

ISSN 0375-9520



TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

Vol. XXII

ISSUE 1(77)

March 1985

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

Vol. XXII
ISSUE 1(77)
March 1985

TARTU

The Editorial Board:

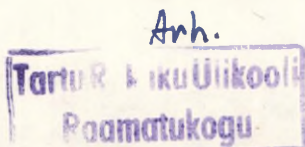
V. Palm, Editor-in-Chief

A. Talvik

I. Koppel

Title of original:

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том XXII. Вып. I (73). Март 1985.
Тартуский государственный университет.



8530

AB INITIO SCF LCAO MO CALCULATIONS OF MOLECULES.
IV. PROTON AFFINITIES. COMPARISON WITH EXPERIMENT

I.A. Koppel, U.H. Milder, and V.A. Palm
Laboratory of Chemical Kinetics and Catalysis and
Department of Geophysics, Tartu State University,
202400 Tartu, USSR.

Received December 17, 1984

Ab initio SCF LCAO MO calculations of proton affinities (PA) of approximately 50 neutral and anionic bases were performed using the Gaussian 80/82 system of programs. The geometries of neutral molecules and molecular ions were fully optimized using the method of gradients. An extensive comparison of the results from literature and authors' calculations (STO-3G, 3-21G, 4-31G, 6-31G⁺, 3-21+G, 4-31+G) with the experimental PA values was made. For the comparison with the results of the single determinant Hartree-Fock calculations the correlation of the experimental PA values with those calculated in the framework of Møller-Plesset perturbation theory was performed.

On the basis of statistical least squares analysis it was shown that for all basis sets the rather general linear relationships $PA_{exp} = a + bPA_{calc}$ (a and b are characteristic for the given basis set and could also depend on the nature of the class of compounds) hold between the experimental and calculated PA values. As a rule, in the least favorable cases the standard deviations from these linearities do not exceed 9 kcal/mol. It was shown

that the latter quantities as well as the standard deviations (STDV) of the calculated proton affinities from the experimental PA values depend significantly on the nature of the basis set. Both quantities are at the lowest level for the most sophisticated basis sets. The above-mentioned correlation equations were used for predictions of the experimental PA values of compounds which are unstable or experimentally hard to handle.

In the first paper¹ of this Series the statistical analysis of the use of the single-determinant nonempirical LCAO MO approach (STO-3G and 4-31G basis sets, Gaussian-70 system of programs²) for the prediction of proton affinities PA of various neutral (B) and anionic (A^-) bases was performed. Based on rather limited and unhomogeneous results of theoretical as well as experimental determination of PA values the approximate linear relationship between experimental and calculated proton affinities was found to hold with an average standard deviation in the range of 10 kcal/mol. At the same time one has to keep in mind that due to the lack the optimization of the geometries of some species (e.g., RO^- , $R_1R_2COH^+$; etc) the calculated PA values^{3,4} themselves are characterized by the errors of the same order. Also, rather significant uncertainty characterizes some of the used experimental PA values. During the last 4-5 years some significant positive shifts⁵⁻⁸ in the use and further improvement of the nonempirical quantum chemical methods of calculation of fundamental properties of molecules have taken place.

Alongside with the development and spread of the economical and rather powerful gradient methods of the optimization of the geometry of molecules for the present time a large number of new, more correct results of nonempirical calculations (particularly those of proton affinities) were performed.

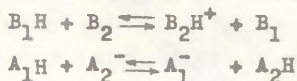
By far the largest number of ab initio calculations with the full optimization of the geometry by the method of gradients were performed using the Gaussian 80⁸⁻¹⁰ system of programs developed by J.A.Pople et al. at Carnegie-Mellon Uni-

versity, PA.

Rather fruitful is also the use of Gaussian 82/83 system designed by W.J. Hehre et al.¹¹ at the University of California, Irvine (CA), the use of the significantly modified and improved by P.v.R. Schleyer¹²⁻¹⁴ Gaussian 76 system at University of Erlangen (FRG), and the use of the Monster-gauss program (Poirot and Petersen¹⁵) at the University of Toronto. Also, rather significant progress took place in the field of the further accumulation and refinement of the experimental values of proton affinities of neutral as well as anionic bases.¹⁶⁻²³

All these circumstances, evidently, call for a new, more contemporary and sufficiently strict quantitative comparison of the results of the theoretical calculation of PA on one hand, and the results of the experimental measurement of PA, on the other.

One has to remember^{8,24} that the close enough correlation between proton affinities calculated in the single-determinant approximation (on the condition of the sufficiently long and flexible basis set) and experimental PA values corrected for contribution arising from the zero-point vibrations is expected only in the case of the compensation of the contributions of the correlational and relativistic effects for the protonated and deprotonated forms of bases. Theoretical considerations and practical experience predict that the probability of the observance of these restrictions, particularly that concerning the cancellation of the contributions from the correlation energy, is the highest for the so called isodesmic reactions which include also the proton transfer reactions:



On the other hand, there is also some evidence that in the case of the proton transfer reactions, at least for the different classes of bases (protonization centers), the difference between the zero-point energies (ZPE) of protonated and deprotonated forms of bases is also relatively constant

and does not depend significantly on the substituent. On one hand, in the present work the quantitative comparison of the calculated (PA_{calc}) and experimental (PA_{exp}) proton affinities was performed calculating for the different classes of compounds (for the fixed basis sets) the standard deviations STDV

$$STDV = \sqrt{\sum_{i=1}^n (PA_{exp(i)} - PA_{calc(i)})^2 / (n-1)}, \quad (1)$$

where subscript i refers to the i -th compound of the given series consisting of n bases

of the experimentally determined PA_{exp} values from the corresponding theoretical quantities PA_{calc} .

On the other hand, the comparison of these two quantities was also performed using the method of least squares in terms of the following linear equation:

$$PA_{exp} = a + b PA_{calc}, \quad (2)$$

where a and b are constants.

It is evident that in the general case the standard deviations s from the linearities of the latter type are not identical to the quantities STDV which characterize the correspondence between theory and experiment in the most explicit way. As a rule, Hartree-Fock single-determinant PA_{calc} values from literature sources as well as those calculated in the present work⁸ using the Gaussian 80^{9,10}, Gaussian 82/83¹¹, Gaussian 70² systems of programs were compared with the experimental proton affinities (vide infra). Only the standard basis sets (STO-3G, 4-31G, etc) were used. As a

⁸ Quantum chemical calculations were performed on the Harris Slash-6 computer at the Department of Chemistry of the University of California, Irvine (I.A.K.), on EC-1060 computer of the Computer Center of Tartu State University (I.A.K., U.H.M.) and on Amdahl 470 V/6-II computer of the University of British Columbia (I.A.K.).

rule, only the PA_{calc} values gotten with the total optimization of the structures of the deprotonated and protonated forms of bases were used. In that respect the literature values of PA_{calc} for the substituted pyridines²⁵, anilines^{25,26}, phenolate²⁷ and toluate-anions^{28,29} were somewhat exceptional (only partial optimization of some bond lengths, valence and torsional angles was performed).

PA_{calc} values were calculated in the present work from the total energies of the fully optimized structures of the protonated and deprotonated forms. Total energies of the latter are given in Table 1 of the Appendix.

In this work the comparison of PA_{calc} values was performed with the uncorrected for the zero-point energy PA_{exp} values as well as with those corrected for the contribution of the latter type. On the basis of Refs. 7,8,12,24,30-32,54 it was assumed that the correction into the experimental proton affinity values is relatively constant, mainly determined by the chemical nature of the protonization center, and depends on the substituent only rather slightly. Throughout the present work the following (probably, somewhat overestimated) contributions for the ZPE were used in order to convert the experimentally determined PA values into PA values corrected for the zero-point energy term. They were gotten averaging the different quantities given in the above-mentioned references. The following values for various protonization centers were used: sp^3 nitrogen in amines RNH_2 and anions RNH^- - 10 kcal/mol, nitrogen in nitriles and N_2 - 7.5 kcal/mol, sp^3 (ROH, RO^-) and sp^2 (RCHO) oxygen - 8.0 kcal/mol, fluorine (RF and F^-) - 6 kcal/mol, sp - carbon ($RC\equiv CH$) - 4.5 kcal/mol, sp^2 - carbon ($R_1R_2C=CH_2$, benzene, etc) - 6.5 kcal/mol, carbon in carbanions ($R_1R_2R_3C^-$) - 7.5 kcal/mol, phosphorus in phosphines - 7.5 kcal/mol, and in RPH^- - 6 kcal/mol, sulfur in RSH - 8.0 kcal/mol and in HS^- - 7 kcal/mol, silicon in SiH_3^- - 8.5 kcal/mol. Due to the presence of three extra vibrational degrees of freedom in the protonated form of the base these corrections always lead to the increase of the absolute values of PA_{exp} .

The complete set of the initial data for the statistical least squares analysis in terms of Eqns. (1) and (2) is given in Table 1. The experimental PA-s are mostly taken from Refs. 16 - 29, 33 - 40. PA values reported in Refs. 33 and 35 are recalculated to take into account the temperature correction.^{16,22}

Ammonia was assumed to be the reference compound for the absolute proton affinity scale of neutral bases. Quite arbitrarily, its PA was put equal 207.0 kcal/mol.²² For the anionic basis the scale accepted in Refs. 16, 17, 34, 37, 40, 42 was assumed. According to our estimates the average experimental uncertainties of proton affinities for individual bases which make up the proton affinity scale over the almost 350 kcal/mol interval are in the range from 2 to 5 kcal/mol.

In order to study the effect of the possible inhomogeneity of the proton affinity scale due to the lack of the equilibrium measurements of PA in the range of bases from helium to water from one hand, and from the strongest neutral bases (amines, etc.) to the weakest anionic bases, from the other, the separate correlations of PA_{calc} quantities with PA_{exp} values were performed using both the gross scale of PA (i.e., including all 165 PA_{exp} values presented in Table 1) as well as the PA values which were derived from the equilibrium ICR or high pressure mass spectrometry experiments only. Besides that, some other bases (H, H₂, H⁻, etc.) whose PA_{exp} values are believed to be reliably determined on the basis of combining the information on the ionization threshold measurements with the other thermochemical data were also included into the latter, "equilibrium" scale of PA_{exp} values (the compounds Nos 1-14, 19-26, 29-31, 37-60, 73-86, 88-119, 121-165 from Table 1).

It turned out that the separate statistical analysis of these two scales of PA_{exp} values in terms of Eqns. (1) and (2) did not lead to drastically different results. Therefore,

One has to remember that this quantity has been the object of still continuing discussions. Mostly the values between 202 and 208 kcal/mol are given (see Refs. 22, 23, 33, 35, 36, 38, 39).

Table 1

Experimental (PA_{exp}) and Calculated (PA_{calc}) for Different Basis Sets
Proton Affinities (in kcal/mol) of Some Neutral and Anionic Bases.^a

PA _{exp}			PA _{calc}						
Compound		STO-3G	3-21G	4-31G	6-31G ⁺	3-21+G	4-31+G	MP4/6-31G ⁺⁺	
1	2	3	4	5	6	7	8	9	10
1. NH ₃	207	259.6 ¹⁰	227.10	221.9 ⁴³	217.4 ¹⁰	-	-	221	
2. MeNH ₂	216.6	268.5 ¹⁰	236 ⁷	230.4 ⁴⁴	228.3 ¹⁰	-	-	231	
3. EtNH ₂	219.5	272.5 ⁴⁵	239 ⁷	232.9 ⁴⁴	-	-	-	-	
4. i-PrNH ₂	222.2	275.2 ⁴⁵	-	236.6 ⁴⁵	-	-	-	-	
5. t-BuNH ₂	224.6	277.6 ⁴⁵	-	-	-	-	-	-	
6. Me ₃ N	228.2	280.0 ⁷	246 ⁷	239.7 ⁴⁴	-	-	-	-	
7. Me ₂ NH	223.7	275.0 ⁷	242 ⁷	236.1 ⁴⁴	-	-	-	-	
8. H ₂ NNH ₂	210.1	257.9 ^{43,46}	226.1 ¹⁰	221.3 ⁴⁶	219.1 ¹⁰	-	-	-	
9. PhNH ₂	213.7	267.6 ^{26,46}	-	-	-	-	-	-	
10. Py	223.9	277.9 ²⁶	-	238.5 ⁴⁷	-	-	-	-	
11. 1,2-diazine	219.4	263.8 ⁴⁷	-	231.4 ⁴⁷	-	-	-	-	
12. 1,3-diazine	213.8	264.5 ⁴⁷	-	228.9 ⁴⁷	-	-	-	-	
13. 1,4-diazine	211.5	256.0 ⁴⁷	-	220.6 ⁴⁷	-	-	-	-	
14. Borazine	196.4	249.0 ⁴⁷	-	203.4 ⁴⁷	-	-	-	-	

Table 1 continued

1	2	3	4	5	6	7	8	9	10
15.	N≡N	124.6	141.3 ⁴⁸	126.0 ⁷	118.6 ⁴³	118 ⁷	-	-	125
16.	NH ₂	186.3	230.7 ⁴³	-	204.4 ⁴³	-	-	-	-
17.	NH	141.3	179.9 ⁴³	-	157.4 ⁴³	-	-	-	-
18.	N	96.9	100.5 ⁴³	-	78.6 ⁴³	-	-	-	-
19.	HCN	177.4	201.6 ¹	179.0 ¹	180.8 ⁴⁹	178.1 ¹⁰	-	-	179
20.	CF ₃ CN	171.1	205.0 ⁴⁶	-	-	-	-	-	-
21.	MeCN	190.7	221.6 ⁴⁶	196.0 ¹⁰	197.5 ⁴⁹	-	-	-	-
22.	CNCN	169.8	188.9 ¹	-	-	-	-	-	-
23.	H ₂ O	172.9	228.7 ⁴³	192.0 ¹⁰	181.8 ⁴⁹	174.8 ¹⁰	-	-	181
24.	MeOH	185.6	238.5 ⁴⁵	205.2 ¹⁰	197.1 ⁴³	190.6 ¹⁰	-	-	194
25.	t-BuOH	198.8	250.8 ⁴⁵	-	-	-	-	-	-
26.	i-PrOH	196.4	247.2 ⁴⁵	-	196.8 ⁴⁵	-	-	-	-
27.	LiOH	240.7	287.6 ¹⁰	284.5 ¹⁰	-	254.8 ¹⁰	-	-	-
28.	NaOH	247.6	378.6 ^{10,50}	-	-	-	-	-	-
29.	Me ₂ O	194.1	239.7 ⁵¹	-	203.0 ⁴⁹	-	-	-	-
30.	PhOMe	203.9	243.5 ⁵²	-	-	-	-	-	-
31.	OH	139	191.3 ⁴³	-	140 ⁴³	-	-	-	-
32.	O	113	153.5 ⁴³	-	104 ⁴³	-	-	-	-
33.	NO	127	164.0 ⁴³	-	-	-	-	-	-
34.	O ₂	101	161.4 ¹⁰	126.0 ¹⁰	100.0 ⁴³	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
35.	Me ₃ NO	238	342.5 ⁴⁶	-	-	-	-	-	-
36.	CO ₂	127	191.6 ^{46,53}	137.0 ¹⁰	131.6 ⁵³	-	-	-	-
37.	H ₂ CO	177.5	221.3 ⁴³	183.4 ¹⁰	177.9 ⁴⁹	-	-	-	-
38.	MeCHO	188.5	236.7 ⁵⁴	-	191.2 ⁵⁴	194.6 ¹⁰	-	-	-
39.	Me ₂ CO	198.6	248.9 ⁴⁶	-	198.8 ⁵⁵	-	-	-	-
40.	(Δ) ₂ CO	213.7	264.0 ⁴⁶	-	-	-	-	-	-
41.	CF ₃ COH	170	218.0 ⁴⁶	-	-	-	-	-	-
42.	F ₂ CO	166.1	214.9 ⁴⁶	-	-	-	-	-	-
43.	(CF ₃) ₂ CO	166.7	211.3 ⁴⁶	-	-	-	-	-	-
44.	HCOOH	183.3	239.0 ⁵⁴	-	185.1 ⁵⁴	187.7 ⁵⁴	-	-	-
45.	HCONH ₂	202.6	263.2 ⁵⁴	-	211.4 ⁵⁴	-	-	-	-
46.	MeCOOH	191.8	255.5 ⁵⁹	-	-	-	-	-	-
47.	C ₆ H ₆	184.8	227.8 ⁵⁷	190 ⁷	187.9 ⁵⁸	-	-	-	-
48.	PhMe	192.6	235.6 ⁵⁷	-	-	-	-	-	-
49.	PhEt	193.5	237.0 ⁵⁷	-	-	-	-	-	-
50.	PhBu	194.8	238.3 ⁵⁷	-	-	-	-	-	-
51.	i-PrPh	194.8	237.9 ⁵⁷	-	-	-	-	-	-
52.	t-BuPh	195.0	238.7 ⁵⁷	-	-	-	-	-	-
53.	PhPr	194.4	237.9 ⁵⁷	-	-	-	-	-	-
54.	PhF	187.5	231.5 ⁵²	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
55.	CH_4	128.2	120.5 ¹⁰	115 ¹⁰	-	121.3 ¹⁰	-	-	-
56.	C_2H_6	140	150 ⁷	143 ⁷	-	142 ⁷	-	-	-
57.	C_2H_4	169	209.7 ⁴³	163 ¹⁰	171.4 ⁴³	175.4 ¹⁰	-	-	173
58.	$\text{FCH}=\text{CH}_2$	168	230.1 ⁵⁹	-	170.8 ⁵⁹	-	-	-	-
59.	$\text{MeCH}=\text{CH}_2$	184.3	230.6 ⁴⁶	-	192.5 ⁶⁰	-	-	-	-
60.	$\text{Me}_2\text{C}=\text{CH}_2$	197.0	246.4 ⁴⁶	-	206.6 ⁶¹	-	-	-	-
61.	$\text{HC}\equiv\text{CH}$	152	193.7 ⁴⁵	163.0 ¹⁰	167.9 ⁴³	-	-	-	163
62.	CO	140	175.6 ⁴³	143 ¹⁰	-	143 ¹⁰	-	-	151
63.	MeCl	162	167.7 ⁶²	-	145.8 ⁶²	-	-	-	-
64.	EtCl	172	177.1 ⁶²	-	-	-	-	-	-
65.	MeF	153	197.2 ⁵⁹	160.0 ¹⁰	153.6 ⁵⁹	-	-	-	-
66.	EtF	164	206.0 ⁵⁹	-	165.0 ⁵⁹	-	-	-	-
67.	HCl	141	141.1 ⁶²	113 ⁷	118.0 ⁶²	130 ⁷	-	-	-
68.	HF	114	182.8 ¹⁰	132 ⁷	118.3 ⁴³	122.3 ¹⁰	-	-	131
69.	CH_3	130.2	136.1 ⁴³	-	119.0 ⁴³	-	-	-	-
70.	CH_2	204.5	215.4 ⁴³	-	189.8 ⁴³	-	-	-	-
71.	CH	175.3	218.8 ⁴³	-	188.8 ⁴³	-	-	-	-
72.	C	137	142.9 ⁴³	-	125.4 ⁴³	-	-	-	-
73.	H	70	68.7 ¹⁰	-	53.2 ⁴³	-	-	-	-
74.	H_2	101.0	81.2 ¹⁰	92.3 ¹⁰	92.4 ⁴⁹	92.6 ¹⁰	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
75.	PH_3	191.1	244 ⁷	184 ⁷	187.2 ⁶³	197 ⁷	-	-	-
76.	MePH_2	206.5	255 ³¹	-	201.2 ⁶⁴	-	-	-	-
77.	Me_2PH	219.5	261.4 ⁶³	-	-	-	-	-	-
78.	PhPH_2	210.8	259.4 ⁶⁴	-	206.8 ⁶³	-	-	-	-
79.	H_2S	176.7	223.0 ⁷	-	160.5 ⁶³	-	-	-	-
80.	MeSH	189.6	228.0 ³¹	-	-	-	-	-	-
81.	H^-	400.4	601.9 ¹⁰	453.4 ¹⁴	442.0 ¹²	442.2 ¹⁰	400.3 ¹⁴	401.8 ¹²	404.8
82.	F^-	371.3	602.1 ¹⁰	431.8 ¹⁴	401.3 ¹⁴	409.2 ⁴⁶	359.2 ¹⁴	361.9 ¹²	351.3
83.	Cl^-	333.3	411.5 ⁴⁶	324 ⁷	337.0 ⁴⁶	335.2 ⁴⁶	325.0 ⁷	-	-
84.	I^-	314.3	407.4 ⁴⁶	-	-	-	-	- ¹²	-
85.	NH_2^-	403.6	547.0 ¹²	462 ¹⁴	448.6 ¹²	444.7 ¹²	417.9 ¹⁴	421.2	408.7
86.	FNH^-	361.9	513.3 ⁴⁶	-	400.3	-	-	-	-
87.	PH_2^-	370.4	525 ⁷	372 ⁷	393.0 ⁷	383.4 ¹⁰	372 ⁷	-	-
88.	HS^-	353.4	506 ⁷	349.0 ⁷	364.0 ⁴⁶	360 ⁷	350 ⁷	-	-
89.	CH_2NH^-	403.2	529.0 ¹²	-	440.3 ¹²	-	419.6 ¹⁴	422.6 ¹²	410.7
90.	CH_3^-	416.6	559.8 ¹²	462.8 ¹⁴	463.1 ¹²	457.3 ¹²	431.7 ¹⁴	433.5 ¹²	425.2
91.	$\text{HO}\equiv\text{C}^-$	375.4	496.4 ¹²	405.0 ¹⁴	408.3 ¹²	403.0 ⁷	381.9 ¹⁴	385.6 ¹²	383.1
92.	$\text{CH}_3\text{C}\equiv\text{C}^-$	379.6	499.9 ¹²	-	414.1 ¹²	-	-	393.2 ¹²	-
93.	CNCH_2^-	372.2	496.8 ⁶⁵	-	402.0 ¹²	402.4 ⁶⁶	384.1 ¹⁴	386.1 ¹²	383.4
94.	$\text{CH}_2=\text{CHCH}_2^-$	391	515.8 ¹²	-	425.7 ⁶⁶	425.6 ⁶⁶	-	405.5 ¹²	399.1

Table 1 continued

1	2	3	4	5	6	7	8	9	10
95.	$\text{CF}_3\text{C}\equiv\text{C}^-$	356.0	466.0 ⁴⁶	-	369.4 ⁴⁶	-	-	-	-
96.	$(\text{CN})_2\text{CH}^-$	337.2	441.2 ⁶⁵	-	355.8 ⁶⁵	-	-	-	-
97.	CN^-	353.1	462.8 ¹²	379.1 ¹⁴	374.2 ¹²	370.0 ¹⁰	354.1 ¹⁴	354.2 ¹²	353.7
98.	PhCH_2^-	379.0	504.4 ²⁸	-	419.6 ⁶⁵	-	-	-	-
99.	CF_3^-	375.6	491.8 ⁶⁵	399.0 ¹⁰	396.8 ⁶⁵	-	-	-	-
100.	NO_2CH_2^-	358.7	475.4 ⁶⁵	362.8 ¹⁴	361.1 ¹²	381.5 ⁶⁵	342.3 ¹⁴	350.5 ¹²	-
101.	CH_2CHO^-	366.4	503.0 ¹²	-	391.6 ¹²	396.9 ⁶⁶	371.6 ¹⁴	374.5 ¹²	369.2
102.	CF_3CH_2^-	386.0	507.5 ⁴⁶	403.8 ⁷	406.3 ⁶⁶	420.4 ⁷	385.7 ⁶⁷	-	-
103.	SiH_3^-	371.5	510.0 ⁷	378 ⁷	-	388 ⁷	383 ⁷	-	-
104.	HCOO^-	347.6	478.1 ⁴⁶	-	359.9 ¹²	-	344.4 ¹⁴	346.9 ¹²	337.3
105.	AcO^-	350.9	478.2 ⁴⁶	-	-	-	349.5 ¹⁴	-	-
106.	CF_3COO^-	325.7	451.0 ⁴⁶	-	-	-	-	-	-
107.	HO^-	390.8	565.3 ¹⁰	450.1 ¹⁴	426.0 ¹²	429.5 ¹⁰	391.3 ¹⁴	394.6 ¹²	381.1
108.	HOO^-	367.9	520.0 ⁴⁶	-	386.7 ⁴⁹	-	365.6 ¹⁴	-	-
109.	MeO^-	379.2	529.0 ⁴⁶	-	409.8 ¹²	-	390.7 ¹⁴	393.1 ¹²	381.4
110.	EtO^-	376.1	526.4 ⁴⁶	-	410.5 ¹⁴	-	389.2 ¹⁴	391.7 ¹²	378.7
111.	PhCH_2O^-	369.6	513.0 ⁴⁶	-	-	-	-	-	-
112.	$i\text{-PrO}^-$	374.1	522.2 ⁴⁶	-	-	-	-	-	-
113.	$t\text{-BuO}^-$	373.3	519.4 ⁴⁶	-	-	-	-	-	-
114.	$\text{CF}_3\text{CH}_2\text{O}^-$	364.4	500.0 ⁴⁶	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
115.	$(\text{CF}_3)_2\text{CHO}^-$	347.9	479.9 ⁴⁶	-	-	-	-	-	-
116.	$(\text{CF}_3)_3\text{CO}^-$	334.3	447.9 ⁴⁶	-	-	-	-	-	-
117.	NO_3^-	324.6	432.8 ⁴⁶	-	321.2 ⁴⁶	-	307.4 ¹⁴	-	-
118.	ONO^-	338.3	471.3 ⁴⁶	-	352.4 ⁴⁶	-	333.0 ¹⁴	-	-
119.	PhO^-	351.4	465.0 ⁷	-	-	-	-	-	-
120.	ClO_4^- ArO^-	280	398.0 ⁴⁶	-	-	-	-	-	-
121.	4- NO_2	323.6	435.8 ²⁷	-	-	-	-	-	-
122.	3-Me	351.9	465.5 ²⁷	-	-	-	-	-	-
123.	4-Me	353.2	466.0 ²⁷	-	-	-	-	-	-
124.	2- NH_2	347.4	465.0 ²⁷	-	-	-	-	-	-
125.	3- NH_2	352.4	469.9 ²⁷	-	-	-	-	-	-
126.	4- NH_2	355.7	469.9 ²⁷	-	-	-	-	-	-
127.	2-OH	341.0	459.5 ²⁷	-	-	-	-	-	-
128.	3-OH	346.4	462.0 ²⁷	-	-	-	-	-	-
129.	3-OMe	350.0	463.9 ²⁷	-	-	-	-	-	-
130.	4-OMe	351.9	468.0 ²⁷	-	-	-	-	-	-
131.	2-F	347.6	462.6 ²⁷	-	-	-	-	-	-
132.	3- CF_3	334.9	456.6 ²⁷	-	-	-	-	-	-
133.	3-F	345.6	459.6 ²⁷	-	-	-	-	-	-
134.	2- NO_2	337.6	437.4 ²⁷	-	-	-	-	-	-
135.	2-CN	335.3	444.3 ²⁷	-	-	-	-	-	-

Table 1 continued


1	2	3	4	5	6	7	8	9	10
136.	3-CN	337.1	450.5 ²⁷	-	-	-	-	-	-
137.	4-OF ₃ ArOH ₂	332.6	453.5 ²⁷	-	-	-	-	-	-
138.	3-Me	379.2	504.5 ²⁸	-	-	-	-	-	-
139.	4-Me	380.5	505.7 ²⁸	-	-	-	-	-	-
140.	3-NO ₂	362.8	487.1 ²⁸	-	-	-	-	-	-
141.	4-NO ₂	354.5	472.5 ²⁸	-	-	-	-	-	-
142.	3-CF ₃	369.2	496.4 ²⁸	-	-	-	-	-	-
143.	4-CF ₃ 	367.3	492.4 ²⁸	-	-	-	-	-	-
144.	3-Me	226.8	280.4 ²⁵	-	-	-	-	-	-
145.	4-Me	228.1	282.9 ²⁵	-	-	-	-	-	-
146.	4-NH ₂	233	294.0 ²⁵	-	-	-	-	-	-
147.	3-NH ₂	223	281.4 ²⁵	-	-	-	-	-	-
148.	4-OMe	231.1	287.2 ²⁵	-	-	-	-	-	-
149.	3-OMe	226.9	277.6 ²⁵	-	-	-	-	-	-
150.	4-CF ₃	207.4	271.1 ²⁵	-	-	-	-	-	-
151.	3-CF ₃	207.1	271.1 ²⁵	-	-	-	-	-	-
152.	4-CN	212.7	266.5 ²⁵	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
153.	3-ON	211.9	265.5 ²⁵	-	-	-	-	-	-
154.	4-F	219.8	277.7 ²⁵	-	-	-	-	-	-
155.	3-F	216.9	271.6 ²⁵	-	-	-	-	-	-
156.	4-NO ₂	211.2	261.2 ²⁵	-	-	-	-	-	-
	ArNH ₂								
157.	3-Me	217.0	268.9 ²⁵	-	-	-	-	-	-
158.	4-Me	216.9	270.1 ²⁵	-	-	-	-	-	-
159.	4-NH ₂	218.9	273.7 ²⁵	-	-	-	-	-	-
160.	3-NH ₂	217.7	271.8 ²⁵	-	-	-	-	-	-
161.	4-CF ₃	206.2	261.7 ²⁵	-	-	-	-	-	-
162.	3-CF ₃	207.6	262.6 ²⁵	-	-	-	-	-	-
163.	4-F	211.4	266.3 ²⁵	-	-	-	-	-	-
164.	3-F	210.3	263.8 ²⁵	-	-	-	-	-	-
165.	3-ON	204.1	258.6 ²⁵	-	-	-	-	-	-

a - PA_{exp} values in column 3 do not include the correction for the zero-point energy. In columns 4-10 the calculated ab initio proton affinities are given for the different basis sets. The abbreviated notations STO-3G, 4-31G etc. are equivalent to STO-3G//STO-3G, 4-31G//4-31G, etc. (i.e. PA values for a given basis set are calculated at geometries fully optimised with the use of the same basis set). Only in column 10 PA_{calo} (Ref.10) MP4/6-31G¹² basis set refer to 6-31G¹² geometries. In the same column PA_{calo} values¹² for anions refer to MP2/4-31+G//4-31G level of calculations.

further in this paper the results of the statistical treatment of the data will be given for the first, more extensive gross PA_{exp} scale, only.

