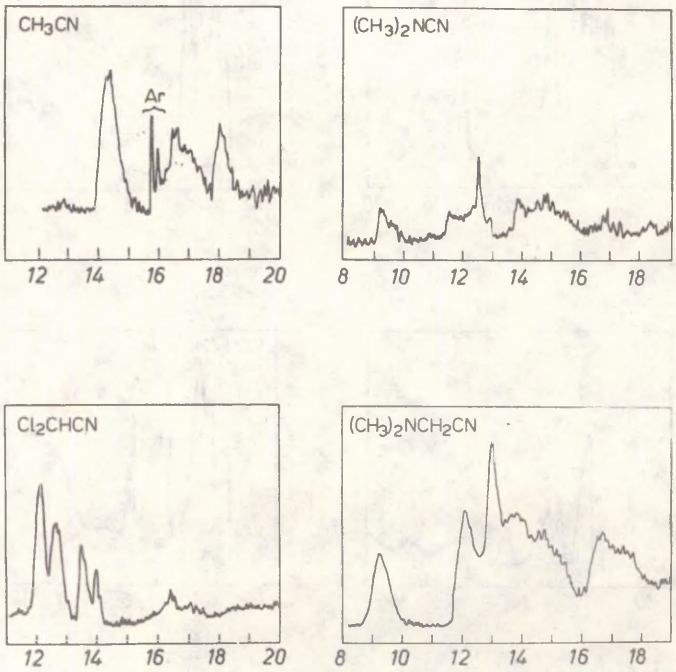

Fig. 1. PES of some nitriles (continuation).

Table 1

Experimental Ionization Potentials of Nitriles (PES) and Calculated Orbital Energies ($-\varepsilon_i$) (in eV units).

1. MeCN

	IP_v[a]	HAM/3[a]		CNDO/2[b]		
		$-\varepsilon$	MO	$-\varepsilon$	MO	
1.	12.46	12.17	2e	15.36	2e	π_{CN}
2.	13.17	13.10	$7a_1$	17.42	$4a_1$	n_N
3.	15.7	15.30	1e	22.79	$3a_1$	σ_{CC}
4.	17.4	16.88	$6a_1$	23.15	1e	π_{CH_3}
5.	24.9	23.16	$5a_1$	36.23	$2a_1$	$2S_N$
6.	29.7	25.97	$4a_1$	40.61	$1a_1$	$2S_C$

a. From Ref. 4, see also.[5-9]

b. This work: E_{tot} = -27.8994 a.u.

2. FCH_2CN

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	12.92	15.60	$3a''$	π_{CN}
2.	13.25	16.74	$8a'$	π_{CN}
3.	13.60	17.26	$7a'$	n_F, n_N
4.	14.58	19.71	$2a''$	n_F
5.	14.94	19.96	$6a'$	n_N, n_F
6.	18.5	23.53	$5a'$	n_F
7.	19.1	26.32	$1a''$	π_{CH_2}, n_F

a - This work ($IP_a^{(1)}$ = 12.81, $IP_a^{(6)}$ = 17.4)

b - This work: E_{tot} = -54.8693 a.u.

3. $ClCH_2CN$

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	12.05	14.22	$3a''$	n_{Cl}
2.		14.32	$8a'$	n_{Cl}
3.	12.3	15.17	$7a'$	π_{CN}, n_{Cl}
4.	12.9	16.46	$2a''$	π_{CN}, n_{Cl}
5.	13.59	18.16	$6a'$	n_N

a - From Ref. 5, see also[9]

b - This work: E_{tot} = -43.3180 a.u.

Table 1 continued

4. CF_3CN

	IP_v[a]	HAM/3[b]		CNDO/2[c]		
		$-\varepsilon$	MO	$-\varepsilon$	MO	
1.	14.39	14.30	$10a_1$	17.48	$6a_1$	n_N
2.	14.39	13.81	6e	18.41	5e	π_{CN}
3.	16.39	16.76	$9a_1$	20.40	4e	n_F
4.	16.57	15.87	$1a_2$	21.26	$5a_1$	n_N
5.	17.0	16.45	5e	21.68	$1a_2$	n_F
6.	18.24	17.30	4e	22.55	3e	n_F
7.	21.6[b]	20.85	3e	27.11	2e	n_F
8.	22.6[b]	21.51	$8a_1$	27.85	$4a_1$	n_F
9.	25.8[b]	24.56	$7a_1$	33.59	$3a_1$	σ_{CC}

a - This work ($IP_a^{(4)}$= 14.0) See also Ref. 18.
b - From Ref. 18
c - This work, E_{tot}= -108.8498 a.u.

5. Cl_2CHCN

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	12.14	13.95	$5a''$	n_{Cl}
2.		14.37	$9a'$	n_{Cl}
3.		14.48	$8a'$	n_{Cl}
4.	12.63	15.11	$4a''$	n_{Cl}
5.		16.05	$3a''$	π_{CN}
6.	13.43	17.14	$7a'$	π_{CN}
7.	13.92	18.83	$6a'$	n_N
8.		21.34	$2a''$	π^*_{CN}
9.		21.59	$5a'$	
10.	16.38	25.97	$4a'$	

a - This work ($IP_a^{(1)}$=12.00), See also Ref. 5.
b - This work: E_{tot}= = -58.9558 a.u.

6. CCl_3CN

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	11.94	13.98	5e	n_{Cl}
2.	12.27	14.51	$6a_1$	n_{Cl}
3.		14.80	$1a_2$	n_{Cl}
4.	12.69	15.45	4e	n_{Cl}
5.	13.06	17.53	3e	π_{CN}
6.	13.87	19.33	$5a_1$	n_N
7.		22.12	2e	π^*_{CN}
8.	16.99	22.49	$4a_1$	
9.		29.32	$3a_1$	
10.	18.38	31.44	1e	

a - This work ($IP_a^{(1)}$=11.89) See also Refs.5,9.
b - This work work: E_{tot}= = -74.2138 a.u.

Table 1 continued

7. Et_2NCN

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	9.32	12.07	12a'	n_N
2.	11.81	13.19	8a''	π_{CH_2}
3.	12.54	15.22	7a''	π_{CN}

a - This work ($IP_a^{(1)}$= 8.97; $IP_a^{(2)}$= 11.23; $IP_a^{(3)}$= 11.93)
b - This work: E_{tot}= -66.3817 a.u.

8. $NCCH_2CN$

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	12.70	14.89	$2b_1$	π_{CN}
2.	13.05	15.60	$4b_2$	π_{CN}
3.		15.77	$5a_1$	π_{CN}
4.	13.57	17.63	$1a_2$	π_{CN}
5.	13.91	18.53	$3b_2$	n_N
6.		19.08	$4a_1$	n_N
7.	17.68	25.51	$3a_1$	π_{CH_2}
8.		25.57	$1b_1$	π_{CH_2}
9.		25.71		

a - This work ($IP_a^{(1)}$≈$IP_v^{(1)}$) See also Refs. 9,19.
b - This work: E_{tot}= -45.6805 a.u.

9. Me_2NCH_2CN

	IP_v[a]	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	9.22	12.47	11a'	n_N
2.	12.14	13.82	10a'	σ_{CN}
3.	12.62	14.53	6a''	π_{CN}
4.	12.98	15.84	5a''	σ_{CH}
5.	13.74	16.26	9a'	π_{CN}
6.	14.58	17.07	4a''	π_{CN}
7.	16.73	17.83	8a'	n_N
8.	17.51	20.62	7a'	π_{CH_2}
9.	20.4	21.47	3a''	σ_{CH}

a - This work ($IP_a^{(1)}$= 8.86)
b - This work: E_{tot}= -57.7369 a.u.

Table 1 continued

10. $ClCH_2SCN$

	IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	10.38	11.98	$4a''$	n_S, n_N
2.	11.69	13.28	$10a'$	n_{Cl}
3.	11.84	14.26	$3a''$	n_{Cl}
4.	12.62	15.54	$9a'$	σ_{CS}
5.	13.04	15.74	$8a'$	n_{Cl}, π_{CN}
6.	13.33	19.07	$7a'$	n_N
7.	14.44	19.97	$2a''$	π_{CN}
8.	15.6	20.40	$6a'$	π_{CN}, n_{Cl}
9.	17.52	22.19	$5a'$	n_N, n_S
		23.20	$1a''$	π_{CH_2}

a - This work ($IP_a^{(1)}$= 10.29, $IP_a^{(2)}$= 11.59)
b - This work : E_{tot}= -54.2270 a.u.

whereas the PES of the nitrile appears on the heating of the reaction mixture (amide + P_2O_5). After the cooling of the ampoule and after some pumping the PES of the initial amide is again recorded. It is worthwhile to notice that the PES of CF_3CN measured using the present technique is in a good agreement with the recently[18] published data.

