TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition
of
Реакционная способность
органических соединений

Vol. XVIII
ISSUE I(65)
September 1981

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition
of
Реакционная способность
органических соединений

Vol. XVIII
ISSUE I(65)
September 1981

TARTU

Organic Reactivity
Vol.18,1(65),1981

FT ICR Study of Structure and Solvent Effects on Basicity of Some Anions in Gas Phase

I. Koppel, R. Pikver, A. Sügis, E. Suurmaa,
and E. Lippmaa

Laboratory of Chemical Kinetics and Catalysis,
Tartu State University, 202400 Tartu,
U.S.S.R.

Department of Physics, Institute of Chemical
and Biological Physics of the Academy of Sciences
of the Estonian S.S.R., 200001 Tallinn, U.S.S.R.

Received December 25, 1980.

A versatile high resolution FT ICR spectrometer was designed and built for the gas phase study of the kinetics and equilibria of ion molecule reactions and solvation phenomena. Gas phase basicities of the anions of some OH- and NH- acids were determined. The comparison of the experimental and predicted by the ab initio and semiempirical calculations values of PA-s has been made. The dependence of the gas phase basicities of several classes of anions and neutral bases on the solvation and substituent effects was discussed.

Ion cyclotron resonance spectroscopy is a new powerful experimental technique[1-3] for the quantitative investigation of kinetics, equilibria, and mechanisms of the gas phase ion molecule reactions in conditions not complicated by the solvation phenomena. On the other hand, this versatile method can be used for the detailed intimate study of solvent effects on the direction and nature of various chemical reactions.

Up to now this technique has been used to obtain new fundamental information[4] concerning the behavior of some types of ion molecule reactions in solution and in gas phase.

As a consequence, several theoretical concepts were either corrected or even reevaluated. However several interesting problems still need to be considered. So, for example, the influence of fluorosubstituted alkyl radicals and fluorine atoms vicinal to the reaction center on the gas phase proton transfer reactions (especially those including negative ions) has not yet received enough attention. The influence of solvation phenomena on the gas phase basicity of anions of various classes also calls for an urgent study.

The present investigation of the substituent and solvent effects on the gas phase basicity of anions of acids A_iH uses ICR spectroscopy as well as quantum chemical ab initio and semiempirical calculations to study the following proton transfer equilibrium:

$$A_iH + A_o^- \rightleftharpoons A_oH + A_i^-$$

where A_i^- and A_o^- are the given and reference bases.

Experimental

The ICR spectrometer designed and built in the laboratories of the present authors was used for the gas phase proton transfer equilibria experiments. It operates either in the pulsed or stationary frequency sweep mode or as an Fourier-transform ICR spectrometer(in the pulsed mode). The block diagram of this spectrometer is shown in Fig. 1.

Cubic one-section cell (20x20x20 mm) functionates as a trap either for the positive or negative ions. The direction and interdependence of various ion molecule reactions were determined by the multi ICR (in the simplest case - double resonance). Partial pressures of different components were in the range of 10^{-5}-10^{-9} Torr. Up to 4 separate compounds could be simultaneously let into the vacuum system through the VARIAN leak valves. F_2N^-, Cl^- and HO^- ions were

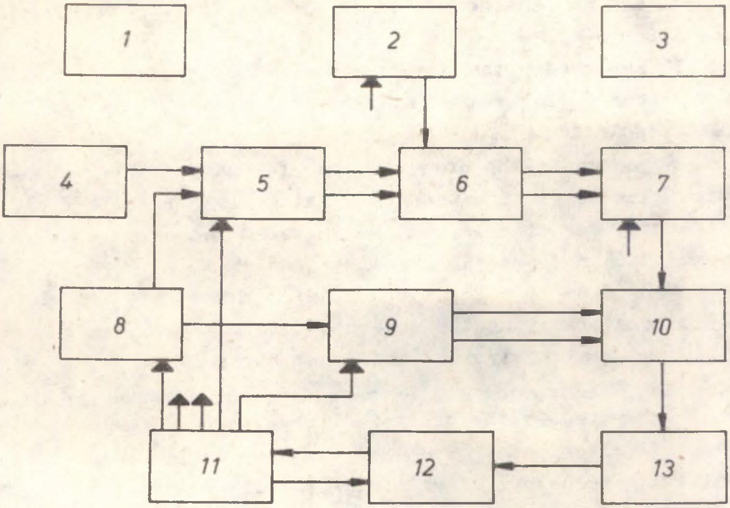


Fig. 1. Block diagrams of the capacitance bridge ICR spectrometer with the Fourier' transformations and options for multiresonance, reaction kinetics and equilibria measurement modes 1. Vacuum (5.10^{-9} Torr) and inlet systems, 2. Cell control. 3. Electromagnet and power supply. 4. Multiresonance oscillators. 5. Power amplifier. 6. Capacitance-bridge ICR cell. 7. Signal amplifier. 8. Frequency synthesizer (10kHz--1MHz). 9. Reference channels and phase shifter. 10. Phase detectors. 11. Pulse programmer. 12. NIC-1086 minicomputer, display, plotter. 13. Filters and ADC.

generated by the dissociative electron capture from F_2NH, t-BuCl and H_2O and were used to promote the ionization of the acids A_iH.

It was shown[5] that the use of FT ICR spectrometer with a superconducting magnet allows one to get extremely high mass resolution.

As shown in the present paper it was possible to obtain high mass resolution even at a rather low magnetic field strength. For example, at the magnetic induction 0.6 T the resolution for several negative ions exceeds 100,000 and for $C_6H_6^+$ ion more than 50,000 which shows that even ICR spectrometers without a superconducting magnet can compete with the best analytical mass spectrometers.

Fig. 2 shows the FT ICR mass spectrum of NOH^- and CH_3O^- ions generated by the dissociative capture of low energy (1.5 eV) electrons from CH_3ONO (5.10^{-8} Torr, 0.62 T). The following procedure of obtaining the spectrum was used: the ions formed by the 100 msec (400 nA) electron beam pulse were excited by a radiofrequency pulse from the frequency synthesizer (306.7 kHz) of 200 μsec duration and 200 mV amplitude (p-p). After a certain delay time the (amplified) induced signal will be digitized (800 Hz) by the ADC and recorded in the 2 K memory of the NIC 1086 minicomputer. The timing sequence will be finished by the quench pulse (100 msec) which ejects the ions from the analyzer cell. The stored time domain transients are Fourier - transformed by the minicomputer to the frequency domain ICR mass-spectrum. The performance of the spectrometer for the study of the gas phase proton transfer equilibria was checked by the redetermination of the equilibrium constants for some well documented[2,3] acid-base equilibria.

For the first time the proton affinities of $(CF_3)_2CHO^-$, $(CF_3)_3CO^-$ and F_2N^- anions were determined.

The experimental results are listed in the Table alongside with the experimental[6] PA_{exp} values for reference compounds A_o^- and anions A_i^- of a large number of the other OH,

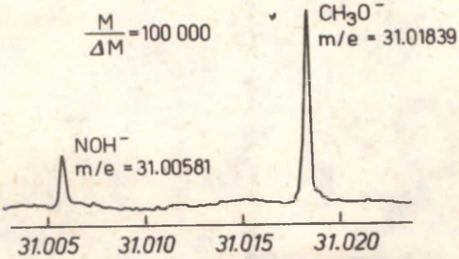


Fig. 2. ICR absorption frequency domain mass-spectrum of the CH_3O^- and NOH^- ions obtained by the Fourier transformation of the time domain transients. 16 sweeps were accumulated yielding the spectrum shown.

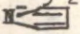
NH, CH, and SH acids A_iH. Also included in the Table are pK_a values of these acids in aqueous solution[7] and "experimental" values (PA_{exp}^{4-31G} and PA_{exp}^{CNDO}) predicted from the ab initio[8] (GAUSSIAN 70) and semiempirical (CNDO/2)[9] calculations for several negatively charged bases.

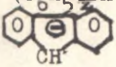
TABLE.

Experimental (PA_{exp}) and Predicted From Quantum Chemical Calculations Proton Affinities (in kcal/mol) of Bases A_i^-; Their Aqueous pK_a Values and Estimates of the Extra Solvent Effects $\Delta pK_{a(solv)}$ (in kcal/mole units).[a]

	Base A_i	PA_{exp}	PA_{exp}^{4-31G}	PA_{exp}^{CNDO}	$pK_a^{H_2O}$	$\Delta pK_{a(solv)}$
1	2	3	4	5	6	7
1.	HO^-	390.8[b]	393.3	402.1	15.7	46.9
2.	FO^-	374[c]	335.3 375.3[d]	380.5	-	-

1	2	3	4	5	6	7
3.	CH_3O^-	379.1	381.0	373.6	15.5	36.0
4.	CF_3O^-	334^c	312.3 340.5^d	335.2	-	-
5.	FCH_2O^-	-	360.4 373.5^d	356.8	-	-
6.	F_2CHO^-	-	362.0^d	-	-	-
7.	$CH_3CH_2O^-$	376.1	-	372.3	16.0	32.0
8.	$CF_3CH_2O^-$	364.4	-	384.4	12.4	28.6
9.	$(CH_3)_2CHO^-$	374.1	-	367.2	17.1	29.2
10.	$(CF_3)_2CHO^-$	347.0^e	-	332.2	9.3	12.9
11.	HOO^-	367.9^c	351.9	382.8	11.6	29.9
12.	$(CH_3)_3CO^-$	373.3	-	363.9	19.2	25.8
13.	$(CF_3)_3CO^-$	331.8^e	-	323.4	5.3	≤2.0
14.	ClO_4^-	285^c	289^d	284	-1.7÷ -8	-29
15.	NO_3^-	324.6	-	295.1	-1.5	4.1
16.	ONO^-	338.0	329.2	320.5	3.4	11.6
17.	$HCOO^-$	345.2^b	334.9	343.8	3.75	18.4
18.	$FCOO^-$	333^c	-	-	-	-
19.	CH_3COO^-	348.5^b	-	346.6	4.75	21.1
20.	FCH_2COO^-	337.6	-	-	2.55	12.2
21.	F_2CHCOO^-	330.0^b	-	-	1.30	6.1
22.	Cl_2CHCOO^-	328.4	-	-	1.30	4.8
23.	CF_3COO^-	322.7^b	-	328.5	-0.3	0
24.	$C_6H_5COO^-$	338.8	-	-	4.20	10.9
25.	$3\text{-}ClC_6H_4COO^-$	332.8	-	-	3.82	5.4
26.	$3\text{-}NO_2C_6H_4COO^-$	327.7	-	-	3.50	≤1.5
27.	$4\text{-}NO_2C_6H_4COO^-$	327.7	-	-	3.43	≤2
28.	$C_6H_5O^-$	349.8	-	-	10.00	15.0
29.	$3\text{-}NO_2C_6H_4O^-$	334.2	-	-	8.40	≤1.5
30.	$3\text{-}NCC_6H_4O^-$	335.2	-	-	8.61	0
31.	$3\text{-}FC_6H_4O^-$	344.0	-	-	9.28	0
32.	$3\text{-}CF_3C_6H_4O^-$	340.1	-	-	-	-
33.	$4\text{-}CF_3C_6H_4O^-$	337.8	-	-	-	-
34.	$3\text{-}CH_3C_6H_4O^-$	350.3	-	-	10.10	15.0
35.	$4\text{-}CH_3C_6H_4O^-$	351.7	-	-	10.27	14.5

1	2	3	4	5	6	7
36.	4-$FC_6H_4O^-$	347.3	-	-	9.90	15.0
37.	HS^-	353.4	-	338.7	7.0	21.1
38.	FS	-	316.8	329.7	-	-
39.	CH_3S^-	359.0	357.7^d	335.7	10.33	24.5
40.	CF_3S^-	-	338.2^d	313.4	-	-
41.	I^-	314.3	-	-	11	6.8
42.	Br^-	323.6	-	-	-9	10.9
43.	Cl^-	333.6^b	-	-	-7	19.7
44.	F^-	371.5^b	-	-	3.18	44.2
45.	H_2N^-	403.6	403.7	403.9	35	34.0
46.	FNH^-	-	380.3	388.8	- -	-
47.	F_2N^-	360.0^e	352.3^d	374.9	-	-
48.	CH_3NH^-	403.2	383.9^d	387.5	-	-
49.	CF_3NH^-	-	368.3^d	362.5	-	-
50.	$(CH_3)_2N^-$	-	375^d	363.2	-	-
51.	$(CF_3)_2N^-$	-	-	324.6	-	-
52.		360.7	-	-	17.5	13.6
53.	$C_6H_5NH^-$	367.1	-	-	27	8.8
54.	3-$CF_3C_6H_4NH^-$	359.1	-	-	25.4	3.4
55.	3-$CH_3C_6H_4NH^-$	367.6	-	-	-	-
56.	3-$FC_6H_4NH^-$	363.1	-	-	-	-
57.	4-$CF_3C_6H_4NH^-$	355.6	-	-	-	-
58.	4-$CH_3C_6H_4NH^-$	368.2	-	-	27	8.2
59.	4-$FC_6H_4NH^-$	365.5	-	-	-	-
60.	CH_3^-	416.6	432.6	424.2	40	41.5
61.	FCH_2^-	390	-	402.0	-	-
62.	F_2CH^-	384	-	386.0	-	-
63.	F_3C^-	375.6	-	366.4	26.5	17.0
64.	$CF_3CH_2^-$	-	-	371.1	-	-
65.	$CH_3CH_2^-$	-	-	422.0	-	-
66.	$(CH_3)_3C^-$	-	-	415.0	-	-
67.	$(CF_3)_3C^-$	-	-	321.6	7	-8.8
68.	$NCCH_2^-$	372.2	-	-	25	16.3
69.	$(NC)_2CH^-$	336.1	-	-	11.2	0
70.	NC^-	353.1	337.5	351.9	12.9	11.5

1	2	3	4	5	6	7
71.	$C_6H_5C(CN)H^-$	351.9	-	-	20.8	≤ 2
72.	$C_6H_5C\equiv C^-$	370.0	-	-	23.2	15.6
73.	$(C_2H_5OOC)_2CH^-$	348.3	-	-	15.2	5
74.	$(CH_3CO)(CF_3CO)CH^-$	328.5	-	-	6.30	0
75.	$(O_2N)_3C^-$	-	-	280	0	-40.8
76.	$O_2NCH_2^-$	358.7	-	-	10.21	20.4
77.	$CH_3SOCH_2^-$	372.7	-	-	34	2.5
78.	$CH_3SO_2CH_2^-$	366.6	-	-	28.5	≤ 3
79.	$C_6H_5SO_2CH_2^-$	362.7	-	-	29.0	0
80.	$C_6H_5COCH_2^-$	363.2	-	-	15.8	18.4
81.	$(CH_3CO)_2CH^-$	343.7	-	-	8.8	8.8
82.	$C_6H_5CH_2^-$	379.0	-	-	42	$(0)^f$
83.	$(C_6H_5)_2CH^-$	364.5	-	-	32.2	$(0)^f$
84.		353.3	-	-	22.6	$(0)^f$

Footnotes: a - If not further specified the PA_{exp} values were taken from Ref. 6. The PA_{exp}^{4-31G} and PA_{exp}^{CNDO} values were predicted on the basis of the corresponding ab intio[8] (GAUSSIAN 70, 4-31G basis set) and semiempirical CNDO/2[9] quantum chemical calculations. In the 6th column the aqueous pK_a values[7] are given for comparison. The last (7th) column lists the estimates of the extra-solvent effects (($\Delta pK_{a(solv)}$(kcal/mol)) calculated as indicated in the text.

b - Reference base A_o^- used in the present gas phase proton transfer equilibria measurements.

c - Termochemical calculations, this work.

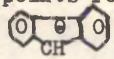
d - Ab initio GAUSSIAN 70 calculations, STO-3G basis.

e - Measured in this work.

f - By definition: see the text.

Discussion

Solvent Effects. For the rough first approximation estimate of the gross-solvent effects[10] accompanying the transition of the ion molecule reaction of proton transfer from the gas phase to solution it has sense to use the simple approach suggested by Bordwell[11] and Taft.[12]

For this purpose in Fig. 3 the gas phase PA values for a large number of anions were plotted against the corresponding pK_a values for the aqueous solution. By definition, the straight line (I) with the unity (+1) slope was put through the points representing anions A_i^- ($C_6H_5CH_2^-$, $(C_6H_5)_2CH^-$ and ) of some aromatic CH-acids which, as well as their conjugated acids A_iH, are the least capable or even not able to be stabilized by the specific solvation while going from the gas phase to solution. For compounds of this type it is assumed that due to the very significant charge delocalization the specific hydrogen bond stabilization of both the anionic (the lack of hydrates $A_i^-...HOH$) **and neutral acid form** (no hydrates of the $A_iH...O{<}^{H}_{H}$ type) **does not** take place.

It is evident that according to this model the horizontal deviations of any other points from the line (I) should serve as a relative measure of the gross (the blend of specific and (often very significant) nonspecific solvent effects) solvation interactions[10] between molecules of the solvent and solutes (A_i^- and A_iH).

The specific nucleophilic solvation of the neutral acid A_iH via the hydrogen bond stabilizes the initial state (reduction of the acidity of A_iH, the increase of the basicity of A_i^-). On the other hand, specific electrophilic solvation of the anionic form A_i^- results in the increase of the acidity of the acid A_iH and in the decrease of the basicity of its conjugated base A_i^-. Therefore, on condition of invariability of nonspecific solvent effects, in the special case of mutual compensation of specific solvent-solute interactions for the acid and its anion the situation might arise where due to the zero gross specific solvent effect compounds of a very different chemical nature and strong but equal in the two states specific solvation effects fit the same straight line with the anions of the aromatic carbon acids. Evidently, in the general case, the zero gross solvent effect in terms of the present approach might also stem from the separate non-equivalent compensation of specific and

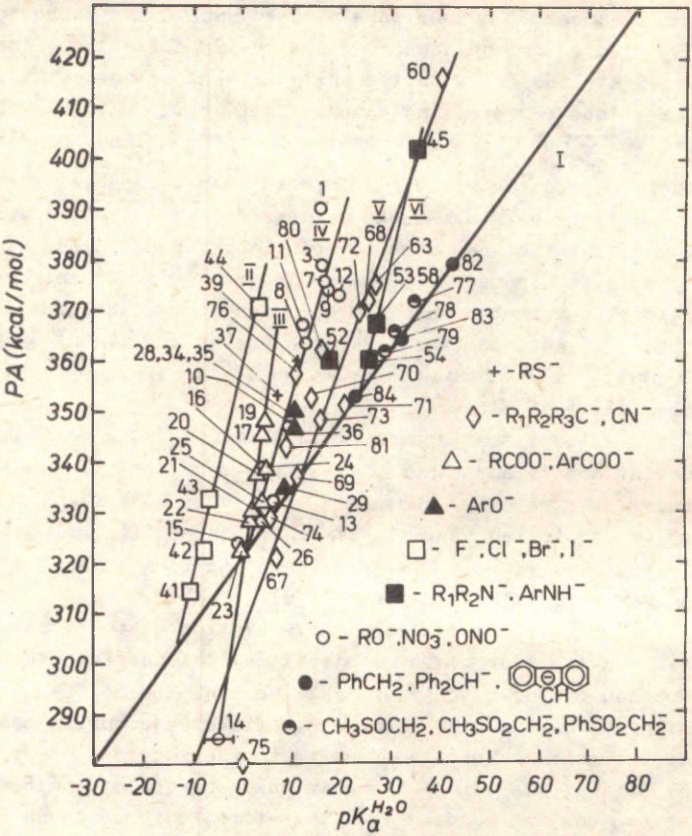


Fig. 3. The dependence of the gas phase proton affinities of anions A_i^- on their aqueous pK_a values.
The straight line (I) has the unity slope and fits the points(●) for the compounds the least stabilized by the specific solvent-solute interactions.

nonspecific solvent-solute interactions.* The deviations of points from the straight line (I) towards the higher acid strength (the decreasing values of pK_a) of A_iH shows evidence of the dominant role of the extra solvent stabilization of the anionic form whereas the deviations to the opposite direction (the increase of the base strength of A_i^-) should stem from the more significant role of the specific nucleophilic solvation of the neutral acid A_iH.

Fig. 3. shows that in most cases dominates the extra-stabilization of the anion A_i^- by the combined influence of nonspecific and specific solvent-solute interactions. The largest deviations from the line (I) belong to the relatively small anions (CH_3^-, HO^-, H_2N^-, F^-, etc.), which are characterized by the higher localization of the negative charge on the solvation and reaction center. One can see from Fig. 3 that within the different subfamilies (halide ions (line (II)), carboxylate ions, NO_3^-, and probably ClO_4^- (III), alcoholate- and phenolate anions, HO^-, $O_2NCH_2^-$ (IV), some carbanions [$(NC)_2CH^-$, $NCCH_2^-$, CH_3^-, $C_6H_5C\equiv C^-$, $(CH_3CO)(CF_3CO)CH^-$, $C_6H_5COCH_2^-$, $C_6H_5C(CN)H^-$, $(C_2H_5OOC)_2CH^-$ (V), H_2N^- and anilide-ions (VI)] the trend of domination of the extra solvent stabilization effects of the anionic form of the acid decreases with the increase of the ionic radius of the anion (i.e., towards the higher similarity with the reference anions) and/or with the introduction of the more electronegative substituents. The nature of this behavior is a complex one.

So, the increase of the effective radius of the ions due to introduction of larger fragments (substituents) or because of the better delocalization of the charge (e.g., due to the resonance stabilization of the moiety) should lead to the decrease of the intensity of the nonspecific

---

* For example, the stronger than in the case of standard series (line (I) non-specific solvent stabilization of the anion A_i^- and the opposing effect of the nucleophilic stabilization of the neutral acid A_iH.

(electrostatic) as well as electrophilic specific solvation of the anionic form of the acid. In its turn, the introduction of the more electronegative substituents should result in the decrease of the intrinsic basicity of the anion A_i^- (followed by the decreased electrophilic solvation of A_i^-) and in the increase of the acid strength of the acid A_iH which should be accompanied by the stronger nucleophilic stabilization of the latter.

The small or practically negligible gross solvent effect is characteristic to $(CF_3)_3CO^-$, CF_3COO^-, $(NC)_2CH^-$, NO_3^-, $(CH_3CO)(CF_3CO)CH^-$, $C_6H_5C(CN)H^-$, 3-$CF_3C_6H_4NH^-$, 3-CN-and 3-NO_2-$C_6H_4O^-$, I^-, and to some other anions (See Table and Fig. 3).

Perchloric acid, trinitromethane, and probably $(CF_3)_3CH$ are the representatives of compounds which are characterized by the extra-stabilization effect of the neutral acid A_iH. In this case (significant delocalization of the charge in the the anionic form, the presence of strongly electronegative substituents) the specific as well as nonspecific solvent stabilization of the anionic form A_i^- is compensated and even overridden by the joint influence of the very strong nucleophilic specific stabilization of the highly electrophilic neutral acid which is assisted by the nonspecific stabilization of the latter.

Some estimates of the intensity of the solvent extra-stabilization effects are given in the last column of the Table where the extent of the horizontal deviation ($\Delta pK_{a(solv)}$) of the given point from the reference line (I) is chosen as its quantitative measure (in kcal/mol*).

---

* The positive value refer to the extra-stabilization of the anionic form whereas the negative $\Delta pK_{a(solv)}$ values indicate to the preferential solvent stabilization of the neutral acid.