The comparison of the experimental PA -s with PA_{calc} values derived on the basis of post-Hartree-Fock model was performed using PA_{calc} values, calculated^{12,30} in the approximation of Möller-Plesset perturbation theory.

The statistical data processing in terms of Eqns. (1) and (2) was performed on our ND-100 computer using the program written by one of us (V.A.P.).

The results of such an analysis are given in Table 2. For the economy of space only the results for PA_{exp} values corrected for the ZPE contribution are included. It should be mentioned that because of the very tight interdependence (see Table 2, series No 1) between the "natural" experimental PA_{exp} values (Table 1), on one hand, and those corrected for the ZPE contribution, on the other hand, the substitution of the latter quantities for the former ones does not lead to the significant changes of the slope b of the straight lines expressed by Eqn. (2). The only major changes would be the increase by ca 8 kcal/mol of the intercept a and the decrease by approximately the same quantity of the corresponding STDV values.

In the general case, the statistical treatment of data for the different basis sets from Table 1 in terms of Eqns. (1) and (2) was done separately for the various subsets (neutral and anionic bases, N-bases, neutral and anionic O-bases, neutral C-bases and carbanions, etc. - all together 16 subsets), as well as for the united, more general data sets which include data from several (or all) subsets.

Standard deviations s (Eqn. (2)) of series consisting of several subsets were, on one hand, calculated on the basis of assumption about the equal statistical weights of the subsets. On the other hand, the parallel calculations of quantities of this type were also performed taking into account the real differences in the statistical weights of the subsets. In Table 2 these quantities (called s_w) are given in column 7 in parentheses under the unweighted ave-

rated standard deviations s from the regression line.

The exclusion of the significantly deviating points (see column 3 of Table 2) from the data processing in terms of Eqn. (2) was made according to the Student's test (99 per cent level). For the most basis sets, as a rule, Table 2 lists only the results of comparison of experimental and calculated PA values for neutral and anionic bases considering them separately in terms of two different subsets as well as a unified general data set. For the basis sets which are characterized by the sufficiently representative number of calculations of PA values some results of the statistical data treatment in terms of Eqns. (1) and (2) are also given separately for some more elementary subsets.

Some typical relationships between PA_{exp} and PA_{calc} values are shown in Fig. 1-3.

Discussion

The results of the statistical analysis of the relationship between experimental and theoretical proton affinities in terms of Eqns. (1) and (2) could be evaluated from two separate points of view. On one hand, it is evident that the standard deviation STDV which characterizes the statistically averaged differences between the experimental and calculated proton affinity values is the most explicit criterion of the quality of calculations of PA_{calc} values. Understandably, in the case of isomorphism between theory and experiment this quantity should be negligible (in the ideal case $STDV=0$) within the uncertainties of the comparable PA_{exp} and PA_{calc} values.

On the other hand, in addition to that condition, the completely adequate correspondence between the results of quantum chemical calculations and experimentally determined PA values should be also characterized by the zero intercept ($a=0$) and unit slope ($b=1.0$) in terms of Eqn. (2).

Within the framework of the approach based on the use of the latter equation one has to mention that besides the closeness of regression coefficients a and b to the ideal val-

ues, the absolute value of standard deviation s from the regression line and the total range of variation of comparable quantities are also rather significant indicators of the closeness between theory and experiment. One can assume that in the case of "sufficiently" long and flexible basis set, and on condition of making "proper" corrections for correlation energy and ZPE effects the observance of the above -stated conditions should not depend neither on the chemical nature, charge type and multiplicity nor the concrete basis set studied.

One can see from Table 2 (see also Fig. 3) that for the simultaneous correlation of the data for the neutral and anionic bases series No 23 (3-21G basis set for neutral bases and diffuse function-augmented basis set 3-21+G for anions), 25 (4-31G basis set for neutrals and 4-31+G for anionic bases) and 29 (post-Hartree-Fock calculations: MP4/6-31G³ for neutral basis and MP2/4-31+G for anions), at least formally, are not too far from satisfying the ideal conditions $a=0$ and $b=1.0$ for the regression coefficients of Eqn. (2). The same conditions are also met for series No 26 (post-Hartree-Fock MP4/6-31G³ calculations of neutral bases). At the same time in these cases the difference between theory and experiment is characterized by STDV and s values which for the very significant variation of PA_{exp} values (in the case of series No 25 ΔPA_{exp} is 347 kcal/mol) range from 3 to 10 kcal/mol. One can also observe that for the comparable range of PA_{exp} values the more sophisticated basis set leads to less pronounced statistical error limits of the correlations.

It should be, however, mentioned that the separate analysis of PA_{calc} values for neutral and anionic bases calculated, corresponding with the use of "regular" (3-21G, 4-31G) split-valence sets and those augmented with the diffuse and flat s and p functions on first row atoms (3-21+G, 4-31+G) leads for these charge types to the statistically significantly different regression coefficients. So, it is evident from Table 2 (series No 7 and 10 for neutrals, 20 and 23 for anionic bases) and Fig. 3 that the corresponding b values are for anions (3-21+G, 4-31+G) lower and intercepts a higher

Table 2

Results of Statistical Data Treatment of Experimental and Calculated Proton Affinities in Terms of Eqns. (1) and (2) for Different Basis Sets[#]

No	Base	Compounds (see Table 1 for numbers), notes	a	b	r	s	STDV	ΔPA_{max}	n
1	2	3	4	5	6	7	8	9	10
1.	PA_{exp} (ZPE) vs. PA_{exp}	1-165, the comparison of PA_{exp} values correct- ed for zero point energy contribution with natural experimental PA values.	8.2 (0.3)	1.001 (0.002)	0.999	1.3 (1.3)	8.5	347	165
2.	STO-3G	1-27, 29-33, 37-67, 69, 71-80, 144-165; neutral bases; deviating points: HF, NaOH, O ₂ , CO ₂ , Me ₃ NO, CH ₂ .	33.4 (4.1)	0.706 (0.017)	0.973	8.1 (8.1)	38.6	171	96
3.	"	81, 83-119, 121-143; anions; deviating points F ⁻ and ClO ₄ ⁻	107.7 (15.9)	0.536 (0.033)	0.906	9.3 (8.8)	120.0	92	61
4.	"	1-27, 29-31, 33, 37-67, 69, 71-80, 83-165; neu- tral and anionic bases; deviating points: F ⁻ , HF, O ₂ , NaOH, NaOH, H ⁻ , CO ₂ , Me ₃ NO, CH ₂ , O.	40.9 (11.9)	0.647 (0.005)	0.995	8.6 (8.6)	79.5	347	156

Table 2 continued

1	2	3	4	5	6	7	8	9	10
5.	STO-3G	1-22, 144-165; all neutral N-bases (amines, nitriles, etc.)	33.8 (14.0)	0.714 (0.018)	0.988	3.8 (3.7)	41.1	91	44
6.	"	23-27, 29-33, 35, 37-46, 104-143 neutral and anionic O-bases; deviating points: NaOH, O ₂ , CO ₂	30.4 (4.0)	0.689 (0.009)	0.995	8.8 (8.5)	97.4	278	55
7.	"	47-57, 59-62, 90-102; neutral and anionic C-bases deviating points CH ₂ and FCH=CH ₂	35.5 (2.7)	0.697 (0.004)	0.998	6.2 (6.2)	85.8	289	37
22 8.	3-21G	1-3, 6-8, 15, 19, 21, 23, 24, 27, 34, 36, 37, 55-57, 61, 62, 65, 67, 68, 74, 75, neutral bases.	31.4 (8.1)	0.821 (0.044)	0.968	10.8 (9.4)	13.8	117	26
9.	"	81-83, 85, 86, 88, 90, 91, 97, 99, 100, 102, 103, 107; anions.	189.8 (23.3)	0.481 (0.057)	0.924	9.2 (8.7)	31.5	84	14
10.	"	1-3, 6-8, 15, 19, 21, 23, 24, 27, 34, 36, 37, 55-57, 61, 62, 65, 67, 68, 74, 75, 81-83, 85, 86, 88, 90, 91, 97, 99, 100, 102, 103, 107; neutral and anionic bases.	22.1 (5.8)	0.887 (0.021)	0.990	15.2 (9.0)	21.3	317	40

Table 2 continued

1	2	3	4	5	6	7	8	9	10
11.	4-31G	1-4, 6-8, 10-19, 23, 24, 26, 29, 31, 32, 34, 36-39, 44, 45, 47, 57-61, 63, 65-69, 71-76, 78; neutral bases, deviating points H_2S and CH_2 .	26.2 (3.6)	0.831 (0.020)	0.986	6.6 (6.6)	9.5	158	50
12.	"	81-83, 85-102, 104, 107-110, 117, 118; anions.	120.7 (10.7)	0.651 (0.027)	0.978	4.8 (4.8)	21.9	92	28
13.	"	1-4, 6-8, 10-19, 23, 24, 26, 29, 31, 32, 34, 36-39, 44, 45, 47, 57-61, 63, 65-76, 78, 79, 81-83, 85-102, 104, 107-110, 118; neutral and anionic bases, deviating point NO_3^- .	27.3 (2.2)	0.881 (0.007)	0.997	7.8 (6.2)	15.8	347	79
14.	"	1-4, 6-8, 10-18, amines, N_2 , etc.	25.7 (4.7)	0.750 (0.019)	0.995	3.9 (3.9)	38.9	131	16
15.	"	23, 24, 26, 29, 31, 32, 36-39, 44, 45; anionic O-bases.	20.4 (5.7)	0.914 (0.033)	0.993	4.3 (3.5)	7.9	103	13
16.	"	104, 107-110, 117, 118; anionic O-bases.	129.1 (13.6)	0.631 (0.036)	0.992	3.3 (3.3)	19.0	66	7
17.	"	47, 57-61, 69-72, 90-102; neutral and anionic C-bases.	25.7 (5.4)	0.887 (0.017)	0.996	9.3 (7.7)	18.3	248	23

Table 2 continued

1	2	3	4	5	6	7	8	9	10
18.	6-310 [±]	1, 2, 8, 15, 19, 23, 24, 27, 38, 44, 55-57, 62, 67, 68, 74, 75; neutral bases.	24.3 (4.3)	0.888 (0.024)	0.994	4.4 (1.6)	8.4	91	18
19.	"	81-83, 85, 86, 88, 90, 91, 93, 94, 97, 100-103, 107; anions.	120.0 (15.2)	0.654 (0.038)	0.978	4.8 (4.3)	23.5	84	16
20.	"	The joint treatment of data for neutral and anionic bases (see series 18 and 19).	25.4 (3.0)	0.886 (0.009)	0.998	6.9 (3.4)	17.0	316	34
21.	3-21+G	81-83, 85, 86, 88-91, 93, 97, 100-105, 107-110, 117, 118; anions.	100.0 (13.4)	0.746 (0.036)	0.977	5.2 (5.2)	11.5	93	23
22.	"	104, 105, 107-110, 117, 118; 1000 ⁻ , 10 ⁺ .	111.3 (21.8)	0.716 (0.060)	0.979	4.9 (4.9)	14.0	66	8
23.	3-21G (neutral bases), 3-21+G (anions)	1-3, 6-8, 15, 19, 21, 23, 24, 34, 36, 37, 47, 55-57, 61, 62, 63, 65, 66, 68, 74, 75, 81-83, 85, 86, 88-91, 93, 97, 100-105, 107-110, 117, 118; neutral and anionic bases; deviating points LiOH and HCl.	0.14 (4.3)	1.009 (0.015)	0.995	10.5 (7.9)	10.8	316	47

Table 2 continued

1	2	3	4	5	6	7	8	9	10
24.	4-31+G	81, 82, 85, 89-94, 97, 100, 101, 104, 107, 109, 110; anions.	97.3 (21.1)	0.750 (0.054)	0.965	5.4 (3.7)	8.3	63	16
25.	4-31G (neutral bases), 4-31+G (anions)	1-4, 6-8, 10-19, 21, 23, 24, 26, 29, 31, 32, 36- 39, 44, 45, 47, 57-61, 63, 65-76, 78, 79, 81, 82, 85, 89-94, 97, 100, 101, 104, 107, 109, 110; neutral and anionic bases.	15.4 (2.6)	0.951 (0.010)	0.996	8.5 (6.3)	10.7	347	68
26.	MP4/6-31G ^{XX}	1, 2, 15, 19, 23, 24, 37, 56, 61, 62, 68; neutral bases.	0.48 (10.3)	0.995 (0.068)	0.985	6.1 (3.2)	5.8	52	11
27.	6-31+G ^{XX}	82, 83, 85, 86, 88, 90, 91, 97, 103, 107; anions.	72.3 (8.4)	0.814 (0.022)	0.997	2.2 (2.2)	6.9	86	10
28.	MP2/4-31+G	81, 85, 89, 90, 91, 93, 94, 97, 101, 104, 107, 109, 110; anions.	64.8 (26.4)	0.845 (0.062)	0.970	5.5 (5.5)	6.4	63	13
29.	MP4/6-31G ^{XX} basis for neutrals, MP2/4-31+G basis for anions	1, 2, 15, 19, 23, 24, 37, 56, 61, 62, 68, 81, 85, 89, 90, 91, 93, 94, 97, 101, 104, 107, 109, 110; neutral and anionic bases.	-3.5 (3.6)	1.021 (0.012)	0.998	6.5 (4.1)	9.0	292	24

Table 2 continued

Throughout this Table, only PA_{exp} values corrected for the zero-point vibrational energy were used (see, however, series No 1) in the data precessing in terms of Eqn. (1) and (2). a and b are regression coefficients from Eqn. (2). In parenthesis under their values are reported their error limits. r - is the correlation coefficient. s - standard deviation from regression line in terms of Eqn. (2) on assumption of the equal statistical weights of the subsets making up the composite data sets; in the same (7th) column in parenthesis under the latter quantities are given the statistically averaged and weighted standard deviations s_w from the regression line which take into account different statistical weights of subseries (see the text). In the 8th column STDV values calculated according to Eqn. (1) are given. 9th column shows the maximum range (in kcal/mol) of variation of the experimental PA values whereas the number of points n (after the exclusion of significantly deviating points) included in the data treatment according to Eqns. (1) and (2). The calculations for series No 27 are based on PA_{calc} values from Ref. 7.

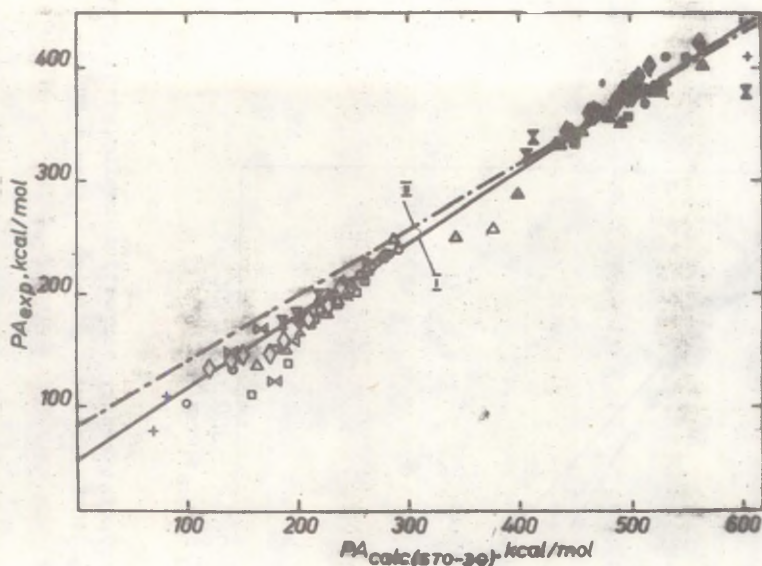


Fig. 1. The dependence of PA_{exp} on PA_{calc} (minimum STO-3G basis set). Straight lines I and II correspond to Eqns. (2) and (3) from Table 2. In the present figure, as well as in Figs. 2 and 3 the following notations of points has been accepted: \bigcirc - N-bases (except nitriles and $N \equiv N$); \triangle - O-bases, sp^3 -protonization center; \square - O-bases, sp^2 -protonization center; \diamond - C-bases (benzenes, ethylenes, carbanions etc.); ∇ - protonization on halide atom, \times - nitriles and N_2 ; \bigcirc - P- and S-bases. Right points correspond to the neutral bases, the filled ones - to anionic bases. Crosses (+) refer to H, H_2 and H^- . The PA_{exp} values do include the zero-point energy correction.

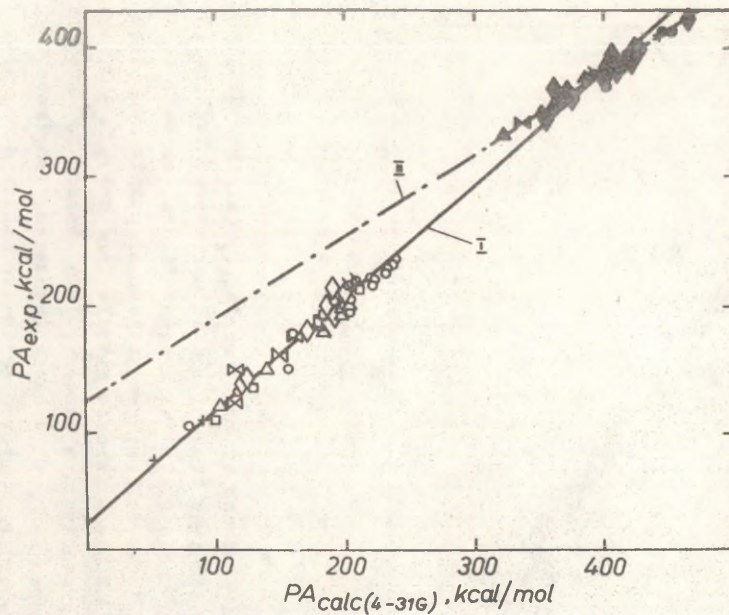


Fig. 2. The dependence of experimental (zero-point energy correction is included) proton affinity values PA_{exp} on PA_{calc} (4-31G basis set). Straight lines I and II refer to Eqns. (13) and (12) from Table 2.

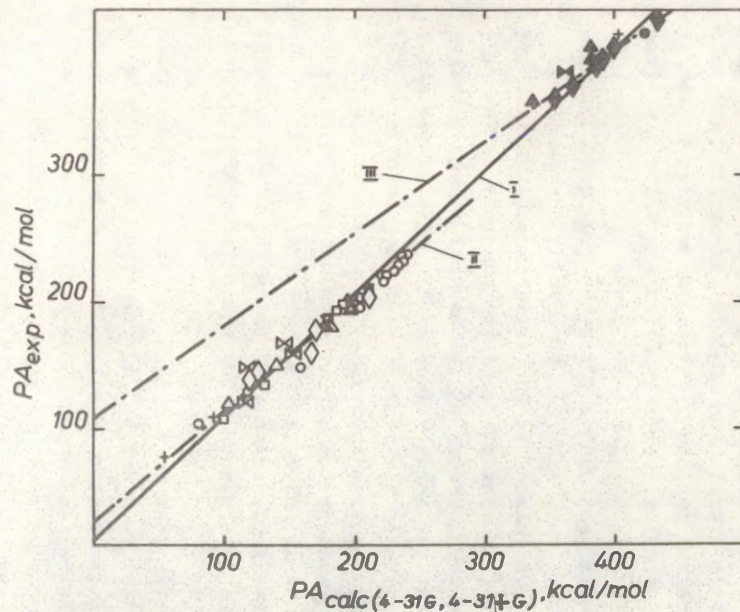


Fig. 3. The dependence of experimental (zero-point energy correction is included) proton affinity values PA_{exp} on PA_{calc} (4-31G basis set for neutral bases, the diffuse-function-augmented 4-31+G basis set for anionic bases). Straight lines I, II and III refer to Eqs. (25), (11), and (24) from Table 2.

than the same quantities for the neutral bases. The same is also true for series 18 and 26, on one hand, and series 27 and 28, on the other hand, although in the case of these subsets STDV as well as s values for neutral and anionic bases are rather comparable with each other and, with some admissions, are also approaching the experimental error limits of determination of proton affinity values.

At the same time, one has to acknowledge that in the case of a separate correlation of data for neutral and anionic bases b values for the neutrals themselves, in the limits of their statistical errors, differ significantly from unity, whereas $b < 1$. So, for 4-31G basis set b value is ca 0.83, for 6-31G⁺ set 0.85 and for the STO-3G it approximately equals 0.7 (series No 2). As a rule, the conditions $a \geq 0$ and $b \leq 1$ correspond to the overestimated values of PA_{calc} . Formally, on assumption of the adequacy of the calculation of the total energy of the neutral molecule (base B or acid AH) the too large values of PA_{calc} evidence about the underestimation of the stability of the ionic forms BH^+ or A^- in the one-electron approximation. The most significantly overestimated proton affinity values are characteristic for such small anions as F^- (more than 60 kcal/mol) and H^- (ca 40 kcal/mol) calculated using the minimum basis set. The same is true also for the basicity of HF , O_2 and CO_2 .

It is possible that in the light of these circumstances the near-the-ideal ($a=0$ and $b=1.0$) values of the regression coefficients in the case of the simultaneous correlation of the data for neutral and anionic bases using the mixed basis sets of 3-21G, 3-21+G type are actually artifacts which are formally accounted for by the accidental coincidence of several circumstances. Indeed, one might imagine that in the case of certain, relatively close values of the slopes b and at the sufficiently large difference for the intercepts a of the two separate, relatively remote straight lines for neutral and anionic bases (see series 8 and 21, 11 and 24, 26 and 28) the latter could be rather satisfactorily approximated by a single straight line with a slope b quite close to

the unity. In that respect, a certain, however hardly the decisive, role can also be played by the possible inhomogeneity of the scale (the lack of the common origin) of PA for the neutral and anionic bases which might result from the absence of the direct experimental equilibrium measurements of these quantities in the range between the strongest neutral bases (with PA c_a 240-250 kcal/mol) and the weakest anionic (PA approximately 310-320 kcal/mol) bases⁴.

Up to now, due to the above-mentioned circumstances the rather limited series No 26 (MP4/6-31G^{***} basis for neutral bases) seems to be the only undisputed example of the approximate observance of conditions $a=0$ and $b=1.0$ at the quantities s and STDV which are both comparable with the experimental error limits.

Practically analogous, rather complicated picture is present also in these cases when the analysis of the data from Table 1 is performed in terms of Eqn. (2) using a single basis set (STO-3G, 4-31G, 6-31G^{***}, etc.) simultaneously for neutral and anionic bases.

By the number of the data points the most primitive and economic (and probably the less successful) from all standard basis sets considered - STO - 3G - is, naturally, also the most representative one. One can see from Table 2 (see series Nos 4-6, 7) that in the case of this basis set the simultaneous analysis of data for the bases of the different charge and multiplicity leads to satisfactory correlations which over the very wide range (almost 350 kcal/mol) of variation of PA are characterized (see also Fig. 1) by the \neq The equilibrium scale of the absolute values of PA of the neutral bases is based on the separate independent determinations of PA values for such a reference compounds as NH₃, isobutylene, propene, etc. The corresponding equilibrium PA scale for anionic bases, in its turn, relies on the exact and independent determination of PA values for F⁻, Cl⁻, PhO⁻, etc.. Strictly speaking, any verifications of the compatibility (homogeneity, the common origin) of these two scales of absolute proton affinities was never given.

standard deviation which does not exceed 6-8 kcal/mol. On the other hand, these relationships have a non-zero intercept a and slopes of the straight lines b which differ significantly ($c\approx 0.68$) from unity. At the same time the STDV value is in the range from 80 to 100 kcal/mol. From the separate analysis of data for the different charge type one can see (series 2,3, and 5) that, as a rule, the slope b for the neutral bases practically coincides with the above-mentioned slope for the simultaneous correlation of data for neutral and anionic bases. In its turn, the same quantity for the anions (0.53) is significantly less than its value for the neutral bases.

Noticeably higher (approximately by 50-70 kcal/mol) than in case of neutrals is also the intercept a for the anionic bases. In addition to the rather high absolute values of STDV the difference between these quantities for neutral ($c\approx 40$ kcal/mol) and anionic ($c\approx 120$ kcal/mol) bases is even higher than the last figures. More detailed analysis of the applicability of the standard minimum Gaussian basis set for the calculation of proton affinities separately for the different classes of compounds reveals that the gross (formal?) relationships which include data for various classes of bases (series 2-4) could be split into several less general "sub-family" linearities. At least part of the latter differ significantly by their regression coefficients, s and STDV values from the relationships of the former type. As a rule, within these subsets the absolute deviations (as evidenced by STDV values) of theoretical values of PA from PA_{exp} are still rather high and comparable with those for the large composite series (e.g. 2 and 3). Contrary to that, the standard deviations s from these separate subset linearities are frequently approaching the level of precision which is characteristic for the correlation equations which describe the dependence of PA values on structure in terms of inductive, resonance and polarizability characteristics of substituents.⁵⁰

Concluding the analysis of the use of the minimum basis set, one can also mention that the basicity of neutral as well as carbanionic C-bases (series No 7) is described in

terms of linear relationships which are essentially identical with correlations for the series 2 and 4. On the contrary, the regression coefficients for the anionic O-bases (not shown in Table 2) differ from the analogous characteristics of series No 6 (neutral and anionic O-bases).

On the natural grounds, there are still much less ab initio calculations (with the full geometry optimization) with the use of split-valence basis sets (3-21G, 4-31G, 6-31G⁺) than in the case of the STO-3G minimum basis set. The largest number of these, more sophisticated calculations have performed using 4-31G basis set (see series 11 - 17 and Fig. 2) Similar to the STO-3G basis set this basis also somewhat overestimates proton affinities of most bases. However, in the case of the comparable correlations (series 2 and 11; 3 and 12, 4 and 13, 5 and 14, and 20) one can see that at the relative constancy of values of the intercept a the slopes b are in this case noticeably higher, and standard deviations s , in its turn, lower (3-7 kcal/mol) than for the minimum basis set. As in the above-mentioned occasion of STO-3G basis set, the 4-31G intercept for the anionic bases is significantly higher and slope b is lower than the corresponding quantities for neutrals only as well as for the latter with anionic bases.

Similar to the situation in the case of STO-3G basis set, the standard deviations s for the latter two subsets differ from each other only insignificantly (see series 11 and 12) simultaneously resembling by their absolute values the error limits of the experimental determination of the proton affinities.

According to the STDV values the 4-31G basis set has noticeable advantages over the minimum basis set in predicting absolute values of proton affinities. So, the STDV value for STO-3G basis set for neutral bases is 38.6 kcal/mol (series No 2), whereas the same quantity for 4-31G basis set is only 9.5 kcal/mol (series No 11). The corresponding figures for anions (120.0 kcal/mol for STO-3G basis and 21.9 kcal/mol for 4-31G basis set) follow the same pattern. In the case of the 4-31G basis set the comparison of standard deviations s

from Eqn. (2) for some subseries (see, e.g., series 14 - 16) with the experimental uncertainties of PA as well as with the standard deviations of the correlations of PA values in terms of substituent constants⁵⁰ is even more favorable than for the minimum basis set. It should be also mentioned that in the case of 4-31G basis set the sharp deviations of F^- , HF, O_2 , CO_2 , O and H^- (compare series 4 and 13 from Table 2) from the generally observed relationship between PA_{exp} and PA_{calc} are absent.

More economic 3-21G basis set has been used for the calculation of the proton affinities for a much shorter time period. Therefore, in contrast to the 4-31G basis set, rather promising results (see series 8-10) are based on much less representative data basis. One can see from Table 2 that as reflected by the standard deviations STDV, this basis set has clear preferences before the minimum basis set. At the same time it somewhat loses in accuracy to the more sophisticated and less economic 4-31G basis set. It seems that rather close to the regression coefficients for the 4-31G basis set a and b values in series 8 and 10, on one hand, and the most deviating from that condition values of these quantities for anions (series 9) call for the further careful check on the basis of more representative data set.