PES of Et_2NCN was followed only up to 12.6 eV due to the presence of the significant amounts of water vapor in the system.

IP-s listed in Table 1 are the average figures from the values determined by the repeated scanning of the spectrum.

Some of the presently reported results were already used[3] for the analysis of the relationship between IP and the energetic characteristics of the molecules. CNDO/2 method with its original parametrization[20] was mostly used for the interpretation of PES throughout the present work.

The order of MO-s and the approximate characters of

their localization are given in Table 1[*] and correspond to the CNDO/2 optimized geometry. The generally accepted symbols for the symmetry and MO characters are used. sp-hydridization is assumed for the CN group ($\angle_{XCN}=180^{\circ}$; the other valence angles are assumed tetrahedral with the exception of CSC (90°)). The CNDO/2 "optimum" bond lengths from Ref. 21 were used; besides that C–S= 1.77 Å and ≡C–S=1.51 Å were used.

Discussion

The interpretation of PES of nitriles is rather complicated due to the problem of the separate determination of the IP localized on C≡N bond and IP-s belonging to the π_{CN} and n_N characters. In Ref. 9 the linear relationship between proton affinity and IP(n_N) of several nitriles was suggested. The extended relationship of the same kind was recently suggested[3a]:

$$PA(RCN) = -0.556(0.010)IP(n_N) + 360.3(3.2) \qquad (1)$$

$r = 0.998$; $s = 0.6$ kcal/mol; $n = 13$,

where r – is the correlation coefficient
s – standard deviation
n – the number of points ($PA(NH_3)$=207 kcal/mol).

Only the point for HCN was found to deviate the relationship (1) significantly.

As in the case of IP(n_O) (see Refs. 1 and 2) IP(n_N) also depends linearly on the shifts of the stretching frequencies of the OH group of the phenol $\Delta\nu_{PhOH}$ (in CCl_4). caused by the complex formation of the latter with the oxygen (alcohols, ethers) and nitrogen bases.

The comparison of $\Delta\nu_{PhOH}$ values with IP(n_N)(See Fig. 2) results in the following approximate linearity:

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[*] As a rule, most semiempirical and nonempirical SCF calculations of nitriles are characterized by the bad convergency of the iteraction cycles in the SCF routine.

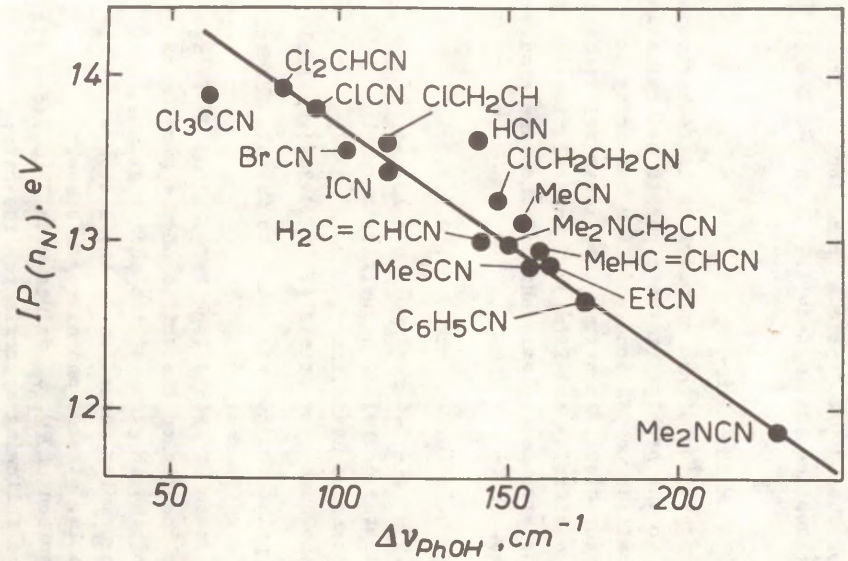

Fig. 2. The dependence of $IP(n_N)$ of the lone pairs of the nitrogen atom of the CN group of the nitriles on the shifts of the stretching frequencies of the OH-group of phenol in CCl_4 $\Delta\nu_{PhOH}$

$$\Delta\nu_{PhOH} = -71.792(6.219)IP(n_N) + 1079.8\ (82.2) \qquad (2)$$

$r = 0.961$; $s = 12.5\ cm^{-1}$; $n = 13$

The observance of Eqns. (1) and (2) again supports the assignment of the IP-s used to the lone pairs of the CN--group.

As a direct consequence from Eqns. (1) and (2), Eqn.(3) could be written:

$$PA(RCN) = 0.169(0.018)\Delta\nu_{PhOH} + 165.77(2.66) \qquad (3)$$

$r = 0.948$; $s = 2.6$ kcal; $n = 12$

In the case of the localized orbitals the method of direct comparison of the gross IP values of the compounds of different classes which resemble each other by the character of the localization of the MO-s could be used to give rather interesting results.

Due to the simultaneous presence of the large enough number of common substituents R the comparison of the corresponding ionization potentials of nitriles ($IP(n_N)$) and aldehydes ($IP(n_O)$) was made. Eqn.(4) represents the result gotten (See also Fig. 3).

$$IP(n_N) = 1.14(0.04)IP(n_O) + 1.48(0.43) \qquad (4)$$

$r = 0.995$; $s = 0.07$ eV; $n = 12$

For the comparison with the $IP(\pi_{CN})$ of nitriles, $IP(\pi_{C\equiv C})$ values of alkynes seem to be most proper partners. Indeed, the corresponding relationship between these quantities is quantitatively incorporated into Eqn.(5) (See Fig. 3*):

$$IP(\pi_{CN}) = 1.47(0.06)IP(\pi_{C\equiv C}) - 3.15(0.68) \qquad (5)$$

$r = 0.992$; $s = 0.11$ eV; $n = 11$.

---

* The deviation of CF_3CN from the straight line in Fig.3 could be caused by the circumstances that the 1st PES band of this molecule (1 eV wide) is possibly formed by two different but strongly overlapping bands $IP(\pi_{CN}) = 14.39$ eV (at maximum) and $IP(n_N) \approx 14.7$ eV.

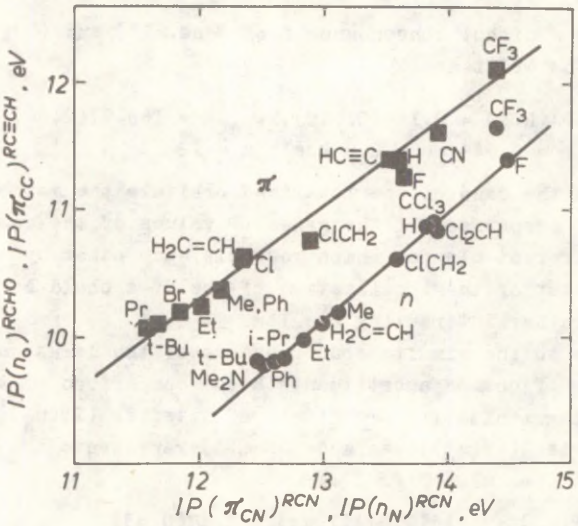

Fig. 3. The comparison of IP(π_{CN}) for nitriles RCN and IP($\pi_{C\equiv C}$)for alkynes RC≡CH (line π) and IP(n_N) for nitriles RCN and IP(n_O) for aldehydes RCHO (line n).

The IP(π_{CN}) and IP(n_N) values calculated by means of these relationships are listed in Table 2.

With the exception of the inverted order of $3a_1$ and 1 1 orbitals the CNDO/2 calculations of the acetonitrile molecule give the spectrum of eigenvalues which in the framework of the Koopmans' theorem agrees with the determinations from PES[8] and with the calculations on HAM/3 and double dzeta levels[8]. The above-mentioned contradiction is overcome by using the modified[7] CNDO method.

In the molecules of the C_{3V} group of symmetry π-MO-s are doubly degenerated. However, in the case of the asymmetric substitution (C_s group) such a degeneration disappears and a doublet of bonds emerges.