Several inversions of the basicity order for the aqueous solutions accompany the transition of the proton transfer equilibrium from the water to the gas phase. Here, reference will be given only to the behavior of compounds studied in the experimental section of this paper. So, in aqueous solution $(CF_3)_3COH$ and $(CF_3)_2CHOH$ are weaker acids (pK_a=5.2 and 9.3) than the acetic acids (4.75). However in the gas phase these compounds are already correspondingly by 12.3 and 1.1 kcal/mol stronger acids than CH_3COOH whereas the solvent effects of these transfers amount to 17.3 and 7.6 kcal/mol.

Even larger differential solvent effect (18.4 kcal/mol) is responsible for the inversion of the aqueous basicity order of Cl^- (pK_a= -7) and $(CF_3)_3CO^-$ anions.

Structural effects of fluorine-containing substituents

The analysis of substituent effects could be started by recalling that in the first approximation[12,13] the gas phase basicity or acidity are determined by the inductive, polarizability, and resonance characteristics of the substituents. For the separate quantitative consideration of these inluencing factors it is reasonable to make use of the specifically chosen model compounds the acid-base preperties of which depend only on one of those structural factors. It is known[13] that the polarizabilities of fluorine and hydrogen atoms are practically equal. Therefore, on condition of the rough equivalency or negligibility of their resonance characteristics the structural effect of the substitution of the fluorine atom for the hydrogen atom or fluoroalkyl radical for the corresponding unsubstituted alkyl group should be determined only by the differences in the inductive characteristics of the substituted and unsubstituted fragments. Judging by the cleseness of the values[14] of the Taft σ^* inductive constants for fluorine (3.19) and CF_3-group ($2.6 \leq \sigma^* \leq 3.3$) one should expect not too different effects of the substitution of F for H and CF_3 for CH_3 radical.

The analysis of the data from Table leads to the situa-

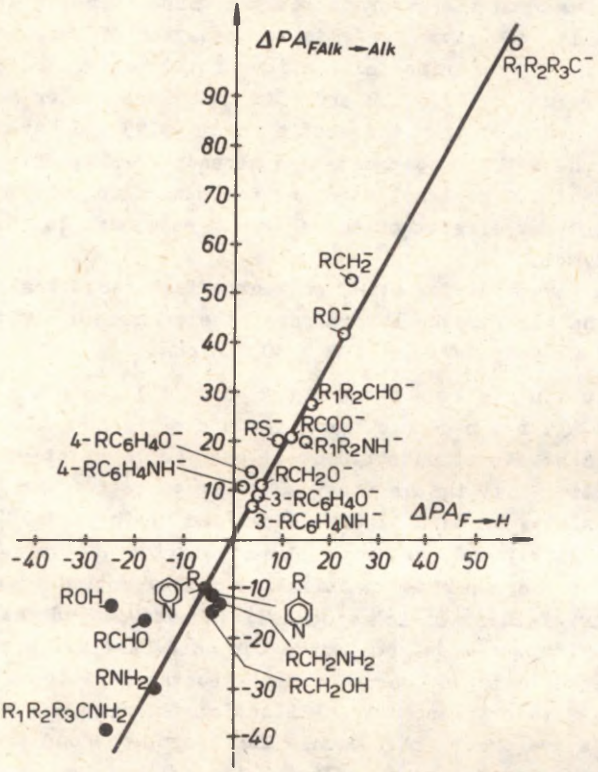


Fig. 4. The comparison of the effect of the substitution of fluoroalkyl substituents for the alkyl group ($\Delta PA_{FAlk \to Alk}$) with the effect of substitution of F-atom for H atom ($\Delta PA_{F \to H}$) on the gas phase basicity of several classes of anions A_i^- (O) and neutral Bases B_i (●).

tion shown in Fig. 4. The available data[2,4,6,8] on the analogous substituent effect on the gas phase basicity of neutral bases B_i (amines, alcohols, ethers, carboxylic acids, ketones, aldehydes) were also included for comparison.

Fig. 4 reveals that both effects vary over an extremely wide range (from ca'+100 to -40 kcal/mol) depending on the charge type and chemical nature of the classes of bases. Within the error limits of the available data the following proportionality was found to exist between the quantities compared:

$$\Delta PA_{FAlk \longrightarrow Alk} = \alpha \Delta PA_{F \rightarrow H} ,$$

where α is close to 2. In other words, the perfluoroalkyl effect exceeds twice the corresponding effect of the substitution of F atom for the hydrogen. One can see from Fig. 4 that the straight line actually intercepts the origin of the coordinates which for all classes of compounds corresponds to the pair of substituents removed to the infinity from the protonization center.

Some neutral bases of the type ROH, RCHO and R_1R_2CO deviate from this very primitive relationship (see Fig.4). In these cases the effect of the vicinal to the reaction center α-fluorine atom is "anomalously" strong most probably because of the resonance stabilization of the protonized form of the base by the fluorine lone pair:

$$FOH_2^+ \longleftrightarrow F^+{=}OH_2; \; FC(OH)H^+ \longleftrightarrow F^+{=}C(OH)H, \text{ etc.}$$

The domination of the perfluoroalkyl effect over the substituent effect of the fluorine atom closely reminds the effects of these substituents on the reactions in solution[15]. The origin of the perfluoroalkyl/fluorine substituent effects will be a topic of a separate publication.

References

1. T. Lehman and M. Bursey, Ion Cyclotron Resonance Spectroscopy, J. Wiley, New York, 1976.
2. J.F. Wolf, R.H. Staley, I. Koppel, M. Taagepera, R.T. McIver, Jr., J.L. Beauchamp, and R.W. Taft, J. Am.Chem. Soc., 99, 5417(1977).
3. J.E. Bartmess, J.A. Scott, and R.T. McIver, Jr., ibid., 101, 6046 (1979).
4. M.I. Kabatschnik, Uspekhi Khimii, 48, 1523 (1979).
5. M. Alleman, H. Kellerhals, and K.-P. Wanczek, Chem.Phys. Lett., 75, 328 (1980).
6. I.A. Koppel, U.H. Mölder, and R.J. Pikver, Organic Reactivity, 17, 457 (1980); P. Kebarle, Ann.Rev. Phys. Chem., 28, 445 (1977); G. Kemister, A. Pross, L. Radom, and R.W. Taft, J. Org. Chem., 45, 1056 (1980).
7. V.A. Palm (Ed.), Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions, Vol. 1(1) and 2(1), Moscow, VINITI, 1975-1976. A. Albert, E. Serjeant, Ionization Constants of Acids and Bases, Moscow-Leningrad, Khimiya, 1964 (Russian translation).
8. I.A. Koppel and M.B. Comisarow, Organic Reactivity, 17, 495 (1980).
9. I.A. Koppel and U.H. Mölder, ibid., 18, 54 (1981).
10. I.A. Koppel and V.A. Palm, in N.B. Chapman and J. Shorter (Eds.), Advances in LFER, Plenum , New York, 1972, p.203. C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, Weinheim, New York, 1979.
11. F.G. Bordwell, W.S. Matthews, G.E. Drucker, Z. Margolin, and J.E. Bartmess, J. Am. Chem. Soc., 97, 3226 (1975).
12. R.W. Taft in: P. Ausloos (Ed.), Kinetics of Ion Molecule Reactions, NATO Advanced Study Institute Series (B-Physics), 40, 271 (1979). Plenum, New York.
13. I.A. Koppel and M.M. Karelson, Organic Reactivity, 11, 985 (1975).
14. I.A. Koppel, M.M. Karelson, and V.A. Palm, ibid., 11, 99 (1974).
15. O.A. Reutov, I.P. Beletskaya, and K.P. Butin, CH-Acids, Moscow, Nauka, 1980 (in Russian).

Organic Reactivity
Vol.18,1(65),1981

AB INITIO SCF LCAO MO CALCULATIONS OF MOLECULES. II. IONIZATION POTENTIALS *

I.A. Koppel, U.H. Mölder, and M.B. Comisarow

Laboratory of Chemical Kinetics and Catalysis,
Department of Chemistry, Tartu State University,
Tartu, Estonian S.S.R., U.S.S.R.
Department of Chemistry, University of British
Columbia, Vancouver, B.C., Canada

Received: January 5, 1981

Ab initio SCF LCAO MO calculations of ionization potentials (IP) of various classes of compounds have been done using the GAUSSIAN 70 system of programs [1-3] with the STO-3G and 4-31G basis sets. These results have been compared with those of semiempirical CNDO/2 calculations.

A rather general linear relationship was established between experimentally determined photoelectron spectra (PES) and ab initio energies of molecular orbitals ε. Ab initio proton affinities (PA) also depend linearly on the energies of the highest occupied MO (HOMO) in good agreement with the earlier found linear relationship between experimental values of PA and IP. The split-valence 4-31G basis was shown to have some advantages over the STO-3G in predicting this and other relationships established in the present work.

The early attempts to compare the results of quantum chemical calculations with the experimental data refer to the energies of the occupied MO-s. According to the

---

* See Ref. 4 for the previous communication of this series.

Koopmans' theorem [5] for the closed shell molecule the ab initio SCF energy of MO is approximately equal to the negative of the energy of ionization of the electron from this orbital. At the same time the invariability of the MO (the lack of the reorganization of the electron shell) and the constancy of the electron correlation energy contribution into the total energy are assumed during the transfer of the molecule to the ion-radical state during the ionization process.

The failure to take into account the stabilization of the ion-radical due to the reorganization of the MO during the ionization process leads to the overestimated values of IP-s. At the same time negligence to account for the non-zero difference in the correlation energies of the cation-radical and the molecular ground state (the former, probably, has larger correlation energy than the latter) is responsible for the underestimated values of ionization potentials.[6]

Hence, only when the sum of these two contributions is constant or depends linearly on the IP one should expect the observance of the linear relationship

$$IP = \alpha \varepsilon_{SCF} + \beta \qquad (1)$$

where α and β are constants.

Only in the limiting special case of the total exact compensation of these two contributions or in the case of invariability of their difference in the process of ionization Eqn.(1) reduces to the simple proportionality $IP = -\varepsilon_{SCF}$ with $\alpha = -1$ and $\beta = 0$.

Naturally, these limitations to the Koopmans' theorem are valid regardless of the nature of the ground state to be ionized (neutral molecule, radical or ion.)

In this work mostly the compounds with the lone electron pairs are considered. In this connection it is necessary to mention that the increase of the extent of the localization of the corresponding MO leads to the increase of the expected contribution from the energy of reorganization.

Also, sometimes there are additional limitations to the Koopmans' theorem for the open shell molecules which are due to the partial inability of the simple Slater determinant to represent adequately the wave-functions of such a species.

However, taking into account all of these additional factors is rather complicated. Moreover, there is no satisfactory general algorithm for making these corrections into the calculated gross-values. Therefore, as a rule, despite its many failures (see e.g., Ref. 17) the Koopmans' theorem is frequently used for comparisons of orbital energies with the experimental ionization potentials.

The comparison of energies of MO calculated from the Koopmans' theorem with the ionization potentials determined from PES has been done for a relatively small number of molecules. Only in a few cases an attempt was made to check up the relationship (1) throughout the homologous row of compounds.

So, for example, in Ref. 6 an Eqn. (2).

$$IP = -0.74\,\varepsilon_{STO-3G} + 3.77 \qquad (2)$$

and in Ref. 7 the following Eqn. for dimethoxybenzenes

$$IP = -0.70\,\varepsilon_{STO-3G} + 3.75 \qquad (3)$$

were found to be valid.

On the other hand, ionization potentials could be, in principle, calculated as the differences ΔE in the total energies E_{tot} of the molecule in the ground state (M) and in its ionized form (cation-radical):

$$IP = \Delta E = E_{tot}(M) - E_{tot}(M^+) \qquad (4)$$

However, the prediction of the higher ionization potentials includes the calculation of the molecular ions in their excited states. Therefore this approach is usually limited to the calculation of the first ionization potentials only. It is evident that the success of this approach as well as that of the Koopmans' theorem depends heavily on the invariability of the energy of electron correlation in the ionization process of the molecule. In the present paper using the data from Ref. 8 (4-31G basis) the applicability of Eqn. (4) was checked up in terms* of the linear Eqn. (5)

$$IP = \alpha' \Delta E + \beta' \qquad (5)$$

where α' and β' are the constants using the least squares analysis of the first IP-s for 25 compounds (See Table 1 and Fig. 1)

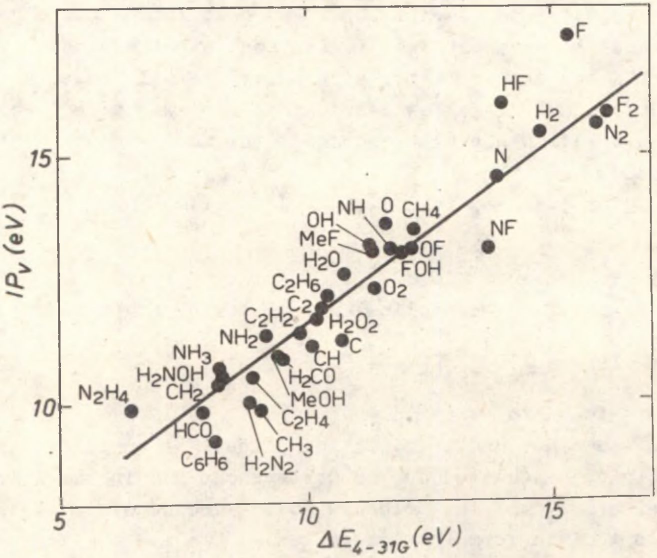


Fig. 1. The dependence (Eqn.(6)) of the 1st vertical ionization potentials on the corresponding ionization energies calculated with the 4-31G basis according to Eqn. (4).

---

* For the sake of generality the presence of the non-zero intercept β' was assumed.

The following equation holds:

$$IP = 0.72(0.03)\Delta E + 4.45(0.32) \qquad (6)$$

$r = 0.982$; $s = 0.33$ eV; $\Delta IP_{max} = 6.5$ eV;
$s\% = (s/\Delta IP_{max}).100 = 5.1$, $n = 34$,

where r - correlation coefficient
s - standard deviation
n - number of points
ΔIP_{max} - the maximum range of changing the experimental IP values

Here and in the following the standard errors of the regression coefficients are given in parenthesis.

As follows from practical consideration it is most easier to carry out the analysis of PES in terms of Koopmans' theorem. Keeping this in mind in the present work extensive ab initio LCAO MO calculations of a relatively large number of molecules and ions were performed using the GAUSSIAN 70 system of programs with the STO-3G and 4-31G basis sets and with the usual scaling factors.[2,3]

Geometries of the molecules considered were given elsewhere.[4] Calculations were made on the Amdahl 470 V/6-11 computer of the Computing Centre of the University of British Columbia, Vancouver, B.C., Canada.

The dependence of the IP-s determined from PES on the energies of MO calculated using ab initio methods was studied.

The results of the least squares analysis of the relationship between the first vertical ionization potentials and energies of HOMO (see Table 2) lead to the following results [*]:

$$IP_1 = 0.94(0.04)\varepsilon_{CNDO} - 2.23\ (0.39) \qquad (7)$$

$r = 0.975$; $s = 0.35$ eV; $\Delta IP_{max} = 7.38$ eV; $s\% = 4.7$;
$n = 62$

---

[*] Eqn. (7) is taken from Ref. 9.

Table 1

The 1st Vertical Ionization Potentials IP and Calculated With 4-31G Basis from Eqn. (4) ΔE Values (in eV)

No	Compound	IP	ΔE	No	Compound	IP	ΔE
1.	H_2	15.43	14.76	18.	C_2H_4	10.51	8.87
2.	C	11.26	10.70[b]	19.	C_2H_6	12.1	10.40
3.	CH	11.13	10.09	20.	HCO	9.83	7.9
4.	CH_2	10.4	8.18	21.	H_2CO	10.88	9.54
5.	CH_3	9.84	9.05[b]	22.	MeF	13.05	11.33
6.	CH_4	13.5	12.14	23.	MeOH	10.96	9.37
7.	N	14.53	13.84	24.	N_2	15.58	15.93
8.	NH	13.1	11.7	25.	HN=NH	10.02	8.83[b]
9.	NH_2	11.4	9.16	26.	H_2NOH	10.56	8.29
10.	NH_3	10.72	8.20	27.	NF	13.1	13.67[b]
11.	O	13.62	11.63[b]	28.	O_2	12.31	11.43
12.	OH	13.17	11.27	29.	H_2O_2	11.7	10.20
13.	H_2O	12.60	10.74	30.	OF	13.1	12.13
14.	F	17.42	15.31[b]	31.	FOH	13.0	11.92
15.	HF	16.03	13.95[b]	32.	F_2	15.82	16.14
16.	C_2	11.9	10.27	33.	N_2H_4	9.93	6.42[b]
17.	C_2H_2	11.4	9.85	34.	C_6H_6	9.25	8.14[a]

a - From Ref. 11, does not obey Eqn. (6)

b - This value does not fit Eqn. (6)

$$IP_1 = 0.75(0.02)\mathcal{E}_{3G} + 3.82(0.20) \qquad (8)$$

$r = 0.983$; $s = 0.57$ eV; $\Delta IP_{max} = 12.2$ eV; $s\% = 4.7$; $n = 35$

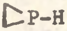
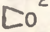
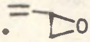
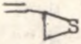
$$IP_1 = 0.77(0.02)\mathcal{E}_{4-31G} + 1.85(0.25) \qquad (9)$$

$r = 0.988$; $s = 0.43$ eV; $\Delta IP_{max} = 13.5$ eV; $s\% = 3.2$; $n = 33$

Table 2.

1st Vertical Ionization Potentials and Energies of HOMO

Compound	IP	Refs.	$-\mathcal{E}_{4-31G}$	Refs.	$-\mathcal{E}_{3G}$	Refs.
1. NH_3	10.72	12	10.94	32	9.75	37
2. $MeNH_2$	9.66	12	10.20	33	-	-
3. $EtNH_2$	9.50	12	10.0	32	-	-
4. $ClNH_2$	10.52	13	10.85	33	-	-
5. N_2H_2	10.02	14	11.14	34	9.07	34
6. Me_3N	8.55	12	9.44	33	-	-
7. F_3N	13.73	15	14.89	35	10.62[a]	35
8. Me_2NH	8.94	16	9.71	16	-	
9. F_2NH	12.36	17	14.04	35	10.18	35
10. $HONH_2$	10.56	18	11.23	35	6.61[a]	35
11. H_2NCHO	10.32	12	11.12	33	9.08	36
12. $(NH_2)_2CO$	10.28	20	-	-	8.66	36
13. Pyridine	9.67	12	11.12	37	9.20	37
14. F_3NO	14.3	21	15.5	38	7.78[a]	35
15. Me_3NO	8.43	19	-	-	4.12[a]	35
16. HNO_3	12.44	22	-	-	7.85[a]	35
17. 1,2-diazine	9.3	12	10.75	37	-	-
18. 1,3-diazine	9.7	12	10.84	37	-	-

19. 1,4-diazine	9.4	12	11.13	37	-	--
20. HCN	13.60	12	13.52^a	33	13.41	37
21. MeCN	12.18	12	12.54	33	-	-
22. $(CN)_2$	13.36	12	-	-	11.84^a	35
23. H_2O	12.6	12	13.57	35	-	-
24. MeOH	10.96	12	12.16	33	-	-
25. Me_2O	10.04	16	11.36	16	-	-
26. CF_3OF	13.63	23	16.65^a	39	11.34	39
27. F_2O	13.25	24	15.65	35	10.64^a	35
28. FOH	13.0	25	14.91	35	10.33^a	35
29. O_2	12.3	12	-	-	10.25	35
30. H_2CO	10.86	12	11.91	33	9.64	36
31. MeCHO	10.23	12	11.51	33	9.17	41
32. Me_2CO	9.70	12	11.12	33	8.76	41
33. $(CHO)_2$	10.52	26	-	-	8.92	36
34. F_2CO	13.6	12	-	-	11.18^a	36
35. FCHO	12.55	27	-	-	10.45	36
36. MeSH	9.44	28	-	-	6.71	35
37. Me_2PH	9.10	16	9.12	16	-	-
38. 	9.03	16	9.36	16	6.92	29
39. 	9.75	16	9.88	16	7.92	16
40. Me_2S	8.68	16	9.03	16	-	-
41. 	10.57	29	-	-	9.91	29
42. 	10.26	29	-	-	9.67	29
43. 	9.94	29	-	-	8.16	29
44. 	8.88	29	-	-	6.65	29
45. 	8.89	29	-	-	6.76	29
46. HCl	12.74	12	12.75^a	33	11.42	42
47. MeCl	11.22	12	11.70	33	10.36	42
48. EtCl	10.97	12	-	-	10.18	42
49. i-PrCl	10.78	30	-	-	10.00	42
50. t-BuCl	10.61	30	-	-	9.81	42
51. FCl	12.77	12	18.14^a	33	-	-
52. HF	16.03	12	17.08^a	33	12.63^a	40

53. MeF	13.05	12	14.20	33	11.38	40
54. i-PrF	11.1	31	12.82	40	10.54	40
55. EtF	12.43	12	13.42	33	10.86	40
56. $FCH=CH_2$	10.58	12	10.55	33	8.50	40
57. F_2	15.82	12	18.14	33	-	-
58. NO_3^-	3.9	10	-	-	-0.02	35
59. ClO_4^-	5.82	10	-	-	2.77	35
60. FO^-	1.4	10	3.67[a]	35	-4.24	35
61. ClO^-	2.9	10	4.23[a]	35	-0.03	35
62. NO_2^-	2.36	10	-0.26	35	--2.03	35
63. HOO^-	3.0	10	0.19[a]	35	-4.67[a]	35
64. F_2N^-	3.0	10	4.12[a]	35	-	-
65. SF^-	2.5	10	1.72	35	-	-
66. O_2^-	-	-	-0.26	35	-	-
67. FCH_2O^-	-	-	0.25	35	-	-
68. H_2NO^-	-	-	0.07	35	-	-
69. FNH^-	-	-	0.55	35	-	-
70. O_2^{2-}	-	-	-8.68	35	-	-
71. CF_3NH_2	-	-	-	-	10.04	35

Footnote: a - This value does not fit Eqns. (8) and (9).

As was shown in Ref. 9 the semiempirical CNDO/2 calculation of the 1st IP-s of various molecules in terms of Eqn.(4) does not lead to a satisfactory result. The use in the same framework of ab initio results gotten with the extended split-valence 4-31G basis set improves the outcome significantly (see Eqn. (6)). However, the comparison of the statistical characteristics of Eqns.(6) and (9) still seems to favor the approach based on the Koopmans' theorem. It is interesting to note that HF molecule does fit neither Eqn. (6) nor Eqns. (8) and (9).

The study of the general relationship between the energies of the occupied MO-s and IP determined from PES is a rather complicated task for several reasons.

So, for example, it was shown [10] that the shortcomings of the Koopmans' theorem are most noticeable for the case of inner molecular orbitals .

On the other hand, there is no guarantee that the essentially complete photo electron spectrum has been determined with the all lines resolved. As a matter of fact frequently there are some lines in the calculated spectra which are so closely spaced that they are hardly unresolvable in the real PES experiment. Unfortunately, it is enough to assign uncorrectly only one spectral line in the PES when all the following lines will also be misinterpreted.