The results of the statistical treatment of data in terms of Eqn. (2) show (see series 18-20) that polarization basis set 6-31G[Ⓜ] has practically no evident preferences before the much more economic and less primitive split-valence 4-31G basis set for predicting of proton affinities of neutral and anionic bases. Indeed, practically unchanged are the values of regression coefficients a and b (see series No 11 - 13 and 18 - 20) as well as STDV values. Some slight decrease was, however, noticed for the standard deviations s from the regression line.

The diffuse function-augmented 3-21+G, 4-31+G and 6-31+G[Ⓜ] basis sets suggested by P.v.R. Schleyer have some unquestionable preferences for predicting the proton affinities of anions. Indeed, as compared with the other standard basis sets 3-21G, 4-31G, 6-31G[Ⓜ]) at the comparable (still rather

high) values of the intercept a the value of the slope of the PA_{exp} vs. PA_{calc} plot is significantly higher than for basis sets (including also the polarisational 6-31G⁺ basis) without the augmented diffuse s- and p-functions. Indeed, the comparison of the slopes b for the series 8 and 21, 11 and 24, 18 and 27 shows that due to the use of these diffuse function augmented basis sets for the anionic bases reduces the differences in the slopes b for neutral and negatively charged bases down to the 7 \pm 8 per cent level. (0.075, 0.081 and 0.074 units, correspondingly).

The transfer from the ordinary split-valence basis sets to diffuse s- and p-function augmented basis sets is also accompanied by a very significant (3 to 4 times) decrease of standard deviations STDV (compare series 9 and 21, 12 and 24, 19 and 27). Some decrease in standard deviations s (the latter now range from 2.2 to 5.4 kcal/mol) from the regression line also takes place. This once more calls the attention to the comparability of the latter values with the experimental error limits of PA_{exp} as well as with the statistical characteristics of correlations⁵⁰ which were based on LFER principle. However, the above-said in the beginning of the present discussion about the use of the "mixed" basis sets, still significantly different from the ideal conditions ($a=0$ and $b=1.0$) regression coefficients, and several concrete under- (F^- , NO_3^-) or overestimates (e.g. EtO^- , MeO^- ; PA_{calc} for latter compounds are calculated as practically identical to the corresponding value for OH^- ion, etc.) of PA values lead to the conclusion that the problem of developing of the "good enough" basis set for the adequate calculation of proton affinities of anions cannot be considered as completely resolved.

The comparison of series 24 and 28 shows that the post-Hartree-Fock Møller-Plesset approach in the 2nd order (MP2/4-31+G) improves somewhat the results of the calculations of the basicity of anions: the intercept a decreases by 33 kcal/mol, and the slope b even somewhat exceeds the same quantity for 6-31+G⁺ basis set. Also from 8.3 (4-31+G basis set, series No 24) to 6.4 kcal/mol (see series No 28)

decreases the standard deviation STDV whereas the standard deviation from the regression line s does not change significantly.

As already mentioned, the transfer from series 18 to series 23 results in the nearly ideal values of the regression coefficients for the limited set of neutral bases. However, it is not quite clear to which of the two reasons the increase in the quality of calculations should be ascribed: a) transfer to the post-Hartree-Fock level or b) addition of the polarization functions also to the hydrogen atoms (the latter factor could be easily the dominant one). It is evident that only the first steps³⁰ have been made towards the study of the role of the electron correlation effects on the proton affinities of a limited number of basis. It still seems that unambiguous evidence about the substantial influence of this factor on the proton affinity of neutral as well as anionic bases has not been presented yet. It was recently⁶⁸ argued that the resources of generating significantly more sophisticated basis sets which could be used either within the limits of a single determinant approach or on the post-Hartree-Fock level of the theory are still far from being totally exhausted.

The following preliminary conclusions about the adequacy of ab initio calculation of proton affinities using the Gaussian 70/80/82 programs can be made:

1. Linear relationships of type of Eqn. (2) exist between experimental and calculated proton affinities for several classes of compounds over a very wide range of variation of PA_{exp} (up to 350 kcal/mol). As a rule, even in the least favourable cases (minimum set) standard deviations of these correlations do not exceed 9 kcal/mol.

The standard deviation s from the regression line as well as the standard deviation STDV of experimentally determined proton affinities from the calculated values PA_{calc} depend significantly on the basis set: the gradual transfer from the minimum STO-3G basis set to more sophisticated basis sets results for some subsets to s values which are comparable with experimental uncertainties of PA_{exp} values, as

well as with those standard deviations which characterize the dependence of PA values on structure in the framework of LFER approach. The STDV values for different basis sets and data sets also approach these limits.

However, based on the existing data sets for the experimental and calculated values of PA in most cases the regression coefficients of Eqn. (2), a and b , differ from their ideal values ($a=0$ and $b=1.0$) which are expected in the case of the total isomorphism between theory and experiment. In a large majority of cases $b < 1$, whereas its value for the anionic bases is always less than that for neutrals.

2. For a further study of the problem it is necessary to perform additional systematic calculations of proton affinities of compounds of different chemical nature and charge type using single determinant Hartree-Fock as well as post-Hartree-Fock approximations. From the other side, systematic extensive experimental gas phase studies are also necessary for tackling of the more distant and very complicated problem of building the homogeneous equilibrium proton affinity scale in the all range from the very weak neutral bases ($PA < 100$) to the most basic anionic basis (CH_3^- , NH_2^- etc.)

3. Correlational relationships from Table 2 could be used for the approximate prediction of proton affinities of compounds which are unstable or otherwise hard to handle. Some predicted PA values (PA_e) are given in Table 2 of the Appendix.

We are grateful to Prof. W.J. Hehre for the Gaussian 82/83 program and Drs. N.M. Vitkovskaya and G.V. Zakhzhevski for the Gaussian 80 program.

References

1. I.A. Koppel and M.B. Comisarov, This journal 17, 495(1980).
2. W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton and J.A. Pople, QCPE, Program No 236, Bloomington, Indiana.

3. L. Radom, *Austr. J. Chem.*, 28, 1 (1975).
4. J.E. DelBene and A. Vaccaro, *J. Am. Chem. Soc.*, 98, 7526 (1976).
5. P. Pulay, *Applications of Electronic Structure Theory*, H.F. Schaefer, III, (Ed.), Plenum, New York, 1977, Chapt.4.
6. H.B. Schlegel, *J. Comput. Chem.*, 3, 214 (1982); H.B. Schlegel, J.S. Binkley and J.A. Pople, *J. Chem. Phys.*, 80, 1976 (1984).
7. W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley Interscience, New York, 1985.
8. *Computational Theoretical Organic Chemistry*, I.G. Csizmadia and R. Daudel (Eds.), D. Reidel Publishing Co, Dodrecht, Boston, London, 1981.
9. J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn, and J.A. Pople, *Univ. of Carnegie-Mellon, Pittsburgh, Pa.* 15213, *QCPE*, 406, 437, 446 (1981, 1982).
10. R.A. Whiteside, M.J. Frisch, J.S. Binkley, D.J. DeFrees, H.B. Schlegel, K. Raghavachari, and J.A. Pople, *Carnegie-Mellon Quantum Chemistry Archive*, 2nd Edition, 1981, Carnegie-Mellon University, Pittsburgh, PA., 15213.
11. R.F. Hout, Jr., M.M. Francl, E.S. Blurock, W.J. Pietro, D.J. DeFrees, S.K. Pollack, B.A. Levi, R. Steckler, and W.J. Hehre, *Univ. of California, Irvine*, 1977-1983.
12. J. Chandrasekhar, J.G. Andrade, and P.v.R. Schleyer, *J. Am. Chem. Soc.*, 103, 5609, 5612 (1981).
13. G.W. Spitznagel, T. Clark, J. Chandrasekhar, and P.v.R. Schleyer, *J. Comput. Chem.*, 3, 363 (1982).
14. T. Clark, J. Chandrasekhar, G.W. Spitznagel, and P.v.R. Schleyer, *ibid*, 4, 294 (1982).
15. Reference 8, pp.15, 413.
16. R.W. Taft, *Progr. Phys. Org. Chem.*, 14, 247 (1983).
17. M. Fujio, R.I. McIver, Jr., and R.W. Taft, *J. Am. Chem. Soc.*, 103, 4017 (1981).

18. K.-P. Wanczek, *Int. J. Mass.Spectr. Ion Processes*, 60, 11(1984).
19. P.R. Moylan and J.I. Brauman, *Annu. Rev. Phys. Chem.*, 34, 187 (1983).
20. *Lecture Notes in Chemistry No 31. Ion Cyclotron Resonance Spectrometry II*, H. Hartmann and K.-P. Wanczek (Eds), Springer, 1983.
21. I.A. Koppel and R.W. Taft, University of California, Irvine, 1982.
22. S.G. Lias, D.M. Shold, and P. Ausloos, *J. Am. Chem. Soc.*, 102, 2540 (1980).
23. S.M. Collyer and T.B. McMahon, *J. Phys. Chem.*, 87, 909 (1983).
24. A.C. Hopkinson, N.K. Holbrook, K. Yates, and I.G. Csizmadia, *J. Chem. Phys.*, 49, 3596 (1968).
25. M. Taagepera, K.D. Summerhays, W.J. Hehre, R.D. Topsom, A. Pross, L. Radom, and R.W. Taft, *J. Org. Chem.* 46, 891 (1981).
26. A. Pross and L. Radom, *Progr. Phys. Org. Chem.*, 13, 1 (1980).
27. A. Pross, L. Radom, and R.W. Taft, *J. Org. Chem.*, 45, 818 (1980).
28. G. Kemister, A. Pross, L. Radom, and R.W. Taft, *J. Comput. Chem.*, 2, 470(1981).
29. G. Kemister, A. Pross, L. Radom, and R.W. Taft, *J. Org. Chem.*, 45, 1056 (1980).
30. J.E. DelBene, M.J. Frisch, K. Raghavachari, and J.A. Pople, *J. Phys. Chem.*, 86, 1529 (1982).
31. M.L. Hendewerk, R. Frey, and D.A. Dixon, *ibid.*, 87, 2026 (1983).
32. A.C. Hopkinson, K. Yates, and I.G. Csizmadia, *Theoret. Chim. Acta (Berl.)*, 23, 369 (1972).
33. J.F. Wolf, R.M. Staley, I. Koppál, M. Taagepera, R.T. McIver, Jr., J.L. Beauchamp, and R.W. Taft, *J. Am. Chem. Soc.*, 99, 5417 (1977).

34. P. Kebarle, *Annu. Rev. Phys. Chem.*, 28, 445 (1977).
35. I.A. Koppel, U.H. Milder, and R.J. Pikver, *This journal*, 17, 460 (1980).
36. D.H. Aue and M.T. Bowers, *Gas-Phase Ion Chemistry*, Vol.2, M.T. Bowers (Ed.), Academic Press, New York, 1979, p. 2.
37. J.E. Bartmess and R.T. McIver, Jr., *ibid.*, p.88.
38. R. Walder and J.L. Franklin, *Int. J. Mass Spectrom. Ion. Phys.*, 36, 85 (1980).
39. *Thermodynamic Properties of Pure Compounds*, Vol. 1 and 2, V.P. Glushko (Ed.), Nauka, Moscow, 1978-1979 (in Russian).
40. J.E. Bartmess, J.A. Scott, and R.T. McIver, Jr., *J. Am. Chem. Soc.*, 101, 6046 (1979).
41. R.A. Bades, K. Scanlon, M.R. Ellenberger, and D.A. Dixon, *J. Phys. Chem.*, 84, 2840 (1980).
42. I.A. Koppel, R.J. Pikver, A.J. Sùgis, R.E. Suurmaa, and E.T. Lippmaa, *This journal*, 18, 3 (1981).
43. W.A. Lathan, L.A. Curtiss, W.J. Hehre, L.B. Lisle, and J.A. Pople, *Progr. Phys. Org. Chem.*, 11, 175 (1974).
44. H. Uneyama and K. Marokuma, *J. Am. Chem. Soc.*, 98, 4400 (1976).
45. L. Radom, *Aust. J. Chem.*, 28, 1 (1975).
46. This work, some of the results are gotten in Ref. 21 and published in I.A. Koppel, *This journal*, 22, issue 3 (1985).
47. J.E. DelBene, *J. Am. Chem. Soc.*, 99, 3617 (1977).
48. K. Hiraoka, P.P.S. Saluja, and P. Kebarle, *Can. J. Chem.*, 57, 2159 (1979).
49. P. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, 99, 1333 (1977).
50. I.A. Koppel and U.H. Milder, *This journal* 20, 3(1983). Part III of the present series of papers.
51. W.J. Hehre and J.A. Pople, *Tetrahedron Letters*, 1970, 2959.
52. Y.K. Lau and P. Kebarle, *J. Am. Chem. Soc.*, 98, 9452 (1976).
53. U. Seeger, R. Seeger, J. A. Pople, and P.v.R. Schleyer, *Chem. Phys. Letters*, 55, 399(1978).

54. J.E. DelBene, Chem. Phys. Letters, 94, 213 (1983).
55. J.E. DelBene and A. Vaccaro, J. Am. Chem. Soc., 98, 7526 (1976).
56. W.R. Davidson, S. Meza-Höger, and P. Kebarle, Can. J. Chem., 57, 3205 (1979).
57. W.J. Hehre, R.T. McIver, Jr., J.A. Pople, and P.v.R. Schleyer, J. Am. Chem. Soc., 92, 7162 (1974).
58. W.J. Hehre, L. Radom, and J.A. Pople, J. Am. Chem. Soc., 94, 1496 (1972).
59. W.L. Jorgensen and M.E. Cournoyer, J. Am. Chem. Soc., 100, 5278 (1978).
60. R. Ditchfield, W.J. Hehre, A. Radom, and J.A. Pople, J. Am. Chem. Soc., 92, 4796 (1970).
61. W.J. Hehre and J.A. Pople, J. Am. Chem. Soc., 97, 6941 (1975).
62. W.J. Jorgensen, J. Am. Chem. Soc., 100, 1057 (1978).
63. D.H. Aue, H.M. Webb, W.R. Davidson, M.T. Bowers, H. Goldwhite, L.E. Vertal, J.E. Douglas, P.A. Kollman, and G.L. Kenyon, J. Am. Chem. Soc., 102, 515(1980).
64. S. Ikuta and P. Kebarle, Can. J. Chem., 61, 97 (1983).
65. K. Edgecombe and R.J. Boyd, Can. J. Chem., 61, 45(1983).
66. A. Pross, D.J. DeFrees, B.A. Levi, S.K. Pollack, L. Radom, and W.J. Hehre, J. Org. Chem. , 46, 1693(1981).
67. P.v.R. Schleyer and A.J. Kos, Tetrahedron, 39, 1141(1983).
68. J.A. Pople, M.J. Frisch, B.T. Luke, and J.S. Binkley, Int. J. Quant. Chem., 17, 307 (1983).

A P P E N D I X

Total SCF MO Energies (E_{tot}) of Some Neutral Molecules and Molecular Ions
Calculated in Present Work^a Table 1

No	Deprotonated form (B or A ⁻)	$-E_{\text{tot}}$ (a.e.)		No	Deprotonated form (B or A ⁻)	$-E_{\text{tot}}$ (a.e.)	
		B or A	BH ⁺ or AH			B or A ⁻	BH ⁺ or AH
1	2	3	4	1	2	3	4
1.	H ⁻	0.4224 ^b	1.1230 ^c	11.	CHF ₂ O ⁻	307.6696	308.4722
2.	Cl ⁻	454.4804		12.	CF ₃ O ⁻	405.2064	405.9571
		459.5260 ^b		13.	MeO ⁻	112.7064 ^d	113.5492 ^d
3.	I ⁻	6850.6052		14.	EtO ⁻	151.2960	152.1331
4.	FO ⁻	171.5531		15.	i-PrO ⁻	189.8840	190.7165
		173.1898 ^c	172.3742 ^d	16.	t-BuO ⁻	228.4720	229.2994
		174.1263 ^b	174.7296 ^b	17.	CF ₃ CH ₂ O ⁻	443.7170	444.5136
5.	ClO ⁻	528.2091	528.9013	18.	(CF ₃) ₂ CHO ⁻	774.7108	775.4753
6.	O ₂ ⁻	146.6230	147.9366	19.	(CF ₃) ₃ CO ⁻	1105.6731	1106.3866
7.	HOO ⁻	147.9366	148.7650 ^d	20.	Me ₃ NO ⁻	244.8884	245.4341
8.	H ₂ NO ⁻	128.4265	129.2631	21.	Me ₃ NCH ₂ COO ⁻	394.7250	395.2970
9.	NCO ⁻	164.8060	165.5112 ^d	22.	ONO ⁻	201.1640 ^d	201.9156 ^d
10.	CH ₂ FO ⁻	210.1961	211.0080	23.	NO ₃ ⁻	274.9690 ^d	275.6585

Table 1 continued

1	2	3	4	1	2	3	4
24.	ClO_4^-	749.2985	749.9337	41.	CF_3CH_2^-	369.8835	370.6920
25.	HCOO^-	185.4563	186.2179	42.	$\text{CF}_3\text{CH}_2\text{CH}_2^-$	408.4260	
26.	MeCOO^-	224.0483	224.8102	43.	CF_3CN	422.6365	422.9631
27.	CF_3COO^-	516.4620	517.1805	44.	$(\text{CN})_2$	182.2195	182.5205
28.	F_2O	273.4535 ^b	273.5986 ^b	45.	NCNH	145.2603	145.9982
29.	HCOF	209.8308	210.1822	46.	O_2NNH^-	255.4438	256.1516
30.	F_2CO	307.3079 ^d	307.6503	47.	CF_3NH^-	385.6580	386.4330
31.	HCOCN	202.9024	203.2322	48.	CF_3NH_2	386.4330	386.8246
32.	$\text{CO}(\text{CN})_2$	293.4412	293.7529	49.	$(\text{CF}_3)_3\text{N}$	1044.5925 ^e	
33.	CCl_3COH	1512.9170	1513.2465			1044.3118 ^f	
34.	CF_3COH	443.3200	443.6673	50.	N_2NNH_3^+	111.3460	111.4454
35.	$(\text{CF}_3)_2\text{CO}$	774.2809	774.6175	51.	$\text{CF}_3\text{CH}_2\text{NH}^-$	424.1872	424.9980
36.	$(\Delta)_2\text{CO}$	341.4240	341.8466	52.	BF_4^-	416.6144	417.2549
37.	CF_3CONH_2	497.6393		53.	CF_3S^-	724.5570	725.2826
38.	F_2N^-	249.5415	250.3060	54.	CF_3SO_3^-	946.0300	
39.	$\text{FC}\equiv\text{C}^-$	172.5296	173.3071 ^d	55.	$\text{Me}_2\text{C}=\text{CH}_2$	154.2460	154.6384
40.	$\text{CF}_3\text{C}\equiv\text{C}^-$	406.0811	406.8222	56.	He	2.8078 ^c 2.8357 ^c 2.8552 ^b	2.8540 ^c 2.8815 ^b 2.9099 ^b

Footnote: a - If not otherwise indicated the STO-3G basis set was used. More detailed description of the results of compounds No 4-25 see: I.A. Koppel, This journal, 27, issue 3(1985).

b - 6-31G⁺ basis set, c - 3-21G basis set, d - see also Refs. 7,10, e - Tetrahedral CNCC configuration, no geometry optimization. f - Planar CNCC - configuration, no geometry optimization.

Table 2
The Predicted "Experimental" Values PA_e for Some
Bases^a

No	Compound	PA_e	No	Compound	PA_e
1	2	3	1	2	3
1.	He	50.4 (4) 42.5(10) 50.0(20)	15.	NCNH ⁻	343.1(4)
2.	F	88.7(20)	16.	O ₂ NNH ⁻	330.4(4)
3.	F ₂	92.4(26) 97.4(20) 93.6(13)	17.	CF ₃ S ⁻	340.9(4)
4.	FOH	140.5(20) 139.7(26)	18.	BF ₄ ⁻	305.8(4)
5.	FO ⁻	377.5(6) 352.9(20) 359.7(19)	19.	ClO ₄ ⁻	317.2(3)
6.	F ₂ O	98.9(13) 96.1(20)	20.	ClO ⁻	301.2(4)
7.	FNH ₂	186.2(26) 185.3(13)	21.	O ₂ ²⁻	296.6(6)
8.	F ₂ N ⁻	350.9(12) 354.3(4)	22.	CF ₃ O ⁻	338.4(4)
9.	F ₃ N	152.2(4) 127.9(13)	23.	NCN ⁻	334.7(6)
10.	F ₂ NH	160.0(13)	24.	H ₂ NO ⁻	331.2(4)
11.	CF ₃ NH ⁻	358.8(4)	25.	(NO ₂) ₃ C ⁻	382.4(4)
12.	CF ₃ NH ₂	196.6(4) 199.3(5)	26.	(NC) ₃ C ⁻	298.0(4)
13.	H ₂ NNH ₃ ⁺	68.3(5) 72.9(4) 72.2(13)	27.	Me ₃ NCH ₂ COO	301.6(7)
14.	H ₂ NOH	199.5(26)	28.	Me ₃ NO	300.9(4)
			29.	CO ₂	304.6(7)
			30.	HOOH	272.8(4)
					263.7(4)
					258.4(6)
					132.8(20)
					135.2(13)
					165.0(26)

Table 2 continued

1	2	3	1	2	3
31.	HGOCH	172.4(4)	33.	(CN) ₂	160.7(4)
32.	CO(CN) ₂	164.8(4)	34.	O ₃	156.3(13)
		157.2(6)			156.9(20)

Footnote: a - PA_e values are given in kcal/mol. After the predicted value, in the parenthesis is shown the sequence number of the corresponding equation from Table 2. PA_{calc} values used for predictions are taken from Table 1 and from Refs. 1, 7, 10, 43, 53-55, 65, 66. PA_{calc} for ozone is from work M. Kausch and P.v.R. Schleyer, J. Comput. Chem., 1, 94(1980). In that paper on the MP2/6-31G^M//4-31G level the PA_{calc} value for ozone is given as 124 kcal/mol. The value reported in the 3rd column of the present Table agrees better with values (149.7 - 155.6 kcal/mol) predicted on the basis of PES and ESCA data for this compound.³⁵

ISOMERISM OF COMPONENTS OF CHEMICAL PROCESSES:
A NEW DIFFICULTY IN COMPARING THEORETICAL AND OBSERVED
REACTIVITY CHARACTERISTICS

Zdeněk Slanina

The J. Heyrovský Institute of Physical Chemistry and
Electrochemistry, Czechoslovak Academy of Sciences ,
Máchova 7, CS-121 38 Prague 2, Czechoslovakia

Received August 10, 1984

Systematic investigation of a potential energy hypersurface often reveals several different minima all represented by one species in an experiment and/or several different saddle points corresponding to activated complexes in a single rate process. Energy criteria can sometimes prove only one structure to play an important role. However, it may also happen that two or more isomeric structures of comparable stability coexist and are indistinguishable under given experimental conditions. Then any structure-dependent observable can be considered as an average value resulting from contributions of all the isomers in question. Evaluation of reaction characteristics (both standard and activation) of processes whose components have been shown by theoretical analysis to be mixtures of isomers is discussed and consequences regarding confrontation of the theoretical and observed characteristics are analyzed.

1. Introduction

The origin of a general concept of isomerism may be traced¹ back to antiquity, when it was first adumbrated in

the writings of the Greek atomists². Modern science has supplied the old general concept with a huge amount of examples in the field of chemical isomerism, of biological isomerism³ and of the isomerism of atomic nuclei⁴. Since Berzelius's definition⁵ over thirty⁶ varieties of chemical isomerism have been recognized and this process still vigorously continues⁷ on both the inorganic^{7a} and Organic^{7b} scenes. Various schemes of isomer classification have been proposed⁸ and recently the algebraic methods⁹ (set theory^{9a,b}, group theory^{9c-e} and graph theory^{9f}) have been employed for this purpose. The algebraic generalization^{9b,10} of the notion of isomerism was given for use in the automatic design of syntheses. Besides algebraic methods, quantum-chemical methods are nowadays applied to the theoretical study of isomerism. In the latter case the individual isomers and the relations between them are treated as minima and their interrelations on the corresponding potential energy hypersurfaces¹¹. The approaches of both the algebraic methods and quantum chemistry have facilitated the rationalization of isomeric relationships (for successful and instructive examples see Refs. 12a,b and Refs. 12c,d, resp.). Moreover, theoretical techniques can lead to the prediction of hitherto unforeseen reactions (e.g. Balaban's graph-theoretical study¹³ of automerizations) or even to the discovery of new isomers experimentally unknown (e.g. quantum-chemical research of the bound, closed form of ozone¹⁴).

Exploitation of the theoretical methods has disclosed several new aspects of the old problem of isomerism¹⁵. The aim of the present article is to discuss one of them which lies on the border-line of theory and experiment, namely the evaluation of the reaction characteristics of chemical processes whose components, according to the theoretical analysis, are mixtures of isomers. There is nothing revolutionary about it, and it can be stated in very conventional terms. Nevertheless, the topic has been proved to play an important role in theoretical interpretation of observables in the field of chemical reactivity and in precise compa-

risons of quantum-chemical outputs with experimental data.

2. Quantum-Chemical Description of Isomers

2.1. Potential Energy Hypersurface

The concept of a potential energy hypersurface is a consequence of the separation¹⁶ of the nuclear and electronic motions as proposed by Born and Oppenheimer^{16a} in 1927. Adiabatic approximation underlies many of our chemical concepts - for example, the notion of molecular structure and energy barriers. The phenomenon of isomerism can be interpreted straightforwardly in these classical terms as the occurrence of more than one local minimum within one hypersurface or within the hypersurfaces of potential energy corresponding to various electronic states. The feasibility of transitions among single minima is determined by the barrier heights separating the adjacent minima and by temperature (at lower temperatures also by the possibility of quantum-mechanical tunnelling), and possibly also by transition probabilities between energy hypersurfaces. The same factors determine in principle the possibility of distinguishing two configurations, some qualitative criteria being outlined for this purpose¹⁷. Ideally, isomeric structures (especially in the case of stereochemically non-rigid systems^{17a,18}) should be treated by means of the whole potential energy hypersurface(s) comprising all possible configurations¹⁹. This level is however nowadays unattainable; nevertheless the question of the experimental distinguishing of structures corresponding to the individual local minima is a cardinal question of the concept of isomerism itself²⁰.

The adiabatic approach is an approximation only and therefore the same holds for the conventional quantum-chemical picture of isomerism. The classical concept of molecular structure is not consistent with requirements of quantum theory and therefore it has recently been criticized²¹. A rigorous quantum-mechanical interpretation of isomerism,

i.e. a description in terms of the eigenfunctions of the total molecular Hamiltonian (which is the same for all species having given summary formula) has not yet been completed. The identification of certain eigenfunctions of the molecular Hamiltonian with particular chemical species is an approximation^{22a}. In other words, the uniqueness of molecular species which consists of the same kind and number of nuclei along with the same number of electrons is only an approximation (which is good in most cases). Wilson^{22b} pointed out that chemists prepared substances by methods which select particular structures rather than exact energy states. Thus, the resulting states need not be eigenfunctions of energy, i.e. stationary states. In fact, the uniqueness of isomers is well founded in terms of the nonstationary states provided the change with time is sufficiently slow.

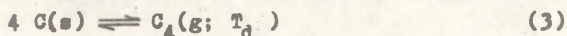
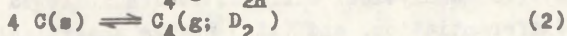
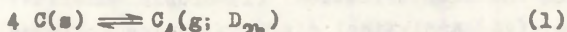
2.2. Location and Identification of Stationary Points

It is well known that the present state of numerical quantum chemistry does not permit the carrying out of a routine evaluation of potential energy hypersurfaces for systems of chemical interest. Low-number atomic systems consisting of nuclei at the very beginning of the periodic system represent an exception^{11c,23}. However, instead of the construction of the whole hypersurfaces quantum chemistry is able to localize and characterize the hypersurface stationary points, i.e. points having zero first derivatives of energy with respect to the nuclear coordinates. Identification of the stationary points is enabled by an analysis of the eigenvalues of the force constant matrix F at these points¹¹. Three kinds of them can be distinguished, namely local minimum, transition state or activated complex, and higher type of stationary point, their F matrixes having no, one, and two or more negative eigenvalues, respectively. There are three²⁴ significant levels of stationary point location and identification: (i) double numerical differentiation, (ii) analytical differentiation followed by numerical differentiation, and (iii) double analytical differenti-

ation. The pioneer works of Palay^{25a} and of McIver and Kormornicki^{25b} showed the way of mastering the (ii) technique. At present the effective (ii) treatment is used²⁶ within various quantum-chemical methods including the ab initio correlated wavefunctions²⁷. Moreover, the technique (iii) has recently been mastered^{27c} for ab initio SCF wavefunctions, which is promising^{27b} for the multiconfiguration SCF level to be settled soon. The F matrix serving the identification of stationary points can also be used for the carrying out of normal coordinate analysis²⁸. This treatment enables to describe the motion of nuclei around the stationary point. We can thus summarize that now in practically all areas of computational quantum chemistry the methodology has reached the level enabling the study of chemical reactivity phenomena in terms of energy hypersurface critical points and their characteristics. However, the harmonic description represents the upper limit; the calculations of higher derivatives of energy are still quite scarce²⁶. That is why it is necessary so far to describe the motion of nuclei in terms of the rigid rotator and harmonic oscillator (RRHO). Let us note that within this simple approach the motions of individual stationary points are independent.