In the case of chlorosubstituted nitriles HOMO refers to the lone pairs of chlorine atom.

Table 2

IP of Electron Pairs of the CN-Group Calculated From Eqns.(1)-(5) for Nitriles

Nr	RCN	IP(π_{CN})	IP(n_N)
1	2	3	4
1.	HCN	13.6	13.82
2.	MeCN	12.18	13.11
3.	EtCN	11.85	12.85
4.	PrCN	11.67	-
5.	i-PrCN	11.85	12.7
6.	t-BuCN	11.6	12.5
7.	FCN	13.65	14.48
8.	ClCN	12.37	13.80
9.	BrCN	12.03	13.56
10.	JCN		13.15
11.	$(CN)_2$	13.93	14.68
12.	FCH_2CN	12.92	13.60
13.	CF_3CN	14.39	14.39
14.	$ClCH_2CN$	12.9	13.59
15.	Cl_2CHCN	13.43	13.92
16.	CCl_3CN	13.87	13.87

Table 2 continued

1	2	3	4
17.	$H_2C{=}CHCN$	12.35	13.0
18.	$MeCH{=}CHCN$		12.89
19.	$HC{\equiv}CCN$	13.54	
20.	PhCN	12.18	12.62
21.	$ClCH_2CH_2CN$	12.25	13.24
22.	H_2NCN	13.12	12.98
23.	Me_2NCN	12.33	12.55
24.	Et_2NCN		12.54
25.	MeSCN		12.85
26.	$NCCH_2CN$	12.69	13.91
27.	Me_2NCH_2CN		14.58

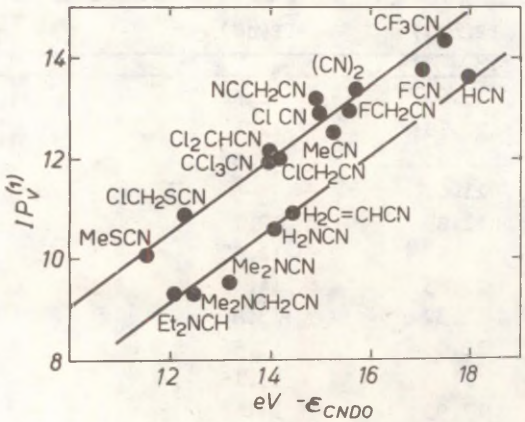

Fig.4. The dependence of $IP_v^{(1)}$ on the energy $(-\varepsilon_i)$ of HOMO for aliphatic nitriles.

Fig. 4 represents the linear relationship between the 1st vertical IP-s of some nitriles and the corresponding CNDO/2 energies of HOMO-s based on the Koopmans' theorem.

It is interesting to notice that the points for HCN, $H_2C{=}CHCN$ and cyanamides deviate from the general relationship and form a separate straight line of approximately the same slope.

$$IP_v^{(1)} = -0.702\ (0.042)\,\varepsilon_1 + 2.01\ (0.63) \qquad (6)$$

$$r = 0.982\ ;\ s = 0.24\ ;\ n = 12$$

The CNDO/2 calculations of the fluorosubstitution of acetonitrile suggest that the mixing of n_N and n_F orbitals should take place. As a result of that the doublet of MO-s (7a', 6a') appears. On the analogous chlorosubstitution π_{CN} and n_{Cl} orbitals will be mixed leading to the MO doublet 7a', 5a' (on the same reason 3è and 2e MO-s in CCl_3CN are also mixed)

According to CNDO/2 calculations the n_N character is assigned to the HOMO of the CF_3CN molecule. As a matter of fact it is very significantly delocalized all over the molecule.

$CNCH_2CN$ molecule belongs to the C_{2v} symmetry. The calculations according to the modified CNDO method lead, with the exception of $1a_2$ and $3b_2$, to the order of MO-s listed in Table 1. The MO characters, however, differ significantly. CNDO/2 predicts for $4a_1$ clearly pronounced n_N character whereas $2b_1$ and $1a_2$ should have π_{CN} character. In its turn, due to the delocalization of $4b_2$, $5a_1$ and $3b_2$ orbitals the assignment of their character is rather unambigous.

According to CNDO calculations[6] the 1st IP in the PES of Me_2NCN has the n_N character. On the other hand, the gas phase protonization of this compound most probably takes place on the CN-group. The analogous behavior could be expected also for Et_2NCN molecule whereas Me_2NCH_2CN should [3a,c]

behave in both cases as a typical aliphatic amine ($IP^{(1)}$ and protonization are associated with the lone pair of the NMe_2 group). Therefore, the more detailed analysis of PES of this compound will be given in the further communication of the present authors jointly with the discussion of the data for the aliphatic amines. The experimental[23] CSC angle in MeSCN is 99°. CNDO/2 calculations indicate that somewhat more stable conformation corresponds to the angle of 90°. In this case the results of the present CNDO/2 calculations agree (with the exception of the order of 6a' and 2a'') with those of nonempirical STO-3G calculations[12]. In molecules of this type the HOMO has a clear cut n_S character even in the chlorosubstituted derivatives. In $ClCH_2SCN$ the mixing of n_{Cl} and π_{CN} orbitals occurs. As a result of that 8a' and 6a' MO-s appear in the spectrum of the eigenvalues.

The correlation diagram of CNDO/2 MO-s of the compounds studied in this work is given in Fig. 5.

Table 3 represents the results of the correlation analysis of experimental (IP) and calculated ($-\varepsilon_i$) orbital energies in terms of the Eqn.(7):

$$IP_i = -a\varepsilon_i + b \qquad (7)$$

where a and b are constants.

For the nitriles the CNDO/2 method, as a rule, leads to slopes a which are considerably less than unity. On the other hand, HAM/3[4] which is specially parametrized for the calculations of PES predicts slopes which practically do not differ from unity (see Table 3).

The present identification of $IP(n_N)$ values of nitriles is also supported by the analysis of the dependence of IP-s on the formal CNDO/2 Mulliken charge distribution in these molecules. As it was shown earlier[3e] IP of the lone pairs depend linearly on the Mulliken charges on condition that the intramolecular Madelung correction potential is taken into account. It is, meanwhile, interesting to notify that the relationship of that kind derived in Ref. 3c for 18 CN-containing compounds predicts for CF_3CN the $IP(n_N)$=14.7 which is identical to the above-accepted value.

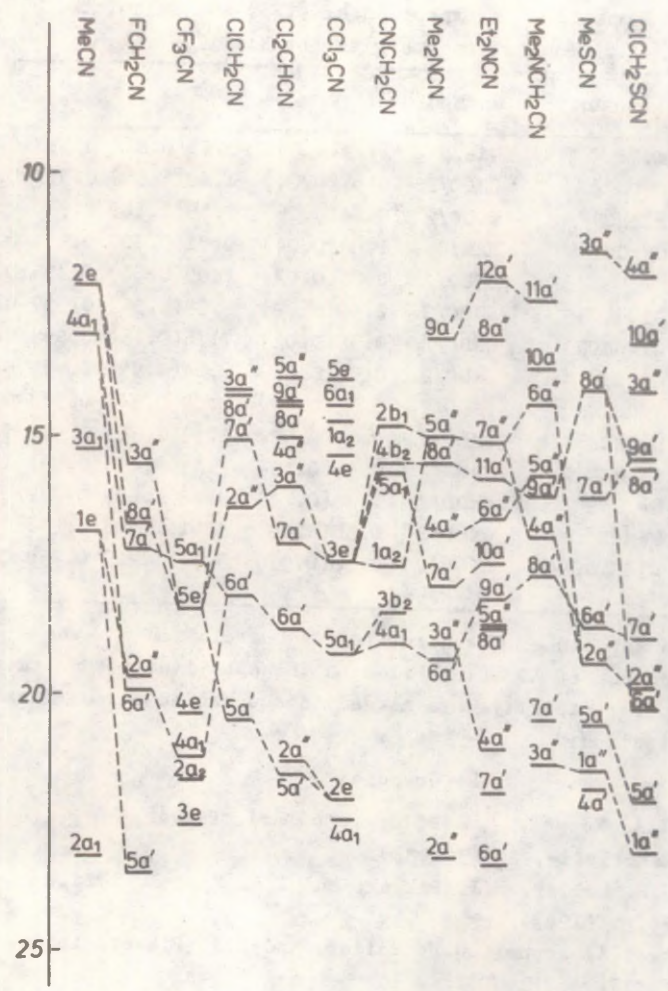

Fig. 5. Correlation diagram of CNDO/2 eigenvalues of some aliphatic nitriles

Table 3

The Comparison of Experimental (IP_i) and Calculated ($-\varepsilon_i$) Ionization Energies For Nitriles