However, despite those difficulties the analysis of a large number of PES shows that a certain rather general relationship holds. It is preferable to make the statistical treatment of the available data in terms of the linear dependence of PES ionization potentials IP_i on the calculated energies ε_{calc} of the i-th MO:

$$IP_i = \alpha'' \varepsilon_{calc} + \beta'' \qquad (10)$$

where α'' and β'' are constants.

Such a treatment anticipates that the data sets with the adequately assigned experimental and calculated PES will be characterized by the highest correlation coefficients and with the slopes α'' which are relatively close to the unity.

The least squares treatment of available data (see Table 3) in terms of Eqn.(10) results in the following relationships* (see also Fig. 2 and 3):

---

* Eqn. (11) is taken from Ref. 9.

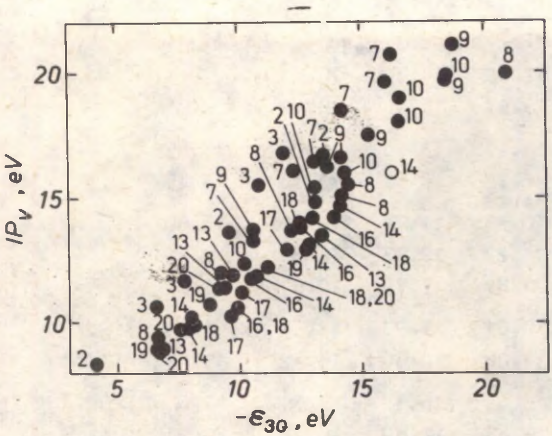


Fig.2. Comparison (Eqn.(12)) of experimental PES with the energies of MO calculated using the STO-3G basis set. The numbering of points corresponds to Table 3.

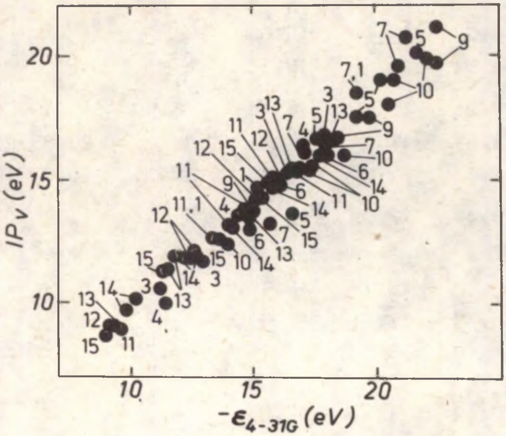
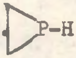
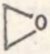
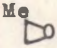
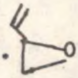
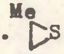
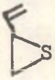


Fig.3. Comparison (Eqn.(13)) of experimental PES with the energies of MO calculated using the 4-31G basis set. The numbering of the points corresponds to Table 3

Table 3

Experimental PES and Calculated with the STO-3G and 4-31G Basis Sets MO Energies (in eV).

	Refs.	PES and energies of MO $-\varepsilon_i$					
1. H_2O	35a	12.62	14.74	18.51			
	35b	13.57	15.15	19.22			
2. Me_3NO	19a	8.43	13.55	14.80	16.65		
	35c	4.12	9.57	13.16	13.45		
		4.18					
3. $HONH_2$	18a	10.59	11.70	15.50	16.80		
	35b	11.23	12.97	16.88	17.91		
	35c	6.61	7.79	10.81	11.83		
4. Me_2O	16a	10.01	11.90	13.55	14.20	16.4	
	16b	11.36	12.66	14.42	15.11	17.03	
5. CF_3OF	23a	13.63	16.6	17.5	19.0	20.1	
	39b	16.65	17.60	19.26	20.21	21.65	
				19.12	20.35		
				19.31	20.89		
				19.45			
6. FOH	25a	13.0	14.8	16.0			
	35b	14.91	16.18	18.13			
7. F_2O	24a	13.25	16.10	16.44	18.50	19.55	20.7
	35b	15.65	17.11	17.95	19.22	20.85	21.15
	35c	10.64	12.24	13.12	14.19	16.03	16.16
8. MeSH	28a	9.44	12.0	13.7	15.1	15.5	20
	35c	6.71	9.28	12.15	14.2	14.48	20.87
9. NF_3	15a	13.73	16.15	16.55	17.52	19.71	
	35b	14.89	18.14	18.33	19.72	22.52	
			18.14		19.72	22.52	
						22.52	
	35c	10.62	13.57	14.23	15.25	18.40	18.71
			13.57		15.25		18.71
			13.57				

	Refs.	PES and energies of MO $-\varepsilon_i$						
10. HNF_2	17a	12.38	15.37	15.54	15.98	18.01	19.0	19.77
	35b	14.04	17.34	17.43	18.73	20.47	20.67	22.12
	35c	10.18	12.96	13.06	14.27	16.52	16.52	18.47
11. Me_2NH	16a	8.93	12.62	13.2	13.8	15.1	15.4	16.65
	16b	9.71	13.59	14.00	14.75	15.76	16.77	17.88
12. Me_2PH	16a	9.10	11.8	12.1	13.65	14.15	15.0	15.0
	16b	9.12	12.36	12.62	15.04	15.14	15.95	16.22
13. 	16a	9.03	11.37	11.93	13.51	15.33	16.58	
	16b	9.36	11.51	11.71	14.91	16.43	18.5	
	29c	6.92	9.39	9.70	13.41			
14. 	16a	9.75	10.21	11.78	13.10	14.75	16.0	
	16b	9.88	10.20	12.33	14.18	15.83	17.76	
	16c	7.92	8.03	10.68	12.88	14.19	16.29	
15. Me_2S	16a	8.68	11.35	12.75	14.25	14.90	15.5	
	16b	9.03	11.30	13.29	15.39	15.63	16.44	
16. 	29a	10.57	11.71	13.7	14.2			
	29c	9.91	10.53	12.54	13.89			
17. 	29a	10.26	11.23	12.88	13.33			
	29c	9.67	10.07	11.99	13.19			
18. 	29a	9.94	10.58	12.21	13.88	14.22		
	29b	8.16	9.86	11.16	12.53	13.04		
19. 	29a	8.88	10.76	11.44	12.89			
	29b	6.65	8.82	9.47	12.80			
20. 	29a	8.89	9.72	11.44	12.23	13.89		
	29b	6.76	7.61	9.31	11.04	12.62		

a - Experimental PES

b - ab initio calculations, 4-31G basis set

c - ab initio calculations, STO-3G basis set

$$IP_i = 0.90(0.01)\varepsilon_{CNDO} - 1.75(0.25) \qquad (11)$$

$r = 0.975$; $s = 0.53$ eV; $\Delta IP_{max} = 11.7$ eV;
$s\% = 4.5$; $n = 192$ (48 molecules)

$$IP_i = 0.88(0.05)\varepsilon_{3G} + 3.36(0.56) \qquad (12)$$

$r = 0.919$; $s = 1.25$ eV; $\Delta IP_{max} = 11.7$ eV;
$s\% = 10.7$; $n = 63$ (13 molecules)

$$IP_i = 0.97(0.02)\varepsilon_{4-31G} + 0.93(0.32) \qquad (13)$$

$r = 0.982$; $s = 0.57$ eV; $\Delta IP_{max} = 11.7$ eV;
$s\% = 4.9$; $n = 70$ (13 molecules)

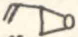
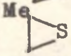
The comparison of statistical characteristics of Eqns. (12) and (13) and Figs. 2 and 3 shows that the extended split-valence 4-31G basis has some definite advantages over the STO-3G basis set. Due to the different data sets involved Eqns. (12) and (13) cannot be directly compared with the Eqn. (11). However it is still evident that, as a rule, CNDO/2 approximation also leads at least to the satisfactory description of the PES of a large number of molecules.

As a rule, the separate linear correlations of PES for the molecules from Table 3 in terms of Eqn. (10) also lead to the slopes α'' which, within their error limits, are rather close to the unity. Correlation statistics of this analysis is presented in Table 4. Some typical examples are also represented in Fig. 4 and 5.

Table 4

Separate Correlations of PES With ab initio Energies of the i-th Molecular Orbital in Terms of Eqn.(10). Data Are From Table 3.

Compound	Method	α''	β''	r	s	n
1. F_2O	a	1.27(0.12)	-6.20(2.29)	0.982	0.58	6
	b	1.22(0.12)	0.62(1.61)	0.982	0.57	6
2. H_2NOH	a	0.94(0.05)	-0.21(0.81)	0.997	0.30	4
	b	1.21(0.04)	2.43(0.32)	0.999	0.15	4
3. NF_3	a	0.78(0.02)	2.04(0.35)	0.999	0.10	5
	b	0.85(0.06)	4.55(0.93)	0.990	0.42	6
4. Me_3NO	b	0.79(0.13)	5.35(1.27)	0.976	0.95	4
5. H_2O	a	1.02(0.09)	-1.00(1.45)	0.996	0.37	3
6. HNF_2	a	0.93(0.06)	-0.76(1.15)	0.989	0.41	7
	b	0.89(0.06)	3.55(0.94)	0.987	0.44	7
7. 	a	0.79(0.06)	2.09(0.80)	0.989	0.45	6
	b	0.67(0.13)	4.86(1.26)	0.965	0.59	4
8.  -H	a	0.79(0.02)	2.03(0.28)	0.999	0.15	6
	b	0.73(0.04)	4.08(0.45)	0.995	0.29	6
9. Me_2NH	a	0.94(0.03)	-0.13(0.51)	0.997	0.23	7
10. Me_2PH	a	0.83(0.03)	1.53(0.44)	0.996	0.20	7
11. Me_2O	a	1.09(0.05)	-2.24(0.05)	0.997	0.20	5
12. CF_3OF	a	1.17(0.19)	-5.05(3.82)	0.983	0.77	5
	b					
13. MeSH	b	0.72(0.03)	4.87(0.42)	0.996	0.36	6
14. Me_2S	a	0.88(0.05)	0.97(0.62)	0.995	0.29	6
15. FOH	a	0.91(0.22)	-0.25(3.58)	0.972	0.50	3
16. 	b	0.98(0.15)	1.95(1.73)	0.974	0.47	4

17.		b	0.84(0.15)	2.50(1.67)	0.970	0.43	4
18.		b	0.94(0.11)	1.86(1.18)	0.981	0.43	5
19.		b	0.64(0.10)	4.97(0.93)	0.977	6.44	4
20.		b	0.82(0.06)	3.46(0.53)	0.993	0.27	5

a - Calculations using 4-31G basis set.

b - Calculations using STO-3G basis set.

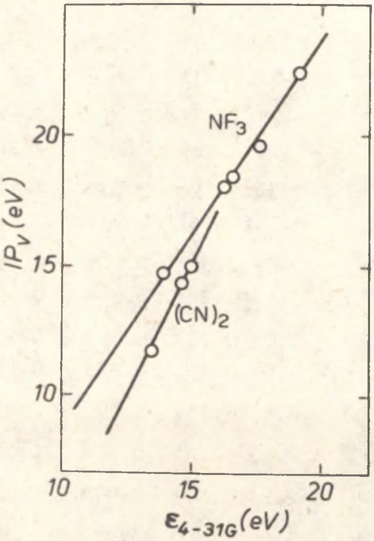


Fig. 4. The dependence of PES for NF_3 and $(CN)_2$ molecules on the ab initio 4-31G MO energies.

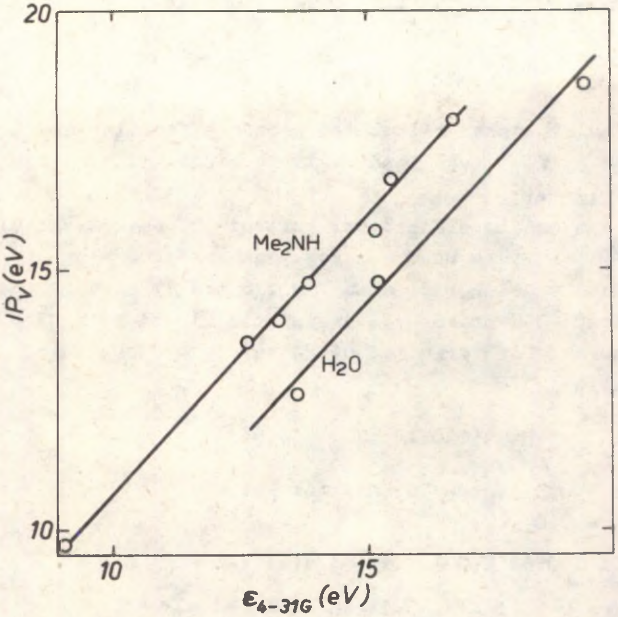


Fig. 5. The dependence of PES for H_2O and Me_2NH molecules on the ab initio 4-31G MO energies.

Evidently Eqns. (1) - (13) as well as the separate correlations from Table 4 should be regarded as rough approximations to the real situation. Despite that they are still useful starting points for the assignment of first 4-5 lines in the corresponding photoelectron spectra.

It should be mentioned that Eqs. (11) - (13) and correlation equations from Table 4 are also backed up by the fact that the data sets with the highest correlation coefficients are simultaneously characterized by the slopes α'' of Eqn.(10) which are the closest to the unity.

It was demonstrated earlier [9] in the framework of CNDO/2 approximation that the linear relationship

$$PA'_{calc} = \alpha''' \varepsilon_{calc} + \beta''' \qquad (14)$$

should hold between calculated proton affinities and energies of MO-s localized on the protonization center of the corresponding bases.

The systematic statistical analysis of data available undertaken in this work assures that the same type of relationship holds (see also Figs. 6 and 7) also on the ab intio (4-31G and STO-3G basis sets) level over the maximum range of variation of PA values by more than 530 kcal/mol:

$$PA_{CNDO} = -0.99(0.01)\,\varepsilon_{CNDO} + 626(3) \qquad (15)^{*}$$

$r = 0.993$; $s = 20$ kcal/mol ; $s\% = 1.3^{**}$;
$n = 110$

$$PA_{3G} = -0.88(0.03)\,\varepsilon_{3G} + 426(6) \qquad (16)$$

$r = 0.992$; $s = 13.1$ kcal/mol ; $s\% = 2.4$;
$n = 15$

$$PA_{4-31G} = -0.76(0.02)\,\varepsilon_{4-31G} + 404(5) \qquad (17)$$

$r = 0.992$; $s = 11.8$ kcal/mol; $s\% = 2.2$;
$n = 29$

---

[*] Eqns. (15) is taken from Ref. 9. It was shown there that on more detailed consideration this general formal relationship splits into several, more limited, but statistically distinguishable dependences of PA_{calc} on ε_{CNDO} which are characterized by the slopes $-0.95 \leq \alpha''' \leq -1.04$

[**] $\Delta PA_{max} = 1565$ kcal/mol.

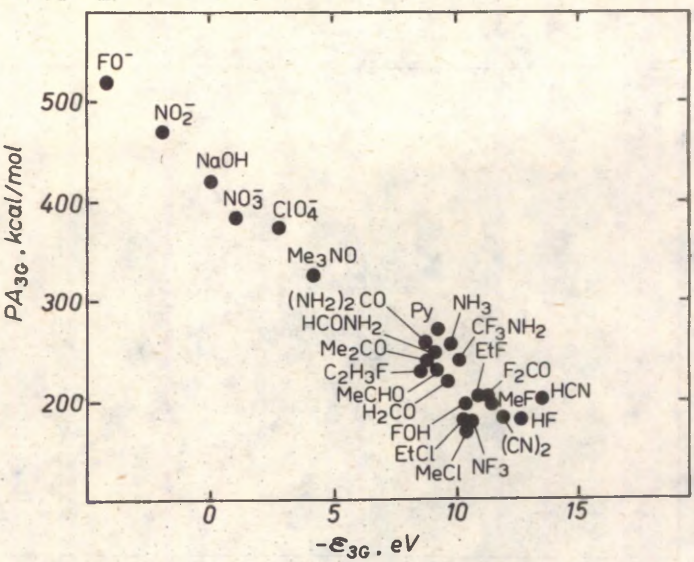


Fig. 6. The STO-3G predicted relationship (Eqn. (16)) between proton affinities and energies of the HOMO of the protonization center.

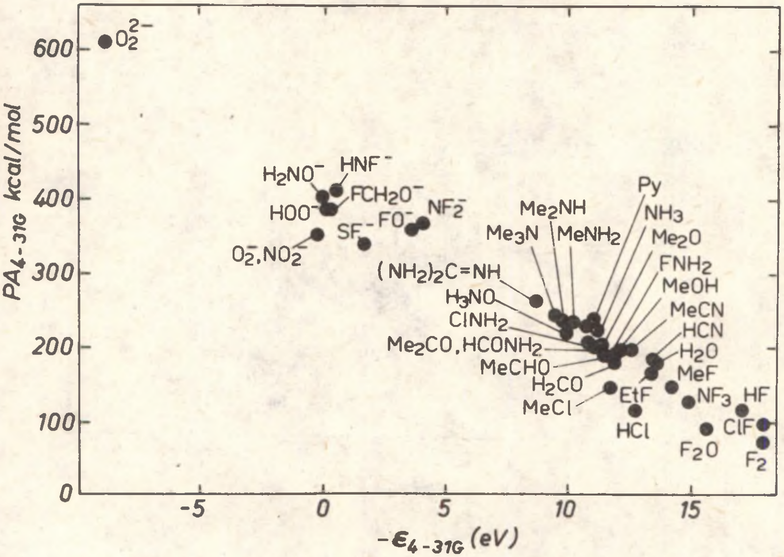


Fig. 7. The 4-31G predicted relationship (Eqn. (17)) between proton affinities and energies of the HOMO of the protonization center.

As a rule, Eqns. (15) - (17) obey for the second period basicity centers. Eqn. (15) does not describe the behavior of compounds with the adjacent fluorine atom to the basicity center. Moreover, even in the ab initio calculations such points deviate somewhat stronger than others from the general relationship characterized by Eqns. (16) and (17).

However, the latter equations, especially Eqn. (17), model qualitatively and quantitatively better than the CNDO/2 approximation the real relationships[43] between experimentally determined proton affinities and ionization potentials (or electron affinities).

References

1. W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton, and J.A. Pople, Gaussian 70, Programm No. 236, Quantum Chemistry Programm Exchange, Bloomington, Indiana.
2. a) W.J. Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys., 51, 2657(1969); b) W.J. Hehre, R.Ditchfield, R.F. Stewart, and J.A. Pople, J.Chem. Phys., 52, 2769(1970).
3. a) R. Ditchfield, W.J. Hehre, and J.A. Pople, J.Chem. Phys., 54, 724(1971); b) W.J. Hehre, and J.A. Pople, J.Chem. Phys., 56, 4233(1972); c) W.J. Hehre, and W.A. Lathan, J.Chem. Phys., 56, 5255 (1972).
4. I.A. Koppel and M.B. Comisarow, This Journal, 17, 495 (1980).
5. T. Koopmans, Physica, 1, 104 (1933).
6. M. Bloch, F. Broglie, E. Heilbronner, T.B. Jones, H. Prinzbach, and O. Schweikert, Helv. Chim. Acta, 61, 1388(1978).
7. G.M. Anderson III, P.A. Kollman, L.N. Domelsmith, and K.N. Houk, J. Am. Chem. Soc., 101, 2344 (1979).
8. W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Progr. Phys.Org.Chem., 11, 175(1974).
9. I.A. Koppel and U.H. Mölder, This Journal, in press.
10. a) D.C. Calabro and D.L. Lichtenberger, Inorg.Chem., 19, 1732(1980); b) W.G. Richards, Int.J.Mass.Sp. Ion Phys., 2, 419(1969); c) T. Minato and D.P. Chong, Chem.Phys.Lett., 72, 252(1980).
11. W.J. Hehre and J.A. Pople, J.Am.Chem.Soc., 94, 6901(1972).
12. V.I. Vovna and F.I. Vilesov in "Advances in Photonics, Issue 5, Leningrad University Press, Leningrad, 1975.

13. M.K. Livett, E. Nagy-Felsobuki, J.B. Pee, and G.D. Willett, Inorg. Chem., 17, 1608 (1978).

14. D.C. Frost, S.T. Lee, and C.A. McDowell, Chem. Phys. Lett., 30, 26 (1975).

15. P.J. Bassett and D.R. Lloyd, J.C.S. Dalton Trans., 1972, 248.

16. D.H. Aue, H.M. Webb, W.R. Davidson, M.Vidal, M.T. Bowers, H. Goldwhite, L.E. Vertal, J.-E. Douglas, P.A. Kollman, and G.L. Kenyon, J. Am. Chem., Soc., 102, 5151 (1980)

17. D.Colbourne, D.C. Frost, and C.A. McDowell,Chem.Phys. Lett., 72, 247 (1980).

18. K. Kimura, S.Katsumata, J.Chem.Phys.,67, 1225(1977)

19. S. Elbel and H. Dieck , J.C.S. Dalton Trans., 1976, 1757.

20. D. Dougherty, K. Wittel, J. Meeks, and S.P. McGlyun, J.Am. Chem.Soc., 98, 3815 (1976).

21. D.C. Frost, F.G. Herring, K.A.R. Mitchell, and I.A. Stenhouse, J. Am. Chem. Soc., 93, 1596 (1971).

22. D.R. Lloyd, P.J. Roberts, and I.H. Hillier, Farad. Trans. II, 1975, 496.

23. M.B. Robin and N.A. Kuebler, J.El. Spectr., 1, 13(1972).

24. C.R. Brundle, M.B. Robin, N.A. Kuebler, and H. Basch, J. Am. Chem.Soc.,94, 1451(1972).

25. J.Berkowitz, J.L. Dehmer, and E.H. Appelman, Chem.Phys. Lett., 19, 334 (1973).

26. J.L. Meeks, H.J. Maria, P.Brint, and S.P. McGlynn, Chem.Revs., 75, 603(1975).

27. K. Wittel, J.El.Spectr. and Relat. Phenom., 8, 245(1976).

28. S. Cradock and R.A. Whitefort, Farad. Trans. II, 68, 281(1972).

29. E.J. McAlduff and K.N. Houk, Can.J.Chem., 55, 318,(1977).

30. K. Watanabe, T. Nakayama, and J. Mottl, J. Quant. Spectros, Rad. Transfer, 2, 369(1962).

31. A.D. Williamson, P.P. LeBreton, and J.L. Beauchamp, J.Am. Chem. Soc., 98, 2705(1976).

32. H. Umeyama and K. Morokuma, J.Am.Chem.Soc., 98.4400(1976).

33. P. Kollman and S. Rothenberg, J. Am. Chem. Soc., 99, 1333 (1977).

34. D.J. Pasto and D.M. Chimpman, J.Am.Chem.Soc., 101, 2290(1979).

35. Calculated in this work.

36. J.E. Del Bene and A. Vaccaro, J. Am.Chem.Soc., 98, 7526(1976).

37. J.E. Del Bene, J.Am. Chem.Soc., 99, 3617 (1977).

38. J.F. Olsen and J.M. Howell, J. Fluorine Chem., 10, 197 (1977).

39. J.F. Olsen, J. Fluorine Chem., 9, 471(1977).

40. W.L. Jorgensen and M.E. Cournoyer, J. Am. Chem.Soc., 100, 5278(1978).

41. J.E. Del Bene and S. Radovick, J.Am.Chem.Soc., 100, 6936(1978).

42. W.L. Jorgensen, J.Am.Chem.Soc., 100, 1057 (1978).

43. I.A. Koppel, U.H. Mölder and R.I. Pikver, This Journal, 17, 457 (1980).

Organic Reactivity
Vol.18, 1(65),1981

CNDO/2 CALCULATIONS OF MOLECULES. I. PROTON AFFINITY. COMPARISON WITH EXPERIMENT.