2.3. An Illustrative Example

Carbon atom aggregates, which are present²⁹ at high temperatures in the gas phase above graphite, have recently been studied³⁰ by means of the MINDO/2 method. Comprehensive search for stationary points on potential energy hypersurfaces of the C_n ($4 \leq n \leq 7$) was carried out³⁰ according to the (ii) technique. Four or more stationary points were found³⁰ on each hypersurface, at least two of them being minima (Figure 1). For example, three isomers (D_{2h} , D_2 , T_d) were found in the case of the C_4 aggregate. Accordingly, three partial equilibria (1)-(3) take place in the gas phase



above graphite. However, the experimental (mass-spectrometrical) values²⁹ of reaction characteristics do not correspond to any of the individual processes (1)-(3) but to the overall equilibrium (4). It is clearly evident that



it is necessary for comparison with the experimental data to sum up weighted contributions of the isomers.

3. Theoretical Calculations of Reaction Characteristics

The present theory of chemical reactivity is entirely based³¹ on representation of energy hypersurfaces by means of their stationary points. Location and identification of these points is however only the first step with calculations of the characteristics of equilibrium and rate processes.. For this purpose it is necessary to link effectively both quantum chemistry and statistical thermodynamics, two fields of science traditionally somewhat disconnected³². Recent comprehensive studies³³ testing the applicability of quantum-chemical methods as source of molecular data for evaluation of partition functions have been successful. The used RRHO approximation of partition functions does not seem^{33a,34} to depreciate the quality of the calculated characteristics. Thus, it has become possible in the case of the calculation of thermodynamic functions^{34,35} to replace the molecular parameters which are conventionally derived from experiment or merely estimated by those obtained from theoretical calculations. The same holds for the evaluation of rate characteristics by means of activated-complex theory³⁶ (ACT). In fact the linking up of the ACT with quantum-chemical methods has brought ACT to its renaissance. Besides the generation of reliable characteristics of activated complexes which follows from this symbiosis, one more thing is contributing to its boom: test studies³⁷ comparing in the case of very simple systems the values of characteristics of the rate processes obtained on the basis of the ACT and on the basis of exact quantum-mechanical calculations have shown surprising

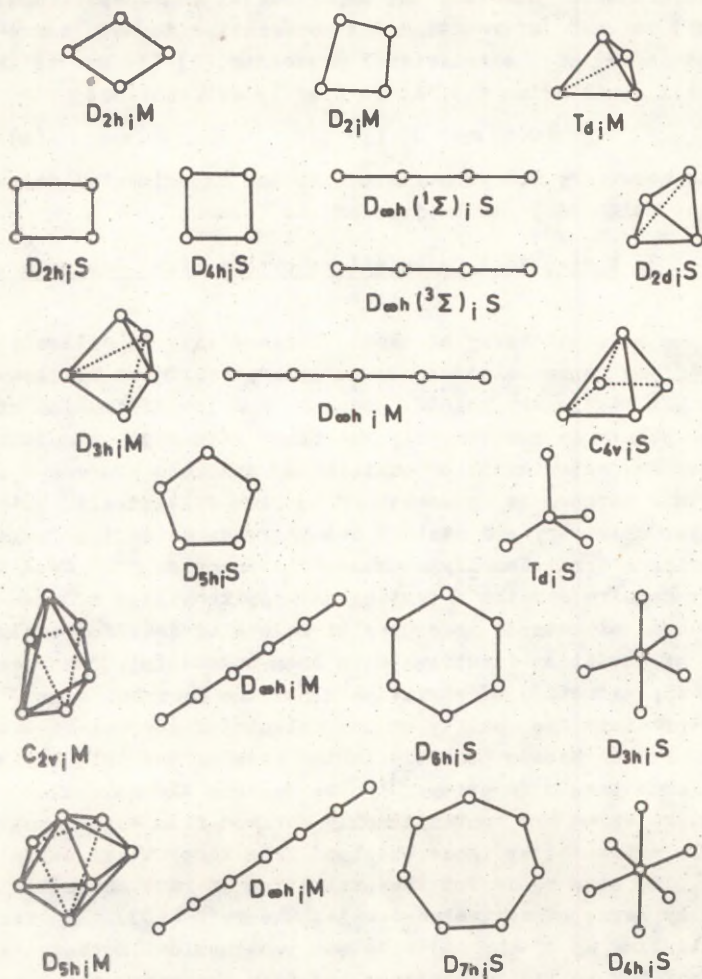


Fig. 1. Schemes of stationary points found on the MINDO/2 potential energy hypersurfaces of C_n ($n = 4$ to 7); M - Minimum.

ly good agreement (except for the low temperature region where tunnelling manifests itself markedly. Thus, a period of evaluating reaction characteristics (standard or activation ones) completely independently of experimental information (with the exception of masses, fundamental constants and Coulomb's law) has begun. Characteristics of a large number of equilibrium and/or rate processes in the gas phase have been calculated in this manner^{15,38}.

4. General Equilibrium Isomeric Problem

The thermodynamics of the perfect gas mixture is a well known textbook problem³⁹. The description of a mixture of isomers is formally a similar task, though there is one qualitative difference - the equilibrium between the components is established by chemical reactions (i.e. isomerizations). The task is important for evaluation of thermodynamic characteristics of a species which is in fact a mixture of several (inseparable) isomeric structures. Calculations of thermodynamic functions of such compounds based on experimental and/or estimated molecular parameters were reported⁴⁰, although these were restricted only to the isomers linked by hindered rotation. An especially important application is that for the description of macromolecules (the rotational isomeric state model⁴¹).

After the introduction of isomerism study by means of quantum-chemical description in terms of energy hypersurface critical points the situation has changed pronouncedly. All the necessary characteristics are obtainable from theoretical calculations for any type of isomeric compounds. Moreover, both quantum chemistry (there are several dozens of such findings, e.g. ^{12c,d,14,30,42}) and molecular mechanics (examples are again very numerous, e.g. ^{11b,43}) calculations have indicated that even relatively simple substances are frequently to be considered mixtures of several isomeric structures. In fact, each chemical species can be (at least formally) treated in this manner provided its electronically excited states (each with its vibrational and rotational sub-

structure) are taken into account. Wide use of numerical techniques for location and identification of stationary points has made it reasonable to consider generalised chemical equilibria, viz. equilibria of which each component is a mixture of isomers⁴⁴. Multiple-configuration thermodynamics was described within the formalism of general equilibrium isomeric problem^{44b}. The resulting weighting relations are especially important for comparison of the experimental and theoretical outputs in case of processes where isomerism of reaction components was revealed only theoretically or (though known) could not be eliminated in the experiment. Each isomeric structure of any reaction component contributes to the total effective values measured in the experiment according to its weight factor^{43a,b,g,44,45}, i.e., according to its Gibbs energy. The application of the quantum-chemical methods has made it possible to consider any difference in the motions of individual isomeric structures and to evaluate the weight factors not only on the basis of simple Boltzmann factors but also using the rotational and vibrational parts of partition functions (at present, however, only within the RRHO approximation). According to the weight factor value it is sometimes possible to eliminate all but one structure of each reaction component to play an important role under the given experimental conditions. However, marked differences between single-configuration and multiple-configuration thermodynamic functions can also appear and these cases are of special interest for us here.

Generally, there are two important presumptions included in the equilibrium isomeric problem: the first is the postulate of full separability of the motion of individual isomers and the other one assumes complying with the conditions of full thermodynamic equilibrium. A very important question is therefore whether the latter conditions were really reached in the experiment. This problem must be thoroughly discussed in every case. It can happen that instead of the equilibrium mixture of isomers, a specific generation of isomers^{46a,b} (even preferential formation of less stable isomers^{46c}) may

take place. Clearly the general equilibrium isomeric problem should be applied only to such cases where realization of full equilibrium conditions is ensured.

4.1. General Formulae

Consider an equilibrium process

$$\sum_{k=1}^n \nu_k A_k = 0 \quad (5)$$

in ideal gas phase between n reaction components A_k having stoichiometric coefficients ν_k . This equilibrium is described by standard changes of enthalpy ΔH_T° , entropy ΔS_T° , and Gibbs energy ΔG_T° . Let us consider now any reaction component A_k to be a mixture of j_k isomers $A_k^{(1)}, A_k^{(2)}, \dots, A_k^{(j_k)}$, where the $A_k^{(1)}$ isomer is lowest in energy. Distinguishing the A_k component into individual isomeric structures causes the overall process (5) to become a superposition of all possible partial equilibria; a part of these equilibria forms a set of partial processes:

$$\sum_{k=1}^n \nu_k A_k^{(i_k)} = 0, \quad (i_k = 1, 2, \dots, j_k). \quad (6)$$

Let the reaction characteristics $\Delta H_{1,1,\dots,1}^\circ$, $\Delta S_{1,1,\dots,1}^\circ$, and $\Delta G_{1,1,\dots,1}^\circ$ belong to the process (5) realized by the isomers having the lowest energy. Finally, let us consider isomerization processes:



that are described by the values of $\Delta H_{1 \rightarrow i_k}^\circ$, $\Delta S_{1 \rightarrow i_k}^\circ$, and $\Delta G_{1 \rightarrow i_k}^\circ$, and by the corresponding equilibrium constant of isomerization $K_{1 \rightarrow i_k}$. Between the characteristics of partial and overall processes the relations (8)-(10) hold^{15,44b}:

$$\Delta H_T^\circ = \Delta H_{1,1,\dots,1}^\circ + \sum_{k=1}^n \sum_{i_k=1}^{j_k} \nu_k w_{i_k} \Delta H_{1 \rightarrow i_k}^\circ \quad (8)$$

$$\Delta S_T^0 = \Delta S_{1,1,\dots,1}^0 + \sum_{k=1}^n \sum_{i_k=1}^{j_k} \gamma_k w_{i_k} (\Delta S_{1 \rightarrow i_k}^0 - R \ln w_{i_k}) \quad (9)$$

$$\Delta G_T^0 = \Delta G_{1,1,\dots,1}^0 + \sum_{k=1}^n \sum_{i_k=1}^{j_k} \gamma_k w_{i_k} (\Delta G_{1 \rightarrow i_k}^0 + RT \ln w_{i_k}), \quad (10)$$

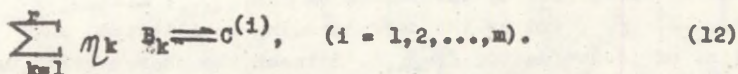
where the weight factors w_{i_k} are given by:

$$w_{i_k} = K_{1 \rightarrow i_k} / \sum_{i_k=1}^{j_k} K_{1 \rightarrow i_k}. \quad (11)$$

Relations (8)-(11) enable to traverse correctly from partial to total characteristics and vice versa. The first direction is typical for the comparison of the experimental and theoretical outputs in case of processes where the isomerism of reaction components was discovered by theoretical means only. For this purpose it is convenient to express^{45b} the weights (11) in microscopic terms, i.e. in terms of partition functions and energy differences among individual isomers. As both these characteristics are obtainable from quantum-chemical calculations, the realization of the weighting treatment indeed becomes possible.

4.1.1. One Frequent Special Case

The results gained so far indicate that for many equilibria isomerism of reaction components is most frequently met with the processes of the type:



Apparently, a special case of general equilibrium problem takes place here, i.e. a case of the isomerism of only one component. The weighting relations have especially simple forms³⁷ now, e.g.:

$$\Delta H_T^0 = \sum_{i=1}^n w_i \Delta H_i^0 \quad (13)$$

$$\Delta S_T^0 = \sum_{i=1}^n w_i (\Delta S_i^0 - R \ln w_i), \quad (14)$$

where the meaning^{44b} of symbols ΔH_i^0 and ΔS_i^0 is obvious. On denoting the highest and the lowest values of the ΔH_i^0 set with ΔH_{\max}^0 and ΔH_{\min}^0 respectively, a useful estimation:

$$\Delta H_{\min}^0 \leq H_T^0 \leq H_{\max}^0 \quad (15)$$

of the magnitude of ΔH_T^0 can be made^{44b}. Similar inequality holds for the overall entropy term^{49c}:

$$\Delta S_{\min}^0 < \Delta S_T^0 \leq \Delta S_{\max}^0 + R \ln n, \quad (n > 1). \quad (16)$$

5. Special Cases of Chemical Processes with Isomerism of a Component

5.1. Chemical Equilibria

Isomerism of reaction component is frequently met with usual chemical association processes and concerns the arising associate. The formation³⁰ of the C_n aggregates mentioned above is an example. The weighting treatment in the case of C_4 formation (Eqs. (1)-(3)) is illustrated in Table 1. It is evident that mere approximation of the characteristics of the overall process (Eq. (4)) using those of the most stable structure (D_{2h}) may be quite misleading. This is especially true with the entropy term: the total entropy term coincides circumstantially with that of D_2 isomer formation. Another example is difluoroamino radical dimerization studied^{47a} using the CNDO/2 method and exhibiting isomerism of the dimer (gauche- and trans- N_2F_4). The effects of the weighting treatment are demonstrated in Figure 2. While the total ΔH_T^0 term is predominantly^{47b} connected with the formation of gauche- N_2F_4 , in case of the ΔS_T^0 term the effect of the

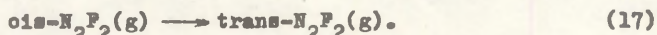
Table 1
Partial and Total MINDO/2 Thermodynamic Characteristics
of $4C(s) \rightleftharpoons C_4(g)$ Reaction at 2400 K

Process	ΔH_T^0 , kJ mol ⁻¹	ΔS_T^0 , J mol ⁻¹ K ⁻¹
$4C(s) \rightleftharpoons C_4(g; D_{2h})$	904.1	210.2
$4C(s) \rightleftharpoons C_4(g; D_2)$	952.2	213.6
$4C(s) \rightleftharpoons C_4(g; T_d)$	1301.5	205.5
$4C(s) \rightleftharpoons C_4(g; \text{Total})$	909.9	213.6

isomerism is more marked - the difference between the summary and any of partial terms being significant in the whole presented temperature range. (For our model purpose the difference in experimental^{47b} and CNDO/2 (Ref.^{47a}) orders of stability of both N_2F_4 rotamers is of less importance here.)

5.2. Rate Processes

The phenomenon of reaction component isomerism should not be considered only with equilibrium processes. The original concept of the ACT simply presumes³⁶ that the transformation of reactants into products goes through a single activated complex. However, recent systematic investigations⁴⁸ of stationary points by various quantum - chemical methods have indicated the possibility of the existence of more than one stationary point meeting¹¹ the requirements set to an activated complex of the given rate process (i.e. parallel transition states^{31e}). A common example is cis - trans interconversion around -N-N- bond^{48a-d} which is realized by two mechanisms, viz. the inversion and the rotation mechanisms, both being connected with a comparable activation energy. Figure 3 illustrates this fact - giving the schemes of stationary points on energy hypersurface of N_2F_2 which are important in the rate process:



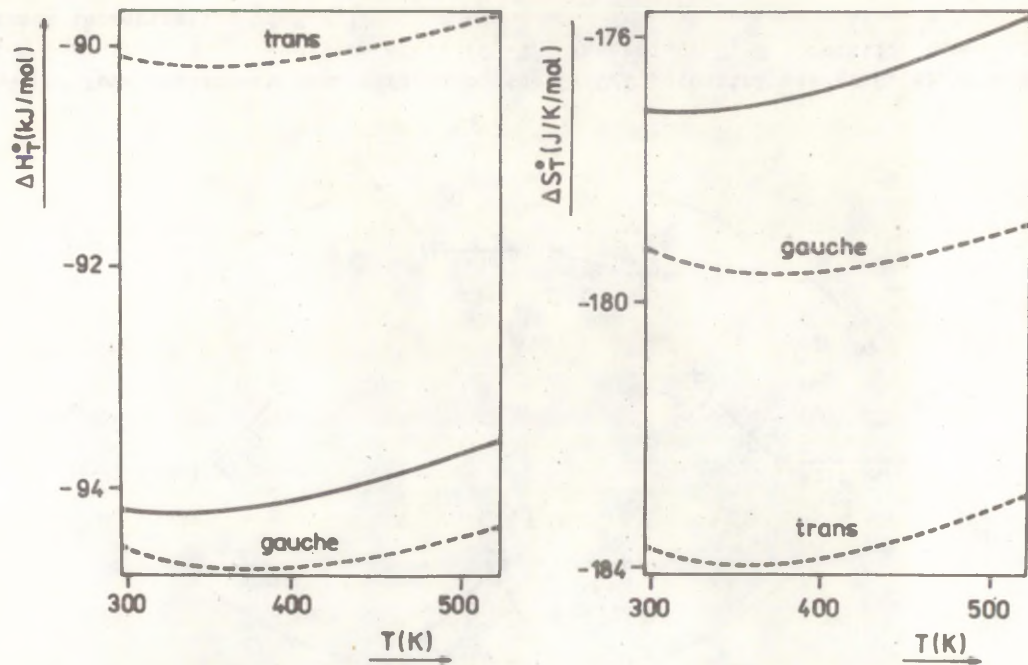


Fig. 2. Temperature dependences of CNDO/2 ΔH_T^0 and ΔS_T^0 terms for the partial dimerizations of NF_2 to gauche- N_2F_4 (g) and to trans- N_2F_4 (g) and for the overall dimerization process (—).

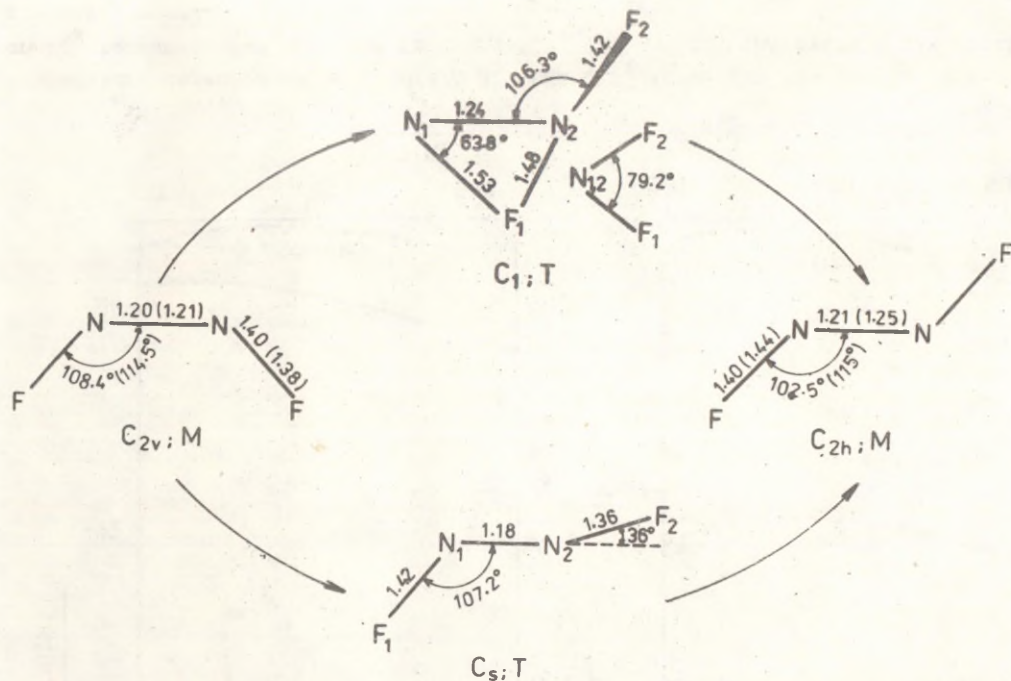


Fig. 3. Schemas of four stationary points found on the CNDO/2 potential energy hypersurface of N_2F_2 ; M - minimum, T - transition state (C_s -T - inversion, C_1 -T - rotation mechanism of cis-trans isomerization of N_2F_2).

On one hand it is clear that an experiment will generally give only the overall rate characteristics involving the contributions of all partial paths from reactants to products through individual activated complexes. Differentiation to separate partial activation processes seems hardly possible in any experiment. However, on the other hand a theoretical description of such rate process in terms of the ACT primarily yields the partial activation parameters corresponding to transitions through individual activated complexes, e.g. C_2 and C_1 transition states realizing^{48c} rate process (5) (Figure 3). Thus, with confrontation of theoretical and experimental data arises the problem of the contribution of each partial path through the particular activated complex to the total effective values of rate characteristics obtained in the experiment. The equilibrium hypothesis (on which the ACT is based) enables a straightforward application of the results of the general equilibrium isomeric problem yielding the required weighting scheme⁴⁹, e.g. in the following form:

$$\Delta H_T^\ddagger = \sum_{i=1}^{n^\ddagger} w_1^\ddagger \Delta H_1^\ddagger \quad (18)$$

$$\Delta S_T^\ddagger = \sum_{i=1}^{n^\ddagger} w_1^\ddagger (\Delta S_1^\ddagger - R \ln w_1^\ddagger), \quad (19)$$

where ΔH_1^\ddagger and ΔS_1^\ddagger denote the partial activation enthalpies and entropies, respectively, while ΔH_T^\ddagger and ΔS_T^\ddagger are the corresponding overall terms. The number of possible different activated complexes is denoted by n^\ddagger . The weighting factors w_1^\ddagger can be expressed in a similar way as in the equilibrium situation.

One can ask whether a contingent passing of one activated complex to another one through a higher type of stationary point would interfere in this scheme. Such transitions should usually be of negligible probability (in comparison with that of the ordinary process). Moreover, formal application of the equilibrium hypothesis indicates that the interconversions between different activated complexes should not influence the distributions of activated complexes.

If the values of the partial activation characteristics and of the corresponding weights are known, the weighting treatment leading to the total effective values can be carried out. Only in this way does the theoretical description reach a level enabling correct comparison with the experimental data. Properties of the weighting treatment were thoroughly studied^{49b} in the case of kinetics of isomerisation (17) (Figure 4). For both ΔH_T^\ddagger and ΔS_T^\ddagger terms there are temperature ranges where the total value differs markedly from any of the corresponding partial ones. The results indicate that the summary ΔS_T^\ddagger term can generally be expected to be (in accordance with its physical interpretation) more influenced by the phenomenon of activated-complex isomerism than the summary ΔH_T^\ddagger term. This can be seen in a more rigorous form from the inequalities^{49c} describing the limit behavior of the summary characteristics: while the total ΔH_T^\ddagger term can never get out of the interval defined by the lowest and the highest partial enthalpic term, the total ΔS_T^\ddagger term can exceed the highest partial entropic term even by the value of $R \ln n^\ddagger$. Thus, interplay between the partial entropic terms and the weight factors can lead to quite important differences between the total and any of the partial entropic terms. This is demonstrated by the figures^{48e, 49a} in Table II where the summary ΔS_T^\ddagger term is about one third higher than the partial one belonging to the path with lower energy barrier. Similarly due to the activated-complex isomerism the summary rate constant can be even n^\ddagger multiple of the rate constant of the most probable partial activation process. The increase of the value of rate constant is much greater than that usually caused by the tunnel effect. It is also generally greater than that due to the possible multiplication factor in the ACT basic equation mentioned by Arnot^{50a} (however later criticized by Mahan^{50b}).

The concept of activated-complex isomerism presented here supposes two or more different activated complexes existing between one common set of reactants and one common set of products. It should be noted that this concept is not equivalent to the classical Curtin-Hammett principle⁵¹. Though the

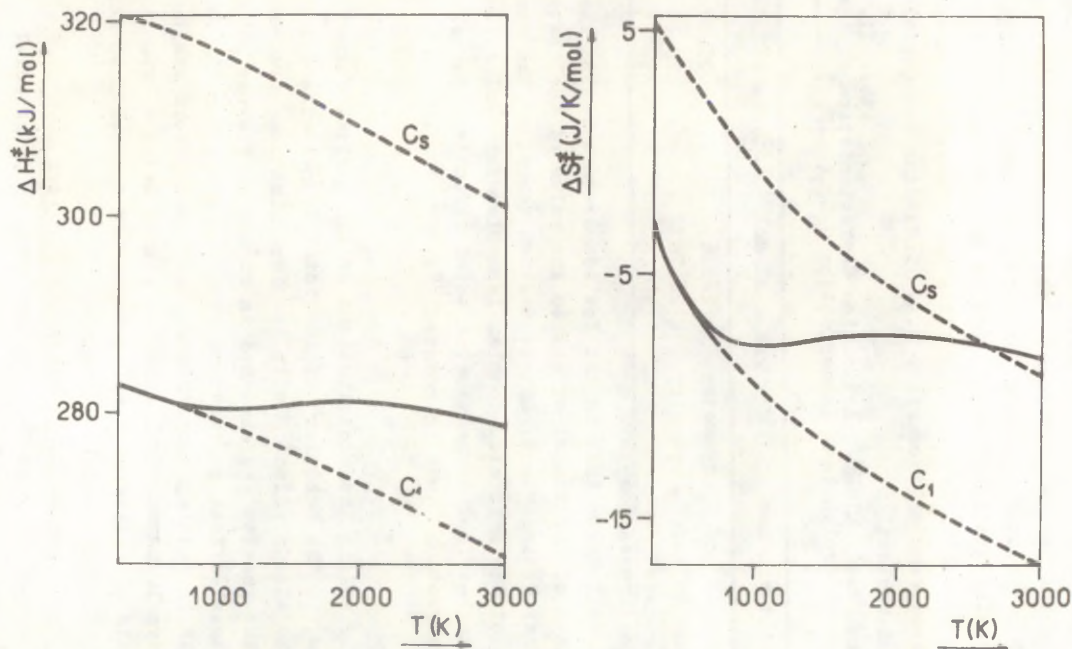


Fig. 4. Temperature dependences of CNDO/2 ΔH^\ddagger_T and ΔS^\ddagger_T terms of the cis-trans isomerization of N_2F_2 for C_s and C_1 activated complexes and for the overall activation process (—).

latter deals with rate processes from the common isomeric set of reactants to different sets of products thus supposing the existence of isomeric activated complexes, it concerns only the partial processes. This is quite natural as different products are within the Curtin-Hammett principle experimentally distinguishable. Let us mention finally that there are possibilities to generalize the presented concept of activated-complex isomerism, e.g. including sequential transition states^{31c}.

Table II.
Partial and Total MINDO/2 Activation Characteristics of the
Chair-to-Boat Cyclohexane Isomerisation $C_6H_{12}(g; D_{3d}) \longrightarrow$
 $C_6H_{12}(g; D_2)$ at 298 K

Rate process	ΔH_T^\ddagger , kJ mol ⁻¹	ΔS_T^\ddagger , J mol ⁻¹ K ⁻¹
Through the AC ^a of C_s symmetry	26.36	25.02
Through the AC ^a of C_2 symmetry	26.78	28.62
Overall process	26.60	32.75

a - AC - activated complex.

It is well known that in the low temperature region the contribution of the tunnel effect to the value of the rate constant may be important. Let us mention therefore the consequences of the activated-complex isomerism for evaluation of the tunnel-effect correction. A total effective tunnel-effect correction was introduced^{49b}:

$$\Gamma = \sum_{i=1}^{n^*} w_i \Gamma_i \quad (20)$$

in order to weight the contributions of the partial correction terms Γ_i . The behavior of the total tunnel-effect correction was also studied^{49b} with the isomerization process (5), and the results are sketched in Figure 5. Whereas the partial tunnel-effect corrections show the usual smooth decrease with increasing temperature, the summary term exhibits an unusual, paradoxical increase; this being a remarkable example of activated-complex isomerism consequences for characteristics of overall processes.

5.3. Formation of Multi-Molecular Clusters

One field of quantum-chemical research is of especial interest in connection with the presented conception of the reaction component isomerism - the field of weak intermolecular interactions. Ample isomerism of multi-molecular clus-

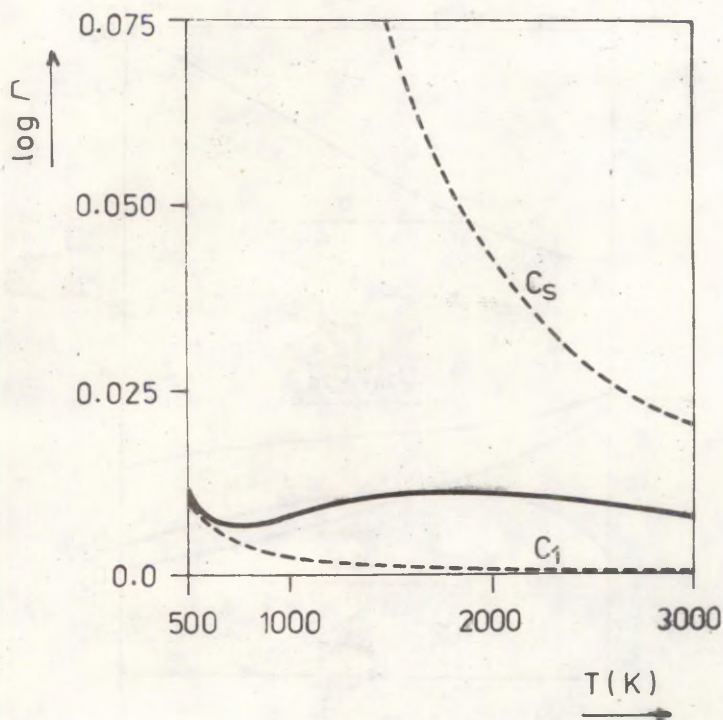


Fig. 5. Temperature dependences of CNDO/2 tunnel-effect corrections f for C_s and C_1 activated complexes and for the overall activation process (—) of cis-trans isomerization of N_2F_2 .