No	Compound	Method	a	b	r	s
1.	MeCN	HAM/3	1.23(0.05)	-3.03(0.81)	0.997	0.57
		CNDO/2	0.67(0.04)	1.48(1.06)	0.993	0.93
2.	FCH_2CN	CNDO/2	0.64(0.06)	2.59(1.16)	0.980	0.55
3.	CF_3CN	HAM/3	1.08(0.04)	-0.71(0.80)	0.994	0.46
		CNDO/2	0.75(0.03)	1.09(0.64)	0.995	0.40
4.	$ClCH_2CN$	CNDO/2	0.40(0.02)	6.29(0.36)	0.997	0.07
5.	Cl_2CHCN	CNDO/2	0.35(0.01)	7.36(0.15)	0.999	0.08
6.	Cl_3CCN	CNDO/2	0.39(0.05)	6.64(0.99)	0.959	0.78
7.	$NCCH_2CN$	CNDO/2	0.32(0.04)	8.09(0.84)	0.973	0.74
8.	Me_2NCN	CNDO/2	0.87(0.08)	-1.53(1.36)	0.977	0.64
9.	Et_2NCN	CNDO/2	0.94(0.48)	-1.49(6.47)	0.891	1.08
10.	Me_2NCH_2CN	CNDO/2	1.08(0.10)	-3.62(1.65)	0.972	0.84
11.	MeSCN	CNDO/2	0.55(0.09)	3.81(1.50)	0.943	0.78
12.	$ClCH_2SCN$	CNDO/2	0.58(0.07)	3.54(1.22)	0.950	0.72

Some aspects of the quantitative correlation of the dependence of IP of nitriles on the substituent constants and polarizability were already discussed in our earlier publication.[3c]

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STRUCTURE INFLUENCE OF POLYCYCLIC ARENES ON THEIR SOLUBILIZATION IN AQUEOUS SOLUTIONS OF IONIC SURFACE-ACTIVE SUBSTANCES

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The paper reports the results of studying the solubilization of a set out of 12 polycyclic arenes (PA) in the aqueous solution of ionic surface-active substances (SAS). The influence of the nature of SAS on the change of standard free energy of the system - ΔG^{o} was determined. It was established that there exists a polylinear correlation between the coefficient of PA distribution in aqueous and micellar phases, the Hansch hydrophobicity constants (log P) and the Streitwieser polar constants σ_r. It was shown that the contribution of each constant of the correlation is conditioned by the nature of SAS.

The penetration of polycyclic arenes (PA) into the building materials of cells and cell membrances as well as their distribution there is the initial point in the process of PA metabolic oxidation.

As is known, in aqueous medium biphilic molecules, due to the forces of hydrophobic interaction , form aggregates: liquid micelles, protein globules, two-layer membranes, micelles of surface-active substances (SAS). The ability of these aggregates to solubilize PA molecules essentially changes their content in water, thus influencing the metabolic processes.

A group of authors[1] have studied the kinetic regularities of neutral arene solubilization in the micelles of ionic SAS. They have presented an empirical model for the solubilization process which unites the position of the solubilized arenes and the factors that determine the speed of their entry and departure from the micelle.

As can be concluded from ref. 2 the bonding of hydrocarbons with micelles is conditioned by the hydrophobic and ionic interactions with nonpolar and charged groups of the solubilized molecules.

In the case of aromatic molecules the interaction of the charged groups of the micelle surface with the π-electron system of the aromatic ring is involved as well. However, no distinct correlations between the structure of hydrocarbons and its ability to solubilize can be found in literature.

We have shown earlier[3] that there exist correlational dependences between the experimental hydrophobicity values of a set of PA and quantum-chemical characteristics F_r^{max}, L_r^{min} and the Streitwieser polar constants σ_r.

In the present communication we have presented the results of studying the influence of PA structure on their solubilization in the micelles of ionic SAS.

Methods and Objects of Investigation

A set of PA served as the object of investigation, they are presented in Table. SAS were used in the experiment as well: anionic - sodium dodecylsulfate (DDS) (the Shostkin Factory of Chemical Reagents) and cationic - cetyltrimethylammonium bromide (CTAB).-"Merck". The commercical reagents DDS and CTAB were further purified by repeated recrystallization from ethanol and the mixture of acetone-acetonitrile (3:1) respectively.

The experiments were conducted in a thermostatically controlled glass reactor which was supplied with a magnetic mixer. 1 ml of the acetone solution of PA (4mM) was introduced into the reactor, after that acetone was elaborately evaporated. To the dry residue 50 ml of SAS solution in water was added. The concentrations of SAS were taken higher

than their critical concentrations of micelle formation (CCM) (Table). The contents of the reactor were mixed for 4 hrs and then left alone for 16-18 hrs. In order to avoid suspended particles the PA solution was filtered through a double green tape (Filtrak 91, Germany).

In the cases when the sensitivity of the device (Specord, UV VIS) didn't enable us to measure the PA concentration directly from the aqueous solution (applying the coefficient of molecular extinction for ethanol) the extraction method was applied.

The mathematically treated results of the experiment are presented in Table.

(The error which is indicated in Table is a mean deviation).

Discussion and Results

Table presents the data on the solubilization of a set out of 12 PA in the aqueous solutions of ionic SAS. When interpreting the results of the experiment the distribution coefficient K has been applied which is established in accordance with the simple law of distributing substances between the micellar and aqueous phases.

$$K = /PA/_m \; / \; /PA/_a,$$

where $/PA/_m$ and $/PA/_a$ are the concentrations of PA in the micellar and aqueous phases, at this $(PA)_a$ is numerically equal to their solubility in water.

The calculation of $(PA)_m$ has been done from the equation:

$$/PA/_m = \frac{/PA/_{gen} - /PA/_a}{(C - CCM).\ V},$$

where $/Pa/_{gen}$ denotes the general PA content in the aqueous solution of SAS, V is the molar volume of SAS equal to 0.32 l, the values for CCM have been taken from ref.1, C is the initial SAS concentration in the solution.

The molar volume (V=0.32 l) has been calculated by applying the numbers of aggregation (N) for DDS - 62, for CT AB-60. Our calculations showed that according to the

Gaussian distribution of micelles as to their size in the aqueous solutions of ionic SAS, 95% of their molecules form micelles with the above numbers of aggregation in the areas of the concentrations studied.

The changes in the standard free energy of PA solubilization have been calculated from the thermodynamic equation:

$$\Delta G^{\circ} = - RT \ln K.$$

As structural characteristics we have selected the empirical Streitwieser constant σ_r which indirectly characterizes the values for electron densities in the r-position of aromatic hydrocarbon[5] and the Hansch hydrophobicity constant[6,7] (log P), where P is the distribution coefficient of the compound between n-octanol and water. According to ref. 7 the hydrophobic constant of a molecule is determined by the sum of the hydrophobic contributions of its fragments:

$$\log P = \sum_{1}^{n} a_n f_n$$

Here f_n stands for the hydrophobicity of the molecular fragment, a is the number of fragments.

Applying the literature values[6,7] of log P to a number of PA and fragments, we have calculated on the basis of additivity and invariancy of f_n the unavailable log P values for a number of PA (Table).

As is known, the process of micelle formation in the aqueous solutions of ionic SAS is to a large extent determined by the forces of hydrophobic interaction. The latter should also exert considerable influence on the solubilization of hydrocarbons which accounts for selecting the constant log P as one of the structural characteristics.

As can be concluded from Table at PA solubilization a decrease in the free energy of the system is highest in the case of benz(a)pyren-arene with the highest hydrophobicity, i.e. the ability of PA to solubilize in the micelles of ionic SAS is closely related to their efforts to leave the aqueous environment.

Taking into account the charge on the surface layer of the micelle (the Stern layer) the π-electron system of the aromatic ring should make a certain contribution to PA solubilization.