I.A. Koppel and U.H. Mölder
Laboratory of Chemical Kinetics and
Catalysis, Tartu State University,
TARTU, 202400 ESTONIA, USSR.

Received: January 15, 1981

CNDO/2 calculations of more than 450 molecules, ions, and free radicals of various classes and chemical nature have been performed. The proton affinities PA of many bases were made and the linear correlation was found between the corresponding experimental and calculated quantities

Up to now a large number of various level ab initio calculations of many molecular systems have been performed. However, semiempirical quantum chemical methods still also maintain their attraction to the practical chemist. The latter situation is mainly due to the easy availability of standard computer programs, rather modest use of CPU time and to the relative simplicity to interpret the results of those calculations

Due to the elimination of the cumbersome problem of the calculation of three and four-center repulsion integrals the semiempirical all valence electron SCF MO methods using the complete neglect of differential overlap (CNDO) approximation remain most widespread.

The calculations of rather large molecular systems are easily performable even on the relatively small computers using either the standard CNDO/2 program of Pople and Dobosh[1] or its various modifications.Most frequently CNDO/2 method was used for calculations of various energetic (proton affinity, ionization potentials, bond dissociation energies, etc.) or other characteristics (e.g., the charge distribution in the molecule) of molecules, ions, and free radicals.

In the framework of this approximation the proton affinity is calculated as the difference of total energies of the molecule/anion and the corresponding protonated form.[2-5] As a rule, those calculations happen to reproduce the real basicity or acidity order of compounds. However, the absolute predicted PA values differ rather significantly from their experimental values. Similar to the relaxation potential method for the calculations of ESCA core level ionization potentials method[6] has been suggested according to which the electrostatic potential towards the proton is calculated using CNDO/2 wave functions. This model was used[6-9] for the prediction of the relative gas phase basicity order of various molecules and anions. It makes possible the analysis of relative PA of similar compounds in terms of inductive and polarizability effects, however, it does not always lead to the quantitative agreement with the experimental data. In Refs. 10 and 11 the CNDO/2 approximation was used for the calculation of gas phase acidity of some hydroxylic acids. It should be mentioned[12] that this method is hardly able to calculated the potential surface of the proton abstraction or attachment process. Only the limiting cases where proton is bound to the molecule (or anion) or transferred to the infinity could be considered with a relative success.

Despite a great number of papers on the semiempirical CNDO/2 calculations of various characteristics of organic molecules the systematic and extensive evaluation of its possibilities and predictive power has not been made on the basis of the comparison of experimental and calculated values.

This series of papers[14] has been designed to partially fulfill this gap. The present calculations have been made for more than 450 compounds of various classes, charge type (neutral molecules, positive and negative ions) and multiplicity.

The proton affinity of the generalized base B PA(B), where B is either a neutral molecule, ion of any possible charge type or a free radical, is calculated as the difference in the total energies E_{tot} of the given base in the ground (deprotonated) and protonated states:

$$PA(B) = E_{tot}(B) - E_{tot}(BH^+) \qquad (1)$$

The calculations were performed using the most common version[1] of the CNDO/2 program adopted to the M-32 computer by Dr. M.M. Karelson of this laboratory.

The geometries of molecules, ions, and free radicals used in these calculations are given in the Appendix* with their total energies and, as a rule, with the corresponding proton affinities. The calculated total energies are mostly calculated on the basis of the standard geometrical parameters listed by Pople and Beveridge[1] using the additional optimization of the bond lengths, valence and conformational angles in the immediate vicinity of the protonization (basicity) center. The comparison of the experimental** and calculated PA values has been made including as much data as possible for the various classes of compounds.

The statistical analysis of these data for 89 compounds (see also Appendix, footnote b) has been performed using the linear least squares treatment on the 95 percent confidence level. Equation (1) was found to hold (see also Fig. 1).

$$PA = 0.63(0.01)PA_{CNDO} + 11.5(2.7) \qquad (2)$$

---

* Some parts of the data given in the Appendix will be used in the following communications of this Series for the discussion of several more special problems (the calculation of ionization potentials, and interpretation of photoelectron spectra, the dependence of the reactivity of various classes of compounds on their structure, charge distribution, etc.).

** Experimental PA values are mostly taken from a recent publication[15] of the present authors.

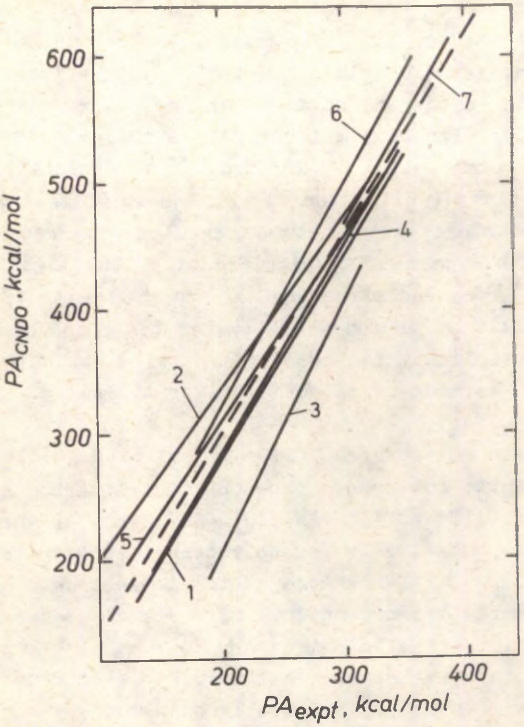


Fig. 1. General comparison of the CNDO/2 and experimental proton affinities for the various classes of compounds. The dotted line corresponds to Eqn.(2) from the text and the full straight lines refer to equations listed in Table 1.

The standard deviations of the regression coefficients are given in parenthesis, PA values are in kcal/mol; the maximal range of variation of the experimental proton affinity values PA exceeds 400 kcal/mol. The correlation coefficient is 0.995 and the standard deviation equals 10.1 kcal/mol. Eqn.(2) shows that in a first rather rough approximation CNDO/2 method is able to describe the behavior of PA values over the wide range of compounds (alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, alcoholate and carboxylate anions, nitriles, etc.) of the different chemical nature, charge type and multiplicity. Eqn. (2) evidently does not describe the data for sulfur compounds R_2S, RSH and RS^- for which the CNDO/2 method predicts (unlike the other classes of bases) PA values "too close" to the experimental ones. Free radicals also deviate from Eqn.(2) significantly. One might speculate that this is caused either by the unhomogeneity of the general scale of proton affinity for the compounds of different multiplicity and charge type or by the uncompatibility of the methods of calculation for the closed and open shell molecules.

A certain scatter from the straight line (2) is also characteristic for some cyano-substituted carbon acids, and their anions ($CH_2(CN)_2$, $(CN)_2CH^-$, CN^-) and for the cyanogen $(CN)_2$. This behavior is probably connected with the fact that the CNDO/2 calculations of total electronic energies of cyano-substituted compounds often need the largest possible number of iterations in order to reach the self-consistent results. The latter behavior might stem from the partial failure to reach the equally satisfactory parametrization of the calculation procedure for some elements.

Analogously alongside with the gross general correlation by Eqn.(2) of experimental PA values with their calculated values these quantities were compared also for the separate classes of bases. The results of such a statistical treatment are listed in Table 1 whereas some typical examples are shown on Fig. 2 and 3. It is evident that in the more detailed consideration the relationship (2) splits into several statistically different subfamily linear relationships which describe the behavior within the separate classes of compounds and are characterized by the different values of the slopes α and intercept β .

Eqn. 2 and equations in Table 1 show that as an average

Table 1

The Results of Separate Regression Analysis in Terms of Equation $PA_{exp} = \beta + \alpha PA_{CNDO}$ for the Several Classes of Compounds

No	Class of Compounds	β^{a}	α^{a}	r^{b}	s^{b}	n^{d}	ΔPA^{e}_{exp}
1.	R_1OR_2,ROH,RO^-	22.1(3.3)	0.63(0.01)	0.998	6.9	22	281.9
2.	RO^-,LiOH NaOH, DMSO	-52.4(14.7)	0.75(0.03)	0.995	6.0	10	186.0
3.	R_1SR_2,RSH,SH	91.3(0.5)	0.52(0.01)	0.999	0.5	5	162.5
4.	$R_1R_2R_3N$, R_1R_2NH,RNH_2 NH_2^-,NH^{2-}	29.4(2.7)	0.60(0.01)	0.999	5.7	20	96.3
5.	R_1COR_2,RCOH, R_1COOR_2,$RCOO^-$,	-13.6(6.0)	0.69(0.02)	0.994	7.3	20	223.7
6.	RCN,CN^-	19.8(4.6)	0.56(0.01)	0.997	4.0	11	170.4
7.	$R_1R_2R_3C^-$	22.6(7.8)	0.60(0.01)	0.998	4.7	8	71.6

Footnotes: a - Regression parameters and their standard deviations (in parenthesis).
b - Correlation coefficient
c - Standard deviation of the correlation
d - The number of points
e - The maximum range of variation of experimental PA values included in the correlation.

CNDO/2 proton affinities exceed the corresponding experimental quantities by 1.6 times. Too high PA values for the negatively charged anions probably indicate that this method does underevaluate the stability of anions whereas the too high values of PA for the neutral bases are due to the overestimated stability of the protonated form. The latter reminds the well-known fact that CNDO/2 method also leads to the too high energies of the hydrogen bond.[16] It is evident the Eqn.(2) and more specific linear equations

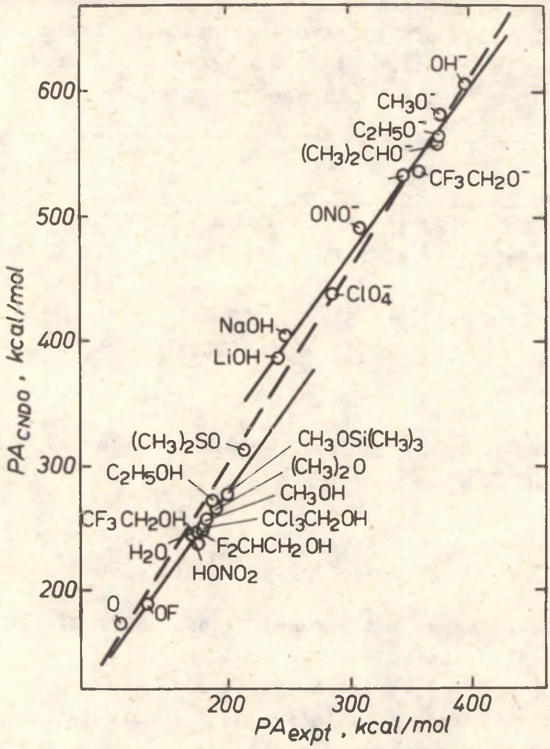


Fig. 2. The comparison of CNDO/2 and experimental proton affinities for some oxygen compounds.

from Table 1 describe the relationship between experimental and CNDO/2 proton affinities only in the first approximation. However, because of the frequent experimental difficulties or, in some cases, even of the principal impossibility to determine the experimental PA values it has some sense to use Eqn. 2 and its special cases for the prediction of these quantities for compounds of practical or theoretical interest. The predicted from these equations "experimental" values of proton affinities PA_e for compounds of different chemical nature, charge type, and multiplicity are listed in Table 2.

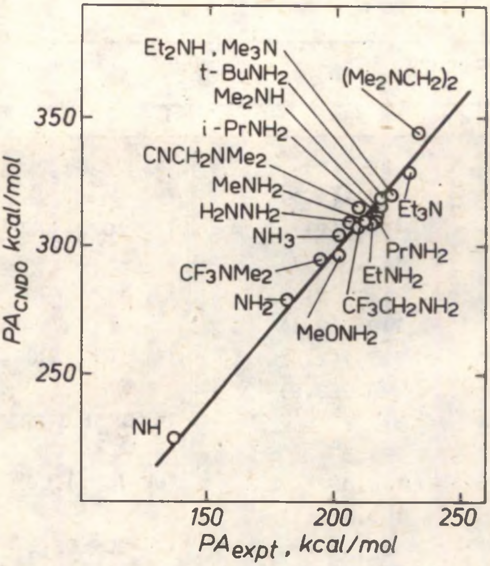


Fig. 3. The comparison of CNDO/2 and experimental proton affinities for some nitrogen compounds.

The process of abstraction or attachment of the proton is characterized by the constancy of the number of lone electron pairs involved and, as a consequence of that, also by the insignificant change of the electron correlation energy during this type of chemical reaction. These circumstances might explain the relative success of the one electron SCF LCAO MO methods to predict the energetics of this type

Table 2.

The Predicted "Experimental" Values of Proton Affinities[a] PA_e

No	Compound	PA_e
1	2	3
1.	O^-	402.2(2)
		412.6(2.2)
2.	OH	150.0(2)
		160.6(2.1)
3.	OF	129.6(2)
		140.2(2.1)
4.	OF^-	375.1(2)
		380.5(2.2)
		375.7[b]
		335.3[c]
5.	FOH	140.0(2)
		150.6(2.1)
		143.3[b]
		162.4[c]
		160.4-163.5[d]
6.	ClO^-	344.3(2)
		344.7(2.2)
7.	FCH_2OH	164.0(2)
		174.6(2.1)
8.	FCH_2O^-	356.8(2)
		358.7(2.2)
		360.4[b]
		373.5[c]
9.	CF_3O^-	337.1(2)
		335.2(2.2)
		312.3[b]
		340.5[c]
10.	CF_3OH	155.2(2)
		165.8(2.1)
11.	$CF_3CH_2O^-$	348.1(2)
		348.4(2.2)
12.	$(CF_3)_2CHO^-$	334.6(2)
		332.2(2.2)
13.	$(CF_3)_3CO^-$	327.1(2)
		323.4(2.2)
14.	$(CF_3)_3CCH_2O^-$	341.2(2)
		340.1(2.2)
15.	$(CF_3)_2C(OH)O^-$	333.1(2)
		330.5(2.2)
16.	$(CF_3)_2CO_2^{2-}$	438.8(2)
		456.3(2.2)
17.	$CCl_3CH_2O^-$	348.9(2)
		349.2(2.2)
18.	HOO^-	377.0(2)
		382.8(2.2)
		351.9[b]
19.	H_2O_2	159.0(2)
		169.6(2.1)
		170.2[b]
		177.2[c]
20.	$HOOH_2^+$	35.8(2)
		10.6(2.1)
21.	O_2^{2-}	594.7(2)
		605.3(2.2)
		552.1[b]
22.	O_2	137.8(2)
		124.7(2.5)
23.	O_3 central oxygen	114.5(2)
		89.8[d]
	terminal oxygen	I48.I(2)
		149.7-155.6[d]

1	2	3
24.	$-OCH_2O^-$	492.6(2)
		520.3(2.2)
25.	$HOCH_2O^-$	364.6(2)
		368.0(2.2)
26.	$(HO)_2CH_2$	175.0(2)
		185.6(2.1)
27.	$HOCH_2OH_2^+$	84.1(2)
28.	F_3NO	192.4(2)
29.	H_3NO	203.0(2)
		175.5(2.2)
		217.4[b]
		213.2[c]
30.	MeOF	I58.2(2)
		I68.8(2.I)
31.	CF_3OF	I30.I(2)
		I4I.0(2.I)
		140.8[d]
32.	F_2O	78.5(2)
		89.1(2.1)
		101.2[b]
		100.0[c]
		103.9[d]
33.	$(CF_3)_2O$	148.7(2)
		159.3(2.1)
		151.7[d]
34.	$(NH_2)_2O$	197.1(2)
		207.7(2.1)
35.	$NH_2ONH_3^+$	95.8(2)
36.	CF_3CHO	172.4(2)
		162.6(2.5)
37.	F_2CO	167.0(2)
		156.8(2.5)
		152.3-168.5[d]
		142.1[b]
		157.2[c]
38.	$(CF_3)_2CO$	164.4(2)
		153.9(2.5)
39.	$(CN)_2CO$	153.1(2)
		141.5(2.5)
40.	CF_3COO^-	323.4(2)
		328.0(2.5)
41.	$(CF_3)_2CHCOO^-$	314.5(2)
		318.2(2.5)
42.	$(CF_3)_3CCOO^-$	308.3(2)
		311.5(2.5)
43.	$CNCOO^-$	324.8(2)
		329.5(2.5)
44.	$CI(CH_2)_2COO^-$	341.9(2)
		348.2(2.5)
45.	$Me_3\overset{+}{N}COO^-$	244.7(2)
		241.8(2.5)
46.	$Me_3\overset{+}{N}CH_2COO^-$	262.7(2)
		261.6(2.5)
47.	$HCONH_2$	206.7(2)
		199.6(2.5)
		198.2[b]
48.	$(NH_2)_2CO$	222.2(2)
		217.2(2.5)
49.	FCH_2CONH_2	205.4(2)
		198.7(2.5)
50.	$(NHMe)_2CO$	235.2(2)
		231.4(2.5)
51.	$NH_2CONHMe$	211.1(2)
		205.1(2.5)
52.	$Me_2NCONHMe$	233.9(2)
		230.0(2.5)
53.	ClO_4^-	287.1(2)
		275.7(2.2)
		279.9[c]
54.	$HClO_4$	159.5(2)
		170.1(2.1)

1	2	3	1	2	3
55.	$MeSO_3^-$	316.0(2)	72.	Me_2N^-	362.1(2)
		310.1(2.2)			363.3(2.4)
56.	HSO_4^-	309.2(2)	73.	$N_2H_5^+$	81.7(2)
		302.1(2.2)			96.5(2.4)
57.	SO_4^{2-}	430.5(2)	74.	FNH_2	180.4(2)
		446.4(2.2)			190.3(2.4)
58.	H_2SO_4	165.3(2)			188.6[b]
		176.0(2.1)			187.9[c]
59.	FSO_3^-	314.2(2)	75.	FNH^-	388.9(2)
		308.0(2.2)			388.8(2.4)
60.	FSO_3H	201.4(2)			380.3[b]
		212.0(2.1)			373.0[c]
61.	$CF_3SO_3^-$	299.9(2)	76.	F_2N^-	374.3(2)
		290.9(2.2)			374.9(2.4)
62.	CF_3SO_3H	205.4(2)			357.2[c]
		216.0(2.1)	77.	HNF_2	157.9(2)
63.	HNO_3	141.3(2)			168.4(2.4)
		151.9(2.1)			163.5[b]
64.	NO_3^-	295.1(2)			157.4-169.5[d]
		285.3(2.2)	78.	NF_3	138.6(2)
65.	N	160.2(2)			150.4(2.4)
		171.1(2.4)			121.8-140.9[d]
66.	$N_2H_3^-$	358.6 (2)	79.	CF_3NH^-	361.2(2)
		360.2 (2.4)			362.5(2.4)
67.	N^{3-}	1021.5(2)			368.3[c]
		991.3(2.4)	80.	CF_3NH_2	186.3(2)
68.	NH^{2-}	663.8(2)			195.8(2.4)
		650.6(2.4)			190.9[c]
69.	$N_2H_2^{2-}$	550.0 (2)	81.	$(CF_3)_2N^-$	321.5(2)
		542.3 (2.4)			324.6(2.4)
70.	NH_2^-	404.7(2)	82.	$(CF_3)_3N$	161.9(2)
		403.9(2.4)			172.7(2.4)
71.	$MeNH^-$	387.5(2)	83.	$ClNH_2$	202.3(2)
		387.5(2.4)			211.1(2.4)
		407.9[b]			200.7-204.5[d]
		383.9[c]			

1	3	4
84.	Cl_2NH	202.2(2)
		211.0(2.4)
		192.1-197.9^d
85.	MeNHCl	206.1(2)
		214.7(2.4)
		208.7-209.4^d
86.	$MeNCl_2$	204.6(2)
		213.3(2.4)
87.	Me_2NCl	209.4(2)
		217.9(2.4)
		212.2-214.0^d
88.	$Me_2N(H)(CH_2)_2NMe_2^+$	148.6(2)
		160.0(2.4)
89.	$Me_2N(CH_2)_4NMe_2$	219.7(2)
		227.6(2.4)
90.	$Me_2N(CH_2)_4N(H)Me_2^+$	177.1(2)
		187.1(2.4)
91.	$HONH_2$	186.5(2)
		196.0(2.4)
		200.2^b
		194.9^c
92.	HONHMe	200.6(2)
		209.6(2.4)
93.	$HONMe_2$	206.7(2)
		215.3(2.4)
94.	MeONHMe	194.7(2)
		201.0(2.4)
95.	$MeONMe_2$	209.8(2)
		218.3(2.4)
96.	MeS^-	335.7(2.5)
97.	H_2S_2	188.4(2.5)
98.	$HSSH_2^+$	93.5(2.5)
99.	FS^-	329.7(2.5)
100.	FSH	117.2(2.5)

1	2	3
101.	$(CF_3)_2S$	176.5(2.5)
102.	CF_3S^-	313.4(2.5)
103.	Cl_2S	176.3(2.5)
104.	Cl_2CHCN	201.9(2)
		189.1(2.6)
105.	H_2NCN	187.0(2.6)
		206.3^d
106.	CH_3^-	433.2(2)
		424.2(2.7)
107.	FCH_2^-	409.9(2)
		402.0(2.7)
108.	$(CF_3)_3C^-$	325.4(2)
		321.6(2.7)
109.	CF_3^-	372.5(2)
		366.4(2.7)
110.	$HC{\equiv}C^-$	403.7(2)
		396.2(2.7)
111.	$MeC{\equiv}C^-$	400.5(2)
		393.2(2.7)
112.	$t\text{-}BuC{\equiv}C^-$	397.6(2)
		390.3(2.7)
113.	$CF_3C{\equiv}C^-$	376.8(2)
		370.5(2.7)
114.	Cl^-	307.7(2)
115.	F^-	388.2(2)
116.	Cl_2	61.2(2)
117.	F_2	80.3(2)
		94.0
		86.1^c
118.	$(CN)_3C^-$	341.8(2.7)^e
119.	$(O_2N)_3C^-$	280.6-291.4(2.7)^e

Footnotes:

a - PA_e values are in kcal/mol. The predicted value is followed in parenthesis either by the number of the Eqn.(2) from the text or by the numbers (2.1-2.7) of its more special variants from Table 1.

b,c - PA_e value predicted[17] on the basis of ab initio calculations. Superscript b refers to the 4-31G basis and superscript c to the STO-3G basis set. PA_e values for the CF_3O^- are calculated on the basis of data from Refs. 17 and 18.

d - PA_e value predicted[15] on the basis of the linearity between experimental PA values and valence or core level ionization potentials.

e - Calculated in this paper using the data of Tupitsin et al.[19]

f,g - Superscript f refers to the protonization of the oxygen of the OH-group, superscript g - to the protonization of the N atom

of reactions. However, the theoretical prediction of the homolytic bond dissociation energies seems to be a far more serious problem. One can (see Fig. 4.) see from the comparison of the CNDO/2 calculated* and experimental dissociation energies of various chemical bonds.