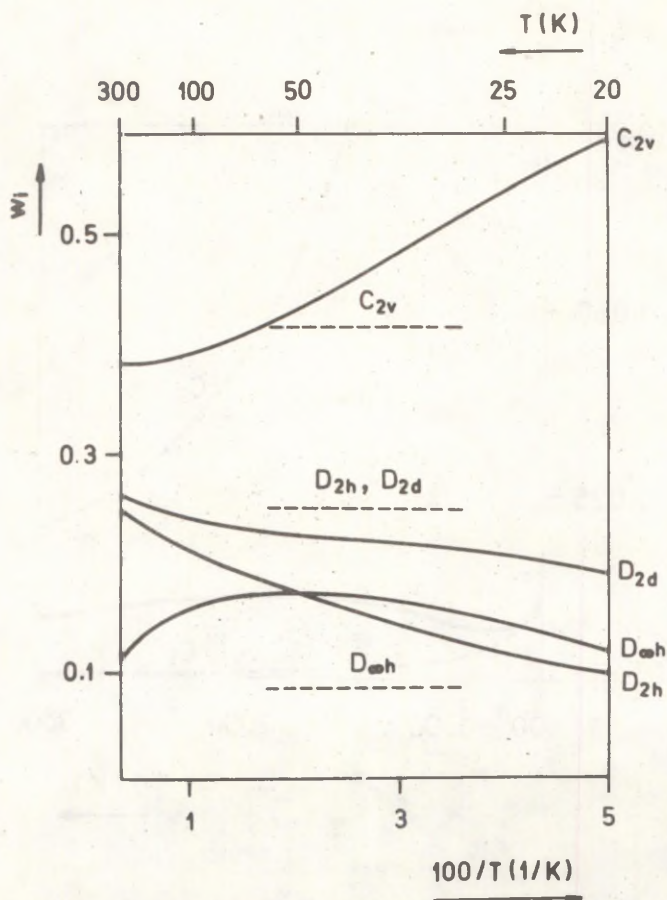


Fig. 6. Temperature dependences of weights w_1 of $(H_2)_2$ with D_{2h} , D_{oh} , D_{2d} , and C_{2v} symmetries (---- approximative values by Bvett and Margenau⁵³).

tere (MMC) is met very often with (e.g. MMC of H_2 (Refs. ^{52a,b}), NO (Refs. ^{52c-e}), H_2O (Refs. ^{52f,g}), CH_3OH (Ref. ^{52h}), and others ^{52i-t}). This isomerism was discovered not only by quantum-chemical methods but also by simple empirical potentials, e.g. ^{44c,52q-t}. Comparable stability of single isomers may frequently be supposed. Temperature dependences of the weight factors of individual MMC may be quite varied ^{49c} due to interchanges in the stability order (Figure 6). Clearly enough, the present experiment can generally yield only the total effective values of the MMC characteristics and the easy establishing of full-inter-isomeric thermodynamic equilibrium is to be quite expected. Thus, the carrying out of theoretical MMC studies up to the level of multiconfiguration thermodynamic functions is quite urgent. Thanks to the thorough study by Owicki et al. ^{52g} information was obtained for example on the isomerism of $(H_2O)_4$. The interplay ^{49c} of partial characteristics of three (known ^{52g}) tetramers is demonstrated in Table III. Both the overall enthalpy and entropy terms differ markedly from those of the energetically most stable isomer (pyramid ^{52g}). Similar results were recently obtained also for other MMC systems ⁵⁴.

Table III.

Partial and Total Theoretical Thermodynamic Characteristics of the Tetramerization of $H_2O(g)$ to Pyramid (P), S_4 Cyclic (C), and Asymmetric Cyclic (A) Isomers of $(H_2O)_4(g)$ at 400 K

Process	ΔH_T° , kJ mol ⁻¹	ΔS_T° , J mol ⁻¹ K ⁻¹
$4H_2O(g) \rightleftharpoons (H_2O)_4(g; P)$	-77.4	-395
$4H_2O(g) \rightleftharpoons (H_2O)_4(g; C)$	-73.0	-330
$4H_2O(g) \rightleftharpoons (H_2O)_4(g; A)$	-59.8	-308
$4H_2O(g) \rightleftharpoons (H_2O)_4(g; \text{Total})$	-74.7	-324

Weights w_i can be expressed ^{45b} in the molecular terms as follows:

$$w_1 = \frac{q_1 \exp \left[-(\epsilon_0^{(1)} - \epsilon_0)/kT \right]}{\sum_{j=1}^m q_j \exp \left[-(\epsilon_0^{(j)} - \epsilon_0)/kT \right]}, \quad (21)$$

where q_k is the partition function of the k -th isomer in the set of m cluster isomers

$$q_k = \sum_j \exp \left[- \frac{\epsilon_j^{(k)} - \epsilon_0^{(k)}}{kT} \right], \quad (22)$$

where the sum is taken over all the eigenstates of the isomer, and the $\epsilon_j^{(k)}$ denote their energies; $\epsilon_0^{(k)}$ is the ground-state energy (the lowest value of the $\epsilon_0^{(k)}$ set is designated ϵ_0). However, sometimes it is recommended as a useful approximation to work with simple steric^{55a} or configurational^{44c,55b} factors:

$$w'_1 = \frac{\exp \left[-\epsilon_0'^{(1)} / kT \right]}{\sum_{j=1}^m \exp \left[-\epsilon_0'^{(j)} / kT \right]}, \quad (23)$$

i.e. to characterize the individual isomers by the depths of the local minima on the potential energy hypersurface, $\epsilon_0'^{(1)}$, only. We have thoroughly studied⁵⁶ interrelations between w_1 and w'_1 values in a set of cluster dimers. The temperature dependences of the weight factors w_1 and simple configurational factors w'_1 of the systems in a broad temperature interval are depicted in Figure 7. It is readily apparent from these results that, even though there are systems for which w'_1 would be an acceptable approximation to w_1 for at least some temperature regions, there are also situations in which this procedure cannot be used at practically any temperature. A good example is the HF-ClF systems (Figure 7d). The applicability of w'_1 is dependent on the cancellation effects in Eq. (21) for which no simple rule can readily be

proposed.

Another common belief in this field concerns the (mentioned above) possibility of approximating the overall ΔH_T^0 and ΔS_T^0 terms by those of (in some sense) "best" single configuration. In order to effectively test the hypothesis, differences $\delta I_{T,E}$ and $\delta I_{T,G}$:

$$\delta I_{T,Y} = \Delta I_T^0 - \Delta I_{T,Y}^0 \quad (I = H \text{ or } S; Y = E \text{ or } G) \quad (24)$$

were introduced⁵⁶, where indices E and G designate the isomers that are most stable at zero temperature and at temperature T, respectively (deficits of the "best" single configuration). The indices correspond to determination of the stability order on the basis of the potential energy scale and the Gibbs energy scale, respectively. The temperature dependences of the $\delta I_{T,E}$ and $\delta I_{T,G}$ functions for the systems of Figure 7 are given in Figure 8. Provided that the most stable structure in the temperature interval from zero to the upper temperature limit chosen is that lying lowest on the potential energy scale, then the courses of functions $\delta I_{T,E}$ and $\delta I_{T,G}$ are essentially identical and continuous. However, when there is a critical point at which a change in the most stable structure on the Gibbs function scale appears (Figs. 7c,d), an interesting situation occurs, leading not only to different courses of functions $\delta I_{T,E}$ and $\delta I_{T,G}$, but also to discontinuous character of function $\delta I_{T,G}$. Apparently, if the discussion is to be limited to a single "best" structure, then, rather than selecting the most stable structure on the potential energy scale, the structure that is most stable at the given temperature on the Gibbs function scale should be chosen (provided that these structures are different). Nonetheless, the results given in Figs. 8a-d clearly indicate that at least at some temperatures deficits $\delta I_{T,Y}$ attain values such that replacement of the overall term by the partial values corresponding to either of the two considered "best" single structures is unacceptable. The possibility that function $\delta I_{T,Y}$ need not necessarily increase with increasing temperature (e.g.

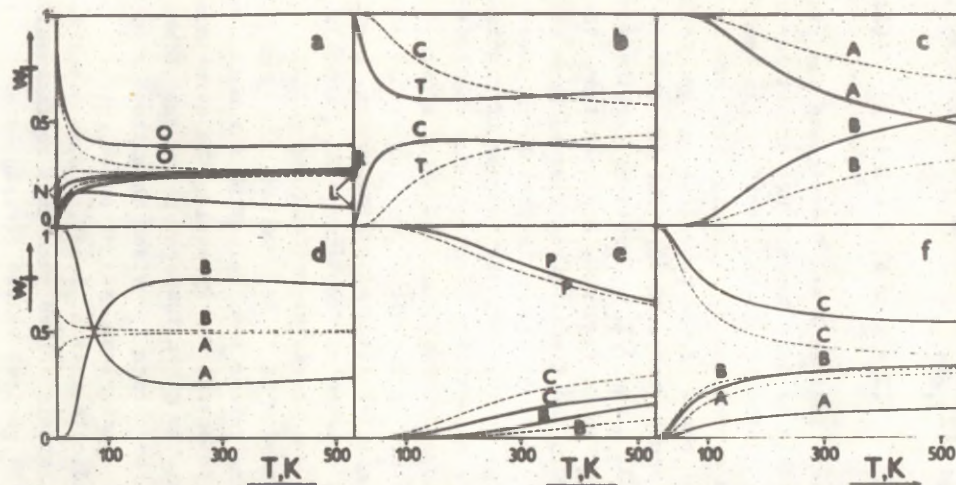


Fig. 7. Temperature dependences of weights w_i (—) and simple configurational factors w'_i (---). (a) Planar-rectangular (R), linear (L), planar-orthogonal (O), and non-planar-orthogonal (N) (H_2O_2); (b) Trans (T) and cis (C) (NO_2); (c) HF.HCl (A) and HCl.HF (B); (d) HF.ClF (A) and ClF.HF (B); (e) Planar-linear (P), closed (C), and bifurcated (B) activated complexes in the (H_2O_2) autoisomerization; (f) Adsorption of O_2 molecule at the center of a graphite hexagon (A), at a carbon atom (B), and at the centre of C-C bond (C).

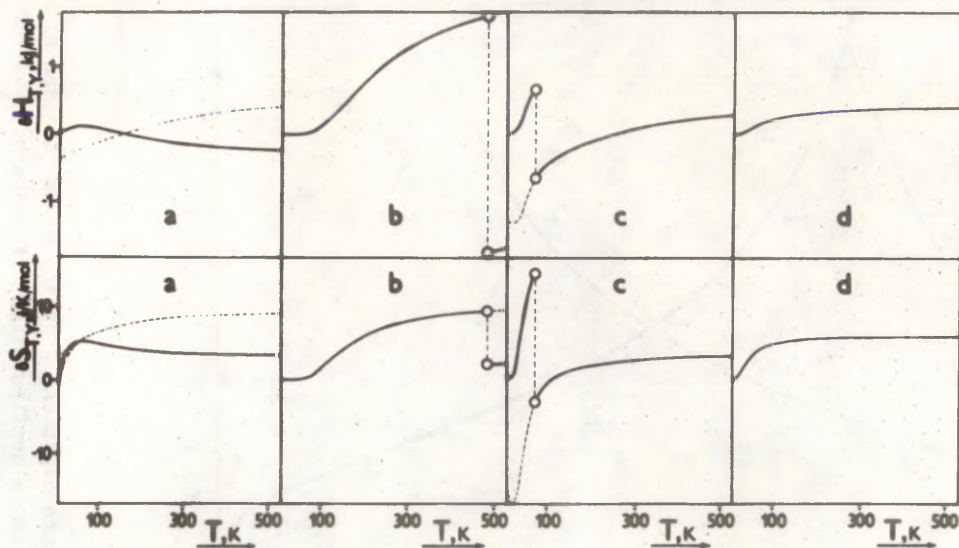


Fig. 8. Temperature dependences of functions $\Delta H_{T,G}$, $\Delta S_{T,G}$ (—) and $\Delta H_{T,B}$, $\Delta S_{T,B}$ (----) for selected cluster formations. (a) $(\text{NO})_2$; (b) HF-HCl ; (c) HF-ClP ; (d) the sorption of O_2 on graphite (cf. Figs. 7b-d,f).

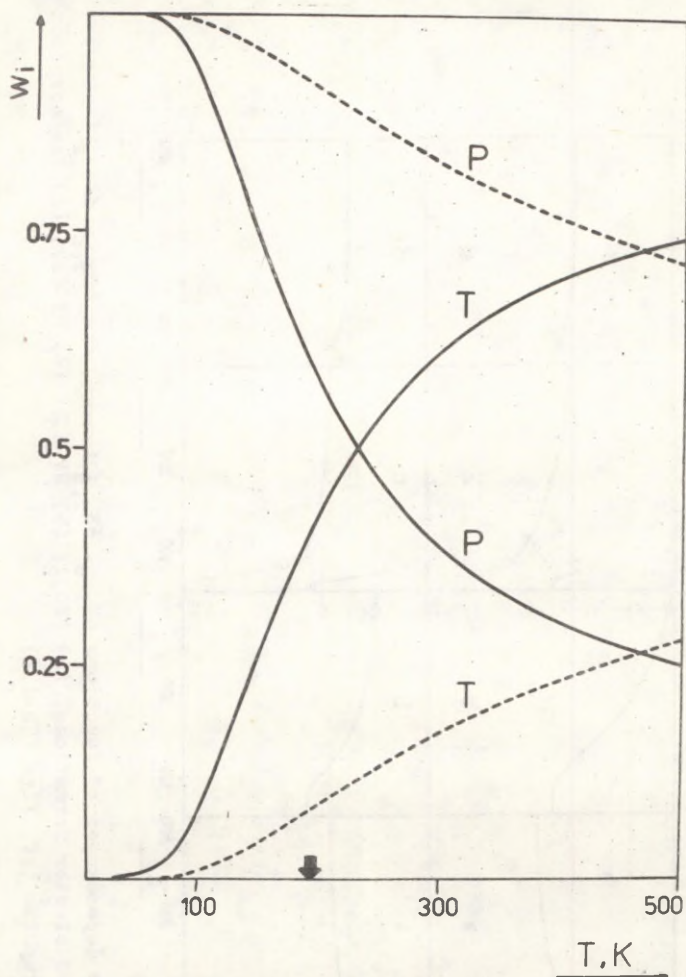


Fig. 9. Temperature dependences of the weight factors w_i and of the simple configurational factors w_i^{\sim} (----) of the parallel (P) and T forms of $(\text{CO}_2)_2$. The arrow indicates the normal sublimation point of CO_2 .

Fig. 8a) is interesting.

The relative stability interchange is apparently an important event for an isomeric set. Quite recently, theoretical study has supplied⁵⁷ us with a very pronounced example of this kind, viz. the $(\text{CO}_2)_2$ system. The ab initio calculations of Brigot et al.^{52k} proved existence of two local minima (called parallel (P) and T form) on potential energy hypersurface of $(\text{CO}_2)_2$ and provided values of harmonic frequencies of intermolecular vibrational normal modes. This amount of information^{52k} enabled construction⁵⁷ of w_1 in the approach of Eq. (21) - see Figure 9. whereas in the region of the lowest temperatures studied the structure P is entirely dominant, a relatively mild temperature increase causes, at first, distinct mutual approaching of the relative stabilities up to the temperature of about 230 K when the equilibrium mixture is equimolar, the T structure being the more stable component above this temperature, although increase in its weight is lower here than below the temperature of inversion of the relative stabilities. Whereas the ratio $w_P/w_T = 3$ is attained at about 150K, the same ratio w_T/w_P is found at the very end of the presented temperature interval. This surprising inversion of relative stabilities of the two isomers is due to contribution of rotational and, especially, vibrational states to the w_1 values. Particularly, the fact that the vibrational frequencies of the T form lie, on the whole, substantially lower than the frequencies of the P form makes it possible to compensate, at relatively low temperatures, for the rather unfavourable (for the T isomer) difference in the potential energy term. After all, this is also well seen in the course of the simple configurational factors. It is particularly important that at the normal sublimation point of CO_2 the two isomeric forms will coexist at comparable concentrations (59% P and 41% T form). In the light of the finding, any possible future experiment in the gas phase near the normal sublimation point of CO_2 should be organized with respect to the possibility of simultaneous presence of the both isomers.

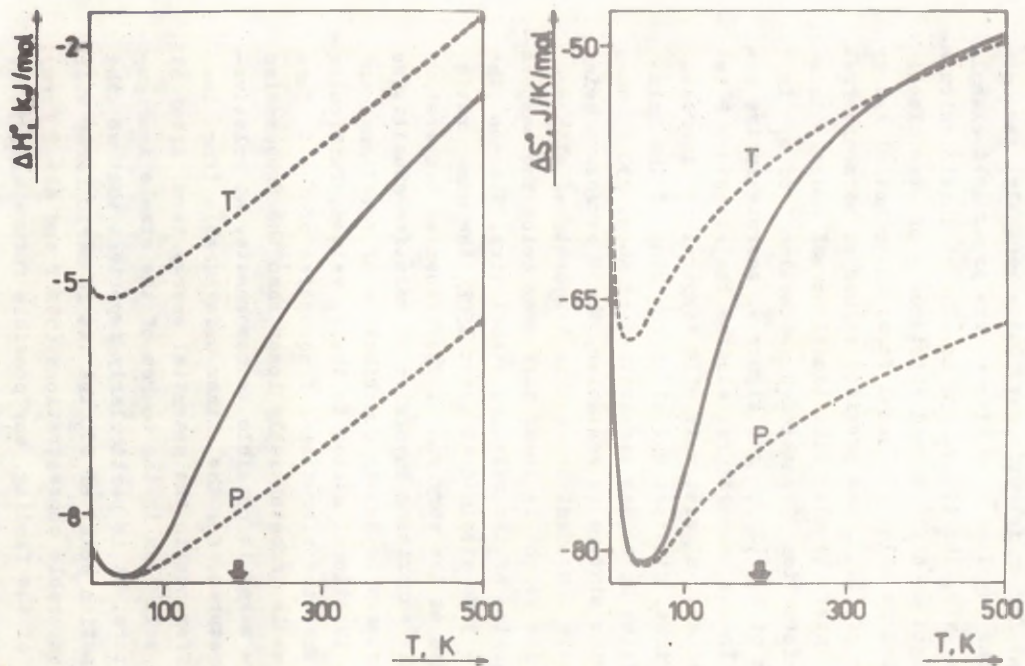


Fig. 10. Temperature dependences of the standard enthalpy ΔH° and entropy ΔS° changes for the partial (P or T - see Fig.9) and overall (—) dimerizations of CO_2 . The arrow indicates the normal sublimation point of CO_2 .

The study⁵⁷ of the relative stabilities of the both isomers of $(\text{CO}_2)_2$ was completed with a prediction of the standard enthalpy and entropy terms of the $(\text{CO}_2)_2$ formation. As it is usual in the field of isomeric multimolecular clusters, depending on the chosen type of experimental technique, it is possible to obtain either the partial values belonging to the individual isomers or the overall values. Temperature dependences of the both types of quantities are presented in Figure 10. Interrelations between these partial and overall terms form an interesting complement of the former results^{44b,45b,49c,55b}, relating the consequences of isomerism for thermodynamics of formation of molecular complexes. At the beginning of the studied temperature interval the overall terms can be well approximated by characteristics of the P isomer, whereas at its end they lie, on the contrary, quite near the terms belonging to the T structure. This fact is surprising in the case of the entropy term; this unusual character is due to considerable difference between the two partial standard entropy terms (almost 17 J/K/mol at 500 K). At the inversion point, ΔH_T° is exactly equal to arithmetic mean of the two partial values, whereas in the case of entropy the arithmetic mean is increased by the value $R \ln 2$. The ΔS_T° term is equal to mere arithmetic mean of the partial values at the temperature as low as 140 K. Obviously, there is no possibility to approximate satisfactorily the overall values, in the whole temperature interval studied, by a single set of any partial characteristics.

5.4. Applications to Heterogeneous Catalysis and Sorption

The cluster approach to the interaction of gases with solid surfaces has provided⁵⁸ us with a great deal of evidence that there are catalytic or sorption processes realized through not only one but several different complexes of the adsorbate and solid adsorbent. Importance of this adsorption-complex isomerism⁵⁹ for confrontation of theoretical outputs with observed data as well as for a deeper interpretation and understanding of the observed data themselves is

again increased by the circumstances that the individual isomeric structures can only exceptionally be distinguished experimentally⁶⁰. Generally, an experimentally determined characteristic of an interaction process must thus be considered as a result of contributions of individual relevant isomeric structures. To enable a correct transition from the partial values primarily yielded by theory to the overall terms resulting from experiment, a weighting treatment is again necessary as in the cases discussed previously. In fact, several different types of adsorption-complex isomerism can be distinguished⁵⁹. First of all, it is a type represented by the isomerism in which formation of a particular adsorption complex does not affect the numbers of sites available for the other kinds of adsorption complexes. This case is established, e.g. when the interaction is represented by a large number of various rigid clusters representing various adsorption sites on the real surface, however, only one adsorption complex is formed on each cluster^{58a}; it is suggested⁵⁹ to call this isomerism type site-caused isomerism. Another important type frequently recognized theoretically^{58b}, is called⁵⁹ as adsorbate-caused isomerism. In the latter case the isomerism is based on different positions of the adsorbed molecule above the site and/or on pronounced differences between isomeric complexes in the manner of structural change of the adsorbed molecule. From the point of view of weighting, the two situations seem to be different, as the latter one clearly supposes an independence between formation of isomeric complexes (formation of a particular adsorption complex decreases the number of the sites available for the other types of complexes). Moreover, various combinations of the both types of isomerism^{58a,b} can frequently take place.

It can be shown⁵⁹ that if the discussion is restricted to sufficiently low coverage (the Henry's Law region), weighting treatments for both above situations become formally identical. The weighting relations themselves are essentially given by Eqs. (13) and (14). The weights w_1 are now expressed in a modified way:

$$w_1 = \frac{s_1 q'_1}{\sum_{j=1}^n s_j q'_j}, \quad (25)$$

where q'_k denote the vibrational partition function of the k -th adsorption complex (the reference energy zero is the state of dissociated complex) and s_k are the steric factors reflecting density of adsorption sites at the surface. Clearly enough, knowledge of not only the depths (and geometrical parameters) of the local minima but also their (harmonic) intersystem vibrational frequencies as well as the surface geometry can be considered to be minimum volume of information sufficient for plausible weighting treatment.

The (physical) interaction of O_2 with graphite can serve^{59a} as an instructive example. The graphite surface was modelled using simple arrays of carbon atoms arranged in a typical hexagonal lattice. More specifically, three types of surface model consisting of 12, 13 and 16 carbon atoms were used (Figure 11). The models were chosen primarily to enable study of three critical adsorption sites conceivable on a real graphite surface. A single orientation of the components of the adsorption complex leading to minimal interaction energy was found for the critical adsorption site of each studied surface model, i.e. threefold site-caused isomerism. These three structures were used^{59a} to demonstrate possible relationships between the partial and overall thermodynamic characteristics in the framework of the concept of perfectly localized adsorption complexes.

The weight factors for the three isomeric structures (A, B, C) in question were evaluated in a broad temperature interval (Figure 7f). Although structure C is the most stable of the three isomeric adsorption complexes considered in the given temperature interval, it is the actual predominant structure only at the lowest temperatures. Already at a temperature of about 210 K, the weight factors of all three structures are of the same order, where only about half the

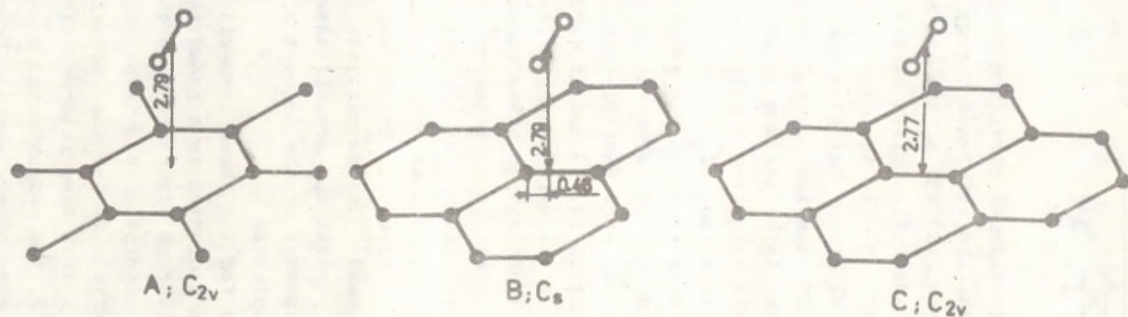


Fig. 11. Optimal structures of model adsorption complexes for physical adsorption of O_2 on graphite (structural data in $10^{-10}m$).

adsorption complexes present under equilibrium conditions are of C type and the rest for the greater part have structure B.

The changes connected^{59a} with transition from partial to overall standard enthalpy and entropy terms can be seen in Figure 12. There are differences between the partial and overall values in the whole given temperature interval. For the enthalpy term, the difference between the partial value corresponding to structure C and the overall value is small at low temperatures, but increases with increasing temperature. This difference is, however, significant for the entropy in the whole interval, and is larger than 5 J/K/mol from temperature of about 110 K. Except for the lowest temperatures, the $T\Delta S_T^0$ term is affected by the phenomenon of isomerism of the adsorption complex to a degree one order larger than for the ΔH_T^0 term. When the qualitative characteristics of the dependence in Figure 12 are considered, not only from the point of view of particular comparison between the theoretical and experimental data for the physical adsorption of oxygen molecules on graphite alone, but as a model study of the conditions for a general interaction process (either physical or chemical) between the gaseous and solid phase leading to isomeric adsorption complexes, it is evident that, at least some of these processes, this isomerism can lead to important results for comparison of the theory and experiment for all three thermodynamic terms ΔH_T^0 , ΔS_T^0 and ΔG_T^0 .

5.5. Inverse Problem

Up to now we have discussed the applications of the weighting treatment which enable the transition from partial reaction characteristics to total ones. However, the scheme is also useful for the solution of the inverse problem^{44b} - the determination of the values of partial characteristics from the total (experimental) ones, especially for the partial enthalpy terms (for both equilibrium and rate processes). The inverse problem is in fact a generalization of the third law analysis which admits isomerism of a reaction component. It requires knowledge of molecular constants for

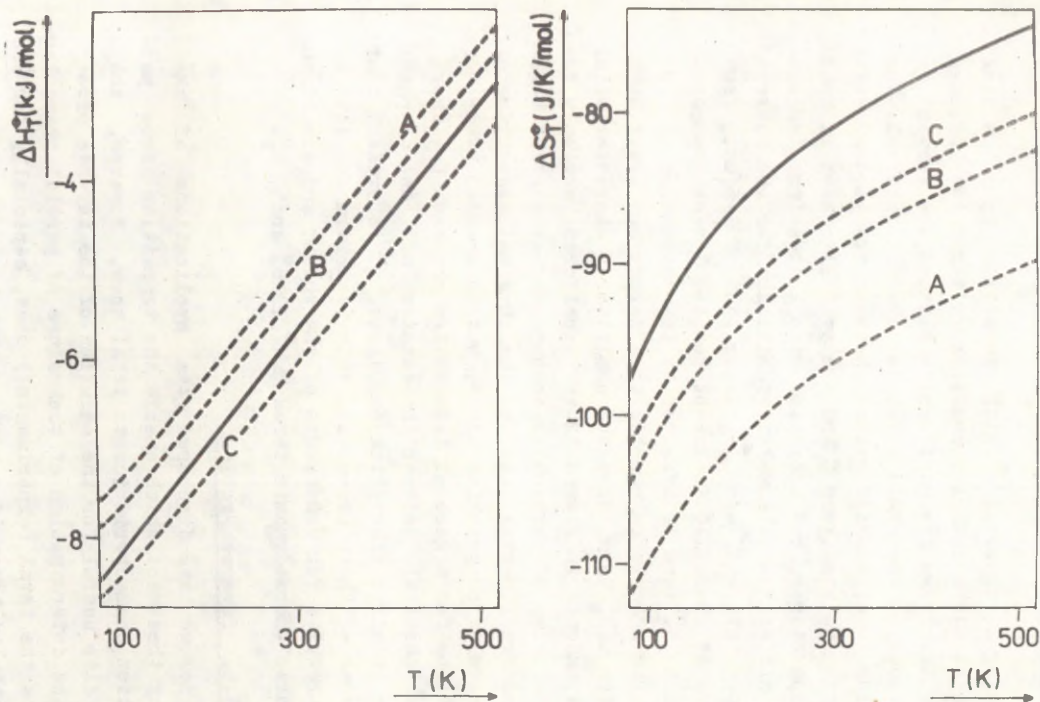


Fig. 12. Temperature dependences of the partial (----) standard enthalpy and entropy terms leading to complexes A, B, and C (Fig. 11) and the overall values ΔH_T° and ΔS_T° .

the construction of partition functions whether from experiment (see the study⁶¹ of N_2F_4 isomers) or from theoretical calculation (cf. the study^{52a,4} of the $(NO)_2$ isomeric system). Especially promising is the application of the inverse scheme with those quantum-chemical methods that fall to provide a satisfactory account of energies but give molecular constants accurate enough for calculation of the entropy.