The mathematical treatment of the results by the step-regression method gave the following correlational equations (1,2).

$$\ln K_1 = (1.58 \pm 2.39) + (0.26 \pm 0.11)\,\sigma_r + (1.79 \pm 0.57) \log P \quad (1)$$

$$n = 10,\ r = 0.95,\ s = 1.07$$

The analysis of the obtained correlational dependences (1,2) shows that in the case of anionic micelles of sodium dodecylsulfate the process of PA solubilization (the confidence level being 95%) is sufficiently well described by polylinear correlation (1). At this the contribution of both independent alternents to the correlation is nearly the same.

Eq. (2) which describes the PA solubilization in the micelles of cationic CTAB is to some extent different. On the confidence level of 95% the introduction of log P as the second independent alternant does not make a noteworthy contribution to the correlation.

Thus, correlation equations (1,2) do reflect the nature of SAS influence on PA solubilization. Since σ_r is the measure of relative basicity of the r'th position in an aromatic molecule, then it can be concluded from the correlation equations that the interaction of the micelle with PA takes place in accordance with the laws of the arene's electrophilic attack. Consequently, the position of PA depends on the former - in the surface layer, the position of the cationic micelle, but in the hydrophobic nucleus, that of the anionic micelle.

Consequently, the results obtained evidence that the correlation equations can be applied to interpret the results of investigating the solubilization of polycyclic arens in the micelles of ionic SAS.

Table

The Results of Determining PA Solubilization in the Aqueous Solutions of Ionic SAS

PA	$R_{16}(CH_3)_3NBr$ (1.5mM)		$R_{12}SO_4Na$ (10mM)		σ_r	log P[c]
	C[a], mmol/l	$-\Delta G^o$ kJ/mol	C[a], mmol/l	$-\Delta G^o$ kJ/mol		
1. Benzene[b]	12300	16.81	2500	12.86	-7.8	2.13
2. Naphthalene[b]	1110	20.76	380	18.16	0	3.37
3. Anthracene	17.0±2.0	26.29	5.3±0.3	23.41	8.1	4.45
4. Phenanthrene	28.0±3.0	19.63	40.0±2.0	20.53	0.5	4.46
5. Pyrene	51.0±8.0	28.43	20.0±1.0	26.12	2.9	5.15
6. Benz(a)anthracene	25.0±3.0	38.42	57.0±0.5	34.86	8.2	5.83
7. Benz(a)pyrene	24.0±4.0	43.61	3.5±0.1	38.92	11.1	6.52
8. Benz(a)pyrene	3.1±0.0	33.28	2.7±0.1	32.94	5.4	6.53
9. Triphenylene	2.1±0.6	23.19	3.5±0.2	24.48	-0.8	5.84
10. Perylene[B]	2.4	34.30	1.9	33.73	8.4	6.36
11. Dibenz(a,j)anthracene	13.0±2.0	31.70	1.3±0.2	31.70	7.7	7.21
12. Dibenz(a,h)anthracene	3.9±1.2	25.61	1.2±0.0	22.79	6.5	7.21

a - the number of PA solubilized in a litre of micelles, b - taken from[1]; c - calculated on the basis of ref. 6 and 7: $\pi_{-CH=CH-CH=CH-} = 1.38-0.036$ and $f_H = 0.23$; d - taken from ref. 6.

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC DATA IN THE GAS PHASE HOMOLYSIS
4. Calculation of Conventional Formation Enthalpies of Free Radicals Based on Experimental Activation Energies, Isokinetic and Isoentropic Models.

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Conventional formation enthalpies of free radicals in the gas phase at $0^{o}K$ have been calculated from experimental activation energies as well as proceeding from the isokinetic and isoentropic models.

Final reliability criteria of the all different models verified are approximately indistinguishable. A primary result before the exclusion of significantly deviating points is somewhat worse using original activation energies. The other treatment versions are approximately identical. The application of activation energies obtained as a result of the treatment according to the Arrhenius equation of the parallel independent data sets for separate reactions makes the result worse.

We have calculated[1] conventional formation enthalpies of free radicals at $0^{o}K$ in the approximation of the constant effective mean value of $\log A_{o}$ for the estimation of rate constants in the gas phase homolysis:

$$R_i - R_j \rightarrow R_i\cdot + R_j\cdot \qquad (1)$$

The working model was based on the expression for the activation energy D_{ij} of reaction (1):

$$D_{ij} = \Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - \Delta H^{o}_{OR_iR_j} \qquad (2)$$

where $\Delta H^{\neq}_{R\cdot}$ and $\Delta H^{\neq}_{R_j\cdot}$ are conventional formation enthalpies of free radicals in the transition state; $\Delta H^{o}_{OR_iR_j}$ is a standard formation enthalpy for a compound R_iR_j at $0^{o}K$. Recalculated values of experimental activation energies served as D_{ij} values obtained according to the formula:

$$D_{ij} = E_{ij} + 2.3\ RT_{mean}\ (\log A_o - \log A_{ij} + \log n_{ij}) \qquad (3)$$

where R is the gas constant, T_{mean} represents the mean temperature for the temperature range studied to calculate the log A and E values, $\log A_o$ is the effective universal value of the logarithm of the preexponential factor obtained from the data treatment in the coordinates $\log k_{T_2} - \log k_{T_1}$ and is equal to 14.64^{2}, n_{ij} denotes the statistical factor equalled to the number of equivalent breaking bonds.

The technique of multilinear regression analysis (MLRA) was used to solve the systems of equations:

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} = D_{ij} + \Delta H^{o}_{OR_iR_j} \qquad (4)$$

or

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} = D_{ij} + I_{R_iR_j} \qquad (5)$$

where

$$\Delta\Delta H^{\neq}_{R_i\cdot} = \Delta H^{\neq}_{R_i\cdot} - \Delta H_{R_i\cdot}\ , \qquad (6)$$

$$\Delta\Delta H^{\neq}_{R_j\cdot} = \Delta H^{\neq}_{R_j\cdot} - \Delta H_{R_j\cdot} \qquad (7)$$

i.e. the differences between the formation enthalpies of the free radicals and the additive enthalpy terms for corresponding substituents, and

$$I_{R_iR_j} = \varphi_{R_i}\varphi_{R_j} + \alpha^{\neq}\sigma^{\neq}_{R_i}\sigma^{\neq}_{R_j}\ , \qquad (8)$$

representing the interaction energy term between substituents R_i and R_j in the initial compound R_iR_j.

In the present study different modifications of the model based on equation (2) are verified. It makes a sense to test equations (4) and (5) using activation energies reported in the literature and obtained by the treatment of the parallel data in the coordinates of the Arrhenius equation[2] as well. Values $\Delta H_T = E_T + RT$, where ΔH_T is the enthalpy and E_T the activation energy for reaction (1), must be served as D_{ij} values, if one assumes the zero value[3] for the activation energy of the recombination of free radicals and if the rate constants are expressed in concentration units. Within the framework of the transition state theory the activation enthalpy is expressed:

$$\Delta H^{\neq}_{ij} = E_{ij} - RT \qquad (9)$$

Consequently one can solve the systems of equations (4) and (5) assuming that the values known are $D_{ij} = E_{ij}$ and $D_{ij} = E_{ij} - RT$.

The presence of the isokinetic relationship should be exposed to a more direct verification comparing with the data treatment in the coordinates $\log k_{T_2} - \log k_{T_1}$ performed in ref. 2. One can assume the isokinetic relationship between "true" values of log A' and of activation energy D':

$$\log A' = \alpha + D'/2.3\,R\beta\,, \qquad (10)$$

where β is the isokinetic temperature. Statistically corrected value of $\log k^c_{ijT}$ characterizing the gas phase homolysis (1) can be represented as follows:

$$\log k^c_{ijT} = \log A_{ij} - E_{ij}/2.3\,RT - \log n_{ij} \qquad (11)$$

and

$$\log k^c_{ijT} = \alpha + D'/2.3\,R\beta - D'/2.3\,RT = \alpha + (1/\beta - 1/T)D'/2.3\,R \qquad (12)$$

Combining equations (11), (12) and either equations of type (4) or type (5) one can obtain equations (13) and (14), respectively:

$$(1 - T/\beta)\,(\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot}) + T\,\Delta H^{o}_{OR_iR_j}/\beta - 2.3\,RT\alpha =$$

$$= \Delta H^{o}_{OR_iR_j} + E_{ij} + 2.3\,RT\,(\log n_{ij} - \log A_{ij}), \qquad (13)$$

$$(1 - T/\beta)\,(\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot}) + T\,I_{R_iR_j}/\beta - 2.3\,RT\alpha =$$

$$= I_{R_iR_j} + E_{ij} + 2.3\,RT(\log n_{ij} - \log A_{ij}) \qquad (14)$$

In the special case of the isoentropic behavior ($\beta = \infty$) these relations are reduced to respective equations (15) and (16):

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - 2.3\,RT\alpha = \Delta H^{o}_{OR_iR_j} + E_{ij} +$$

$$+ 2.3\,RT\,(\log n_{ij} - \log A_{ij}) \qquad (15)$$

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} - 2.3\,RT\alpha = I_{R_iR_j} + E_{ij} +$$

$$+ 2.3\,RT\,(\log n_{ij} - \log A_{ij}) \qquad (16)$$

In equations (15) and (16) the constant $\alpha = \log A_o$ represents the universal effective value of the logarithm of the preexponential factors.