---

* In this paper the homolytic bond dissociation energies were calculated as the differences of the total energies of the two-or polyatomic molecule A-B and the total (open shell) energies of the final products (atoms or the other fragments with the open electron shell) A° and B°:

$$\Delta E_{A-B} = E_{tot}(A-B) - E_{tot}(A^\circ) - E_{tot}(B^\circ)$$

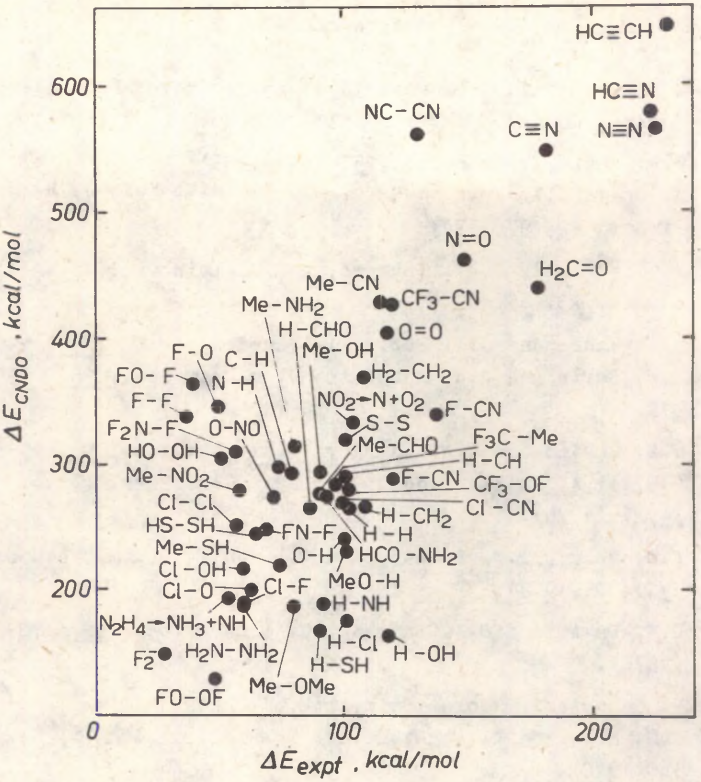


Fig. 4. Comparison of CNDO/2 and experimental homolytic bond dissociation energies.

that in several cases not only the absolute values but even the trend of the change of the corresponding bond energies is predicted inadequately. Such a conclusion is also supported in terms of the regression analysis which leads to the Eqn. (3):

$$\Delta E_{exp} = 1.6(0.2)\Delta E_{CNDO} + 89(16) \qquad (3)$$

which is characterized by the low correlation coefficient (0.893) and a high standard deviation (39 kcal/mol) of the regression.

References

1. J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill Book Co., N.-Y.(1970).
2. T.P. Lewis, Tetrahedron,25, 4117(1969).
3. M. Graffeuil, J.-F. Labarre, and C. Leibovici, J. Mol. Struct. 22, 97(1974)
4. M. Graffeuil, J.-F. Labarre, and C. Leibovici, J. Mol. Struct. 23, 65(1974)
5. W.J. Hehre and J.A. Pople, Tetrahedron Lett. 1970, 2959.
6. D.W. Davis and J.W. Rabalais, J.Am.Chem.Soc., 96, 5305 (1974)
7. R.L. Martin and D.A. Shirley, J.Am.Chem.Soc., 96, 5299 (1974); A. Pullman and P. Brochen, Chem.Phys. Lett., 34, 7 (1975).
8. W.B. Perry, T.F. Schaaf, and W.L. Jolly, J.Am.Chem.Soc. 97, 4899(1975).
9. D.W. Davis and D.A. Shirley, J.Am.Chem.Soc. 98, 7898 (1976).
10. P. Schuster, Theoret.Chim.Acta, 19, 212(1970)
11. B.M. Rode and A. Engelbrecht, Chem.Phys.Lett., 16, 560(1972).
12. W.Jakubetz, H.Lischka, P. Rosmus, and P. Schuster, Chem.Phys.Lett. 11,38(1971).
13. G.A. Segal (Ed.), Modern Theoretical Chemistry.Vol.7. Semiempirical Methods of Electronic Structure Calculation, Part A. Techniques. Vol.8. Semiempirical methods of Electronic Structure Calculation,Part B: Applications, Plenum, New York, London. 1977.
14. The preliminary communication has been published: I.A. Koppel, U.H. Mölder, and R.I. Pikver in the book: E.Kundla, E. Lippmaa, and T. Saluvere (Eds).Magnetic Resonance and Related Phenomena Springer Verlag, Heidelberg,1979, p.265.

15. I.A. Koppel, U.H. Mölder, and R.I. Pikver, This Journal, 17, 457(1980).

16. P.A. Kollman and L.C. Allen, Chem.Revs. 72, 283(1972).

17. I.A. Koppel and M.B. Comisarow, This Journal, 17,495 (1980)

18. J.F. Olsen and J.M. Howell, J. Fluorine Chem., 10, 197 (1977)

19. N.N. Zatsepina, A.A. Kane, and I.F. Tupitsin, This Journal, 12, 179(1975).

20. R.B. Hermann, J. Am. Chem.Soc., 92, 5298(1970).

21. J.P. Tollenaere and H. Moereels, Tetrahedron Lett., 1978, 1347.

Appendix

The Geometries of Molecules, Ions, and Free Radicals and Their CNDO/2 Total Energies and Proton Affinities [a]

Oxygen Bases

1.	O	-18.0820, 173.3[b]
2.	O^-	-18.0036, 620.1
3.	OH	OH=1.026; -18.9913, 219.8[b]
4.	OH^-	OH=1.07 ; -18.9250, 606.4[b]
5.	OH^+	OH=1.04 ; -18.3581
6.	H_2O	OH=1.03 , HOH=104.7; -19.8909, 249.3[b]
7.	H_2O^+	OH=1.04 , HOH=118.7; -19.3411
8.	H_3O^+	OH=1.04 , HOH=120, planar -20.2880
9.	MeO	CO=1.43, , CH=1.09, HCO=109.5; -27.6800
10.	MeO^-	CO=1.3 , CH=1.119, HCO=109.5; -27.6684, 566.1[b]
11.	MeOH	OH=1.04, CH=1.12 , CO=1.37, HCH=108.2, HCO=110.7, COH=107.3; -28.5091, 257.3[b]
12.	$MeOH_2^+$	OH=1.034, CH=1.119, CO=1.37, HOH=109.5, HCH=109.5; -28.9929
13.	EtOH	OH=1.034, CO=1.367, CC=1.457, CH=1.119, HCH=109.5, COH=107; -37.2772, 269.2[b]
14.	$EtOH_2^+$	OH=1.04, CO=1.43, CC=1.54, CH=1.09, HCH=HCO=109.5, HOH=120; -37.6863.
15.	OF	OF=1.18; -46.1807, 187.5[b]
16.	OF^-	OF=1.20; -46.1743, 577.2
17.	FOH	OF=1.18, OH=1.04, FOH=106.9; -47.0936, 203.9.
18.	FOH^+	OF=1.18, OH=1.04, FOH=120; -46.4793.
19.	FOH_2^+	OF=1.18, OH=1.04, FOH=120; -47.4184.
20.	ClO	ClO=1.6; -34.4454
21.	ClO^-	ClO=1.50; -34.5113, 526.2[b]
22.	ClOH	ClO=1.50, OH=1.04, ClOH=90; -35.3495.
23.	FCH_2OH	CO=1.427, OH=0.96, CH=1.092, CF=1.36, HCO=FCH=109, COH=108.9; -55.5000, 242.1.

24. FCH_2O^- CO=1.47, OH=0.96, CH=1.092, CF=1.36,
HCO=FCH=109; -54.6241, 548.1.

25. $FCH_2OH_2^+$ c, COH=HOH=120; -55.8856.

26. CF_3O^- CO=1.36, CF=1.34, FCF=107.3, FCO=111.5;
-108.7603, 516.8

27. CF_3OH CO=1.36, OH=1.04, CF=1.34, COH=109.4,
FCO=111,5; -109.5834, 228.1.

28. $CF_3OH_2^+$ CO=1.36, OH=1.04, CF=1.332, COH=HOH=120,
FCO=111,5, FCF=107.3, -109.9468.

29. FCH_2CH_2OH CO=1.43, OH=1.04, CC=1.54, CF=1.1.384,
COH=109.5; -64.2311, 259.6.

30. $FCH_2CH_2OH_2^+$ c, COH=120; -64.6446

31. F_2CHCH_2OH CO=1.367, OH=1.034, CC=1.457, CF=1.332,
CH=1.1, HOC=107; -91.2404, 258.4^{b}.

32. $F_2CHCH_2OH_2^+$ CO=1.4, OH=1.04, CF=1.332, CC=1.451,
COH=120; -91.6516.

33. $CF_3CH_2O^-$ CO=1.43, CC=1.54, CH=1.09, CF=1.332,
OCH=HCC=109.5, FCF=108.8; -117.3185, 534.4^{b}.

34. CF_3CH_2OH c, OH=0.96, COH=108.9; -118.1698, 245.4^{b}.

35. $CF_3CH_2OH_2^+$ c, COH=120; -118.5607.

36. $(CF_3)_2CHO^-$ CO=1.43, CF=1.332, CC=1.54, CCO=109.5;
-207.0637, 512.8.

37. $(CF_3)_2CHOH$ c, OH=0.96, COH=105; -207.8805

38. $(CF_3)_3CO^-$ CO=1.36, CC=1.54, CF=1.34, OCC=111.5,
CCF=107.3; -296.7420, 501.0.

39. $(CF_3)_3COH$ c, OH=1.04; -297.5399.

40. $(CF_3)_3CCH_2O^-$ CO=1.43, CC=1.54, CH=1.09, CF=1.332,
OCC=CCF=109.5; -305.4141, 523.3.

41. $(CF_3)_3CCH_2OH$ c, OH=0.96; -306.2476.

42. $(CF_3)_2C(OH)O^-$ CO=1.43, CC=1.52, CH=1.09, OH=0.96,
CF=1.332, OCC=CCF=109.5; COH=105,
-225.5140, 510.5.

43. $(CF_3)_2C(OH)_2$	c, -226.3271.
44. $(CF_3)_2CO_2^{2-}$	c, OCO=110.2, FCF=108.8; -224.4338, 678.2.
45. $CF_3C(OH)_2H$	c; -136.6605.
46. CCl_3CH_2OH	CO=1.43, CCl=1.76, CC=1.54, OH=0.96, COH=105, HCH=109.5; -83.5188, 252.9[b].
47. $CCl_3CH_2O^-$	c, -82.6658, 535.5.
48. $CCl_3CH_2OH_2^+$	c, HOH=120; -83.9216.
49. $HC{\equiv}CCH_2OH$	CO=1.43, OH=0.96, CC=1.46, C≡C=1.21, CH=1.04, COH=108.9; -42.5085.
50. $H_2NCH_2CH_2OH$	OC=1.47, CC=1.52, CH=1.09, NH=1.04, OH=1.04, HNH=109.5, CNH=COH=107; -49.4221.
51. O_2	OO=1.132; -36.8048, 200.5
52. O_2^+	OO=1.095; -36.2685
53. O_2H^+	OH=1.04, OO=1.1, OOH=120; -37.1242.
54. O_2^-	OO=1.25; -36.7110
55. O_2^{2-}	OO=1.3; -36.0667, 925.7[b]
56. HOO^-	OH=1.04, OO=1.22; -37.5412, 580.2.
57. H_2O_2	c, HOO=108.8; -38.4653, 234.1.
58. $HOOH_2^+$	c, HOH=120; -38.8382, 38.5.
59. $H_2\overset{++}{O}OH_2$	c, HOH=HOO=120; -38.8995.
60. t-BuOH	CO=1.43, OO=1.22, CC=1.52, CH=1.09, HCH=109.5, HOO=OOC=108.8; -73.1924.
61. O_3	OO=1.17, OOO=117.0; -55.3085, 93.2[d], 216.8[e].
62. HO_3^+	OO=1.25, OH=1.04, OOO=120, OOH=120; -55.6539.
63. $OO^+(H)O$	c, -55.4577.
64. $^-OCH_2O^-$	CO=1.37, CH=1.09, OCH=109.5; -44.9253, 763.6.

65. $HOCH_2O^-$	c, OH=1.04, HOC=107.3; -46.1415, 560.5.
66. $(HO)_2CH_2$	c, OCO=109.5; -47.0343, 259.6.
67. $HOCH_2\overset{+}{O}H_2$	c, HOH=120; -47.4478, 115.2.
68. $H_2\overset{+}{O}CH_2\overset{+}{O}H_2$	c, -47.6313.
69. F_2SO	SO=1.41, FS=1.59, FSO=107, FSF=93; -84.7464.
70. Cl_2SO	SO=1.44, ClS=2.08, ClSO=107, ClSCl=96; -61.9854.
71. F_3NO	NO=1.36, FN=1.25, FNO=109.5; -113.5549, 287.1.
72. F_3NOH^+	c, OH=1.04, HOH=107; -114.0123.
73. H_3NO	NO=1.36, NH=1,038, HNO=HNH=109.5; -32.3761, 303.9.
74. H_3NOH^+	c, OH=1.04, NOH=107.3; -32.8602.
75. Me_3NO	NO=1.36, NC=1.479, CH=1.09, CNO=112, HCH=109.5; -58.4530, 353.7.[b]
76. Me_3NOH^+	c, NOH=103.0 , OH=0.96; -59.0164.
77. Me_2SO	SO=1.47, CS=1.81, CH=1.09, CSO=107, CSC=97, HCH=109.5; -47.9766, 314.8[b].
78. Me_2SOH^+	c, OH=1.04, SOH=120; -48.4780.
79. $MeSO_3^-$	SO=1.45, CS=1.81, CH=1.09, CSO=109.5; -75.3544, 483.3.
80. $MeSO_3H$	SO=1.43, SO=1.54, OH=0.96, CS=1.81, CH=1.09, OSO=CSO=109.5, SOH=120; -76.1243.
81. SO_4^{2-}	SO=1.57, OSO=109.5; -84.2275, 665.0.
82. HSO_4^-	SO=1.63, S=0=1.57, OH=1.022, HOS=120, OSO=109.5; -85.2867, 472.6.
83. H_2SO_4	SO=1.6, S=0=1.57, OH=1.022, HOS=120, OSO=109.5; -86.0394, 244.2.
84. $H_2SO_4H^+$	c, HOS=120; -86.4284.
85. FSO_3^-	FS=1.58, SO=1.43, FSO=109.5; -93.6751, 480.4.
86. FSO_3H	c, SO=1.54, OH=1.022, SOH=120; -94.4508,301.4.

87. $FSO_3H_2^+$	S=O=1.42, SO=1.54, FS=1.58, OH=0.96, FSO=109.5, SOH=120; -94.9309.
88. $CF_3SO_3^-$	S=O=1.45, CS=1.81, CF=1.332, OSO=CSO=FCF=109.5, -156.3563, 457.7.
89. CF_3SO_3H	S=O=1.43, SO=1.54, OH=1.04, CS=1.81, CF=1.332, SOH=120, CSO=FCF=109.5; -157.0962, 307.8.
90. $CF_3SO_3H_2^+$	c, HOH=120, -157.5865.
91. NO_2^-	NO=1.236, ONO=118.3; -48.4476, 490.4[b].
92. HONO	NO=1.43, N=O=1.17, OH=0.96, ONO=111, NOH=102; -49.2286.
93. NO_3^-	N=O=1.24, ONO=120; -67.0244, 450.2.
94. $HONO_2$	N=O=1.22, NO=1.27, OH=1.035, ONO=HON=120;; -67.7896, 206.0[f], 199.7[g].
95. $H_2\overset{+}{O}NO_2$	c, HOH=120; -68.1177.
96. $HONO_2H^+$	HON=120; OH=1.035, OH^+= 1.04, NO=1.27, N=O=1.22, -68.1078
97. ClO_4^-	ClO=1.49, OClO=109.5; -89.8130, 437.5[b].
98. $HClO_4$	Cl=O=7.48, OCl=1.64, OH=1.035, OClO=109.5, HOCl=120; -90.5099, 234.9[f], 225.9[h]
99. $H_2\overset{+}{O}ClO_3$	c, HOH=120; -90.8841.
100. $(HO)_2ClO_2^+$	c, HOCl=120; -90.8692
101. NaOH	NaO=2.55, OH=1.04, NaOH=90; -19.2707, 412.5[b].
102. $NaOH_2^+$	NaO=2.60, OH=1.04, NaOH=120; -19.9278.
103. LiOH	LiO=2.05, OH=1.04, LiOH=90; -19.3506, 381.6[b].
104. $LiOH_2^+$	LiO=2.3, OH=1.04, LiOH=120; -19.9584.
105. Me_2O	CO=1.42, HC=1.09, HCO=109.5, COC=111; -37.0955, 266.2[b].

106. Me_2OH^+	c, OH=1.04, HOC=120; -37.5195.
107. MeOEt	CO=1.367, CC=1.457, CH=1.119, COC=HCH=109.5; -45.9557, 276.5^b.
108. $Me\overset{+}{O}(H)Et$	c, OH=1.034, HOC=109.5; -46.3961.
109. t-BuOMe	CO=1.43, CH=1.09, CC=1.54, COC=HCH=109.5; -63.2757.
110. Et_2O	CO=1.367, CC=1.457, CH=1.119; COC=HCH=109.5; -54.6510, 284.6^b.
111. Et_2OH^+	c, OH=1.034, COH=109.5; -55.1043.
112. $t\text{-}Bu_2O$	CO=1.367; -89.2345.
113. $MeOSiMe_3$	CO=1.43, CH=1.09, OSi=1.63, SiC=1.87, COSi=OSiC=109.5; -60.1737, 276.9^b.
114. $Me\overset{+}{O}(H)SiMe_3$	c, OH=1.04, HOC=120; -60.6146.
115. $(Me_3Si)_2O$	OSi=1.63, SiC=1.87, CH=1.09, SiOSi=CSiC=HCH=109.5; -83.1750.
116. MeOF	CO=1.37, FO=1.18, CH=1.12, FOC=109.5, OCH=109.5; -55.7163, 232.8.
117. $Me\overset{+}{O}(H)F$	c, OH=1.04, COF=HOC=120; -56.0871.
118. CF_3OF	CO=1.37, FO=1.19, CF=1.332, FOC=107.2, OCF=110.7; -136.7152, I88.8.
119. $CF_3\overset{+}{O}(H)F$	CO=1.34, FO=1.19, CF=1.34, OH=1.04, HOC=120; -137.0159.
120. F_2O	OF=1.18, FOF=106.6; -74.3063, 106.3.
121. F_2OH^+	OF=1.18, OH=1.04, HOF=FOF=109.5; -74.4756.
122. $(CF_3)_2O$	CO=1.42, CF=1.332, FCO=FCF=108.8,COC=111; -199.2581, 217.8.
123. $(CF_3)_2OH^+$	c, OH=0.97, COC=HOC=120; -199.6049.
124. F_2O_2	FO=1.19, OO=1.23, FOO=108.4; -92.1562.

125. $(CF_3O)_2O$	CF=1.34, CO=1.367, OO=1.22, FCO=108.2, OOO=109.5; -233.9874.
126. CF_3CH_2OMe	CO=1.367, CF=1.332, CC=1.457, CH=1.10, COC=105; -126.9218, 261.2.
127. $CF_3CH_2\overset{+}{O}(H)Me$	CO=1.4, CF=1.332, CC=1.457, CH=1.1, OH=1.04, HOC=109.5; -127.3379.
128. CF_3CH_2OEt	CO=1.43, CC=1.50, CF=1.332, CH=1.09, FCC=110.2, FCF=108.8, COC=108; -135.5788.
129. t-BuOCl	ClO=1.64, CO=1.367, CC=1.457, CH=1.119, ClOC=CCO=109.5; -70.1122.
130. Cl_2O	ClO=1.50, ClOCl=90; -50.9353.
131. $ClCH_2OEt$	CO=1.43, CCl=1.76, CC=1.54, CH=1.09, COC=111, ClCH=109.5; -61.3465.
132. Cl_2CHOMe	c; -68.0790.
133. $H_2C=CHOEt$	CO=1.42,CC=1.54,C=C=1.35,CH=1.06(vinyl), CH=1.09(ethyl) HC=C=120, CCC=OCH=109.5; -52.8723.
134. $(NH_2)_2O$	NO=1.28, NH=1.04, HNH=HNO=110.2, NON=109.5; -44.9132, 294.6.
135. $NH_2ONH_3^+$	c, $H\overset{+}{N}H$=109.5; -45.3825, 133.8.
136. $H_3\overset{+}{N}ONH_3$	c, -45.5956.
137. CO_2	CO=1.239, OCO=180; -43.6439, 180.0^b.
138. CO_2^-	c,;-43.4162.
139. CO_2H^+	C=O=1.162, CO=1.36, OH=0.97, OCO=125, COH=105; -43.9307.
140. H_2CO	CO=1.25, CH=1.09, HCO=120; -26.8366, 268.0^b.
141. H_2COH^+	OH=0.985, CO=1.27, CH=1.09, HOC=HCH=120; -27.2209.

142. MeCHO CO=1.25, CH=1.09, CC=1.44, HCO=120, HCH=109.5; -35.5505, 292.7.

143. $MeCHOH^+$ OH=0.985, CO=1.27, CH=1.09, CC=1.5, HOC=HCC=120, HCH=109.5; -36.0168.

144. PrCHO CO=1.25, CC=1.44, CH=1.09, CC=1.54, HCO=120, HCH=109.5; -52.9297.

145. t-BuCHO c; -61.6161.

146. CF_3CHO CO=1.25, CH=1.09, CC=1.44, CF=1.332, HCO=120; FCF=109.5. -116.5077, 255.4.[b]

147. CF_3CHOH^+ HO=0.985, CO=1.27, CH=1.09, CC=1.5, CF=1.332, HOC=CCO=120, FCF=109.5; -116.9145.

148. CCl_3CHO CO=1.15, CH=1.09, CC=1.52, CCl=1.76, CCO==CCH=HCO=120, ClCCl=109.5; -81.7609.

149. Me_2CO CO=1.22, CC=1.55, CH=1.09, OCC=120, HCH==109.5; -44.2255, 320.9.

150. Me_2COH^+ HO=1.04, CO=1.3, CC=1.52, CH=1.09, COH=105, HCH=109.5; -44.7367.

151. FCHO CO=1.25, CH=1.12, FC=1.33, FCH=120; -53.8414.

152. MeCOEt CO=1.28, CC=1.44, CC=1.54, CH=1.09, OCC=120, HCH=109.5; -52.9440.

153. F_2CO CO=1.25, FC=1.33, FCF=120; -80.8557,246.9[b].

154. F_2COH^+ HO=1.04, CO=1.3, FC=1.33, COH=107; -81.2490.

155. Cl_2CO CO=1.18, ClC=1.74, ClCCl=120; -57.6433.

156. $MeCOCF_3$ CO=1.25, CC=1.44, CH=1.09, CF=1.332,CCO=120, FCF=109.5; -125.2191.

157. $(CF_3)_2CO$ CO=1.22, CC=1.52, CF=1.332, CCC=120, FCF=109.5; -206.1580, 242.7[b].

158. $(CF_3)_2COH^+$ CO=1.3, CC=1.52, OH=1.04, CF=1.332, COH=105, CCC=120; -206.5446.