6. Usefulness of Non-Numerical Techniques

In spite of the wonderful advance of computers and of quantum-chemical methodology itself it is evident that there are certainly limits in the quantitative, numerical approach to the problem of reaction component isomerism. The methods of isomer enumeration⁶² are valuable supplementary means. The theorem of Pólya⁶³ plays a key role in these enumerations. Remarkably enough, this theorem is considered⁶⁴ to be a milestone not only in graph theory but in mathematics as a whole. Both graph theoretical and iterative techniques of isomer enumeration (for reviews, see^{6c,62}) enable the a priori estimation of the order of magnitude of the number of stationary points on the given hypersurface. Moreover, recent progress in these non-numerical approaches makes it possible to respect⁶⁵ molecular nonrigidity with enumerations. However, the enumerations are still not able to distinguish the individual structures as minima, transition states, etc. The works of Krivoshey et al⁶⁶, also belonging to the field of algebraic chemistry, present another promising approach to the study of potential energy hypersurfaces. In this topological approach the multidimensional hypersurface is presented by a graph. In such a representation, all the differential properties are ignored, but the topological properties⁶⁷ of the hypersurface are retained.

7. Concluding Remarks

The phenomenon of reaction component isomerism is to be considered as a general feature of chemical processes, particularly in the field of organic chemistry. However, this isomerism has been identified (or even correctly respected) only rather exceptionally so far in the theoretical studies. This

can be due to the fact that quantum-chemical studies deal at present with relatively small systems and that such an isomerism is not presumed a priori so that the search is limited to a single structure. Further progress would be desirable in the development of mathematical means ensuring the complete location of stationary points on the hypersurface and in improving the quality of descriptions of the motions within individual structures, as well as of the collective motion interconnecting isomers.

Acknowledgements

The author is indebted to Prof. Dr. Ivar Ugi for his interest and valuable comments on the matter. Continued support of the Czechoslovak Academy of Sciences is gratefully acknowledged.

References

1. H.A. M. Snelders, Chem. Weekbl., 60, 217 (1964).
2. Aristoteles, "Metaphysik", Aus dem Griechischen Übersetzt von F. Bassange, Aufbau-Verlag, Berlin, 1960, paragraph 985^b.
3. V.B. Kasinov, "Biological Isomerism", Nauka, Leningrad, 1973, (in Russian).
4. S.M. Polikanov, "Isomerism of Atomic Nucleus Shape" Atomisdat, Moscow, 1977, (in Russian).
5. J.J. Berzelius, Ann. Phys. Chem., 19 (der ganzen Folge 25), 305 (1830).
6. a) G.W. Wheland, "Advanced Organic Chemistry", 3rd Ed., John Wiley & Sons, New York, 1960; b) K. Mislow, "Introduction to Stereochemistry", W.A. Benjamin, Inc., New York, 1966; c) D.H. Rouvray, Chem. Soc. Rev., 3, 355 (1974).
7. a) J. Gažo, Pure Appl. Chem., 38, 279 (1974); b) K. Mislow, Acc. Chem. Res., 9, 26 (1976).

8. a) I.W.D. Hackh, Chem. News, 121, 85 (1920), Chem. Abstr., 14, 3405 (1920); b) A.C. Lunn and J.K. Senior, J. Phys. Chem., 33, 1027 (1929); c) P.P.A. Tellegen, Chem. Weekbl., 32, 3, 40 (1935), Chem. Abstr. 29, 3295⁷, 3295⁸ (1935); d) M. Bargalló, Ciencia (Mex.) 10, 257 (1950), Chem. Abstr., 45, 78331 (1951); e) R.L. Bent, J. Chem. Educ., 30, 220, 328 (1953); f) J.J. Jennen, Ind. Chim. Belge, 19, 1051 (1954), 20, 1067 (1955); g) W.K. Noyce, J. Chem. Educ., 38, 23 (1961).
9. a) G. Ege, Naturwissenschaften, 58, 247 (1971); I. Ugi, P. Gillespie, and C. Gillespie, Trans. N.Y. Acad. Sci., 34, 416 (1972); c) E. Ruch, Theor. Chim. Acta, 11, 183 (1968); d) E. Ruch, W. Hässelbarth, and B. Richter, *ibid.*, 12, 288 (1970); e) W. Hässelbarth and E. Ruch, *ibid.*, 29, 259 (1973); f) K. Mislow, Bull. Soc. Chim. Belg., 86, 595 (1977).
10. J. Dugundji, P. Gillespie, D. Marquarding, I. Ugi, and P. Ramirez, in A.T. Balaban, Ed., "Chemical Applications of Graph Theory", Academic Press, London, 1976.
11. a) J.W. McIver, Jr. and A. Komornicki, J. Am. Chem. Soc., 94, 2625 (1972); b) O. Ermer, Structure and Bonding, 27, 161 (1976); c) J.N. Murrell, *ibid.*, 32, 93 (1977); d) P.G. Mezey, Progr. Theor. Org. Chem., 2, 127 (1977).
12. a) J.G. Nourse and K. Mislow, J. Am. Chem. Soc., 97, 4571 (1975); b) J.W. Essam, J.W. Kennedy, M. Gordon and P. Whittle, J. Chem. Soc., Faraday Trans. II, 73, 1289 (1977), and references therein; c) D. Poppinger, L. Radom, and J.A. Pople, J. Am. Chem. Soc., 99, 7806 (1977); d) C.W. Jefford, J. Mareda, J.-C. Perlberger, and U. Burger, *ibid.*, 101, 1370 (1979).
13. A.T. Balaban, Rev. Roum. Chim., 12, 875 (1967).
14. a) J.S. Wright, Can. J. Chem., 51, 139 (1973); b) E.R. Talaty, A.K. Schwartz, and G. Simons, J. Am. Chem. Soc., 97, 972 (1975); c) P.G. Burton, Int. J. Quantum Chem., Quantum Chem. Symp., 11, 207 (1977); d) Karlström, S. Engström, and B. Jönsson, Chem. Phys. Lett., 57, 390 (1978), and references therein.

15. Z. Slanina, "Theoretical Aspects of the Phenomenon of Chemical Isomerism", Academia, Prague 1981, (in Czech), and references therein.
16. a) M. Born and R. Oppenheimer, Ann. Phys., 4. Folge, 84, (der ganzen Reihe 389), 457 (1927); b) M. Born, Nachr. Akad. Wiss. Göttingen, Math. Phys. Kl., No 6, (1951); c) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices", Oxford University Press, London, 1954, p.406; d) I. Özkan and L. Goodman, Chem.Rev., 79, 275 (1979).
17. a) E.L. Muetterties, Inorg. Chem., 4, 769 (1965); b) I.B. Bersuker, "Structure and Properties of Coordination Compounds", Khimiya, Leningrad, 1971, p. 192, (in Russian).
18. a) W.E. von Doering and W.R. Roth, Angew. Chem., 75, 27 (1963); b) F.A. Cotton, Acc. Chem. Res., 1, 257 (1968); c) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, Acc. Chem. Res., 4, 288 (1971); d) O. Bastiansen, K. Kveseth, and H. Møllendal, Top. Curr. Chem., 81, 99 (1979); e) G.O. Sørensen, ibid., 82, 97 (1979).
19. a) A.D. Liehr, J. Phys. Chem., 67, 471 (1963); b) S.H. Bauer in D. Henderson, Ed., "Physical Chemistry, An Advanced Treatise", Vol. IV, Academic Press, New York, 1970, p.7.
20. a) K. Mislow and P. Bickart, Isr. J. Chem., 15, 1 (1976/77); b) E.L. Eliel, ibid., 15, 7 (1976/77).
21. a) R.G. Woolley, Advan. Phys., 25, 27 (1976); b) R.G. Woolley, Chem. Phys. Lett., 44, 73 (1976); c) R.G. Woolley and B.T. Sutcliffe, ibid., 45, 393 (1977); d) R.G. Woolley, Int. J. Quantum Chem., 12, Suppl. 1, 307 (1977); e) H. Essén, ibid., 12, 721 (1977); f) R.G. Woolley, J. Am. Chem. Soc., 100, 1073 (1978); g) R.G. Woolley, Chem. Phys. Lett., 55, 443 (1978).
22. a) S. Aronowitz, Int. J. Quantum Chem., 14, 253 (1978) b) E.B. Wilson, Int. J. Quantum Chem., Quantum Chem. Symp., 13, 5 (1979).

23. a) R.F.W. Bader and R.A. Gangi in R.N. Dixon and C. Thomson, Eds., "Theoretical Chemistry, Specialist Periodical Reports", Vol. 2, The Chemical Society, London, 1975; ;
 b) A. Devaquet, Fortschr. Chem. Forsch., 54, 1 (1975);
 c) E.E. Nikitin and L. Zúlicka, "Selected Topics of the Theory of Chemical Elementary Processes", Springer-Verlag, Berlin, 1978.
24. a) C.J.H. Schutte, Structure and Bonding, 9, 213 (1971);
 b) M. Kanakavel, J. Chandrasekhar, S. Subramanian, and S. Singh, Theor. Chim. Acta, 43, 185 (1976), and references therein.
25. a) P. Pulay, Mol. Phys., 17, 197 (1969), 18, 473 (1970), 21, 329 (1971); b) J.W. McIver, Jr. and A. Komarnicki, Chem. Phys. Lett., 10, 303 (1971).
26. P. Pulay in H.F. Schaefer, III, Eds., "Applications of Electronic Structure Theory", Plenum Press, New York, 1977 .
27. a) S. Kato and K. Morokuma, Chem. Phys. Lett., 65, 19 (1979); b) J.D. Goddard, N.C. Handy, and H.F. Schaefer, III, J. Chem. Phys., 71, 1525 (1979), R.N. Camp, H.F. King, J.W. McIver, Jr., and D. Mullally, J. Chem. Phys., 79, 1088 (1983), D.J. Fox, Y. Osamura, M.R. Hoffmann, J.P. Gaw, G. Fitzgerald, Y. Yamaguchi, and H.F. Schaefer, III, Chem. Phys. Lett., 102, 17 (1983);
 c) J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, Int. J. Quantum Chem., Quantum Chem. Symp., 13, 225 (1979); d) K. Yamashita, A. Tachibana, T. Yamabe, and K. Fukui, Chem. Phys. Lett., 69, 413 (1980); e) B.R. Brooks, W.D. Laiding, P. Saxe, J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, III, J. Chem. Phys., 72, 4652 (1980);
 f) R. Krishnan, H.B. Schlegel, and J.A. Pople, J. Chem. Phys., 72, 4654 (1980).
28. a) E.B. Wilson, J.C. Decius, and P.C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955; b) M.A. Eliahevich, Dokl. Akad. Nauk SSSR, 28, 605 (1940).
29. J. Drowart, R.P. Burns, G. De Maria, and M.G. Inghram, J. Chem. Phys., 31, 1131 (1959).

30. Z. Slanina and R. Zahradnik, *J. Phys. Chem.*, 81, 2252 (1977).
31. a) R. Daudel, "Quantum Theory of Chemical Reactivity", D. Reidel Publishing Company, Dordrecht, 1973; b) S. Beran, P. Čársky, P. Hobza, J. Panciř, R. Polák, Z. Slanina, and R. Zahradnik, *Usp. Khim.*, 47, 1905 (1978), *Russ. Chem. Rev.*, 47, 1025 (1978); c) G.M. Zhidomirov, A.A. Bagaturjanc, and I.A. Abbronin, "Applied Quantum Chemistry", Khimiya, Moscow, 1979 (in Russian); d) R. Daudel, A. Pullman, L. Salem, and A. Veillard, Eds., "Quantum Theory of Chemical Reactions", Vol. 1, D. Reidel, Dordrecht, 1980; e) K. Jug, *Theor. Chim. Acta*, 54, 263 (1980).
32. E. Clementi, *Bull. Soc. Chim. Belg.*, 85, 969 (1976).
33. a) Z. Slanina, P. Berák, and R. Zahradnik, *Collect. Czech. Chem. Commun.*, 42, 1 (1977); b) M.J.S. Dewar and G.P. Ford, *J. Am. Chem. Soc.*, 99, 7822 (1977).
34. S.G. Frankiss and J.H.S. Green in M.L. McGlashan, Ed., "Chemical Thermodynamics, A Specialist Periodical Report", The Chemical Society, London, 1973.
35. a) W.H. Rodebush, *Chem. Rev.*, 2, 319 (1931); b) L.S. Kassel, *ibid.*, 18, 277 (1936); c) E.B. Wilson, Jr., *ibid.*, 27, 17 (1940); d) I.N. Godnew, "The Calculation of Thermodynamic Functions from Molecular Data", GITTL, Moscow, 1955, (in Russian); e) H.W. Woolley, *J. Res. Nat. Bur. Stand.*, 56, 105 (1956).
36. a) H. Eyring, *J. Chem. Phys.*, 3, 107 (1935); b) M.G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 31, 875 (1935),.
37. a) D.G. Truhlar and A. Kuppermann, *Chem. Phys. Lett.*, 2, 269 (1971); b) M. Baer, U. Halavet, and A. Persky, *J. Chem. Phys.*, 61, 5122 (1974); c) D.G. Truhlar, J.A. Merrick, and J.F. Duff, *J. Am. Chem. Soc.*, 98, 6771 (1976); d) H. Essén, G.D. Billing, and M. Baer, *Chem. Phys.*, 17, 443 (1976); e) W.H. Miller, *Acc. Chem. Res.*, 2, 306 (1976); f) J.N.L. Connor, W. Jakubetz, and A. Lagana, *J. Phys. Chem.*, 83, 73 (1979); g) D.G. Truhlar, *ibid.*, 83, 188 (1979).

38. a) Z. Slanina, *Radiochem. Radioanal. Lett.*, 22, 291 (1975); b) Z. Slanina, *Advan. Quantum Chem.*, 13, 89 (1981).
39. a) K. Denbigh, "The Principles of Chemical Equilibrium", The University Press, Cambridge, 1961, p.112; b) J.S. Rowlineon, "The Perfect Gas", Pergamon Press, Oxford, 1963, p. 77.
40. a) J.G. Aston, O. Szasz, H.W. Woolley, and F.G. Brickwedde, *J. Chem. Phys.*, 14, 67 (1946); b) C.W. Beckett, K.S. Pitzer, and R. Pitzer, *J. Am. Chem. Soc.*, 69, 2488 (1947); c) J.P. McCullough, H.L. Finke, W.N. Hubbard, W.D. Good, R.E. Pennington, J.F. Messerly, and G. Waddington, *ibid.*, 76, 2661 (1954); d) J. Lielmess and A. Bondi, *Chem. Eng. Sci.*, 20, 706 (1965) e) D.W. Scott and G.A. Crowder, *J. Chem. Phys.*, 46, 1054 (1967); f) F. Heatley, *J. Chem. Soc., Faraday Trans. II*, 68, 2097 (1972); g) S.G. Frankiss, *ibid.*, 70, 1516 (1974); h) D.A.C. Comp-ton, *J. Chem. Soc., Perkin Trans. II*, 1307 (1977).
41. a) V.M. Volkenshtein, "Configurational Statistics of Polymeric Chains", Acad. Sci. USSR, Moscow, 1959, (in Russian); b) P.J. Flory, "Statistical Mechanics of Chain Molecules", Wiley-Interscience, New York, 1969.
42. a) W.C. Herndon, J. Feuer, and L.H. Hall, *Theor. Chim. Acta*, 11, 178 (1968); b) P.K. Pearson, H.F. Schaefer, III, J.H. Richardson, L.H. Stephenson, and J.I. Brauman, *J. Am. Chem. Soc.*, 96, 6778 (1974); c) J.A. Pople, Tetra-hedron, 30, 1605 (1974); d) G. Favini, C. Rubino, and R. Todeschini, *J. Mol. Struc.*, 41, 305 (1977); e) W.J. Hehre in H.F. Schaefer, III, Ed., "Applications of Electronic Structure Theory", Plenum Press, New York, 1977; f) N.D. Epiotis, W.R. Cherry, S. Shaik, R.L. Yates, and F. Bernardi, *Fortschr. Chem. Forsch.*, 70, 1 (1977); g) W.J. Bouma, D. Poppinger, and L. Radom, *J. Am. Chem. Soc.*, 99, 6443 (1977); h) W.D. Laiding and H.F. Schaefer, III, *ibid.*, 100, 5972 (1978); i) W.J. Bouma and L. Radom, *Aust. J. Chem.*, 31, 1649 (1978); j) T.J. Zielinski and R. Rein, *Int. J. Quantum Chem.*, 14, 851 (1978);

- k) J.B. Moffat, *J. Mol. Struct.*, 52, 275 (1979);
 l) S. Green and E. Herbst, *Astrophys. J.*, 229, 121 (1979); m) D.A. Dougherty and K. Mislow, *J. Am. Chem. Soc.*, 101, 1401 (1979); n) M. Kausch and P.R. von Schleyer, *J. Comput. Chem.*, 1, 94 (1980); o) L.T. Redmon, G.B. Purvis, III, and R.J. Bartlett, *J. Chem. Phys.*, 72, 986 (1980); p) K.B. Lipkowitz, R.M. Larter, and D.B. Boyd, *J. Am. Chem. Soc.*, 102, 85 (1980).
43. a) H.A. Scheraga, *Chem. Rev.*, 71, 195 (1971); b) P.N. Lewis, F.A. Momany, and H.A. Scheraga, *Isr. J. Chem.*, 11, 121 (1973); c) N. Go and H.A. Scheraga, *Macromolecules*, 6, 525 (1973); d) N.L. Allinger, M.J. Hickey, and J. Kao, *J. Am. Chem. Soc.*, 98, 2741 (1976); e) D.N.J. White and C. Morrow, *Tetrahedron Lett.*, 3385 (1977); f) S.R. Niketic and K. Rasmussen, "The Consistent Force Field, A Documentation, "Springer-Verlag, Berlin, 1977; g) N.C.P. Hald and K. Rasmussen, *Acta Chem. Scand. A.*, 32, 879 (1978); h) D.A. Dougherty, F.M. Llort, K. Mislow, and J.F. Blount, *Tetrahedron*, 34, 1301 (1978); i) L.G. Dunfield, A.W. Burgess, and H.A. Scheraga, *J. Phys. Chem.*, 82, 2609 (1978); j) D.N.J. White and C. Morrow, *Comput. Chem.*, 3, 33 (1979); k) G.A. Jeffrey and R. Taylor, *J. Comput. Chem.*, 1, 99 (1980).
44. a) L.E. Orgel and R.S. Mulliken, *J. Am. Chem. Soc.*, 79, 4839 (1957); b) Z. Slanina, *Collect. Czech. Chem. Commun.*, 40, 1997 (1975); c) M.R. Hoare, *Advan. Chem. Phys.*, 40, 49 (1979).
45. a) W. Oñ and H.A. Scheraga, *J. Chem. Phys.*, 51, 4751 (1969); b) Z. Slanina, *Int. J. Quantum Chem.*, 16, 79 (1979); c) R.H. Davies, D.A. Smith, D.J. McNeillie, and T.R. Marris, *Int. J. Quantum Chem., Quantum Biol. Symp.*, 6, 203 (1979).
46. a) G.H. De Puy, V.M. Bierbaum, L.A. Flippin, J.J. Grabowski, G.K. King, and R.J. Schmitt, *J. Am. Chem. Soc.*, 101, 6443 (1979); b) Z. Slanina and Z.R. Grabowski, *Collect. Czech. Chem. Commun.*, 44, 3441 (1979); c) J.S. Chang, A.C. Baldwin, and D.M. Golden, *J. Chem. Phys.*, 71, 2021 (1979).

47. a) Z. Slanina, J. Schlanger, and R. Zahradnik, *Collect. Czech. Commun.*, 41, 1864 (1976); b) C.B. Colburn, F.A. Johnson, and C. Haney, *J. Chem. Phys.*, 43, 4526 (1965).
48. a) M.S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, 90, 2471 (1968); b) J.M. Howell and L.J. Kirschenbaum, *ibid.*, 98, 877 (1976); c) Z. Slanina, *Chem. Phys. Lett.*, 50, 418 (1977); d) G. Favini and R. Todeschini, *J. Mol. Struc.*, 50, 191 (1978); e) A. Komornicki and J.W. McIver, Jr., *J. Am. Chem. Soc.*, 95, 4512 (1973); f) W.J. Hehre, *ibid.*, 96, 5207 (1974); g) W.W. Scheeller, *ibid.*, 97, 1978 (1975); h) L. Valko and P. Kovařík, *J. Phys. Chem.*, 80, 19 (1976); i) R. Seeger, R. Krishnan, J.A. Pople, and P.R. von Schleyer, *J. Am. Chem. Soc.*, 99, 7103 (1977); j) R. Gimiraglia, M. Persico, and J. Tomasi, *Theor.Chim. Acta*, 49, 13 (1978); k) W.J. Bouma, M.A. Vincent, and L. Radom, *Int. J. Quantum Chem.*, 14, 767 (1978); l) V.V. Penkevsky, *Dokl. Akad. Nauk SSSR*, 243, 375 (1978); m) M. R. Peterson and I.G. Csizmadia, *J. Am. Chem. Soc.*, 101, 1076 (1979); n) W. Schleker and J. Fleischhauer, *Z.Naturforsch.*, 34a, 488 (1979).
49. a) Z. Slanina, *Collect. Czech. Chem. Commun.*, 42, 1914 (1977); b) Z. Slanina, *ibid.*, 43, 2358 (1978); c) Z. Slanina, *Advan. Mol. Relax. Interact. Process.*, 14, 133 (1979).
50. a) G.L. Arnot, *J. Chem. Educ.*, 49, 480 (1972); b) B.H. Mahan, *ibid.*, 51, 709 (1974),
51. a) D.Y. Curtin, *Rec. Chem. Progr.*, 15, 111 (1954); b) L.P. Hammett, "Physicalische Organische Chemie", Akademie-Verlag, Berlin, 1976 , p.121.
52. a) E. Kochanski, B. Roos, P. Siegbahn, and M.H. Wood, *Theor. Chim. Acta*, 32, 151 (1973); b) M. Jaszuński, E. Kochanski, and P. Siegbahn, *Mol. Phys.*, 33, 139 (1977); c) S. Skaarup, P.N. Skancke, and J.E. Boggs, *J. Am. Chem. Soc.*, 98, 6106 (1976); d) Z. Slanina, *Chem. Phys. Lett.*, 52, 117 (1977); e) Z. Slanina, *Collect. Czech. Chem. Commun.*, 43, 1974 (1978); f) H. Kistenmacher, G.C. Lie, H. Popkie, and E. Clementi, *J. Chem. Phys.*, 61, 546 (1974);

- g) J.C. Owicki, L.L. Shipman, and H.A. Scheraga, *J. Phys. Chem.*, 79, 1794 (1975); h) L.A. Curtiss, *J. Chem. Phys.* 67, 1144 (1977); i) Z. Slanina, *Collect. Czech. Chem. Commun.*, 39, 3187 (1974); j) B. Jönsson, G. Karlström, and H. Wennerström, *Chem. Phys. Lett.*, 30, 58 (1975); k) N. Brigot, S. Odiet, S.H. Walmsley, and J.L. Whitten, *ibid.*, 42, 157 (1977), N. Brigot, S. Odiet, and S.H. Walmsley, *ibid.*, 88, 543 (1982); l) L.A. Curtiss, *Int. J. Quantum Chem., Quantum Chem. Symp.*, 11, 459 (1977); m) J. Prieze and E. Kochanski, *J. Am. Chem. Soc.*, 99, 7352 (1977), 100, 6609 (1978); n) L.A. Curtiss, D.J. Frurip, and M. Blander, *ibid.*, 100, 79 (1978); o) D.J. Frurip, L.A. Curtiss, and M. Blander, *J. Phys. Chem.*, 82, 2555 (1978); p) P. Hobza, K. Boček, H.J. Hofmann, Z. Slanina, and R. Zahradnik, *Collect. Czech. Chem. Commun.*, 43, 665 (1978); q) M.R. Hoare and P. Pal, *Nature Phys. Sci.*, 230, 5 (1971); r) M.R. Hoare and P. Pal, *Advan. Phys.*, 20, 161 (1971); s) M.R. Hoare and P. Pal, *Nature Phys. Sci.*, 236, 35 (1972); t) J.B. Kaelberer, R.D. Ettere, and J.C. Raich, *Chem. Phys. Lett.*, 41, 580 (1976).
53. A.A. Evett and H. Margenau, *Phys. Rev.*, 90, 1021 (1953), G.A. Gallup, *Mol. Phys.*, 33, 943 (1977), G.A. Gallup, *J. Chem. Phys.*, 66, 2252 (1977).
54. a) M.R. Hoare and J. McInnes, unpublished, quoted in Ref. ^{44c}; b) Z. Slanina, *Advan. Mol. Relax. Interact. Process.*, 19, 117 (1981).
55. a) K.S. Pitzer, *J. Chem. Phys.*, 8, 711 (1940); b) D.J. McGinty, *Chem. Phys. Lett.*, 13, 525 (1973), J.J. Burton, *ibid.*, 17, 199 (1972), J.J. Burton, *J. Chem. Soc., Faraday Trans. II*, 69, 540 (1973), S.H. Bauer and D.J. Frurip, *J. Phys. Chem.*, 81, 1015 (1977).
56. Z. Slanina in "Proc. 13th Int. Symp. Rarefied Gas Dynamics", Plenum Press, New York (in press).
57. Z. Slanina, *J. Mol. Struct.*, 94, 401 (1983).
58. a) A.J. Bennett, B. McCarroll, and R.P. Messmer, *Phys. Rev. B.*, 3, 1397 (1971), M.R. Hayns, *Theor. Chim. Acta*, 39, 61 (1975), C.W. Bauschlicher, Jr., C.F. Bender, and

- H.F. Schaefer, III, *Chem. Phys.*, 15, 227 (1976); A. Gavezotti and M. Simonetta, *Chem. Phys. Lett.*, 48, 434 (1977), G.V. Gadiyak, A.A. Karpushin, Ju. N. Morekov, and S.M. Repinskij, *Zh. Fiz. Khim.*, 54, 419 (1980), G.B. Hoflund and R.P. Merrill, *J. Phys. Chem.*, 85, 2037 (1981); R. Dovesi, C. Pisani, and C. Roetti, *Chem. Phys. Lett.*, 81, 498 (1981), G.F. Tantardini and M. Simonetta, *Surf. Sci.*, 105, 517 (1981), D. Post and E.J. Baerends, *ibid.*, 109, 167 (1981), K. Matsumura, S. Yamabe, Y. Yanagisawa, and R. Huzimura, *ibid.*, 109, 311 (1981), P. Marcusson, C. Opitz, and H. Müller, *ibid.*, 111, L657 (1981); b) A. B. Anderson and R. Hoffmann, *J. Chem. Phys.*, 61, 4545 (1974), A.B. Anderson, *J. Am. Chem. Soc.*, 99, 696 (1977), Z. Slanina, S. Beran, and P. Knížek, in "Heterogenous Catalysis", Part 2, D. Shopov, A. Andreev, A. Palazov, and L. Petrov, Eds., Publishing House of the Bulgarian Academy of Sciences, Sofia, 1979.
59. a) Z. Slanina, *Theor. Chim. Acta*, 60, 589 (1982); b) Z. Slanina, *Zh. Fiz. Khim.*, 57, 1164 (1983). Z. Slanina, *Int. J. Quantum Chem.*, 23, 1563 (1983).
60. J.E. Demuth, K. Christmann, and P.N. Sanda, *Chem. Phys. Lett.*, 76, 201 (1980), G.B. Fisher, *ibid.*, 79, 452 (1981), E. Umbach and D. Menzel, *ibid.*, 84, 491 (1981).
61. Z. Slanina, *J. Fluorine Chem.*, 6, 465 (1975) .
62. a) D.H. Rouvray, *Endeavour*, 34, 28 (1975); b) R.C. Read, in A.T. Balaban, ed., "Chemical Applications of Graph Theory", Academic Press, London, 1976; c) A.T. Balaban, *ibid.*
63. G. Polya, *C.R. Acad. Sci.*, 201, 1167 (1935).
64. N.L. Biggs, E.K. Lloyd, and R.J. Wilson, "Graph Theory 1736-1936", Clarendon Press, Oxford, 1976, p. 68.
65. a) J.E. Leonard, G.S. Hammond, and H.E. Simmons, *J. Am. Chem. Soc.*, 97, 5052 (1975); b) R.L. Flurry, Jr., *J. Phys. Chem.*, 80, 777 (1976); c) J.E. Leonard, *ibid.*, 81, 2212 (1977); d) K. Balasubramanian, *Theor. Chim. Acta*, 51, 37 (1979), 53, 129 (1979).