Technique of Data Treatment.

The statistical treatment of data in the coordinates of equations (4) - (5) and (15) - (16) was carried out using the program of MLRA. Equations (13) and (14) require the use of nonlinear least square (NLLS) method. The same program was used for the version with $1/\beta = 0$ leading to equations (15) and (16) after the exclusion of significantly deviating points. The last procedure was performed in all cases according to Student's criterion on the confidence level of 0.95. The calculations were carried out using the Nairi-2 computer. Instead of the complete data set the date for the most represented radicals were processed. The maximum number of unknown coefficients for MLRA and NLLS

programs was equal to 15.

In ref. 1 only a mean temperature T_{mean} of studied temperature range for each pair of literature log A and E values was used to solve the systems of equations (4) and (5). In the present report three temperature values corresponding to lower (T_{min}) and upper (T_{max}) limits of temperature ranges and T_{mean} are used for each pair of log A and E values. In all versions the value $\Delta H^{\neq}_{H\cdot}$ = 51.63 kcal/mol from the handbook[4] was assumed. Alternative values[5] for $\sigma^{*}_{NO_2}$ and α^{*} were used in calculations of $\Delta\Delta H^{\neq}_{R\cdot}$ values. Compiled literature values of log A, E and $\Delta H^{o}_{OR_iR_j}$ are listed in ref. 1.

Results and Discussion.

The data treatment in the coordinates of eq. (4) where $D_{ij} = E_{ij}$ or $D_{ij} = E_{ij} - RT$ leads to the results presented in Table 1. The result obtained using the values of activation energies reported in the literature is comparable with that obtained for D_{ij} values corresponding to the effective mean value of log A_o. The latter one is somewhat preferable owing to better showings of the primary result before the exclusion of points. For D_{ij} according to equation (3) s = 2.6 kcal/mol (134 points, 41 reactions, and 15 radicals). At the same time assuming $D_{ij} = E_{ij}$ s = 3.74 kcal/mol (100 points, 35 reactions, and 14 radicals). After the exclusion of significantly deviating points respective values are s = 1.3 kcal/mol (107 points, 35 reactions)[1] and s = 1.52 kcal/mol (75 points, 35 reactions). If one takes into account that different radical sets were used then the final reliability is approximately identical for both versions. Besides of that when $D_{ij} = E_{ij}$ was assumed not a single one from 35 reactions was excluded.

The use of the values $D_{ij} = E_{ij} - RT$ at T_{mean} leads to lower value of standard deviation (s = 1.34 kcal/mol) after the exclusion of 31 points and one reaction (i-C_3H_8-NO_2). However, the same number of points (NE = 75) as in the version 1) in Table 1 leads to s = 1.66 kcal/mol and the

reaction for i-C_3H_7-NO_2 is not yet excluded. The value of s is essentially lower in result of the data treatment for $D_{ij} = E_{ij}$ - RT at the three indicated temperatures. However in this case the data for three reactions (i-C_3H_7- NO_2, CH_2 = $CHCH_2$ - I and $C_6H_5CH_2$- CH_3) are already excluded and 120 points from 300 as well.

One can see from the variants 4) and 5) of Table 1 that the use of the E_{ij} values obtained for the parallel literature values according to the Arrhenius equation[2] makes the result significantly worse. This conclusion unjustifies the respective averaging procedure in the coordinates of the Arrhenius equation.

The MLRA treatment of the system of equations (5) gives the results analogous to the obtained above (see Table 2). One can explain comparatively high s values of final results for the versions 1) and 3) because of the interruption of the point exclusion procedure. It was so since the program used was not suited with the routine of the exclusion of all points for any radical. A great difference in the $\Delta\Delta H^{\neq}_R$. values for CH_3O. radical in the version 1) compared with that one for the versions 2) and 3) is explained since the treatment of the parallel independent data for the CH_3O - CH_3 bond homolysis in the coordinates of the Arrhenius equation leads to E = 59.1±11.9 kcal/mol[2]. At the same time the literature values are equal to 76.0 and 81.0 kcal/mol. The present reaction is the only one available for the calculation of the $\Delta\Delta H^{\neq}_{CH_3O}$. value.

The results of the data treatment in the coordinates of equations (13) and (15) using the NLLS program are listed in Table 3. At that time in the version 1) the close enough independent values of the right side of equation (13) based on the parallel experimental E_{ij} and $\Delta H^{o}_{OR_iR_j}$ values were averaged in order to include all the data at the present number of radicals (due to the limited memory of the computer used). In the version 3) of Table 3 close

values were not averaged and the number of radicals was reduced to 10. Using NLLS program the versions with unknown β or $1/\beta$ were tested. The results coincided with the high reliability (including the data of Table 5) except the version 3) in Table 3 in which the solution did not converge and β as unknown coefficient approached $-\infty$.

The $1/\beta$ and β values are unstable in the course of the solution. For example the β values for the version 1) in Table 3 change from 4594° K to 13600°K and $1/\beta$ from 0.00007 to 0.00013 while the final results are $\beta = 7494 \pm 2532$°K and $1/\beta = 0.00013 \pm 0.0004$. In the version 3) of Table 3 the $1/\beta$ value changes from 0.00001 to 0.00010, the difference being in the order of the magnitude . However, the distinction of the $1/\beta$ value from zero is reliable from the point of view of Student's criterion on the confidence level 0.95.

One can see from Table 3 that the standard deviation s is somewhat less than in Table 1 at the very beginning of the data treatment and equals approximately to the value for the scheme reported in ref. 1. However the final s value is somewhat higher.

Assuming $1/\beta = 0$ (i.e. the treatment according to equation (15)) the standard deviation s for the same data set somewhat increases. When then the solution process has been continued and some additional points excluded s became somewhat lower (see versions 2) and 4) in Table 3).

The data treatment in the coordinates of equation (15) was carried out in addition to the procedure described above by the MLRA program at T_{mean} for two different sets of radicals listed in Table 4. The first of them corresponds to the set of the versions 1) and 2) in Table 3 and also to the sets of Tables 1-2 and 5-6. This set includes the radicals represented by largest numbers of data both for the treatment schemes using the experimental formation enthalpies of compounds R_iR_j and the interaction terms $I_{R_iR_j}$. The version 2) corresponds to the set of the most represented radicals taking into account only models with the experimental $\Delta H^{\circ}_{OR_iR_j}$ values. The different sets of radicals in

Table 4 lead to approximately identical formation enthalpies of free radicals within the range of their uncertainties. These results are close to that ones for the versions 2) and 4) in Table 3 as well.

The data treatment according to equations (14) and (16) at T_{mean} leads to the results reported in Table 5. In this case the s value is insignificantly lower for the isokinetic model according to equation (14) both for initial and final data sets. Within the framework of the scheme (16) and used data set one is not able to prefer one of the $\sigma^{*}_{NO_2}$ values (3.55 and 4.5).

The results of the verification of equations (15) and (16) using three temperatures for each independent estimate of the right sides of the indicated equations are listed in Table 6. Using the set of radicals identical to the version 1) in Table 4 the number of equations (points) at T_{mean} is equal to 100 instead of 107 in Table 4. This decrease is connected with the exclusion of experimental data for which the temperature ranges are not reported in the compilation[1]. For the comparison the variant 1) is reported where only T_{mean} are used. The use of three temperatures diminishes the final s value evidently owing to more considerable exclusion of deviating points. Thus, at the same number of reactions (29) involved, 31 points from 100 are excluded using the data only for T_{mean} while 107 from 297 are excluded in the case of three temperatures. One can note more that all corresponding regression coefficients obtain very close values for the final sets. The $\Delta H^{\neq}_{R}$. values for three temperatures are about 0.1 - 0.3 kcal/mol lower than using T_{mean}. The log A_o value is somewhat lower as well.