159. $(F_2HC)_2CO$	CO=1.22, CC=1.55, FC=1.36, HC=1.09, HCF=109.5; -152.1492, 261.4^b.
160. $(F_2HC)_2COH^+$	CO=1.3, CH=1.09, CF=1.358, CC=1.52, OH=1.04, COH=105; -152.5656.
161. $(FCH_2)_2CO$	CO=1.22, CC=1.55, CH=1.09, CF=1.384, HCF=109.5; -98.1749, 298.8^b.
162. $(FCH_2)_2COH^+$	CO=1.3, CC=1.55, CH=1.09, CF=1.384, OH=0.96, CCC=120, COH=105; -98.6508.
163. FCH_2COMe	CO=1.22, CC=1.55, CH=1.09, CF=1.384, CCO=120; -71.0781, 312.5^b.
164. $FCH_2CO(H)Me^+$	CO=1.3, CC=1.55, OH=0.96, CH=1.09, CF=1.384, COH=105, COC=120; -71.5766.
165. CF_3COCCl_3	CO=1.22, CC=1.55, CF=1.332, CCl=1.76; CCl=120, FCF=108.8, ClCCl=109.5; -171.4651
166. $(CN)_2CO$	CN=1.16, CC=1.46, C=O=1.22, CCC=120; -62.3737, 224.8.
167. $(CN)_2COH^+$	CN=1.16, CC=1.46, CO=1.3, OH=1.04, HOC=120; -62.7318.
168. $(ClCH_2)_2CO$	CO=1.22, CC=1.54, CCl=1.76, HCCl=109.5, OCC=120; -75.1100.
169. $HCOO^-$	CO=1.3, HC=1.12, HCO=OCO=120;-44.4891, 518.0^b.
170. HCOOH	CO=1.25, HC=1.09, CO=1.36, OH=0.97, HCO=120, COH=105; -45.3143, 303.3^b.
171. $HCO(H)OH^+$	CO=1.30, CH=1.12, OH=1.04, HCO=OCO=120; -45.7974.
172. $MeCOO^-$	CO=1.30; CC=1.54, CH=1.09, OCO=120; -53.0982, 521.0.
173. MeCOOH	CO=1.24, CO=1.43, CC=1.54, CH=1.09, OH=0.97, COH=105, OCO=120; -53.9282, 218.2.

174.	$EtCOO^-$	CO=1.3, CC=1.5, CC=1.457, CH=1.119, OCO=120; -61.9006, 525.5.
175.	$EtCOOH$	OH=1.034, CO=1.358, CC=1.449, C=O=1.267, CC=1.457, CH=1.119, HOC=105, OCO=120, HCH=109.5; -62.7376.
176.	$PrCOO^-$	See $EtCOO^-$; -66.7680, 518.8.
177.	$PrCOOH$	See EtCOOH; -67.5945.
178.	FCH_2COO^-	CO=1.30, FC=1.332, CC=1.54, CH=1.09, OCO=120; -80.1673, 510.0^b.
179.	FCH_2COOH	CO=1.43, C=O=1.24, CC=1.54, CF=1.332, CH=1.09, HOC=105, CCO=OCO=OCC=120; -80.9744, 300.8^b.
180.	$FCH_2CO(H)OH^+$	CO=1.3, CC=1.54, OH=0.96, CF=1.384, CH=1.09, COH=105; -81.4587.
181.	CF_3COOH	CO=1.22, CO=1.43, CC=1.54, OF=1.332, OH=0.97, HOC=105, OCO=OCC=120, CFF=108.8; -134.9584, 305.7.
182.	$CF_3CO(H)OH^+$	CO=1.3, CC=1.52, OH=1.04, CF=1.332, COH=CCO=120, FCF=109.5; -135.4453.
183.	CF_3COO^-	c, OCO=OCC=120, FCF=109.5; -134.1698 , 495.0^b.
184.	CCl_3COOH	C=O=1.15, CO=1.36, CC=1.52, CCl=1.76, OH=0.96, COH=105, COO=120, ClCl=109.5; -100.2289.
185.	$(CF_3)_2CHCOO^-$	CO=1.3, CC=1.54, CF=1.332, CH=1.09, OCO=120, FCF=108.8; -232.5665, 480.9.
186.	$(CF_3)_2CHCOOH$	C=O=1.22, CO=1.43, CC=1.54, OH=0.96, CF=1.332, FCF=108.8, OCO=120; -233.3324.
187.	$(CF_3)_3CCOO^-$	CO=1.3, CC=1.54, CF=1.332, FCF=108.8, OCO=120; -322.2479, 471.1.
188.	$(CF_3)_3CCOOH$	C=O=1.22, CO=1.43, CC=1.54, OH=0.96, CF=1.332, COH=105, FCF=108.8; -322.9984.

189.	$NCCOO^-$	CN=1.16, CC=1.46, CO=1.3, OCO=120; -62.2706, 497.3.
190.	CNCOOH	N≡C=1.16, CC=1.46, CO=1.43, C=O=1.22, OH=0.96, OCO=120, HOC=105; -63.0627.
191.	$Cl(CH_2)_2COO^-$	See $PrCOO^-$, CCl=1.76, HCCl=109.5; -77.3185, 524.4.
192.	$Cl(CH_2)_2COOH$	OH=1.034, CO=1.358, CC=1.449, C=O=1.267, CH=1.119, CCl=1.76, COH=105, ClCH=109.5; -78.1539.
193.	$H_2NCH_2COO^-$	See $PrCOO^-$, CN=1.408, NH=1.071, HNH=112; -65.6554, 534.7.
194.	H_2NCH_2COOH	OH=1.034, CO=1.358, CC=1.449, C=O=1.267, CN=1.408, CH=1.119, COH=105, HNH=112, OCO=120; -66.5071.
195.	$Me_3\overset{+}{N}COO^-$	CH=1.09, CN=1.47, CO=1.3, NC=1.38, CNC=109,5, OCO=120; -83.7521, 370.1.
196.	Me_3NCOOH^+	OH=0.96, CO=1.43, C=O=1.25, CH=1.09, NC=1.38, CN=1.47, HOC=105, CNC=109.5; -84.3416.
197.	$H_3\overset{+}{N}CH_2COO^-$	CO=1.27, CC=1.52, CN=1.39, CCN=1.2, OCC=OCO=120; -66.3063.
198.	$Me_3\overset{+}{N}CH_2COO^-$	CO=1.3, CC=1.5, CN=1.47, CH=1.09,OCO=120, CNC=109.5; -92.3944, 398.8.
199.	$Me_3NCH_2COOH^+$	OH=0.96, CO=1.43, CC=1.44, C=O=1.25, CN=1.47, CH=1.09, CNC=HCH=109.5, HOC=105; -93.0296
200.	HCOOMe	C=O=1.22, CO=1.37, CH=1.09, HCO=118.8, COC=112; -53.9774, 316.3[b].
201.	$HCO(H)OMe^+$	CO(H)=1.3, CO=1.38, $OC(H_3)$=1.47, CH=1.08, OCO=120; -54.4812.
202.	$HCOOCH_2CF_3$	C=O=1.22, CO=1.37; CH=1.09, $OC(H_2)$=1.43, CC=1.52, CF=1.332; COC=112, HCO=FCF=108.8, OCO=123, CCF=111,5; -143.6570, 291.5[b].

203. $HCO(H)OCH_2CF_3^+$	C=O=1.3, CO=1.37, HC=1.09, $OC(H_2)$=1.43, CC=1.54, CF=1.332, OH=1.04, COH=120; -144.1213.
204. MeCOOMe	C=O=1.25, CC=1.44, CO=1.36, CH=1.09, CO=1.47, OCO=120, HCH=109.5; -62.6964.
205. CF_3COOMe	C=O=1.22, CC=1.52, CH=1.09, CF=1.332, OCO=124, CCF=111.5, FCF=108.8, COC=113; -143.6466.
206. ClCOOMe	C=O=1.19, CO=1.36, CCl=1.75, $OC(H_3)$=1.47, COC=112; -69.3828.
207. $Me_2NCOOMe$	C=O=1.25, NC=1.38, CO=1.36, CN=1.47, CH=1.09, COC=112; -83.8500.
208. FCH_2COOEt	C=O=1.21, CC=1.55, CO=1.36, CF=1.332, CH=1.09, COC=112, HCF=109.5, OCO=120; -98.3426.
209. $F_2CHCOOEt$	C=O=1.25, CC=1.44, CO=1.36, CF=1.332, CH=1.09, COC=112, FCF=HCH=109.5; OCO=120; -125.3437.
210. CF_3COOEt	C=O=1.22, CC=1.52, CO=1.36, CF=1.332, OCC=116, OCO=124, COC=111; -152.3448, 296.9[b].
211. $CF_3CO(H)OEt^+$	CO=1.3, CO(Et)=1.36, $OC(H_2)$=1.46, CC=1.52, CF=1.332, FCF=108.8, COC=111, COH=105; -152.8178.
212. NCCOOEt	CN=1.16, CC=1.52, C=O=1.22, CO=1.36, OC(Et)=1.46, OCO=120; -80.4296, 280.4.[b]
213. $NCCO(H)OEt^+$	c, CO=1.3; -80.8762.
214. $HCONH_2$	CO=1.207, CN=1.334, CH=1.139, NH=1.016. HCO=116.7, ONH=126.1, ONH=123.7; -39.2809, 309.0[b].

215. $HCONH_3^+$	CO=1.3, CN=1.334, CH=1.139, NH=1.016, OH=1.04, HCO=120, HOC=120; -39.7730.
216. HCONHMe	CO=1.21, CN=1.38, NC= 1.47, CH=1.09, NH=1.04, HCO=120, CNC=HCH=109.5; -48.0094, 304.3[b].
217. $HC(OH)NHMe^+$	CO=1.34, CN=1.31, NC= 1.47, OH=1.04, CH=1.09, NH=1.04, HCO=HOC=120, CNC=HNC=109.5, -48.4940.
218. $HCONMe_2$	CO=1.21, NC=1.35, CN=1.47, CH=1.09, CHN=120, CNC=HCH=109.5; -56.7072, 319.9.
219. $HC(OH)NMe_2^+$	CO=1.3, CN=1.35, CN=1.47, CH=1.09, OH=1.04, HOC=HCO=120, CNC=109.5; -57.2168.
220. $MeCONH_2$	CO=1.21, NC=1.35, CC=1.55, CH=1.09, NH=1.02, HNH=107, CCN=120, HCH=109.5; -48.0020, 336.2.
221. $MeC(OH)NH_2^+$	CO=1.3, CN=1.35, CC=1.55, CH=1.09, NH=1.02, OH=1.04, HOC=NCO=120, HNH=107, -48.5376.
222. MeCONHMe	CCO=1.21, CN=1.35, NC=1.47, CC=1.55, CH=1.09, NH=1.02, CCO=120, NCO=120, HNC=107; -56.6981, 342.1.
223. $MeC(OH)NHMe^+$	CO=1.3, CN=1.35, CC=1.55, NC= 1.47, CH=1.09, OH=1.04, HNC=107, HOC=CCN=120; -57.2430.
224. $MeCONMe_2$	CO=1.25, CN=1.35, CC=1.44, NC=1.47, CH=1.09, CCN=120, CNC=109.5; -65.4097,332.7.
225. $MeC(OH)NMe_2^+$	CO=1.3, CN=1.35, CC=1.55, NC=1.47, CH=1.09, OH=1.04, HOC=CCN=120; -65.9397.
226. $(NH_2)_2CO$	CO=1.25, NC=1.35, NH=1.02, HNH=HNC=107, NCN=120, -51.7998, 334.5
227. $(NH_2)_2COH^+$	CO=1.3, CN=1.35, NH=1.02, OH=1.04, HNH=107, HOC=HCN=120; -52.3326.

228.	CF_3CONH_2	CO=1.21, CN=1.36, CC=1.53, NH=1.02, CF=1.332; CCO=122, NCO=125, CNH=HNH=107, FCF=108,8; -129.0346, 260.1[b]
229.	$CF_3C(OH)NH_2^+$	c, CO=1.3, OH=1.04, CCF=111.0, COH=105; -129.4488.
230.	$(Me_2N)_2CO$	CO=1.27, CN=1.47 NC=1.35, CH=1.09, OCN=120, CNe=109.5; -86.5672, 334.3[b].
231.	$(Me_2N)_2COH^+$	c, CO=1.3, OH=0.96, COH=105; -87.0996.
232.	FCH_2CONH_2	CO=1.22, CC=1.53, CN=1.36, CF=1.384, CH=1.097, NH=1.02, CCO=120, CCF=108.5, NHH=107, HCC=109.5; -75.0080, 307.7.
233.	$FCH_2C(OH)NH_2^+$	c, CO=1.3, OH=1.04, COH=110; -75.4981.
234.	$(MeNH)_2CO$	CO=1.21, CN=1.47, NC=1.36, NH=1.02, CH=1.09, HCN=120, HNC=109.5; -69.1744, 355.0.
235.	$(MeNH)_2COH^+$	c, CO=1.3, OH=1.04, COH=120; -69.7399.
236.	$H_2NCONHMe$	CO=1.21, CN=1.35, NH=1.02, NC=1.47, NCN=120, HNC(O)=107, HNC(H)=HCH=109.5; -60.4794, 316.9.
237.	$H_2NC(OH)NHMe^+$	c, OH=1.04, COH=105; -60.9841.
238.	$Me_2NCONHMe$	CO=1.21, CN=1.35, NC=1.47, NH=1.02, CH=1.09, OCN=120, CNC=HNC=109.5; -77.8557, 353.0.
239.	$Me_2NC(OH)NHMe^+$	c, CO=1.3, COH=120, HNC=107; -78.4180.

NITROGEN BASES

240.	N_2H^+	NN=1.10, NH=1.07, NNH=120; -23.4561.
241.	N	-11.0769, 236.1.
242.	N^-	-10.9900, 646.2.
243.	N^{3-}	-8.6912, 1603.2.

244. NH	NH=1.061; -12.0193, 260.8.^{b}
245. NH^{2-}	NH=1.1; -11.2447, 1035.4.
246. NH^{-}	NH=1.1; -11.9476, 633.5.
247. NH^{+}	NH=1.084; -11.4529.
248. NH_2	NH=1.07, HNH=104.8; -12.9567, 278.7^{b}.
249. NH_2^{+}	c, -12.4347
250. NH_2^{-}	NH=1.1, HNH=110; -12.8940, 624.1.^{b}
251. NH_3	NH=1.07, HNH=106.4; -13.8882, 300.8.^{b}.
252. NH_3^{+}	NH=1.07, HNH=120; -13.4007.
253. NH_4^{+}	NH=1.07, HNH=109.5; -14.3673.
254. N_2	NN=1.14; -23.0906, 231.6.
255. $MeNH^{-}$	NH=1.04, CN=1.47, CH=1.09, HNC=112, HCH==109.5; -21.6233, 596.8.
256. $MeNH_2$	NH=1.04, CN=1.474, CH=1.093, HCN=CNH=112.2; -22.5740, 308.6.^{b}
257. $MeNH_3^{+}$	c, HCN=HNH=109.5; -23.0656.
258. Me_2N^{-}	CN=1.46, CH=1.09, HCH=109.5, CNC=120, -30.3443, 556.5.
259. Me_2NH	CN=1.46, CH=1.08, NH=1.04, CNC=109.5; -31.2307.
260. Et_2NH	NH=1.04, NC=1.474, CC=1.54, CH=1.09, HNC==112, HCH=109.5; -48.5359.
261. $t\text{-}BuNH_2$	c, -48.6112.
262. $t\text{-}Bu_2NH$	c, -82.9562.
263. Me_3N	CN=1.47, CH=1.09, CNC=108, HCN=109.5; -39.9531, 319.9^{b}
264. Me_3NH^{+}	CN=1.479, CH=1.09, NH=1.038, CNC=HNC=109.5; -40.4627.
265. Et_3N	CC=1.54, HC=1.09, CN=1.474, CNC=112, HCH =109.5;-65.8949.

266. $N_2H_2^{2-}$	NN=1.33, NH=1.08 HNN=120; 23.9751 854.8.
267. $N_2H_3^-$	NN=1.33, NH=1.08, HNN=120, HNH=120; 25.3368, 551.4
268. N_2H_4	NN=1.33, NH=1.08, HNN=110.6; -26.3887, 304.6[b]
269. $N_2H_5^+$	c; -26.8740, 111.9.
270. $N_2H_6^{2+}$	c, NNH=120; -27.0522.
271. NF_2	NF=1.23, FNF=104; -67.1169.
272. NF_2^-	c; -67.1403, 575.8.
273. $H_2NF_2^+$	NF=1.25; NH=1.09, FNH=HNH=109.5; -68.4277
274. HNF_2	NF=1.25, NH=1.09, HNF=105.2, FNF=109.5; -68.0579, 232.4.
275. NF_3	NF=1.25, FNF=104.6; -95.1586, 201.7
276. F_3NH^+	NF=1.25, HN=1.09, FNF=109.5; -95.4799.
277. F_2NFH^+	HF=1.0, FN=1.25, FNF=104.2, HFN=180; -95.4172.
278. FNH_2	HN=1.09, NF=1.25, FNH=105; -40.9679, 268.1
279. FNH_3^+	c, FNH=HNH=109.5; -41.3950
280. FNH^-	FN=1.3, NH=1.072, FNH=120; -40.0037, 599.0
281. CF_3NH^-	NH=1.04, CF=1.332, CN=1.47, FCF=109.5, HNC=112; -102.6904, 555.1.
282. CF_3NH_2	c; -103.5745, 277.4.
283. $CF_3NH_3^+$	c, HNH=109.5; -104.0164.
284. $(CF_3)_2N^-$	CN=1.43, CF=1.332, FCN=111, FCF=108.8, CNC=120; -192.4608, 492.0.
285. $(CF_3)_2NH$	CN=1.43, CF=1.332, NH=1.01, HNC=109.5, NCF=110, FCF=108.8; -193.2445.

286.	$(CF_3)_3N$	CN=1.43, CF=1.332, FCN=110.5, FCF=108.8; -282.9570, 238.8.
287.	$(CF_3)_3NH^+$	CN=1.48, CF=1.34, NH=1.04, FNH=109.5; -283.3374.
288.	CF_3NMe_2	CN=1.408, CF=1.343, CH=1.119 CNC=105, FCF=HCH=109.5; -120,9608, 292.2
289.	$CF_3\overset{+}{N}(H)Me_2$	CN=1.48, CF=1.34, CH=1,09, NH=1.04, CNC=HCH=FCF=109.5; -121.4263.
290.	$CF_3CH_2NH_2$	CN=1.43, CC=1.54, NH=1.07, CF=1.332; CNH=107, FCC=110.9, FCF=108.8; -112.2508, 306.9.[b]
291.	$CF_3CH_2NH_3^+$	CN=1.47, CC=1.54, NH=1.038, CH=1.091, CF=1.332, HCH=HNH=109.5, FCF=108.8; -112.7397.
292.	$CF_3CH_2NMe_2$	CF=1.332, CC=1.54, CH=1.09, CN=1.474, CNC=112, FCF=108.8, HCH=109.5; -129.6162.
293.	$FCH_2CH_2NH_2$	c, NH=1.04, HNH=112; -58.2590, 305.6.[b]
294.	$FCH_2CH_2NH_3^+$	NH=1.07, NC=1.47, CC=1.457, CF=1.332, CH=1.119, HNH=FCH=HCH=109.5; -58.7458.
295.	$F_2CHCH_2NH_2$	CH=1.119, CC=1.54, CF=1.343, CN=1.408, NH=1.071, HNH=112, FCF=108.8, HCH=109.5; -85.2531, 304.1[b].
296.	$F_2CHCH_2NH_3^+$	CH=1.119, CC=1.457, CF=1.332, NH=1.07, NC=1.47, HNH=FCF=HCH=109.5; -85.7375.
297.	$ClNH_2$	NCl=1.76, NH=1.07, HNCl=109.5; -29.2966, 302.9.
298.	$ClNH_3^+$	c; -29.7791.
299.	Cl_2NH	c; -44.7184, 302.7.
300.	$Cl_2NH_2^+$	c; -45.2006.
301.	NCl_3	NCl=1.55, ClNCl=90; -60.5188, 256.3.
302.	Cl_3NH^+	NCl=1.55, NH=1.07, HNCl=125, ClNCl=90; -60.9270.

303. $MeNHCl$	CH=1.091, CN=1.47, NH=1.07, NCl=1.76, CNH=CNCl=109.5; -37.9950, 308.9.
304. $MeNH_2Cl^+$	c, -38.4871.
305. $MeNCl_2$	c, -53.4246, 306.5.
306. $MeNCl_2H^+$	c, -53.9128.
307. Me_2NCl	c, -46.6913, 314.2.
308. Me_2NClH^+	c, -47.1918.
309. $(CF_3)_2NCl$	NCl=1.76, NC=1.47, CF=1.332, FCF=CNCl= =109.5; -208.6775, 270.0.
310. $(CF_3)_2NHCl^+$	c, NH=1.07, HNCl=109.5; θ209.1076.
311. $(HC\equiv CCH_2)_2N$	NC=1.47, CC=1.54, CH=1.09, C≡C=1.2 ≡CH=1.1, CNC=109.5;-81.7651.
312. $(HC\equiv CCH_2)_3NH$	c, NH=1.07, CNH=109.5; -59.1428.
313. $H_2N(CH_2)_4NH_2$	NH=1.04, CC=1.54, NC=1.47, CH=1.04, HNC=109.5; -61.0827, 322.8^{i}.
314. $H_2N(CH_2)_4NH_3{}^+$	c; -61.5969^{i}, 229.5.
315. $H_3\overset{+}{N}(CH_2)_4\overset{+}{N}H_3$	c; -61.9625
316. $CNCH_2\overset{-}{N}Me_2$	C≡N=1.191, CC=1.425, CN=1.408, CH= =1.119, CNC=HCH=109.5; -57.7562, 294.0^{b}.
317. $CNCH_2\overset{+}{N}HMe_2$	c, NH=1.04, CNH=120; -58.2245.
318. $Me_2NCH_2CH_2NMe_2$	CH=1.09, CC=1.54, CN=1.47, CNC=HCH= =109.5; -78.4550, 344.5^{i}.
319. $Me_2\overset{+}{N}H(CH_2)_2NMe_2$	c, NH=1.04, -79.0037^{i}, 217.6.
320. $Me_2N(CH_2)_2NHMe_2$	c, -79.3503.
321. $Me_2N(CH_2)_4NMe_2$	CH=1.09, CN=1.47, CC=1.54, CNC=HCH= =109.5; -95.8247, 330.4.
322. $Me_2N(CH_2)_4\overset{+}{N}HMe_2$	c, NH=1.04, HNC=109.5; -96.3510, 262.8.
323. $Me_2\overset{+}{N}H(CH_2)_4\overset{+}{N}HMe_2$	c; -96.7696.