66. a) I.V. Krivoshey, Zh. Strukt. Khim., 10, 316 (1969);
b) V.I. Zhuravlev and I.V. Krivoshey, L.A. Sleta, *ibid.*,
16, 951 (1975); c) I.V. Krivoshey, *ibid.*, 17, 227 (1976);
d) I.V. Krivoshey and L.A. Sleta, Theor. Chim. Acta, 43,
165 (1976).
67. P.G. Mezey, Theor. Chim. Acta, 54, 95 (1980), 58, 309
(1981), 60, 97 (1981), 60, 409 (1982), P.G. Mezey, Int.
J. Quantum Chem., Quantum Biol. Symp., 8, 185 (1981),
P.G. Mezey, Int. J. Quantum Chem., 22, 101 (1982), P.G.
Mezey, Chem. Phys. Lett., 82, 100 (1981), 86, 562 (1982),
P.G. Mezey, in R.B. King, Ed., "Chemical Applications of
Topology and Graph Theory", Elsevier, Amsterdam, 1983,
P.G. Mezey, Can. J. Chem., 62, XXX (1984).

KINETICS OF FORMATION OF GRIGNARD REAGENT
WITH SMALL ADDITIONS OF ETHYL ETHER.

A. Tuulmets, M. Hõrak, E. Pill, and A. Riikoja
Dept. of Organic Chemistry, Tartu State University,
202400, Tartu, Est. SSR

Received Jan. 14, 1985

A formerly unknown course of the reaction of butyl bromide with magnesium in toluene in the presence of the amounts of ethyl ether (less than one mole to a mole of the halide) has been found. After a rapid formation of the monosolvated Grignard reagent a slow completion of the reaction occurs under the influence of solvated alkylmagnesium halide present. Quantitative characteristics of both reaction stages are determined.

In our previous report¹ we investigated the kinetics of the reaction of n-butyl halides with magnesium in mixtures of toluene with some organic bases. It was revealed that at high concentrations a base influenced the reaction rate by altering the viscosity of the medium. At low contents of the base (less than two moles to a mole of the halide) a rough decrease of the rate constant, accompanied with the decrease in the yield of Grignard reagent, increase of Wurtz reaction, and decrease in the reaction heat were observed. The induction period has also been roughly prolonged.

The region of small additions of the base (less than one mole to a mole of halide) is of certain interest for elucidation of details of the reaction mechanism, as well as in connection with the application of bases in catalytic amounts in industrial organomagnesium syntheses.

In this investigation the reaction of n-butyl bromide

with magnesium in toluene was chosen as a model process. Ethyl ether was added in amounts from 0.17 to 1.02 mole to a mole of the halide. Relative amounts of magnesium and of halide were increased in comparison with previous work in order to cut down the induction period and increase reaction rate: The process was followed thermographically, and by taking aliquots (by titration Grignard reagent and magnesium halide formed).

EXPERIMENTAL SECTION

Reagents and Solvents.

Toluene was treated with conc. sulfuric acid, washed, dried over heated calcium chloride and fractionated over sodium wire.

Ethyl ether was purified from peroxides with potassium hydroxide, washed, dried over heated calcium chloride, distilled over sodium and, before use, over the Grignard reagent.

Butyl bromide was dried over heated calcium chloride and rectified.

Magnesium metal was used in the form of granules from 1.0 to 1.6 mm in diameter.

Kinetic Measurements by the Thermographic Method.

The method worked out by V.A. Palm (and one of us)^{2,3} was used in such a modification as in previous work¹.

The reaction flask (a 35 ml Erlenmeyer flask) was capped with a teflon stopper which was equipped with a silicon rubber disk. Through the disk was placed a thermistor MT-54 which was connected into a Wheatstone bridge-system of direct current. The thermograms were recorded on a potentiometer EZ-8.

The reaction flask was placed into a glass vessel, whose temperature was kept at $30 \pm 0.1^\circ\text{C}$ by means of a thermostat U-10. The reaction mixture was stirred by means of a magnetic stirring bar.

Before the kinetic runs 7.00 g of magnesium (0.29 g.atom, total surface about 185 cm^2) was placed into the flask. Toluene and ethyl ether (altogether 20.0 ml in each run) were in-

troduced into the flask by calibrated pipets. When the system had reached a constant temperature (30°C), 3.0 ml of butyl bromide was introduced through the silicon rubber disk by a hypodermic syringe (0.028 g-mole, about 10% of the initial quantity of magnesium; a complete reacting of the halide causes the diminishing of the magnesium surface about 7%). After the beginning of the heat evolution the thermogram was recorded.

The thermograms were transferred into kinetic curves by numerical integration from the plot of ΔT vs. t in accordance with the formula.

$$\Delta T_0 = \Delta T + \rho \int_0^t \Delta T(t) dt ,$$

where ΔT is the temperature difference between the reaction flask and the thermostat at any time t ; ΔT_0 is the integral temperature difference; ρ is the cooling coefficient.

Coefficient ρ was determined for the system from a separate experiment as described earlier¹.

Kinetic measurements by the Method of Aliquots.

The reaction was carried out as described above with the only difference that during the reaction at appropriate times aliquots of 1.0 ml were withdrawn and analyzed acidometrically for the content of basic magnesium. In the same aliquots the amount of halide was determined by the Volhard method.

The kinetic curves were produced by plotting the yield of Grignard reagent against time.

Analysis of Reaction Mixture by GLC

Aliquots (2 ml) withdrawn from the reaction mixture were decomposed by 0.1 N solution of sulfuric acid. Organic layer was separated, dried with anhydrous calcium chloride, and analyzed on a chromatograph "Vyruchrom 1A" supplied with an integrator. column (2.5 m) was filled with Chromato-N-Super (0.2-C₁₈; n-0.25 mm) coated with 3% OV-225, the carrier gas was nitrogen, column temperature 56°C, ethylbenzene was used as an inner standard. The content of n-butyl bromide and n-octane was determined.

RESULTS AND DISCUSSION

The thermograms and kinetic curves reveal a complicated course of the reaction (Fig. 1 and 2). After a certain induction period a heavy evolution of heat begins and the rate of the reaction increases. Then the rate decreases rapidly and a relatively short rapid stage of the reaction (up to point C in Fig. 1) ends. During this stage a considerable amount of Grignard reagent is formed. The rapid stage of the reaction is followed by the slow one. During the latter butyl bromide is consumed completely. The rates of both stages increase with increasing additions of ethyl ether, but the relative part and duration of the slow stage (Fig. 2) decrease until complete disappearance at the molar ratio of ether to bromide 1:1.

Let us consider the both stages separately.

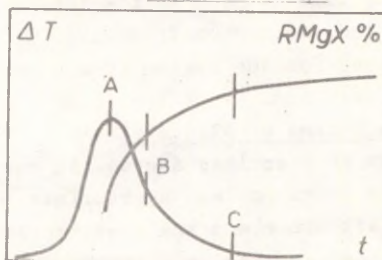


Fig. 1.
A thermogram of the process ($\Delta T-t$) and plot of yield of the reaction ($RMgX\%$) against time.

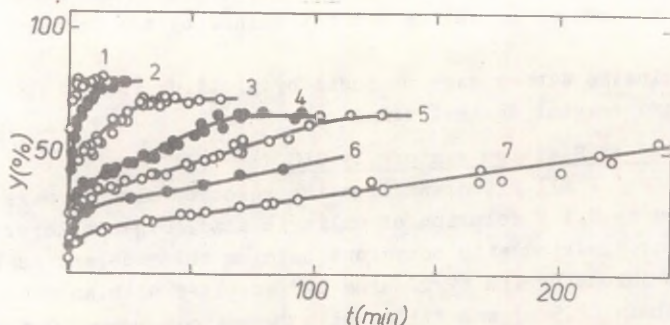


Fig.2. The time-dependence of the yield of Grignard reagent at molar ratios of ether to bromide: 1 -0.85; 2 -0.68; 3-0.51; 4 -0.41; 5 -0.34; 6 -0.27; 7 -0.17.

The rapid stage of the reaction is of complicated kinetic character. Approximately up to reaching the thermic maximum (A in Fig. 1) occurs the increase of the rate, typical of reactions with an induction period. A certain part of the process (from A to B in Fig. 1) can be described by the first-order kinetics. The rate constants were calculated by a differential method⁴ from the slope of a plot of $\ln(\Delta T_0/\Delta t)$ vs. τ where τ is the time corresponding to the intermediate of the time-interval Δt . The constants obtained from such "linear" (up to $\pm 5\%$) parts of differential curves are presented in Table 1. With the increase of relative content of ether the length of the linear portion of rapid stage diminishes, but the extent of the reaction at the end of this stage markedly increases (Table 2). The values of the first-order rate constants almost linearly depend on the ratio ether - bromide (Fig. 3), however, nearly at the ratio 1:1 a sudden increase in reaction rate occurs.

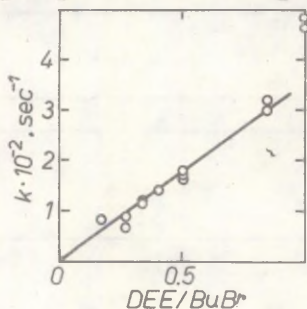


Fig. 3.

Dependence of first-order rate constants of rapid stage of the reaction on molar ratio of ether and butyl bromide

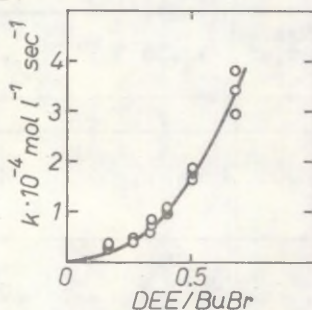


Fig. 4.

Dependence of zero-order rate constants of slow stage of the reaction on molar ratio of ether and butyl bromide.

* These constants coincide with those estimated by titration of Grignard reagent formed while reaction rate permitted to withdraw sufficient number of aliquots.

The "linear" part of the curve is followed by that (BC in Fig. 1) of more complicated kinetics. Apparently, this is a transition region between rapid and slow stages of the reaction. It is conspicuous that at the end of the rapid stage (at point C in Fig. 1) the yield of Grignard reagent (Table 2) corresponds to the amount of ether. Consequently, in rapid stage of the reaction monosolvated Grignard reagent forms, and after the added position of the ether is exhausted, the reaction slows down. Analogous yield of the monoetherate of *sec*-butylmagnesium bromide, corresponding to the added amount of ether, and the following cease of the reaction, when carried out in hexane, are described by Smith⁵.

Table 1

Rate Constants of Rapid (k_1 , sec^{-1}) and Slow (k_2 , $\text{mole} \cdot \text{l}^{-1} \cdot \text{sec}^{-1}$) Stages of the Reaction and Yields of Grignard Reagents.

Relative content of ether	$k_1 \cdot 10^{-2}$	$k_2 \cdot 10^{-4}$	Yield %
1	2	3	4
0.17	...	0.38	55.6
	0.84	0.25	...
	...	0.31	56.6
0.27	0.91
	...	0.42	...
	0.71	0.47	...
0.34	1.16	0.69	65.2
	...	0.71	65.2
	1.19	0.86	...
	...	0.60	64.2
0.41	...	0.97	66.0
	...	0.99	65.0
	1.41	0.96	65.2
	...	1.09	68.5
	...	1.01	...

Table 1 continued

1	2	3	4
0.51	1.70	1.67	69.9
	...	1.87	70.8
	1.65	1.84	71.1
	1.78	1.79	69.1
0.68	...	2.93	76.8
	...	3.42	76.8
	...	3.79	75.6
0.85	2.99	...	76.0
	3.20	...	77.9
1.02	4.85	...	77.5
	4.64

Table 2
Some Characteristics of the Process

Reaction content of ether	Extent (%) of the reaction at the end of the "linear" part of the rapid stage	Yield of Grignard reagent (%) at the end of the rapid stage	Yield of Grignard reagent (%)	Yield of Würtz reaction (%)
0.17	56	42
0.34	15	30	65	35
0.41	28	33	66	28
0.51	38	45	70	...
0.68	52	69	76	17
0.85	67	72	77	...
1.02	...	78	78	...

After the rapid stage of the reaction the formation of the Grignard reagent does not discontinue but the reaction is very slow. As it is seen from Fig. 2, the kinetics of this stage is of zero-order. Rate constants (with mean ac-

curacy $\pm 7\%$) are presented in Table 1. The values of rate constants of the slow stage exert a square dependence on ether content in the reaction mixture (Fig. 4). The relative contribution of the slow stage in whole process decreases with an increase in ether additions, and at the molar ratio 1:1 of ether to bromide only a rapid formation of monosolvated Grignard reagent proceeds (Cf. Fig. 2).

By the end of the reaction the yield of Grignard reagent does not reach 100%. The analyses of the reaction mixture for the content of magnesium bromide, n-butyl bromide and n-octane showed that butyl bromide reacted completely, however, with some formation of Würtz reaction products (with an equilibrium about 93-100%). The contribution of the Würtz reaction is considerable at low contents of ether (Table 2). It decreases with increased additions of ether. The Würtz reaction proceeds also in the rapid stage of the process, however, as it is seen in Fig. 5, it is more essential in the slow stage.

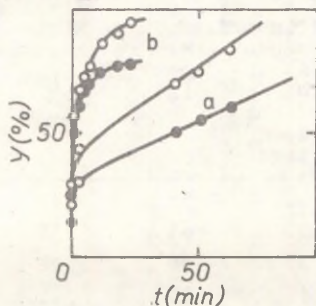


Fig. 5.

Dependence of the yields of Grignard reagent (●) and magnesium bromide (○) on the reaction time at molar ratios of ether to butyl bromide 0.34 (a) and 0.68 (b).

Although the details of the mechanism of the reaction remain obscure, one can imagine the general features of this process to be as follows. First, at low content of ether a rapid formation of monosolvated Grignard reagent occurs. Ether acts as a catalyst but is consumed as a reagent. Nevertheless, the kinetics of the reaction is more complicated, probably, because of various association and solvation equilibria involved. The physical meaning of the first-order rate constants obtained still remains open.

Then follows a reaction under the influence of solvated Grignard reagent. The more of the latter is present the faster alkyl halide converts into the Grignard reagent. In each act of the reaction probably participate two particles of monosolvated Grignard reagent.

At relative content of ether from one to two mole per mole of the halide a steep increase in reaction rate occurs. At higher concentrations of the ether reaction rate is determined by viscosity of the medium, as concluded in our previous work¹.

The Würtz reaction apparently proceeds concurrently and reaches a considerable extent when the rate of Grignard reaction is low. If the ether even does catalyze the Würtz reaction, then in a less extent than that of Grignard.

References.

1. A. Tuulmets, M. Hõrak, E. Jakob, and M. Vapper, *Organic Reactivity*, 18, No 2 (66), 225 (1981).
2. V.A. Palm, and M.P. Hõrak, *Dokl. AN SSSR*, 130, 1260 (1960).
3. M.P. Hõrak and V.A. Palm, *Trudy po khimii i khimicheskoi tekhnologii (Gorki)*, 1961, (1), 189.
4. E.S. Rudakov, *Akad. nauk USSR, Kinetika i kataliz*, vol. 1, No 2, 177 (1960).
5. W.N. Smith, *J. Organometal. Chem.*, 64, 25 (1974).

STUDY OF ELECTRONIC SUBSTITUENT EFFECT
TRANSMISSION IN 5-SUBSTITUTED 2-HYDRAZINOPYRIMIDINES

S.P. Pambolvidius, L.P. Saliskaitė, and P.I. Vainilavičius
V. Kapsukas Vilnius State University, Department of Organic
Chemistry, 232006, Vilnius, Partizanu 24, USSR.

Received December 7, 1984

Proton NMR spectra of 5-R-2-hydrazinopyrimidines, R = CH₃O, CH₃, H, Cl, Br, COOCH₃, have been studied in dimethylsulfoxide solutions. The method of correlation analysis was used in order to study the substituent electronic effects in the 5th position of the pyrimidine ring on the chemical shifts of the amine-group's hydrazine residue. The effect of polar resonance has been observed in the investigated compounds between substituents R and the amine groups. Their contribution has been calculated according to the following equation:

$$\delta = \delta_0 + \rho\sigma^+ + \rho_R^-\sigma_R^-$$

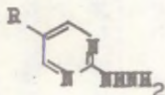
The data of hydrazinopyrimidines correlation analysis are compared with those of the similar series of para-substituted phenylhydrazines and 2-aminopyrimidines.

To continue the studies of the dependence between the structure and biologically significant physico-chemical properties of pyrimidine hydrazine derivatives, the data concerning the substituent electronic effect on the chemical shifts (δ) of the protons belonging to the primary (NH₂) and secondary (NH) amine groups of 5-substituted 2-hydrazinopyrimidines (I) are presented in this report.

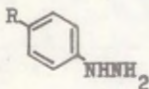
The influence of substituent electronic effects on the

frequency and intensity of the NH_2 group absorption bands in the IR spectra as well as the protons CS of the same group in ^1H -NMR spectra of certain substituted phenylhydrazines was examined in paper³. As the signals of the NH -group are suppressed by the signals of benzene ring protons, in the present paper the CS of the secondary amino group are indicated in case of meta- and para-nitrophenylhydrazines only.

Thus, in order to comparatively estimate the electron effect transfer of the substituent, the analogous para-substituted phenylhydrazines (II) were studied in the pyrimidine series.



I



II

The ^1H -NMR spectra of compounds I, II were taken in the dimethylsulfoxide (DMSO) solutions. The reasons for using DMSO as the solvent were as follows: 1) Certain 2- hydrazino-pyrimidines cannot be easily dissolved in such solvents as C_6H_{12} , CCl_4 and CDCl_3 . 2) Owing to its electron-releasing properties, DMSO hinders the formation of associates via the hydrogen bonds between active groups (amino groups) and the substituents of the compounds⁴ studied. Consequently, there is no need to carry out any concentration studies, since in substantially diluted solutions the proton CS of active groups do not depend any more on the compound concentration and has a constant value, characterizing the monomeric state of the molecules in the observed compounds associated with the solvent⁵. This phenomenon was noticed also while studying the hydrazides of 5-substituted 2-pyrimidinecarboxylic acids using the method of ^1H -NMR¹.

In ^1H - NMR spectra of compounds I, II (with the exception of I, $\text{R}=\text{Cl}$, Br and II, $\text{R}=\text{CH}_3\text{O}$, Cl) slightly broadened singlet proton signals of the $-\text{NH}-$ and $-\text{NH}_2$ group protons of hydrazine residue were detected.

The spin-spin interactions between the protons of these groups were not observed. In the hydrazinepyrimidine (I, R = -Cl, Br) and phenylhydrazine (II, R-CH₃O, Cl) spectra the signals of the -NH-group proton fall into the resonance regions of the pyrimidine or benzene ring. If the temperature rises, these signals shift towards a stronger field, their CS being linearly dependent on temperature. The CS temperature dependences of -NH-groups of 5-bromine and 5-chlorine-2-hydrazinepyrimidines are given in Fig. 1. Similar dependences were also obtained for hydrazines II (R-CH₃O, Cl). These values were used for the CS calculations of the secondary amine groups of these compounds at temperature 37°C (Table 1).

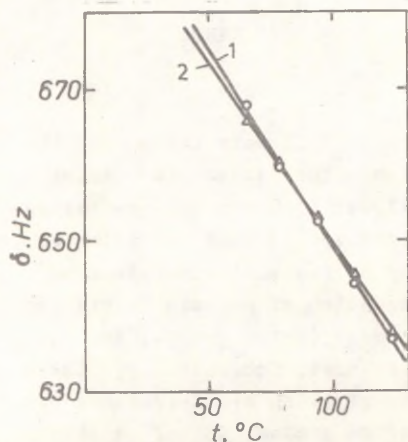


Fig. 1. CS temperature dependences of -NH-groups of 5-bromine-(I) and 5-chlorine-2-hydrazinepyrimidines (2).

The data presented in Table 1 show that the signals of hydrazinepyrimidine amino groups (I) are situated on a weaker magnetic field than those of phenylhydrazines. This phenomenon can be explained by the more clearly expressed electron-withdrawing character of the pyrimidine ring in comparison with benzene⁶. The non-screening effect of the pyrimidine ring was the strongest in case of the secondary aminogroup proton. In addition to that the values of CS aminogroups of the both compound series highly depend on the electronic nature of sub-

stituents R.

The quantitative estimation of the dependence was carried out by means of correlation analysis, with the application of various substituent constants. It should be mentioned that the CS of the aminogroups of hydrazines I, II tend to have the best correlation with the nucleophilic constants of substituents σ^- (Table 2). Application of some other substituent constants in correlations considerably decreases the value of the correlation coefficient.

Table 1

Chemical Shifts^{*} of -NH- and -NH₂ Group Protons of 5-Substituted 2-Hydrazino-pyrimidines (I) and Para-Substituted Phenyl-hydrazines (II).

R	Compounds I		Compounds II	
	δ , ppm	δ , ppm	δ , ppm	δ , ppm
CH ₃ ⁰	7.69	4.05	6.31	3.83
CH ₃	7.84	4.09	6.45	3.88
H	8.12	4.21	6.64	3.93
Cl	8.49	4.23	6.90	4.03
Br	8.51	4.21	6.96	4.06
CO ₂ CH ₃	9.16	4.51	7.60	4.22
NO ₂	-	-	8.40	4.52

* The CS of amino groups were measured relative to the protons of the methyl group of dimethylsulfoxide and transferred tetramethylsilane scale according to equation

$$\delta = \delta_{\text{meas.}} + 2.59.$$

For instance, the correlation coefficients of the δ_{NH} and δ_{NH_2} dependences on the σ -constant are 0.985 and 0.893 for series I and 0.975, and 0.977 respectively for series II. Still lower values of correlation coefficients characterize the correlation of the CS aminogroups of the hydrazine residue of compounds I, II with the σ^0 substituent constants.

For the purposes of comparison we also calculated the correlation equation, connecting CS aminogroups of 5-substituted

2-aminopyrimidines with the σ^- substituent constants (Table 2, Eq. 9).

Table 2

Data of Correlation Analysis of Chemical Shifts of Hydrazines
of I, II Aminogroup from Substituent Constants

Eq. Se- No ries	δ	δ_o^a	ρ	ρ_R^-	s^b	r^c	n^d	Substi- tuent cons- tant
1 I	δ_{NH}	8.12 ± 0.004	1.57 ± 0.013	-	0.01	0.999	6	σ^-
2 ^e I	δ_{NH_2}	4.18 ± 0.01	0.452 ± 0.029	-	0.022	0.980	5	σ^-
3 I	δ_{NH}	8.11 ± 0.008	1.63 ± 0.036	1.408 ± 0.07	0.014	0.999	6	σ^o, σ_R^-
4 I	δ_{NH_2}	4.199 ± 0.019	0.266 ± 0.085	0.8 ± 0.16	0.034	0.953	6	σ^o, σ_R^-
5 II	δ_{NH}	6.65 ± 0.04	1.367 ± 0.064	-	0.028	0.999	7	σ^-
6 II	δ_{NH_2}	3.94 ± 0.02	0.443 ± 0.032	-	0.012	0.997	7	σ^-
7 II	δ_{NH}	6.67 ± 0.016	1.23 ± 0.073	1.58 ± 0.112	0.029	0.998	7	σ^o, σ_R^-
8 II	δ_{NH_2}	3.944 ± 0.011	0.436 ± 0.05	0.453 ± 0.077	0.02	0.993	7	σ^o, σ_R^-
9 ^f 5-R- δ_{NH_2} 2-NH ₂ - pyrimi- dines		6.46 ± 0.06	1.293 ± 0.093	-	0.051	0.999	8	σ^-

a - δ_o, ρ, ρ_R^- - coefficients in eqs. $\delta = \delta_o + \rho \sigma^-$,
 $\delta = \delta_o + \rho \sigma^o + \rho_R^- \sigma_R^-$

b - mean square deviation

c - number of points used for calculation of equations

d - point for compound I (R=Br) is excluded

e - CS of aminogroup presented in⁷ have been used for calculation of the equation.

The data of Table 2 indicate that eqs. (1), (5) and (2), (6) have close values. Consequently, the total electronic substituent effect on the CS values of $-\text{NH}-$ and $-\text{NH}_2$ groups is practically similar in both compound series. The insignificant increase of value ρ in Eq. (1) in comparison with ρ in Eq. (5), is, most probably, conditioned by the growth of the N-H bond polarity, under the effect of the pyrimidine ring. A high polarity of the N-H bond of the secondary amino-group in 2-hydrazinepyrimidines, caused by the electron withdrawing effect of the $-\text{NH}_2$ group, also accounts for the high susceptibility of the CS of the $-\text{NH}-$ hydrazine group towards substituent effects, if compared to the CS of the NH_2 -group in 2-aminopyrimidines (cf. values ρ in eqs. 1 and 9). The electronic conductivity of the NH group, estimated by eqs (2) and (9), proved to be equal to 0.35, which corresponds to the data^{1,8,9}.

The fact that the CS of both aminogroups of compounds I, II have the best correlation with the substituent constants σ^- evidences according to^{10,11} about the existence of the first order polar resonance effect between substituents R and the hydrazine group in the molecules of the compounds studied. In order to estimate the polar resonance contribution to the total electronic substituent effect on the CS of the hydrazine residue aminogroups, the parameters of correlation $\delta = \delta_0 + \rho\sigma^0 + \rho_R^- \sigma_R^-$ (Table 2) were calculated. Constants σ^0 and σ_R^- were chosen according the data¹¹.

Comparison of ρ_R^-/ρ ratios in equations (3) and (7) leads to the conclusion that the polar resonance effect of the substituents on the CS values of the $-\text{NH}-$ group are more clearly expressed in the phenyl hydrazine series ($\rho_R^-/\rho = 0.85$ and 1.28 for I and II, respectively). However, the contribution of polar resonance into the total/summary substituents electronic effect on the CS value of the $-\text{NH}_2$ group in the hydrazine series is three times greater than in the phenylhydrazine series (see ratio ρ_R^-/ρ in eqs. 4,8). The latter, evidently refers to the existence of the more clearly expressed triple bond of N-N in hydrazinepyrimidines in comparison with

that of phenylhydrazines.

Experimental

The parameters of correlation equations were calculated on a computer "Minsk-22", applying the programs prepared by V. Balavičius. The substituent constants were taken from the following literature reports: σ , σ^- ¹⁰, σ^0 , σ_R^- ¹¹.

Compound Synthesis

5-substituted 2-hydrazinopyrimidines (I).

The mixture of 0.1 M of 5-substituted 2-methylsulfonylpyrimidine and of 0.2 moles of 99 per cent hydrazinehydrate is heated in dimethylsulfoxide at temperature 60-100°C for 0.5-2 hours. Then the cooled solution is poured into cold water, the residue is filtrated and recrystallized from ethanol. The yields of compounds I form 70-85 per cent. The melting point of the obtained hydrazines corresponds to literature data¹²⁻¹⁵.

Para - substituted phenylhydrazines (II)

The commercial ones were used. Their constants were in accordance with literature data.¹⁶

The compounds were purified either by means of cristallization or distillation in vacuo in the atmosphere of nitrogen.

Chromatography was applied in order to check the purity of hydrazines I, II.

¹H - NMR Spectra

The ¹H - NMR spectra of compound solutions in DMSO-d₆ were taken on a spectrometer BC 487S "Tesla" (80 MHz) at temperature 37±1°C. The experimental error is ±0.01 ppm. Internal reference - DMSO. The CS of amino groups are presented relative to tetramethylsilane. The concentrations of compounds were 0.005 by molar fraction scale. DMSO-d₆ was stored over the 4Å molecular sieves during a prolonged period of time, distilled in vacuo in the atmosphere of dry nitrogen and stored again over the 4 Å sieves. The ampuls were filled in a box, previously dried with anhydron.