When solving equations (15) and (16) the parameters to be estimated were both $\alpha_1 = \log A_{oNO_2}$ for nitrocompounds and $\alpha_2 = \log A_o$ for other compounds. These modifications of the isoentropic model are not reflected in Tables 4-6. The log A_{oNO_2} values (14.8 - 16.0) exceeded respective log A_o values (13.8 - 14.1), however the reliability of the

description remained approximately identical for all versions tested.

One can draw a general conclusion from the above results of the treatment of the kinetic data for the gas phase homolysis that the final reliability of the all models tested is approximately identical and do not lead to the appreciable improvement of description compared with the approach in ref. 1 where $\log A_o = 14.64$ was assumed. Besides, the primary result before the exclusion of significantly deviating points is somewhat worse using the original literature activation energy values being approximately identical for all other treatment versions. The use of the activation energies obtained by the treatment of the parallel data sets according to the Arrhenius equation leads to even higher values of the standard deviation.

Within the framework of the isoentropic model expressed by equations (15) and (16) the data treatment gives somewhat lower values (close to 14) for the effective universal $\log A_o$ if compared to the treatment result in the coordinates of $\log k_{T_2}$ and $\log k_{T_1}$. This may be related to the different initial data sets used. The different obtained $\log A_o$ values were associated with some changes in the $\Delta H_R^{\neq}$. and $\Delta\Delta H_R^{\neq}$. values as well. However the reliability of description remains identical. One can see this from the data in Table 7. There are the results of the treatment of D_{ij} values according to equations (4) and (5). D_{ij} values were calculated according to equation (3) assuming for the $\log A_o$ values 14.64[1], 14.1 and 13.0. One can see that at similar numbers of accounted points and reactions the values of the standard deviation for the different $\log A_o$ values are practically identical.

So one can confirm the conclusion that the variation of log A values can not be described within the framework of the isokinetic model. The validity of the isoentropic and isokinetic models must be considered as purely formal which indicates to significant uncertainties in the kinetic parameters of the gas phase homolysis.

Table 1

Results of the Data Treatment According to Equation (4)

NE - the number of independent equations

NRN - the number of different reactions (combinations of R_i and R_j)

s - standard deviation, kcal/mol

Versions:

1) $D_{ij} = E_{ij}$

2) $D_{ij} = E_{ij} - RT$ at T_{mean}

3) $D_{ij} = E_{ij} - RT$ at T_{min}, T_{mean}, and T_{max}

4) The activation energies calculated in the coordinates of the Arrhenius equation are used for the reactions which have the parallel literature data of log A_{ij} and E_{ij}. For others $D_{ij} = E_{ij}$

5) $D_{ij} = E_{ij} - RT$ where E_{ij} are analogous to the version 4) at T_{min}, T_{mean} and T_{max}

The data for the final set after the exclusion of significantly deviating points are listed. The number of independent equations used for the calculation of the present value is given in the parenthesis after the $\Delta H_R^{\neq}$. values and their standard deviations. In parenthesis after the NE, NRN and s values the respective characteristics are indicated for the initial set before the exclusion of significantly deviating points.

R·	$\Delta H_R^{\neq}$·, kcal/mol for the versions				
	1)	2)	3)	4)	5)
1	2	3	4	5	6
Cl	21.0±1.6(I)	20.1±1.4(I)	20.4±0.6(3)	20.6±2.6(I)	19.4±1.4(3)

Table 1 continued

1	2	3	4	5	6
Br	24.0±0.9(4)	23.5±0.8(4)	23.4±0.4(7)	24.0±1.4(4)	23.5±0.7(12)
I	25.5±0.6(7)	24.9±0.6(7)	24.4±0.3(18)	26.5±1.1(5)	24.8±0.6(14)
NH_2	39.8±0.4(3)	38.6±0.4(3)	38.8±0.2(7)	48.3±0.8(2)	47.3±0.4(5)
NO_2	8.4±0.4(9)	8.6±0.4(6)	8.6±0.2(17)	8.7±0.6(7)	7.0±0.4(16)
SH	14.0±0.8(4)	13.3±0.7(4)	12.8±0.3(12)	14.5±1.2(4)	13.9±0.6(12)
OCH_3	4.9±0.4(6)	4.4±0.3(6)	4.7±0.1(15)	2.2±0.7(3)	1.3±0.5(4)
OC_2H_5	-3.9±0.3(11)	-4.4±0.2(11)	-4.4±0.1(33)	-4.4±0.5(6)	-5.1±0.3(18)
CH_3	35.0±0.2(29)	34.1±0.2(25)	34.3±0.1(61)	33.6±0.7(9)	32.5±0.4(20)
C_2H_5	27.2±0.5(10)	26.1±0.4(10)	26.2±0.2(30)	26.8±0.7(8)	25.7±0.4(24)
$CH(CH_3)_2$	21.1±0.5(9)	20.8±0.4(7)	20.6±0.2(21)	20.8±0.8(6)	19.9±0.4(16)
$C(CH_3)_3$	13.9±0.5(8)	13.1±0.4(7)	12.8±0.2(18)	14.6±0.9(4)	13.0±0.5(10)
$CH_2CH = CH_2$	41.2±0.5(7)	40.2±0.5(7)	39.9±0.2(18)	41.6±1.4(4)	41.0±0.8(12)
$CH_2C_6H_5$	50.8±0.6(10)	49.6±0.5(10)	50.6±0.3(19)	50.7±0.9(9)	49.4±0.5(25)
NE	75(100)	69(100)	180(300)	44(51)	115(135)
NRN	35(35)	34(35)	32(35)	31(35)	32(35)
s	1.52(3.74)	1.34(3.76)	0.93(3.58)	2.17(7.66)	1.99(7.25)

Table 2.

Results of the Data Treatment in the Coordinates of Equation (5).

Variants:

1) $D_{ij} = E_{ij}$

2) $D_{ij} = E_{ij}$, for reactions represented by parallel literature log A_{ij} and E_{ij} data the E_{ij} values calculated by the averaging procedure according to the Arrhenius equation[2] were used

3) $D_{ij} = E_{ij} - RT$, E_{ij} are analogous to the variant 2) at T_{max}, T_{min} and T_{mean}.

The symbols are same as in Table 1

R·	$\Delta\Delta H^{\neq}_{R\cdot}$, kcal/mol for variants		
	1)	2)	3)
Cl	48.2±1.6(2)	53.2±1.8(1)	47.0±1.2(4)
Br	31.0±1.6(2)	30.3±1.4(2)	30.1±1.0(6)
I	18.2±1.2(4)	21.4±1.1(3)	19.8±0.8(10)
NH_2	44.4±1.7(2)	45.5±1.8(1)	44.2±1.3(3)
NO_2	29.4±0.9(6)	31.0±1.0(3)	30.1±0.7(9)
SH	32.7±1.3(3)	33.7±1.0(3)	32.9±0.7(9)
OCH_3	53.8±1.6(2)	36.0±1.7(1)	35.3±1.3(3)
OC_2H_5	54.8±2.3(1)	55.5±1.7(1)	55.1±1.3(3)
CH_3	50.6±0.3(37)	48.9±0.6(8)	48.0±0.4(21)
C_2H_5	43.9±0.8(9)	43.1±0.6(6)	41.8±0.5(21)
$CH(CH_3)_2$	41.6±0.7(8)	41.6±0.6(5)	40.4±0.5(13)
$C(CH_3)_3$	38.3±0.6(9)	37.4±0.7(3)	36.5±0.5(9)
$CH_2CH{=}CH_2$	32.6±0.8(6)	34.5±1.2(3)	32.5±0.8(11)
$CH_2C_6H_5$	34.6±0.8(11)	34.2±0.7(8)	33.4±0.6(21)
NE	60(77)	27(33)	80(95)
NRN	30(31)	27(31)	28(31)
s	2.17(4.24)	1.63(10.29)	2.04(8.63)

Table 3

Results of the Data Treatment According to Equations (13) and (15) at T_{mean}

Variants:

1) NLLS treatment according to eq.(13) for 13 radicals

2) After the NLLS treatment according to eq.(13) in the variant 1) 1/β was equalled to zero and excluded from the unknown coefficients. Transition to eq. (15) was so achieved.