324.	$HONH_2$	NO=1.41, OH=0.96, NH=1.01, NOH=103, HNO=HNH=107; -32.4204, 277.7.
325.	$HONH_3^+$	NO=1.28, OH=0.96, NH=1.07, NOH=105, HNH=109.5; -32.8627.
326.	$HONHMe$	NO=1.28, OH=0.96, CN=1.47, CH=1.09, NH=1.07, HON=105, CNO=HNO=HCH=109.5; -41.0848, 300.3.
327.	$HONH_2Me^+$	c; -41.5631.
328.	$HONMe_2$	c; -49.7681, 309.8.
329.	$HONHMe_2^+$	c; -50.2616.
330.	$MeONH_2$	NO=1.28, CO=1.43, NH=1.08, CH=1.09, ONH=110.2; -41.0869, 301.1[b].
331.	$MeONH_3^+$	NO=1.28, CO=1.367, CH=1.119, NH=1.07, CON=105; -41.5665.
332.	$MeONHMe$	NO=1.43, CO=1.43, NC=1,47, CH=1.09, NH=1.011, HNC=108, HNO=105, HCH=109.5; -49.7207, 286.0.
333.	$MeONH_2Me^+$	c; -50.1762.
334.	$MeONMe_2$	NO=1.28, CO=1.43, CN=1.47, CH=1.09, CNC=CON=HCH=109.5; -58.4508, 314.8.
335.	$MeONHMe_2^+$	c, NOH=105; -58.9523.

SULFUR BASES

336.	SH	SH=1.4; -11.5579, 197.0
337.	SH^-	SH=1.46; -11.5933, 475.7.
338.	H_2S	SH=1.45; HSH=92; -12.3524, 149.3.
339.	H_2S^+	c, -11.8630.
340.	H_3S^+	SH=1.346, HSH=120, planar; -12.5903.
341.	MeS^-	CS=1.78, CH=1.104, HCS=120; -20.2755, 470.0.

342.	MeSH	CS=1.82, SH=1.45, HSC=100.3; -21.0242, 181.0.
343.	$MeSH_2^+$	c; -21.3224.
344.	Me_2S	CH=1.01, CS=1.82, CSC=105, HCH=109.5; -29.6749, 206.1.
345.	Me_2SH^+	c, SH=1.35, CSC=120; -30.0033.
346.	H_2S_2	SH=1.35, SS=2.06, HSS=92; -23.5036, 186.8.
347.	$HSSH_2^+$	SH=1.35, SS=2.06, HSS=120; -23.8011, 4.2.
348.	$H_2\overset{++}{S}SH_2$	c; -23.8078.
349.	SF	SF=1.6; -38.5816.
350.	SF^-	SF=1.6; -38.6273, 458.5.
351.	FSH	SF=1.33, SH=1.59, FSH=98; -39.3586, 49.9
352.	FSH_2^+	SF=1.33, SH=1.59, SHF=109.5; -39.4381.
353.	F_2S	SF=1.59, SFF=98; -66.3934.
354.	$(CN)_2S$	CN=1.16, CS=1.70, CSC=108, SCN=180; -47.7828.
355.	$(CF_3)_2S$	CF=1.332, CS=1.82, CSC105, FCF=109.5; -191.6420, 163.9.
356.	$(CF_3)_2SH^+$	c, SH=1.35, CSC=120; -191.9031.
357.	CF_3S^-	CS=1.83, CF=1.332, SCF=108.8; -101.2793, 427.1.
358.	CF_3SH	c, SH=1.33, CSH=100.3; -101.7878.
359.	Cl_2S	SCl=2.0, ClSCl=103; -43.6963, 163.4.
360.	Cl_2SH^+	SCl=2.0, SH=1.35, ClSCl=ClSH=120; -43.9570.
361.	$HSCH_2SiMe_3$	SH=1.33, SC=1.82, CH=1.09; CSi=1.87, HSC=100, CSiC=109.5; -52.7925.
362.	$NCSCH_2Cl$	NC=1.216, SC=1.56, CS=1.82, CH=1.09, ClC=1.76, HCH=HCCl=109.5, CSC=105; -54.1276, 184.0.

363.	$NC\overset{+}{S}HCH_2Cl$	c, SH=1.35, HSC=120; -54.4207.

CN - BASES[j]

364.	CN	CN=1.169; -18.1174, 263.4.
365.	CN^+	CN=1.169; -17.5343.
366.	CN^-	CN=1.2; -18.1796, 593.0[b].
367.	HCN	CH=1.092, CN=1.191; HCN=180;-19.1515, 279.6[b].
368.	HCN^+	c; -18.5370.
369.	$HCNH^+$	CH=1.10, CN=1.20, NH=1.07; -19.6019.
370.	$NCCH_2^-$	CC=1.42, CH=1.10, HCH=120; -26.9867, 583.9[b].
371.	$MeCN$	CN=1.16, CC=1.46, CH=1.1, HCC=109.5; -27.9168, 305.2.[b]
372.	$MeCNH^+$	NH=1.038, CN=1.20, CC=1.52, CH=1.09, HNC=180; -28.4030.
373.	FCN	CN=1.19, CF=1.319; -46.1376.
374.	$ClCN$	CN=1.191, CCl=1.66; -34.5622, 280.4.[b]
375.	$ClCNH^+$	CN=1.2, CCl=1.63, NH=1.04; -35.0088.
376.	CF_3CN	CN=1.191, CC=1.425, CF=1.343, FCF=109.5; -108.8498, 250.4[b].
377.	CF_3CNH^+	CN=1.266, NH=1.072, CF=1.332, CC=1.425, FCF=109.5; -109.2481.
378.	Cl_3CCN	CN=1.16, CC=1.46, CCl=1.76, ClCCl=109.5; -74.1597, 298.0[b].
379.	Cl_3CCNH^+	CN=1.20, CC=1.46, CCl=1.76; -74.6344.
380.	FCH_2CN	CN=1.16, CC=1.46, CH=1.1, CF=1.332, FCH=109.5; -54.9131, 303.1.
381.	FCH_2CNH^+	CN=1.20, CC=1.46, CH=1.1, CF=1.332, NH=1.04; -55.3964.

382. $ClCH_2CN$	CN=1.16, CCl=1.76, CC=1.46, HCCl=109.5; -43.3011, 306.4.^{b}.
383. $ClCH_2CNH^+$	CN=1.2, NH=1.04, CC=1.425, Cll=1.76, CH=1.072, HCCl=109.5; -43.7891.
384. Cl_2CHCN	CN=1.16, CC=1.46, CH=1.09, CCl=1.76, ClCCl=109.5, -58.7240, 302.3.
385. Cl_2CHCNH^+	CN=1.20, CC=1.46, NH=1.04, CCl=1.76; -59.2055.
386. $CNCH_2CN$	CH=1.09, CC=1.52, C≡N=1.16, HCH=109.5; -45.6805, 290.5^b.
387. $CNCHCNH^+$	CH=1.09, CC=1.52, CN=1.16, NH=1.04; -46.1432.
388. $(NC)_2CH^-$	CH=1.09, CC=1.52, C≡N=1.16; -44.7300, 596.7^b.
389. $(CN)_2$	C≡N=1.191 CC=1.401; -36.9553, 281.8.^{b}
390. $NCCNH^+$	CN=1.16, CC=1.39, CN=1.2, NH=1.04; -37.4042.
391. H_2NCN	C≡N=1.191, CN=1.375, NH=1.071, HNH=HNC=110.6; -31.6577, 298.5.
392. H_2NCNH^+	C≡N=1.20, NC=1.35, NH=1.01(NH_2), NH=1.04, HNH=120; -32.1332.
393. Me_2NCN	C≡N=1.191, NC=1.375, CN=1.408, CH=1.119, CNC=HCH=109.5; -49.0606, 309.4^b.
394. Me_2NCNH^+	c, NH=1.04; CNH=120; -49.5535.
395. $H_2C{=}CHCN$	CN=1.16, CC=1.44, C=C=1.337, CH=1.071, HCH=CCC=120, CCN=180; -34.8471.
396. MeSCN	CN=1.216, CS=1.56, SC=1.82, CH=1.09, CSC=105, NCS=180; -38.7066, 304.4^b.
397. $MeSCNH^+$	c, NH=1.04; CNH=120; -39.1914.

398.	C	-6.1650
399.	CH	CH=1.09; -7.1570, 277.4.
400.	CH_2	CH=1.094, HCH=108.6; -8.1454, 328.7.
401.	CH_2^+	CH=1.09, HCH=120; -7.5988.
402.	CH_2^-	CH=1.1, HCH=140; -8.0466, 672.0.
403.	CH_3	CH=1.1, HCH=120; -9.1172, 188.2.
404.	CH_3^+	c; -8.6690.
405.	CH_3^-	CH=1.13, HCH=120; -9.0497, 669.3^b.
406.	CH_4	CH=1.09, HCH=109.5; -10.1160.
407.	CH_4^+	CH=1.09, HCH=109.5; -9.4170.
408.	CO	CO=1.191; -25.0620, 282.7.
409.	HCO^+	CO=1.181, CH=1.12; -25.5100.
410.	HCO	c; -25.8885, 289.4(c).
411.	H_2CO^+	c, HCH=120; -26.3495.
412.	FCH_2^-	CH=1.097, CF=1.384, HCH=FCH=120; -36.0153, 632.4.
413.	FCH_3	CH=1.097, CF=1.384, HCH=FCH=109.5; -37.0239.
414.	$CF_3CH_2^-$	CH=1.09, CC=1.54, CF=1.332, FCF=108.8, HCF=120; -98.7866, 580.8.^{b}
415.	CF_3CH_3	c; -99.7129.
416.	$(CF_3)_3C^-$	CH=1.09, CC=1.54, CF=1.332, CCC=120, FCF=108.8; -278.3269, 498.3.
417.	$(CF_3)_3CH$	c, CCC=HCC=109.5; -279.1206.
418.	CF_3	CF=1.32, FCF=113.5; -90.1450.
419.	CF_3^-	CF=1.35; -90.1823, 573.0^b.
420.	HCF_3	CF=1.32, FCF=113.5, CH=1.09; -91.0951.
421.	CF_4	CF=1.34, FCF=109.5; -118.1113.

422.	$HC\equiv C^-$	CC=1.205, CH=1.092; -14.3529, 622.6.
423.	$HC\equiv CH$	c; -15.3446, 256.3.
424.	$H_2C=CH^+$	CC=1.28, CH=1.11, HCC=120; -15.7528.
425.	$MeC\equiv C^-$	C≡C=1.205, CC=1.425, CH=1.119; -23.0952, 617.6.
426.	$MeC\equiv CH$	CH=1.092, C≡C=1.205, CC=1.425, CH=1.119; -24.0790.
427.	$PrC\equiv C^-$	See No 422; -39.4232,
428.	$PrC\equiv CH$	c; -41.4759.
429.	$t\text{-}BuC\equiv C^-$	c; -49.1852, 612.9
430.	$t\text{-}BuC\equiv CH$	c; -50.1615.
431.	$CF_3C\equiv C^-$	c; CF=1.343, FCF=109.5; -104.1180, 579.8.
432.	$CF_3C\equiv CH$	c; -105.0416.

VARIA

433.	H	-05275
434.	H^-	-0.5275, 594.6.
435.	H_2	HH=0.74; -1.4746.
436.	H_2^+	HH=0.746; -1.4747.
437.	Cl	-16.0467.
438.	Cl^+	-15.4642.
439.	Cl^-	-16.1043, 470.2.
440.	HCl	HCl=1.35; -16.8534, 113.5.
441.	H_2Cl^+	HCl=1.35, HClH=180; -17.0341.
442.	HCl^{2+}	HCl=1.6; -15.2756.
443.	Cl_2	ClCl=2.0; -32.4929, 78.9
444.	Cl_2H^+	c, HCl=1.28; -32.6186.
445.	F	-27.5491; 123.1.

446.	F^-	-27.4841,598.0.
447.	F^+	-26.6697, -137.5.
448.	HF	HF=1.00;-28.4367, 180.0.
449.	HF^+	HF=1.0; -27.7452.
450.	HF^{2+}	HF=2.4; -26.4506.
451.	F_2	FF=1.12; -55.6354, 109.2.
452.	F_2^-	FF=1.15; -55.2710.
453.	F_2H^+	FF=1.12, FH=1.0; -55.8094.
454.	PH_2	PH=1.52, HPH=91.5; -8.3818
455.	PH_3	PH=1.42, HPH=93.8; -9.1456, 206.9.
456.	PH_3^+	c; -8.6648.
457.	PH_4^+	PH=1.42, HPH=109.5; -9.4767.
458.	SO_2	SO=1.432, OSO=119.5; -47.5508, 278.0.
459.	HSO_2^+	S=O=1.432, SO=1.6, OH=1.022, OSO=HSO=120; -47.9979.

Footnotes:

a - The following order of representation of the data has been used: in the general case (e.g., polyatomic molecule) after the chemical formulae the bond lengths are given (in Å units) followed by the total energies (in a.u. with the precision of four decimal numbers) and as a rule, by the corresponding proton affinities (in kcal/mol, with one decimal point) calculated from the data of the present Appendix.

b - This compound is included into the data set used in defining Eqn.(2) from the text. CNDO/2 PA values for EtO^-, $i\text{-}PrO^-$, and $t\text{-}BuO^-$ are taken from Ref. 20 and for Me_2NH, $EtNH_2$, $PrNH_2$, $i\text{-}PrNH_2$, $t\text{-}BuNH_2$, and Et_3N from Ref. 21.

c - Unless otherwise specified the structural parameters of the previous compound have been used.

d - Protonization on the central oxygen
e - Protonization on the terminal oxygen
f - Protonization on the oxygen of the OH-group
g - Protonization on the oxygen of the N=O bond
h - Protonization on the oxygen of the Cl=O bond
i - Cyclical protonated form.
j - Some negatively charged CN-substituted carbon bases (carbanions of the CH-acids) are also included in this section of the Appendix.

Organic Reactivity
Vol.18 1(65),1981

CNDO/2 Calculations of Molecules.
II. Ionization Potentials.

I.A. Koppel, U.H. Mölder and R.I. Pikver

Laboratory of Chemical Kinetics and Catalysis, Tartu State University, 202400 Tartu,
Estonian S.S.R., U.S.S.R.

Received February 15, 1981

The CNDO/2 calculations of various classes of neutral molecules, molecular ions and free radicals have been made. Rather general correlation has been found between the PES ionization potentials and the corresponding CNDO/2 energies of MO (ε_i).

In accordance with the behavior of the experimental proton affinities (PA) and ionization potentials (IP) the linear relationship between the calculated PA and the energy of MO localized on the protonization center was found to hold.

Amongst several semiempirical SCF MO methods the CNDO approximation is the most widespread due to its simplicity, and availability of standard programs[1].

In the present work the original standard parametrization of Pople and Dobosh[1] was maintained in order to compare the results with the calculations of various authors. The molecular geometries used and the total energies calculated were listed in the previous publication of this series[2]. For the relatively large molecules the assumed optimum geometry was found by the method of "try and error" varying bond lengths, valence and conformational angels in close vicinity to the ionization or protonization center. The calculations were made for the closed shell (the molecular ground state, ions of various charge type) as well as for the open electron shell (molecular ions, radicals, several atoms) systems. The standard set of energetic and other parameters was calculated in order to verify various aspects of the applicability of the given method of calculation.

In our previous communication[2] the attention was focused on the comparison of the CNDO/2 proton affinities with their experimental values determined for the proton transfer reactions including bases of various charge type.

$$B + H^+ \rightarrow BH^+$$

and

$$A^- + H^+ \rightarrow AH$$

The analogous problems (including also the analysis of photoelectron spectra) were also considered[3,4] by the present authors in the framework of ab initio SCF LCA MO calculations using the GAUSSIAN 70 system of programs.

This work concentrates on the study of the possibility to predict the ionization potentials of various molecular systems using the semiempirical CNDO/2 calculations.

Two main approaches could by used to tackle this problem. On the one hand, the IP can be calculated as a difference in the total energies (E_{tot}) of the initial molecule M and of the corresponding cation radical M^+.

$$IP = E_{tot}(M) - E_{tot}(M^+) \qquad (1)$$

The rigorous use of this approach to the calculation of higher-than-1st ionization potentials leads to the complicated calculations of the excited states of molecular ions where the contribution of the electron correlation energy (not taken into account by the one-electron approximation) should already play a significant role.

Some data on the 1st ionization potentials of small systems calculated from Eqn.(1) are listed in Table 1 along with their experimental values and energies of the HOMO ε_1.

Table 1

Ionization Energies of Molecules ΔE(in eV) Calculated as the Differences in Total Energies of the Molecule and the Corresponding Cation - -Radical

No	Compound	ΔE	$-\varepsilon_1^a$	IP_1^b	
1.	FOH	16.71	16.24	13.0	
2.	HCN	16.85	17.98	13.60	
3.	O_2	14.59	14.85	12.31	
4.	H_2O	14.95	17.80	12.61	
5.	NH_3	13.26	16.14	10.92	
6.	OH	17.17	18.83	13.17	13.36
7.	PH_3	13.11	13.19	10.60	
8.	H_2S	13.31	13.39	10.47	
9.	CO_2	15.36	15.70	13.78	
10.	NO	12.47	12.65	9.56	
11.	HF	18.81	21.12	16.03	
12.	H_2CO	13.27	14.82	10.88	
13.	HCO	13.29	11.82	9.8	9.88
14.	NH	15.41	16.32	13.10	
15.	NH_2	14.20	15.85	11.4	
16.	CN	15.86	15.94	14.20	
17.	CH_3	12.19	13.18	9.84	
18.	CH_2	13.86	15.2	10.40	
19.	F	23.92	23.92	17.42	
20.	Cl	15.84	15.84	12.97	
21.	CO	17.41	17.51	14.02	
22.	NF_3	15.50	16.72	13.73	
23.	FCN	16.93	17.07	13.65	
24.	F_2O	15.82	16.37	13.25	
25.	N_2	18.35	18.28	15.76	
26.	F_2	17.66	19.18	15.82	

27. Cl_2	14.21	14.32	11.57
28. HCl	15.00	15.44	12.75

a The negative value of the energy of HOMO
b The experimental 1st ionization potential.

Linear regression analysis of these data leads to the following relationship between the experimental IP_1 and calculated quantities ΔE (See also Fig. 1):

$$IP_1 = 0.976(0.063)\,\Delta E - 2.278(0.970) \qquad (2)$$

$r=0.952$, $s=0.59$ eV, $IP_{max}=7.62$ eV, $s\%=(s/\ IP_{max})100 = 7.7$,

where r - correlation coefficient,
s - standard deviation,
IP_{max}- maximum range of variation of experimental IP,
n - number of points.
Here and in the following text the errors of the regression coefficients are given in parenthesis.

Besides, Eqn. (2) describes rather approximate data on some free radicals but fails by unknown reasons to account for the IP_1 of the F atom. The deviations of the points for CH_4, $H_2C{=}CH_2$ and CH_2 for which the ionization takes place from the binding MO could be connected with the significant changes of the molecular geometry due to the ionization process.

Another approach to the calculation of IP of the molecular systems uses the Koopmans' theorem[5] according to which the calculated SCF energy of the given molecular orbital is approximately equal to the negative value of the ionization energy of the electron from this orbital. Simultaneously, the invariability of the MO concerned is being assumed. In other words, it is taken for granted that the loss of the electron from the electron shell does not lead to the reorganization of the latter. The increased localization

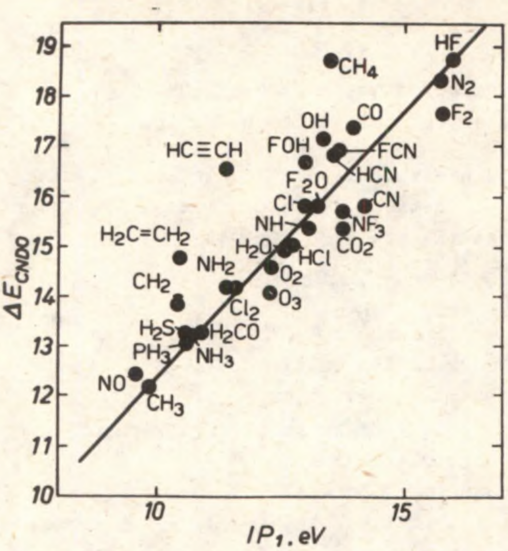


Fig. 1. The comparison of ionization energies calculated from Eqn. (1) with experimental vertical 1st ionization potentials.

of the MO on the ionization center should lead to the increased contribution of this effect. In its turn, the stabilization of the cation-radical due to the reorganization of the electron shell should result in the increased values of the IPs.

The present work deals mostly with the compounds containing the lone electron pairs the MO of which are usually rather localized on a certain atom. Therefore the reorganization energy contribution might be in some cases (especially for the small molecules) significant or even dominant. The latter could explain the situation why the application of the Koopmans' theorem approach to the same set of compounds from Table 1 leads to worse agreement between theory and experiment than in case of the approximation in terms of Eqn. (1):

$$IP_1 = 0.790(0.086)\varepsilon_1 - 0.021(1.366) \qquad (3)$$

$r=0.883$, $s=0.90$ eV, $s\%=14.5$; $n=26$,

where ε_1 is the energy of HOMO (in eV).

The use of the Koopmans theorem assumes also the invariability of the correlation energy contribution in the ground and ionized states of molecules. However, the relative importance of this factor is probably more significant in the cation-radical which should lead to the decrease in the IP values. However, for larger molecules, the Koopmans approximation is generally more reliable. This is because the orbital relaxation effects are sensitive to the degree of localization of an MO, indicating that lone pair MO's in particular have to be considered with care. Also, orbital correlation effects are more equal when the symmetry is low as is generally the case for larger molecules.

In the ideal case of the exact observance of the Koopmans theorem (the constancy or full cancellation of the reorganization and correlation energy contributions) the equality $IP = -\varepsilon_{SCF}$ should be the case.

For the sake of generality the statistical analysis of the data for the verification of the applicability of the Koopmans' theorem was undertaken in terms of the linear equation (4) which assumes that the non-zero intercept and the arbitrary slope do not necessarily equal the minus unity.

$$IP = \alpha \varepsilon_{SCF} + \beta \qquad (4)$$

where α and β are constants.