References

1. S.P. Tumkevičius and P.I. Vainilavičius; *Organic Reactivity*, 20, 85 (1983).
2. S.P. Tumkevičius and P.I. Vainilavičius, *Organic Reactivity*, 20, 568 (1983).
3. E.V. Titov, L.M. Kaplan, V.I. Rybachenko, and A.Yu. Chervinsky, *Ukr. khim. zh.*, 39, 9, 927-929 (1973).
4. R.J. Ouellette, *Can. J. Chem.*, 43, 3, 707-709 (1965).
5. V. Bekarek, J. Klicnar, F. Kristek, and M. Večeřa, *Coll. Czech. Chem. Commun.*, 33, 3, 994-998 (1968).
6. O.P. Shkurko and V.P. Mamaev, *ZhOrKh*, 15, 8, 1737-1739 (1979).
7. O.P. Shkurko and V.P. Mamaev, *KhGS*, 12, 1683-1686 (1979).
8. A.J. Biggs and R.A. Robinson, *J. Chem. Soc.*, 388-393 (1961).
9. A. Fischer, D.A. Happer, and J. Vaughan, *J. Chem. Soc.*, 4060-4063 (1964).
10. Yu. A. Zhdanov and V.I. Minkin, *Correlation Analysis in Organic Chemistry (in Russ.)* The Rostov University Press, 1966, 470 pp.
11. V.A. Palm, *Foundations of Quantitative Theory of Organic Reactions*, Leningrad, "Khimiya", 1977, 359 pp. (in Russ.)
12. J. Dick, J. Ristici and L. Pod, *Acad. Rep. Populare Romine, Base Cercetari Stiint, Timisaare Studii Cercetari, Stiint.Chim.*, 8, 233-237 (1961); *C.A.*, 58, 3429 (1963).
13. Z. Budešinsky and J. Vavrina, *Coll. Czech. Chem. Commun.*, 37, 1721-1733 (1972).
14. K. Shirakawa, S. Ban, and H. Yoneda, *J. Pharm. Soc. Japan*, 73, 598-601 (1953).
15. Pat. USA, 3041339 (1962), *C.A.*, 57, 113774 (1962).
16. *Manual of Chemistry*, (in Russ.), Moscow, "Khimiya", 1965.
17. A. Gordon and R. Ford, *Chemist's Companion (in Russ.)*⁷, Moscow, "Mir" 1976, 541 pp.

FACTORS EFFECTING RATE OF MENSCHUTKIN REACTION.

1. EFFECT OF AMINE STRUCTURE

A.A. Matveev, Zh.P. Piskunova, V.A. Palm, and A.P. Popov
Institute of Physico-Organic and Coal Chemistry of the
Academy of Sciences of the Ukrainian S.S.R., Donetsk,
Tartu State University, Department of Organic Chemistry,
Tartu, Estonian S.S.R.

Received February 14, 1985

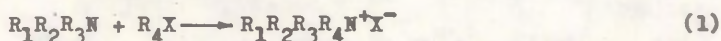
It has been shown on the basis of the Menschutkin reaction (MeI , EtI , $n\text{-PrI}$ with amines, in acetonitrile at 25°C) and by means of the multilinear regression analysis program that the substituent induction effect at the nitrogen atom and the total steric effect of the amine molecule determine the nucleophilic reactivity of aliphatic amines. The polarizability effects as well as the number of N-H bonds in an amine do not practically influence its reactivity. The contributions of each separate factor into the total rate of the process have been estimated.

The dependence of reactivity on structure still remains one of the key problems of physical organic chemistry. The nucleophilic reactivity of the amines belongs to the same area.

The solution of this problem is hindered by a number of difficulties¹ connected with the effect of several factors on the nucleophilicity of nitrogen bases. Literature data on the effect of amines' structure on their reactivity in the S_2 reactions mention mainly two effects - the inductive and the steric^{1,2} ones, though the influence of some other factors should also be kept in mind. In this connection it was

interesting to study the statistical significance of such characteristics as the number of the N-H bonds in an amine molecule and the molecule's polarizability, since they are of great importance in case of basicity and proton affinity of aliphatic amines^{3,4}.

We have chosen the Menshutkin reaction to solve the above mentioned problems



where R_1, R_2, R_3 H or Alk; R_4 - Me, Et, n-Pr; X denotes I.

This classical reaction of bimolecular nucleophilic substitution depends largely on the reagent structure, giving great possibilities for varying both the substance and the nucleophile structures. The rate of the reactions under discussion (Table 1) obey the second order equation, the first for each reagent. The measurements were carried out at the large amine excess, which can be explained by the fact that in case of the first order and second order amines polyalkylation might be possible and the nucleophile excess is necessary for taking the reaction rate (1).

The experimentally obtained data (Table 1) were processed according to equation (2)

$$\log k = \log k_0 + \rho^\Sigma \Sigma \sigma^\Sigma + \sigma_{E_N} + \alpha_1 \Sigma MR + a_2 n \quad (2)$$

$\Sigma \sigma^\Sigma$ is the total of substituent induction constants in the presence of nitrogen atom in amine; E_N - the steric effect of the amine molecule as a whole^{1,2}; ΣMR - denotes the amine molecular refraction⁵, which is equal to the refraction sum of the structural elements for the sodium D-line; n is the number of N-H bonds in amine; ρ^Σ , δ , α_1 and α_2 denote the coefficients of the process susceptibility to the corresponding factors.

The data processing was done using the program of multilinear regression analysis (MLRA). It enables to exclude the statistically insignificant argument scales. The results are presented in Table 2. Of essential importance is the fact that only two variables - $\Sigma \sigma^\Sigma$ and E_N characterizing the sub-

stituents induction effect and the amine steric effect as a whole, will be enough to describe the nucleophilic reactivity of amines with a fixed substance: such factors as the number of N-H bonds in an amine molecule and their polarizability in case of reactivity turned out to be statistically negligible in comparison with the basicity³ and the proton affinity.⁴ Thus, eq.(2) goes back to eq.(3), presented earlier.¹

$$\log k = \log k_0 + \rho^{\Sigma} \Sigma \sigma^{\Sigma} + \delta E_N \quad (3)$$

Besides, comparatively high values of standard deviation within the normalized scale refer to the possible existence of such factors of the amine structure which effect the rate of the observed reactions.

The obtained coefficients ($\log k_0$, ρ^{Σ} , δ) allow to compare the intensity of the amines structural factors effect on the reaction rate within a reaction series as well as the changes of the corresponding effects during transmission from one effect to another. On the natural scale the ρ^{Σ} values do not especially depend on the substituent type in a substance. At the same time the δ values increase from 0.77 for MeI to 1.15 for n - PrI. This phenomenon is conditioned by a stronger steric screening of the reaction center, decreasing the total rate of the process (cf. the $\log k_0$ values). It should be mentioned that the solvent type which remarkably affects the process rate (the values of $\log k_0$ in Table 3), has practically no effect on its susceptibility to both electronic (ρ^{Σ}) and spacial (δ) effects of the amine structure.

In order to find the relative inductive and steric substituent effects in nucleophile it is convenient to use the standardized coefficient (i.e. the coefficients reduced to the same scale⁷,) ρ^{Σ} and δ (See columns 5 and 7 in Table 2). In series 1 the substituent induction effect in the amine is greater than the steric screening effect of the nitrogen atom (the corresponding absolute values equal 1.99 and 1.63). In series 2 ($\rho^{\Sigma}_{\text{stand.}}=1.48$; $\delta_{\text{stand.}}=1.78$) and, especially in series 3 (1.30 and 1.75) a remarkable effect

Table 1

Rate Constants ($k_2 \cdot 10^3$, $M^{-1} \cdot s^{-1}$) of Amines' Reactions with Alkyl iodides in Acetonitrile at 25°C

No	Nucleophile	S u b s t a n c e		
		MeI, No 1	EtI, No 2	n-PrI, No 3
1	2	3	4	5
1.	MeNH ₂	41.2 \pm 2.0	1.83 \pm 0.10	0.781 \pm 0.030
2.	EtNH ₂	27.4 \pm 0.8	1.03 \pm 0.06	0.406 \pm 0.020
3.	BuNH ₂	30.6 \pm 0.6	1.10 \pm 0.02	0.460 \pm 0.005
4.	i-BuNH ₂	20.7 \pm 0.4	0.774 \pm 0.035	0.340 \pm 0.010
5.	i-PrNH ₂	14.7 \pm 0.2	0.459 \pm 0.016	0.173 \pm 0.005
6.	γ -BuNH ₂	8.90 \pm 0.10	0.190 \pm 0.006	0.0685 \pm 0.0032
7.	α -HexNH ₂	19.2 \pm 0.4	0.570 \pm 0.010	0.226 \pm 0.004
8.	Me ₂ NH	319 \pm 14	13.4 \pm 0.3	4.25 \pm 0.05
9.	Et ₂ NH	77.8 \pm 1.0	1.27 \pm 0.01	0.329 \pm 0.003
10.	Bu ₂ NH	63.9 \pm 0.3	1.00 \pm 0.02	0.268 \pm 0.003

Table 1 continued

1	2	3	4	5
11.	1-Bu ₂ NH	22.1 ± 0.2	0.274 ± 0.008	0.0517 ± 0.0030
12.	1-Pr ₂ NH	3.22 ± 0.04	0.0187 ± 0.0007	0.000272 ± 0.00003
13.	Piperidine	358 ± 6	11.2 ± 0.2	3.80 ± 0.08
14.	MeEtNH	182 ± 9	5.34 ± 0.20	1.95 ± 0.03
15.	Me ₃ N	490 ± 12	10.2 ± 0.4	2.93 ± 0.04
16.	Me ₂ BuN	177 ± 2	2.45 ± 0.02	0.578 ± 0.010
17.	Me ₂ HexN	185 ± 3	2.36 ± 0.02	0.580 ± 0.016
18.	Me ₂ BzN	47.2 ± 0.3	0.594 ± 0.010	0.154 ± 0.003
19.	Et ₂ MeN	102 ± 2	0.974 ± 0.030	0.182 ± 0.009
20.	N-Me-piperidine	112 ± 2	0.855 ± 0.024	0.245 ± 0.004
21.	Et ₃ N	40.2 ± 4.0	0.228 ± 0.005	0.0382 ± 0.0006

table 2

Correlation Parameters^{a, b} of Reaction Rate Constants of Aliphatic Amines
with Alkyl iodides According to Eq. (2)

	Substance	log k		ρ^{\pm}		δ		Standard deviation		R^c
		norm.	nat.	norm.	nat.	norm.	nat.	perm.	nat.	
1	2	3	4	5	6	7	8	9	10	11
1.	MeI	1.80^{\pm} ± 0.30	0.87^{\pm} ± 0.15	-1.99^{\pm} ± 0.13	-2.36^{\pm} ± 0.15	1.63^{\pm} ± 0.13	0.77^{\pm} ± 0.06	0.27	0.13	0.967
2.	EtI	-0.65^{\pm} ± 0.21	-0.42^{\pm} ± 0.14	-1.48^{\pm} ± 0.09	-2.37^{\pm} ± 0.15	1.78^{\pm} ± 0.09	1.03^{\pm} ± 0.06	0.23	0.15	0.977
3.	n-PrI	-1.03^{\pm} ± 0.21	-0.75^{\pm} ± 0.16	-1.30^{\pm} ± 0.09	-2.36^{\pm} ± 0.17	1.75^{\pm} ± 0.09	1.15^{\pm} ± 0.06	0.23	0.17	0.977

^a "norm" - in normalized scale; "nat" - in natural scale;

^b scales ΣMR and n are excluded according to the Fischer criterion at 95% level.

^c R is the multiple correlation coefficient.

of the vicinity of the reaction center can be observed.

Table 3.
Rate Constants' Correlation Parameters^a in Reactions
of Aliphatic Amines with Methyl iodide According to
Eq. (3)

No	Reaction conditions	log k ₀	ρ [≡]	δ	s	R
1.	Methanol 30°, ¹	-1.06 ±0.22	-2.21 ±0.21	0.67 ±0.09	0.15	0.977
2.	Benzene 25°, ⁸	-0.91 ±0.22	-2.34 ±0.24	0.67 ±0.09	0.15	0.974
3.	Nitrobenzene 25°, ⁸	-0.69 ±0.25	-2.40 ±0.20	0.75 ±0.11	0.15	0.974
4.	Acetonitrile 25°	0.87 ±0.15	-2.36 ±0.15	0.77 ±0.06	0.13	0.967

^a Data treatment has been carried out in natural scale

It is also noteworthy that the changes in the ρ[≡] and δ values depending on the substance type do not coincide with the corresponding values given in natural scale. This can be explained by the fact that in standardized scale the coefficients are calculated as follows⁷:

$$\rho^{\equiv}_{\text{norm.}} = \rho^{\equiv}_{\text{nat}} \frac{s(\sum \sigma^{\equiv})}{s(\log k)} \quad \text{and} \quad \delta_{\text{norm.}} = \delta_{\text{nat}} \frac{s(E_N)}{s(\log k)},$$

$$\text{where } s(x) = \sqrt{\frac{1}{n(n-1)} [n \sum x^2 - (\sum x)^2]}$$

in case $\bar{Y} = \log k, \sum \sigma^{\equiv}$ or E_N .

As the amine set is constant within all three series, the values $s(\sum \sigma^{\equiv})$ and $s(E_N)$ also remain constant. The increase of $s(\log k)$ during the transmission from MeI to PrI (see differences in the k values for 8 and 12 in Table 1) brings about a decrease in ρ[≡]_{norm.}. Here is but a small change of this value because the growth of δ_{nat} in series MeI < EtI <

< n-PrI compensates the increase of $s(\log k)$. Besides, if the induction and steric effect contribution is evaluated by ρ^{\pm}/δ , it will follow (either for natural or standardized scales) that at the transition from MeI to n-PrI the reaction becomes more susceptible to the special effect of amine structures.

Experimental

Dimethylbutylamine, dimethylhexylamine, diethylmethylamine and N-methylpiperidine were synthesized according to method⁹, iso-butylamine and iso-propylamine according to method³ (p. 871). The purification of acetonitrile, amine, and alkyl iodide was conducted by the known methods. The physico-chemical constants of purified compounds correspond the literature data. The purity was checked using the g.l.c. method on a chromatograph LHM-8MD.

Depending on the reaction rate and character of the obtained products the following ways of control were employed:

1. The potentiometric argentometric titration of the forming iodide ion. This method can be applied for all studied reagents, although it is inconvenient for a high process rate.
2. The conductometric measurement of the changes in ion concentration during the reaction by means of universal bridge E7-4. The method can be used for monitoring the rapid processes. Some rate constants have been obtained applying both methods given above. The difference of their values does not exceed 7 per cent.

The calculation of rate constants was carried out in accordance with the generally accepted formulae on the basis of measuring 2-3 kinetic curves at different initial amine concentrations for each reaction.

References

1. S.V. Bogatkov, A.F. Popov, and L.M. Litvinenko, Reakts. sposobn. organ. soed., 6, 1011 (1969).
2. S.V. Bogatkov, L.V. Bystrov, and R.I. Kruglikova, Organic Reactivity, 15, 172 (1978).

3. A.F. Popov and Zh. P. Piskunova, "Structure and Basicity of Amines". In coll. "Problems of Physico-Organic Chemistry" (In Russ.), Kiev, "Naukova Dumka", 1978.
4. I.A. Koppel and U.H. Møller, Organic Reactivity, 20, 3 (1983).
5. B.V. Ieffe, Refractometric Methods in Chemistry" (In Russian), Leningrad, "Khimiya", 1974.
6. A. Uri, A. Taulmetz, and V. Palm, Organic Reactivity, 20, 122 (1983).
7. E. Ferster and B. Rents, "Methods of Correlation and Regression Analysis", (in Russ.), Moscow, "Finantsy i Statistika", 1983, p. 86.
8. A.F. Popov and Zh. P. Gelbina, Organic Reactivity, 14, 145 (1977).
9. Weigand-Hilgetag, "Experiment and Methods in Organic Chemistry", (in Russ.), Moscow, "Khimiya", 1968, p.486.

STUDY OF REACTIVITY OF AZOLES

A.F. Popov, Zh. Piskunova, V.N. Matvienko,
and A.A. Matveev

Institute of Physico-Organic Chemistry and
Coal Chemistry of the Academy of Sciences of the
Ukrainian SSR, Donetsk, 340114

Received February 14, 1985

The results of interaction kinetics of imidazole, N-methylimidazole and aliphatic amines with a number of substances (phenacylbromide, iodide methyl, trans-p-nitrophenyl- β -chlorovinylsulfone and p-nitrophenyltyoacetate) in various solvents were used in order to quantitatively estimate the inductive ($\Sigma\sigma^+$) and steric (E_N) structural characteristics of these azoles.

The conclusion has been drawn on the basis of the obtained data that taking into consideration of the mentioned effects is not enough for the description of imidazole and N-methylimidazole nucleophilic reactivity.

Imidazole and its derivatives play a remarkable rôle in various chemical and biochemical processes. In reactions of nucleophilic substitution at the carbonylic atom of carbon their reactivity is much higher than that of aliphatic and aromatic series. However, up to now there is no unanimous stand on the causes of the compounds' high activity in the nucleophilic substitution reactions. In connection with that it is important to get the quantitative characteristics of the structural effect of imidazole and its derivatives on their nucleophilicity.

The problem was solved as follows. It has already been

shown³ that the nucleophilic reactivity of aliphatic amines is well described by eq. (1),

$$\log k = \log k_0 + \rho \Sigma \sigma^{\pm} + \delta E_N, \quad (1)$$

where $\Sigma \sigma^{\pm}$ denotes the inductive effect of hydrocarbonic fragments, which are linked with the nitrogen atom; E_N is the sterical accessibility of this atom; values ρ^{\pm} and δ denote the reaction's susceptibility to the described effects. I.e., if the quantity of reaction series (more than two) whose values $\log k_0$, ρ^{\pm} and δ in eq.(1) are known is great enough, it is possible according to the known rate constants of the reactions with participation of imidazole and its derivatives to estimate the $\Sigma \sigma^{\pm}$ and E_N values for any of the azoles under discussion (see⁴). This approach can only be successful provided that the nucleophilicity of azoles is determined by these two factors. In case of some other structural effects besides the inductive and steric ones influencing the azoles activity, the $\Sigma \sigma^{\pm}$ and E_N values found from the data for different series (and their combinations) differ considerably.

The nucleophilicity of amines with different structures has been thoroughly enough examined in the reactions with phenacylbromide in benzene³, with trans-p-nitrophenyl- β -chlorovinylsulfone in chlorobenzene⁵ and with iodide methyl in acetonitrile⁶. The interaction kinetics of these electrophiles with imidazole and N-methylimidazole, as well as that of phenacylbromide with aliphatic amines and with the mentioned azoles in acetonitrile (Table 1,2).

It was shown by special experiments that the rate of aminolysis reaction of various substances obey prevalingly the second order (the first for any of the reagents) reaction (see^{3,5,6}). Sometimes in addition to these flows a flow conditioned by the catalytic action of the second molecule of the initial amine can be observed. In such cases the second order rate constants were calculated according to the known methods (see, e.g.⁵).

The results of treatment of rate constants of the phenacylbromide interaction with different amines in acetonitrile

(Table 1) according to eq. (1) and the analogous data for the other reaction series are presented² in Table 3.

Table 1
Rate Constants of Reactions of Aliphatic Amines with
Phenacylbromide in Acetonitrile at 25°C

No	Amines	$k \cdot 10^3$ $M^{-1} \cdot sec^{-1}$	No	Amines	$k \cdot 10^3$ $M^{-1} \cdot sec^{-1}$
1.	methylamine	578 \pm 5	10.	diisobutylamine	37 \pm 1
2.	ethylamine	321 \pm 3	11.	methylpropylamine	1020 \pm 10
3.	butylamine	326 \pm 2	12.	piperidine	5310 \pm 60
4.	isopropyl- amine	91 \pm 1	13.	trimethylamine	1600 \pm 10
5.	cyclohexyl- amine	133 \pm 1	14.	dimethylbutyl- amine	170 \pm 1
6.	tert-octyl- amine	14.0 \pm 0.1	15.	dimethylbenzyl- amine	38.5 \pm 0.5
7.	dimethyl- amine	3320 \pm 30	16.	diethylmethyl- amine	53.7 \pm 0.5
8.	diethylamine	201 \pm 1	17.	triethylamine	8.34 \pm 0.07
9.	dibutylamine	175 \pm 2	18.	tripropylamine	3.85 \pm 0.1

Table 2
Rate Constants ($k \cdot 10^3$, $M^{-1} \cdot sec^{-1}$) of Imidazole and
N-methylimidazole Reactions with Various Substances
at 25°C

No	Substance	Solvent	Imida- zole	N-methylimidazole
1.	phenacyl- bromide	benzene		0.533 \pm 0.030
2.	phenacyl- bromide	acetonitrile	16.3 \pm 0.2	16.1 \pm 0.5
3.	trans-p-nitro- phenyl-8- chlorovinyl- sulfone	chlorobenzene	2.26 \pm 0.09	2.87 \pm 0.05
4.	methyl iodide	acetonitrile	0.574 \pm 0.030	0.612 \pm 0.023
5.	p-nitrophenyl-acetate	acetonitrile	116 ⁷	

² Values $\Sigma \sigma^{\ddagger}$ and E_A for various amines are taken from ref.³.

The comparison of the obtained parameters of phenacyl-bromide reactions in benzene and acetonitrile (Table 3; 1 and 2) lead to the fact that a greater reactivity of the system ($\log k_0$) brings about a significant drop of its susceptibility towards the substituent electronic effect (ρ^{π}) in amine. Its susceptibility to the amine molecule steric effect (δ) remains stable. Unfortunately, owing to a rather limited data set (two solvents only) it is still difficult to explain the mechanism of the described phenomenon.

Table 3
Correlation Parameters of Amines' Reactivity According to Eq. (1)

Substance	Solvent at 25°C	$\log k_0$	$-\rho^{\pi}$	δ	N (number of points)
1. phenacyl-bromide ³	benzene	0.82 ± 0.20	3.24 ± 0.20	1.38 ± 0.07	20
2. phenacyl-bromide	aceto-nitrile ^a	2.22 ± 0.22	2.34 ± 0.23	1.31 ± 0.08	18
3. trans-p-nitrophenyl- β -chloro-vinyl-sulfone ⁵	chloro-benzene	4.00 ± 0.31	4.78 ± 0.29	1.70 ± 0.11	22
4. methyl-iodide ⁶	acetonitrile	0.87 ± 0.11	2.36 ± 0.12	0.77 ± 0.06	21
5. p-nitro-phenyl-tioacetate ⁸	acetonitrile	4.80 ± 0.19	3.34 ± 0.19	2.53 ± 0.10	8

^a $s = 0.21$; $R = 0.974$

According to the $\log k_0$, ρ^{π} and δ values for four series (2 - 5, Table 3) and the corresponding rate constants (2 - 5), Table 2) it was established that for imidazole $\Sigma 6^{\pi} = 1.26 \pm 0.53$ and $E_N = -0.63 \pm 0.27$. For N-methylimidazole (1 - 4, Table 2 and 3) the deviations in finding $\Sigma 6^{\pi}$ and E_N exceed the real values ($\Sigma 6^{\pi} = 1.18 \pm 1.78$ and $E_N = -0.64 \pm 0.71$), i.e. the results of different series do not correlate with each other. The obtained $\Sigma 6^{\pi}$ and δ values for imidazole are (within the error range) close to the analogous values for piperidine ($\Sigma 6^{\pi} = 1.50 \pm 0.19$ and $E_N = -0.24 \pm$

$\pm 0.14^4$). It results from the aforesaid that the functional nitrogen atom in a five-member imidazole ring is statically screened almost similarly (if not even more) with that in a six-member pyridine ring.

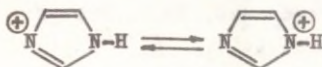
To estimate the $\Sigma 6^{\pi}$ and E_N values a somewhat different approach can be used. It is known⁹ that the basicity of tertiary amines does not practically depend on the spatial effect, being defined by the structural inductive effect only. It can be described¹⁰ by equation

$$pK_a = 9.55 - 3.23 \Sigma 6^{\pi} \quad (2)$$

When inserting the pK_a of imidazole which is equal to 7.0^2 into the equation, its value will be $\Sigma 6^{\pi} = 0.79$. If the value is applied in eq. (1) for series 2-5 (Table 2 and 3), it will result in $E_N = -2.18 \pm 0.32$. According to the data concerning the basicity of N-methylimidazole ($pK_a = 7.3^2$) were calculated $\Sigma 6^{\pi} = 0.70$ and $E_N = -2.05 \pm 0.41$, similarly, from series 1-4 (Table 2,3).

The observed differences in the inductive and spatial characteristics evidence about a probable dependence of the imidazole and N-methylimidazole nucleophilic reactivity not only on the inductive and steric structure effects but also on some other factors which are not considered in eq. (1). The contributions of these factors change during their transition from one reaction series to another. This actually brings about a sharp change of the $\Sigma 6^{\pi}$ and E_N values in case of the different characters and quantity of the reactions, according to which the parameters are calculated.

Consequently, the inductive and steric effects only do not guarantee sufficient description of the nucleophilicity of the studied azoles. The stabilization of a positive charge with the imidazole nucleus, cropping up during the process as a result of its distribution between the nitrogen atoms¹¹ can be observed as a supplementary effect:



In case of absence of such stabilization in some other cyclic amines (e.g. in piperidine), calculation of the $\Sigma 6^{\pi}$ and E_N values in various reaction series, applying different methods gives coinciding results.⁴

Experimental

The amines, substances and solvents were purified according to the known methods.

Kinetic measurements were conducted spectrophotometrically (by consumption of the substrate), conductometrically (by accumulation of ions) or by argentometric titration of the halogenide ion, separated in the course of the reaction. Rate constants were calculated from several parallel runs.

The products of phenacylbromide interaction with imidazole and N-methylimidazole not mentioned in literature were separated: α -imidazolylacetophenone (yield - 80%), melting point - 118-119.5° (from the hexane - benzene 3:1 mixture). % found: C 71.26; H 5.51; N 15.07; $C_{11}H_{10}ON_2$. % calculated: C 70.95 - H 5.41; N 15.04. Bromine hydrate of α -N-methylimidazolylacetophenone (yield - 85%), melting point - 114-120°C. % found: C. 51.40; H 4.74; N 10.09; Br 28.31. $C_{12}H_{13}ON_2Br$ - % calculated: C 51.57; H 4.66; N 9.96; Br. 28.42. The NMR spectra correspond to the compounds presented.

References

1. L.M. Litvinenko and V.A. Dadali, In Coll.: "Mechanisms of Organic Reactions and Molecular Interactions", (in Russ.), Kiev, "Naukova Dumka", 1979.
2. V.A. Dadali, In Coll.: "Molecular Interaction and Reactivity" (in Russ.), Kiev, "Naukova Dumka", 1983.
3. L.M. Litvinenko, A.F. Popov, and Zh. P. Gelbina, DAN SSSR, 203, 343 (1972).
4. A.F. Popov and Zh.P. Gelbina, Organic Reactivity, 14, 145 (1977).
5. A.F. Popov, V.V. Kravchenko, Zh.P. Piskunova, and L.I. Kostenko, Organic Reactivity, 16, 325 (1979)

6. A.A. Matveev, Zh.P. Piskunova, V.A. Palm, and A.F. Pepov, This Journal, p. 110.
7. T. Kömives, A.P. Marton, and F. Dutka, Z. Naturforsch., B 30b, 138 (1975).
8. F. Dutka, T. Kömives, and A.P. Marton, Chem. Folioirat, 82, 465 (1976).
9. V.A. Palm, "Foundations of Quantitative Theory of Organic Reactions," (in Russ.), Leningrad, "Khimiya", 1977.
10. E. Fölkers and O. Runquist, J. Org. Chem., 29, 830 (1964).
11. V.A. Dadali, L.M. Litvinenko, S.A. Lapshin, and Yu. S. Simanenko, DAN SSSR, 219, 1161 (1974).

CONTENTS

I.A. K o p p e l, U.H. M ö l d e r, and V.A. P a l m, Ab Initio SCF LCAO MO Calculations of Molecules. IV. Proton Affinities. Comparison with Experiment	3
Z. S l a n i n a, Isomerism of Components of Chemical Processes: A New Difficulty in Comparing Theoretical and Observed Reactivity Characteristics	46
A. T u u l m e t s, M. H ö r a k, E. P i l l, and A. R i i k o j a, Kinetics of Formation of Grignard Reagent with Small Additions of Ethyl Ether	93
S.P. T u m k e v i ċ i u s, I.P. S a l i c k a i- t e, and P.I. V a i n i l a v i ċ i u s, Study of Electronic Substituent Effect Transmission in 5-Substituted 2-Hydrazinopyrimidines	102
A.A. M a t v e e v, Zh.P. P i s k u n o v a, V.A. P a l m, and A.F. P o p o v, Factors Effecting Rate of Menshutkin Reaction. 1. Effect of Amine Structure	110
A.F. P o p o v, Zh.P. P i s k u n o v a, V.N. M a t v i e n k o, and A.A. M a t v e e v, Study of Reactivity of Azoles	119

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.

Том XIII. Вып. I(77). Март 1985.

На английском языке.

Тартуский государственный университет.
ЗССР, 202400, г.Тарту, ул.Пялсона, 18.

Ответственный редактор В. Чалым.

Подписано к печати 3.06.1985.

Формат 60x84/16.

Бумага писчая.

Машиннопись. Ротапринт.

Условно-печатных листов 7,44.

Учетно-издательских листов 6,84. Печатных листов 8,0.

Тираж 350.

Заказ № 634.

Цена I руб.

Ишпография ТГУ, ЗССР, 202400, г.Тарту, ул.Пялсона, 14.