3)NLLS treatment according to eq. (13) for 10 radicals

4) Analogous to the variant 2) for 10 radicals

The symbols are the same as in Table 1

R·	$\Delta H^{\neq}_{R\cdot}$, kcal/mol for variants			
	1)	2)	3)	4)
Br	28.1±1.5	27.5±1.2	28.8±1.0	29.4±1.0
I	28.5±1.1	29.6±0.9	29.6±0.8	30.2±0.6
NH_2	45.9±1.2	43.3±0.9	-	-
NO_2	6.4±0.8	7.2±0.6	6.5±0.5	6.8±0.4
SH	20.3±1.6	19.3±1.2	-	-
OCH_3	3.7±0.7	3.9±0.6	-	-
OC_2H_5	-3.2±0.8	-2.8±0.7	-3.0±0.3	-2.9±0.3
CH_3	33.2±1.1	31.0±0.5	32.7±0.8	31.0±0.4
C_2H_5	24.9±1.1	23.3±0.7	24.5±0.9	23.1±0.6
$CH(CH_3)_2$	17.1±1.0	15.9±0.7	16.9±0.8	15.8±0.6
$C(CH_3)_3$	10.3±1.0	9.1±0.7	10.5±0.8	9.4±0.5
$CH_2CH{=}CH_2$	41.7±1.0	41.2±0.7	40.0±0.9	39.2±0.8
$CH_2C_6H_5$	50.2±1.0	50.2±0.9	51.1±0.8	50.7±0.7
1/β	0.00013±0.00004	-	0.00009±0.00003	-
β	7494±2532	-	(10821)	-
∝	12.73±0.44	14.11±0.19	13.34±0.38	14.13±0.16
NE	67(74)	64(67)	78(90)	77(78)
NRN	33(35)	33(33)	25(28)	25(25)
s	2.07(2.88)	1.87(2.20)	1.62(2.63)	1.57(1.64)

Table 4

Results of the Data Treatment According to Equation (15) by MLRA Program at T_{mean}

Variants:

1) 14 the most represented radicals taking into account both the schemes expressed by equations (15) and (16)

2) 14 the most represented radicals taking into account only equation (15)

R·	ΔH_R°·, kcal/mol for variants	
	1)	2)
Cl	27.1±1.7(1)	-
Br	29.7±1.0(3)	28.7±0.9(3)
I	30.1±0.6(9)	31.0±0.6(11)
NH_2	43.4±0.6(3)	-
NO	-	20.6±0.5(11)
NO_2	6.8±0.4(14)	6.7±0.3(17)
SH	18.9±0.8(4)	-
OCH_3	3.5±0.4(5)	3.5±0.3(8)
OC_2H_5	-2.7±0.3(12)	-3.0±0.3(19)
$HgCH_3$	-	49.4±0.4(13)
CH_3	31.2±0.4(39)	30.4±0.3(49)
C_2H_5	23.2±0.5(12)	21.6±0.5(10)
$CH(CH_3)_2$	16.1±0.6(7)	14.2±0.7(6)
$C(CH_3)_3$	9.3±0.5(11)	8.8±0.5(10)
$CH_2CH=CH_2$	39.1±0.7(7)	39.3±0.7(5)
$CH_2C_6H_5$	50.3±0.6(13)	50.5±0.6(11)
C_6H_5	-	71.9±0.7(6)
$\alpha = \log A_o$	14.13±0.15(88)	13.92±0.13(104)
NE	88(107)	104(130)
NRN	32(36)	29(37)
s	1.52(2.61)	1.30(2.40)

Table 5

Results of the Data Treatment in the Coordinates of Equations (14) and (16) at T_{mean}

Variants 1) and 2) are analogous to those in Table 3. $\sigma^*_{NO_2}$ = 3.55 is assumed

Variant 3) corresponds to the variant 2), except $\sigma^*_{NO_2}$ = 4.5 and MLRA program is used.

R·	$\Delta\Delta H^{\neq}_{R\cdot}$, kcal/mol for variants		
	1)	2)	3)
Cl	51.2±1.5	49.0±1.3	48.9±1.2(2)
Br	37.1±1.2	36.8±1.2	36.6±1.2(2)
I	23.5±0.9	24.8±0.9	24.5±0.8(5)
NH_2	53.5±1.4	51.0±1.2	51.3±1.1(3)
NO_2	26.3±0.9	27.8±0.7	28.1±0.6(8)
SH	39.1±1.1	38.0±1.0	38.0±1.0(3)
OCH_3	51.7±1.3	50.5±1.2	50.5±1.1(2)
OC_2H_5	-	-	60.0±1.6(1)
CH_3	49.1±0.8	46.7±0.4	46.8±0.4(37)
C_2H_5	41.7±0.8	39.8±0.6	39.9±0.5(10)
$CH(CH_3)_2$	37.7±0.8	36.1±0.7	36.4±0.6(6)
$C(CH_3)_3$	36.2±0.8	34.4±0.6	35.1±0.6(8)
$CH_2CH{=}CH_2$	31.0±0.7	30.4±0.6	30.4±0.6(8)
$CH_2C_6H_5$	34.6±0.8	33.5±0.7	33.2±0.6(15)
1/β	0.00015±0.00004	-	
β	6756±1873	-	
α	12.54±0.44	13.98±0.17	14.01±0.16(64)
NE	61(74)	61	64(78)
NRN	29(32)	29	29(32)
s	1.43(2.65)	1.59	1.52(2.73)

Table 6

Results of the Data Treatment in the Coordinates of Equations (15) and (16) using T_{min}, T_{max} and T_{mean}

Variants:

1) Eq. (15) at T_{mean}

2) The same at T_{min}, T_{max} and T_{mean}

3) Eq. (16) at T_{min}, T_{max} and T_{mean} assuming $\vec{\sigma}_{NO_2} = 4.5$

R·	$\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$, kcal/mol for variants		
	1)	2)	3)
Cl	26.6±1.1(1)	-	49.2±0.3(6)
Br	29.5±0.7(3)	29.3±0.3(9)	37.1±0.3(6)
I	28.1±0.5(7)	27.8±0.3(19)	24.0±0.2(15)
NH_2	42.7±0.4(3)	42.2±0.2(8)	51.9±0.3(9)
NO_2	7.0±0.3(8)	6.9±0.1(26)	27.4±0.2(17)
SH	18.2±0.6(4)	18.0±0.3(12)	37.7±0.3(9)
OCH_3	3.2±0.3(5)	3.1±0.1(14)	51.5±0.5(3)
OC_2H_5	-2.9±0.2(11)	-3.0±0.1(33)	59.2±0.5(3)
CH_3	31.0±0.3(26)	30.7±0.2(69)	47.0±0.1(75)
C_2H_5	24.0±0.4(10)	23.7±0.2(29)	39.9±0.2(20)
$CH(CH_3)_2$	16.1±0.4(5)	15.8±0.2(10)	35.8±0.2(8)
$C(CH_3)_3$	8.5±0.4(8)	8.2±0.2(16)	34.9±0.2(16)
$CH_2CH{=}CH_2$	38.7±0.5(7)	38.6±0.2(18)	29.5±0.2(21)
$CH_2C_6H_5$	49.4±0.5(11)	49.2±0.2(33)	31.8±0.2(30)
$\alpha = \log A_o$	13.90±0.11(69)	13.79±0.05(190)	13.83±0.05(137)
NE	69(100)	190(297)	137(210)
NRN	29(35)	29(34)	27(31)
s	1.01(2.53)	0.85(2.46)	0.76(2.49)

Table 7

Results of the Data Treatment According to Equations (4) and (5). D_{ij} values are calculated at different log A_o values according to equation (3)

Equation	log A_o	The number of points	The number of reactions	Standard deviation in kcal/mol
(4)	14.64	134	41	2.55
		125	39	1.92
		118	37	1.59
	14.10	134	41	2.40
		125	39	1.84
		120	37	1.64
	13.0	134	41	2.53
		122	38	1,90
(5) $\sigma^{*}_{NO_2} = 4.5$	14.64	82	36	2.91
		74	35	1.91
		68	34	1.49
	14.10	82	36	2.70
		74	35	1.85
		68	33	1.50

The estimation of the formation enthalpies for substituted methyl free radicals taking into account substituent effects within the isoentropic and isokinetic models will be discussed in the following paper of this series.

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C O N T E N T S

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