Formally, Eqn (4) should hold in the case of the linear dependence (in the simplest case - constancy) of the ground and ionized state differences of the reorganization and/or correlation effects on the corresponding IP or MO energy values. Most probably, these conditions should be observed in the homologous rows of compounds with the lone pairs of electrons. So, the statistical treatment of the data from Table 2 on the 1st ionization potentials of alcohols, ethers and Li_2O results in the following relationship

Table 2

Photoelectron Spectra of Various Molecules and CNDO/2 Energies of MO($-\mathcal{E}_i$)^{a,b}

No	Compound	Refs.	PES and calculated energies of MO- $\mathcal{E}_i$						
1.	H_2O	11	12.61	14.73	18.55	32.2			
		c	17.80	19.07	20.61	39.14			
2.	MeOH	12	10.96	12.62	15.21	15.64	17.62		
		c	15.13	16.03	19.85	22.95	23.84		
3.	EtOH	13	10.65	12.10	13.30	13.90	15.96	17.48	
		c	14.80	15.82	17.23	18.47	20.23	23.61	
4.	FOH	14	13.0	14.8	16.0				
		c	16.24	17.12	24.18				
5.	ClOH	15	11.22	12.27	14.6	15.6			
		c	14.92	15.10	17.58	19.17			
6.	$HC\equiv CCH_2OH$	16	10.59	10.92	11.53	13.40	16.26	17.51	18.58
		c	14.51	15.54	17.01	17.35	20.31	22.87	24.61
7.	CF_3CH_2OH	16	11.70	13.29	15.35	16.46	17.01	18.01	
		c	15.71	16.11	18.76	19.53	19.69	21.15	
8.	$(CF_3)_2CHOH$	16	12.26	13.65	15.81	16.72	17.41		
		c	15.29	16.82	18.91	19.88	20.07		
9.	$(CF_3)_3CCH_2OH$	16	11.68	13.09	14.19	15.71	16.58	17.46	
		c	15.70	16.23	16.98	17.52	19.45	20.25	
10.	$CF_3C(OH)_2H$	16	10.80	11.81	13.26	15.38	16.83		
		c	14.85	16.79	17.40	19.48	19.65	20.34	
11.	H_2O_2	17	11.51	12.56	15.26	17.35			
		c	15.00	15.14	21.49	23.96			

12. Me_2O	18	10.04	11.91	13.43	14.2	16.5		
	c	14.44	16.16	16.50	19.39	21.52		
13. Et_2O	19	9.61	11.08	11.92	16.23	19.67		
	c	13.66	15.02	15.23	15.34	16.77^d	18,46^d	
		19.40	21.49^d	23.47				
14. tBu_2O	17	9.16	10.24	10.95				
	c	12.61	12.87	13.99	14.55	14.80		
15. $MeOSiMe_3$	16	9.85	10.64	12.33	13.8			
	c	13.61	13.79	14.70	14.95	17.34	17.92	18.09
16. $(Me_3Si)_2O$	16	9.69	10.54	12.21	13.84			
	c	13.61	13.63	13.96	13.99	14.29	16.12	16.59
		16.73	16.80					
17. F_2O	20	13.25	16.10	16.44	18.50	19.55^d	20.7	
	c	16.37	19.79	20.73	22.95	27.55		
18. Cl_2O	21	11.02	12.37	12.65	12.79	15.90	16.65	17.68
	c	14.52	14.60	15.37	15.55	19.90	20.33	21.30
19. CF_3OF	12	13.63	15.35	16.6	17.5	19.0	20.1	
	c	17.50	17.63	20.37	20.62	22.10	22.49	
20. CF_3CH_2OMe	16	10.69	12.38	13.80	14.40	15.49	16.70	17.18
	c	15.16	15.20	16.96	18.69	19.44	19.73	20.52
		21.08	21.30	21.95				
21. CF_3CH_2OEt	16	10.27	10.38	10.56	12.26	13.2	15.49	16.67
	c	14.12	14.94	15.68	16.99	17.57	19.58	19.79
22. Me_2SO	22	9.01	10.17	12.57	13.40	13.9	15.35	
	c	11.35	15.14	16.67	16.89	19.24	19.38	
23. F_2SO	23	12.58	14.0	14.75	15.93	16.6	16.95	18.3
	c	16.72	18.19	18.38	19.68	20.7	21.58	22.97
24. Cl_2SO	23	11.07	11.89	12.15	12.53	13.1	15.70	16.25
		16.6						
	c	14.26	14.31	15.09	15.59	16.86	17.66	19.21
		19.98						
25. HCOOH	24	11.52	12.5	14.8	15.8	17.2	17.8	
	c	14.88	15.09	17.36	21.69	21.69	23.34	

26. MeCOOH	24	10.86	12.11	14.0	14.2	16.30	17.1	
	c	$\underline{14.08}$	$\underline{14.16}$	16.30	18.60	18.70	22.23	23.02
27. EtCOOH	24	10.72	12.04	12.69	13.41	13.8	14.63	15.2
		16.53	17.04					
		13.30	14.33	16.23	16.42	17.39	18.44	20.40
		21.99	24.09					
28. CF_3COOH	24	12.0	13.2	14.9	15.8	16.7	17.5	18.0
		19.7						
	c	14.93	16.55	17.93	20.07	21.24	21.63	21.76
		22.23						
29. HCOOMe	25	11.02	11.55					
	c	14.52	14.90					
30. $HCOOCH_2CF_3$								
	16	11.65	12.09	13.75	14.52	15.26	17.09	19.41
	c	$\underline{15.01}$	$\underline{15.56}$	16.48	17.75	18.66	$\underline{19.63}$	$\underline{19.88}$
		$\underline{21.28}$	$\underline{21.38}$	23.02				
31. H_2CO	11	10.88	14.39	16.01	16.60			
	c	14.82	17.86	20.11	24.67			
32. MeCHO	26	10.26	13.24	14.15	15.34	16.47	19.1	
	c	13.91	15.41	17.14	20.76	23.17	23.60	
33. tBuCHO	27	9.82	12.0	12.6	13.4	14.1	15.6	16.5
	c	13.20	14.50	14.86	$\underline{16.89}$	$\underline{17.17}$	$\underline{18.11}$	$\underline{18.41}$
		20.21	20.50					
34. CF_3CHO	16	11.66	15.27	15.65	16.34	17.10	17.58	19.4
	c	15.09	18.19	19.19	19.91	20.24	$\underline{21.52}$	$\underline{21.56}$
		22.49						
35. CCl_3CHO	16	10.88	11.62	12.07	12.68	13.03	14.47	15.62
	c	13.54	$\underline{14.13}$	$\underline{14.14}$	14.85	$\underline{15.58}$	$\underline{15.59}$	16.25
		16.65	17.27	17.6				
		17.93	18.44	21.46	22.15	22.42		
36. Me_2CO	26	9.70	12.59	13.41	14.04	14.8^d	15.6	16.1^d
		16.6^d	18.1					
	c	13.25	15.31	16.99	18.18	19.73	22.38	

37. F_2CO	20	13.6	14.6	16.6	17.2	19.15	19.8	21.1
	c	17.28	17.39	19.89	21.47	22.20	24.69	26.46
		26.58	28.07					
38. Cl_2CO	28	11.83	12.6	13.05	13.50	16.15	16.73	17.11
	c	13.76	15.21	15.49	15.57	20.76	22.11	23.12
		19.48						
		24.33						
39. $(CF_3)_2CO$	20	12.09	16.0	16.5	17.1	17.75	18.4	
	c	14.74	18.58	19.02	20.36	20.44	20.49	20.85
		21.48						
40. FCH_2COMe	16	10.20	12.60	13.61	15.19	16.89	17.72	19.18
	c	13.49	15.71	16.83	17.39	19.61	20.32	21.19
41. CF_3COMe	16	10.94	13.74	14.25	15.64	16.44	17.25	18.04
	c	14.28	16.21	17.40	19.53	19.79	20.64	21.18
42. $(F_2HC)_2CO$	16	11.23	14.49	15.91	17.48	19.93		
	c	14.27	17.30	18.32	18.41	19.65[d]	20.35	20.67
		21.04	21.87					
43. CCl_3COCF_3	16	11.19	12.16	12.51	12.81	13.33	14.49	15.74
	c	13.93	14.48	14.51	15.20	15.87	15.97	16.23
		16.41	17.44	18.31	17.82	18.76	20.19	20.63
		21.63						
44. CO	11	14.02	16.92	19.69				
	c	17.51	20.11	24.46				
45. NH_3	29	10.92	15.8	16.8				
	c	16.14	19.58	19.89				
46. $MeNH_2$	30	9.64	13.22	14.42	15.45	16.85		
	c	14.26	16.57	18.83	22.23	23.56		
47. Me_2NH	31	8.94	12.64	13.27	13.85	15.05	15.49	16.70
	c	12.91	14.64	17.70	17.90	21.01	23.63	25.98
48. Me_3N	32	8.45	12.36	12.88	13.81	15.88		
	c	12.11	14.52	16.92	17.25	17.98		
49. F_2NH	33	12.36	15.37	15.54[d]	15.98	18.01	19.0[d]	19.77
	c	15.50	18.87	19.97	21.96	25.62		

50. NF_3	34	13.73	16.45	16.55	17.52	19.71		
	c	16.72	19.96	20.07	21.60	22.94		
51. $CF_3CH_2NH_2$	16	10.35	13.86	15.18	16.91	17.70	19.19	20.29
	c	14.59	15.95	18.72	19.37	19.81	20.12	21.02
		21.52						
52. $(CF_3)_2NCl$	35	11.45	13.0	14.30				
	c	15.63	16.01	17.45				
53. $CNCH_2NMe_2$	16	9.22	12.14	12.62	12.98	13.74	14.58	
	c	12.96	14.80	14.94	16.08	17.05	17.83	17.85
		16.73	17.51	20.4	20.47	20.82	24.56	
54. $ClNH_2$	36	10.52	11,92	13.50	15.72	17.50		
	c	14.10	14.58	16.51	18.75	21.33		
55. Cl_2NH	36	10.56	11.88	12.39	12.50	14.54	16.11	17.39
	c	14.03	14.33	14.99	15.31	17.88	18.29	20.93
56. NCl_3	36	10.69	11.66	12.08	13.02	15.41	16.70	
	c	13.28	13.79	15.23	16.45	19.52	20.67	
57. MeNHCl	36	9.8	11.52	12.42	13.68	15.05[d]	15.75	16.99
	c	13.66	14.33	14.96	16.65	19.49	22.12	
58. Me_2NCl	36	9.25	11.19	13.2	13.6	14.3	15.9	
	c	13.17	14.17	14.3	16.34	16.71	19.42	
59. $MeNCl_2$	36	10.01	11.45	11.96	12.14	13.2	14.11	15.54
		16.53						
	c	13.51	14.07	14.62	14.97	16.12	16.62	20.06
		22.32						
60. HCN	37	13.60	13.82	19.9				
	c	17.98	18.17	26.17				
61. MeCN	38	12.18	13.11	15.15	17.4			
	c	15.36	17.42	22.79	23.15			
62. FCN	39	13.65	14.56	19.3				
	c	17.07	19.22	24.99				
63. ClCN	40	12.37	13.80	15.37	19.0			
	c	14.93	17.80	20.05	22.09			

64. FCH_2CN	16.	12.92	13.25	13.60	14.58	14.94			
	c	15.60	16.74	17.26	19.71	19.96			
65. $ClCH_2CN$	41	12.05	12.9	13.59					
	c	14.45	15.04	16.37					
66. Cl_2CHCN	16	12.14	12.63	13.43	13.92	16.38			
	c	14.19	14.65	15.29	16.13	17.31[d]	18.65		
67. CCl_3CN	16	11.94	12.27	12.69	13.06	13.87	16.99	18.38	
	c	14.11	14.71	15.04	15.52	17.20	19.15	21.91	
68. $CNCH_2CN$	42	12.70	13.05	13.57	13.59	13.89	14.02	17.28	
	c	14.89	15.60	15.77	17.63	18.53	19.08	25.51	
69. Me_2NCN	43	9.44	11.87	12.55	12.79	14.0	14.7	16.5	18.3
	c	13.20	15.12	15.60	17.02	18.00	19.12	19.43	23.27

Footnotes to Table 2.

a - Eqns (5)-(7) also describe the following values of IP_1 (the energies of the HOMO are included in parentheses) Li_2O 6.8(-10.83), FCH_2CH_2OH 11.05(-14.96), PrOH 10.52[13] (-14.52), $ClCH_2CH_2OH$ 10.85[16](-14.13), MeCOEt 9.52[27](-13.31), Me_2NCF_3 9.99(-13.62), $FCH_2CH_2NH_2$ 9.86(-13.80), Et_3N 8.19(-12.06), $F_2CHCH_2NH_2$ 10.15(-14.32), Et_2NH 8.51(-12.57), t-$BuNH_2$ 8.83(-13.14), $CF_3CH_2NMe_2$ 8.98(-12.70), $(Me_2NCH_2)_2$ 8.3[16](-12.14); Eqn. (8) also includes the following data: CCl_3CH_2OH 11.34[16](-13.75) Me_3SiCl 10.58 (-13.81), O_3 12.75[45] (-14.43), O_2 12.305[44](-14.85), Cl_2CHOMe 10.98[16] (-13.48), $(CF_3)_3COH$ 12.58[16] (-15.20), (cyclo-$C_3H_5)_2CO$ 9.27[16] (-12.31), N_2 15.76 (-18.28), N_2H_4 9.93[16] (-12.42), Me_3SiCH_2SH 9.0 (-12.05), Me_2S 8.65 (-11.68), $(CF_3)_2S$ 11.11 (-14.83), Cl_2S 9.7 (-12.26), CF_3SH 11.35 (-14.25), MeSH 9.44 (-12.44), H_2S (10.47 (-13.39), H_2S_2 10.01 (-12.81), $H_2C=CH_2$ 10.51

(-14.8), Cl_2CH_2 11.4 (-13.99), CI_3CH 11.48 (-14.09), CCl_4 11.69 (-14.01), MeC≡CH 10.37 (-14.84), CF_3Cl 13.08 (-16.24), MeCl 11.22[4] (-14.21), FCl 12.77 (-15.66), $F_2CHCOOEt$ 11.09[16] (-13.95), MeCOOMe 10.59 (-13.96), PrCHO 9.83 (-13.76), CF_4 16.2 (-20.23), NO 9.56 (-12.65), HCl 12.75 (-15.44), F_2 15.82 (-19.18), PH_3 10.6 (-13.19), MeF 13.05 (-17.27), $MeCF_3$ 13.8 (-16.42), HCF_3 14.80 (-17.69), C_6H_6 9.24 (-13.89), C_6H_5N 9.66 (-13.05). As a rule, the first vertical IPs were taken from Refs 4,6,10.

b - For this sequence of the underlined MO energies the average value was used.

c - Calculated in this work

d - This value was not included in defining the Equations from Table (4).

(see also Fig. 2):

$$IP_1 = 1.008(0.043)\,\varepsilon_1 - 4.025(0.631) \qquad (5)$$

$r = 0.982$, $s = 0.26$ eV, $IP_{max} = 6.83$ eV, $s\% = 3.8$, $n = 22$

The point for H_2O deviates from this Eqn. towards too high values of the predicted energy of HOMO (too low IP_1). The analogous relationships also hold for the aldehydes and ketones (Fig.3) and for tertiary amines (Fig.4) being represented by Eqns. (6) and (7):

$$IP_1 = 0.932(0.085)\,\varepsilon_1 - 2.350(1.230) \qquad (6)$$

$r = 0.954$, $s = 0.42$, $IP_{max} = 4.46$ eV, $s\% = 9.4$, $n = 14$, and

$$IP_1 = 1.199(0.036)\,\varepsilon_1 - 6.353(0.486) \qquad (7)$$

$r = 0.995$, $s = 0.17$, $IP_{max} = 5.54$ eV, $s\% = 3.1$, $n = 13$.

It is interesting to note that Eqn. (6) holds also for O_2 but fails to account for the behavior of CO_2. Like the water in Eqn.6 the point for NH_3 also deviates from Eqn.7 towards the higher values of the predicted energies of HOMO. Just the opposite is however true for the hydrazine.

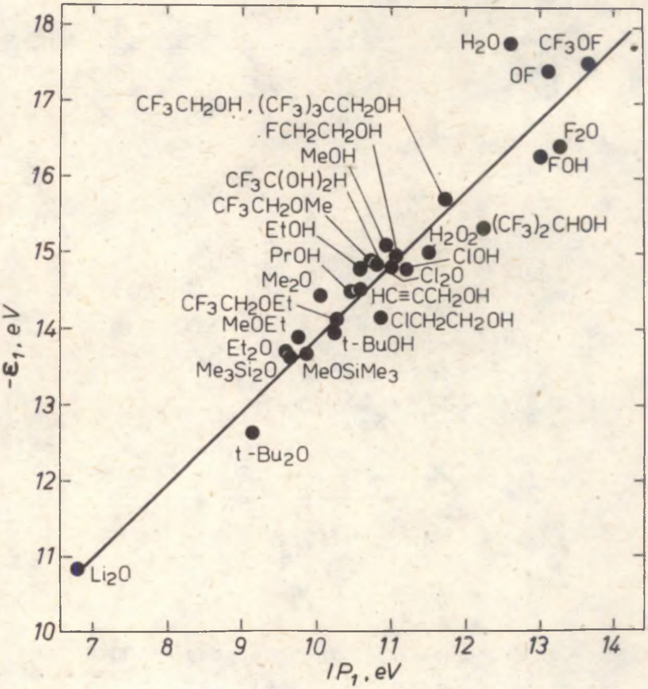


Fig. 2. Comparison of the energies of HOMO with the 1st vertical ionization potentials of alcohols and ethers.

Formally the unified analysis of data from Table 2 for 71 compounds of various classes reveals (see also Fig. 5) a rather general relationship between the 1st vertical ionization potentials and the calculated energies of HOMO:

$$IP_1 = 1.083(0.032)\,\varepsilon_1 - 4.835(0.471) \qquad (8)$$

$r = 0.971$, $s = 0.47$ eV, $IP_{max} = 8.00$ eV, $s\% = 5.8$ $n = 71$.

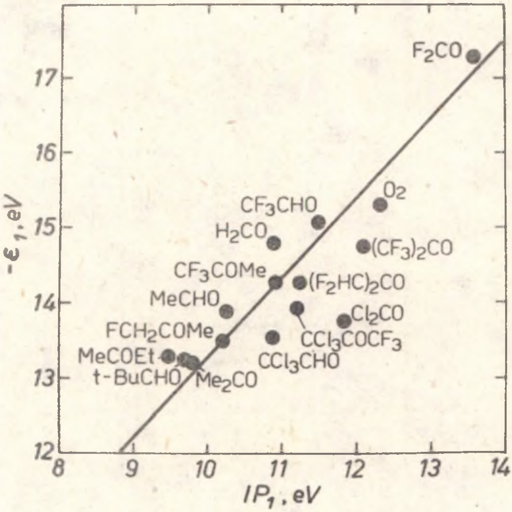


Fig.3. Comparison of the energies of HOMO for carbonyl compounds with their 1st vertical ionization potentials.

The correlation statistics being considerably worse when compounds containing third period elements are included:

$$IP_I = I.009(0.034)\ \varepsilon_1 - 3.564(0.500)$$

$r = 0.942$, $s = 0.56$ eV, $IP_{max} = 8.00$ eV, $s\% = 7.0$, $n = I08$.

It is interesting to note that the data for the simple

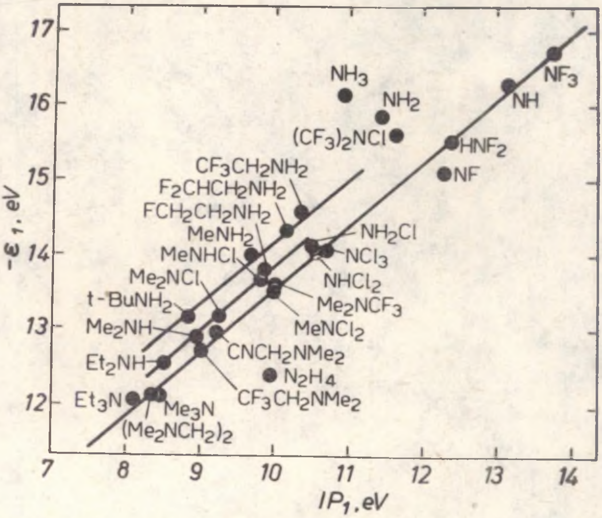


Fig. 4. Comparison of the energies of HOMO for amines with their 1st vertical ionization potentials.

hydrides (-H_2O, NH_3, CH_4, HF and H_2 - fit another straight line (IP_1= 0.968(0.104)-4.800(1.986), r= 0.983; s= 0.44, n=5) characterized approximately by the same slope but by the different more negative intercept. At the same time, hydrides of the 3rd period (HCl and PH_3) obey Eqn.(8).

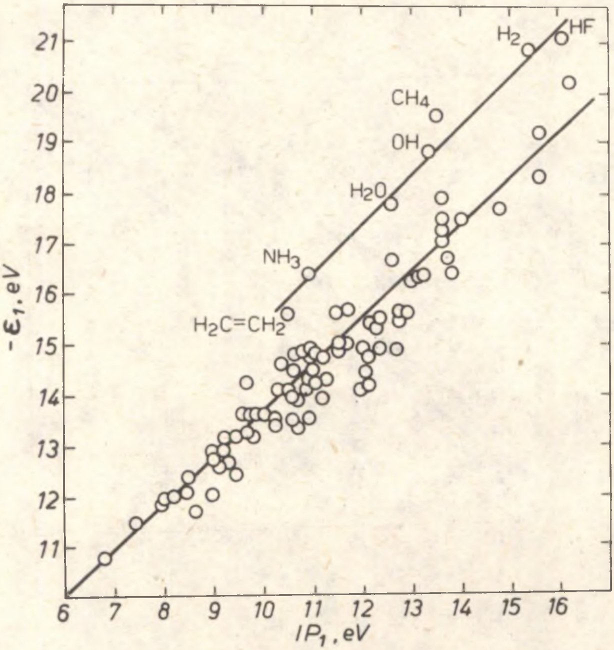


Fig. 5. The general comparison of the energies of HOMO for various classes of compounds with their 1st vertical ionization potentials.

Within their error limits the slopes of Eqns.(5)-(8) are close to unity (compare also with Ref.4). However, all these relationships are characterized by non-zero intercepts.

The photoelectron spectroscopy (PES) determines the spectrum energies of electrons eliminated by the exciting photons from the electron shell of the molecule. It is essential to compare the experimental PES with the calculated energies of the occupied MO-s of the given molecule. Therefore there is steady progress in the field of various level quantum-chemical interpretation of the experimental PES[7]. Meanwhile encouraging results have been gotten [4] by the present authors on the ab initio level using the GAUSSIAN 70 set of programs. In this paper the same problem will be briefly considered also in the framework of the semiempirical CNDO/2 method.

It is clear from the very beginning that any calculations in order to interprete PES should at least, lead to the correct order, number and distances between the spectral lines. Unfortunately, in several cases[8] ab initio and CNDO/2 calculations give contradictory results. It is also well-known that the discrepancies of the Koopmans' theorem are more noticable in the case of the energies of the inner MOs with very rare exceptions the calculated spectrum of the MO energies of the molecule has more lines than the experimental PE spectrum. The calculated energies of the higher occupied MOs are relatively insensitive to the small deviations of the used molecular geometry from its optimum characteristics. However, the situation might change drastically when the complete PES including the lowest IPs is being considered. It understandably complicates the quantum chemical interpretation of the experimental PES. However, the problem could be somewhat simplified by the analysis of PES of molecules of various classes with the definitely resolved lines. As will be demonstrated this approach enables one to find some rather general relationship between the experimental IP_i and calculated values of the MO energies ε_i.

The following procedure was adopted. The semiempirical CNDO/2 method was used not as a real MO method but as a certain algorithm for the calculations of IPs and for the formal comparison of their order. As a rule, the Koopmans' theorem MO energies could be used for the identification of PES only in case the vicinal lines differ from each other at least by 1 eV. For the two or several consecutive experimentally hardly separable lines the arithmetic mean values were used. The experimental and predicted spectra for a large number of molecules were used in this kind of statistical analysis in terms of the linear equation (see also Ref.4):

$$IP_i = \alpha' \varepsilon_{i(calc)} + \beta' \qquad (9)$$

where α' and β' are constants were taken from Table 2. As a rule, experimental ionization potentials not exceeding Ca 20 eV were used.

Analogously to the findings in Ref. 4 one should expect that from the statistical viewpoint the data sets with the highest correlation coefficients, with the lowest standard deviations and with the slopes α' reaching the unity should correspond to the adequately interpreted and identified spectrum.

Within these limitations the rather general correlation equation was found to describe the PES data for 68 molecules from Table 2.

$$IP_i = 0.90(0.01)\,\varepsilon_{i(calc)} - 1.75\ (0.25) \qquad (10)$$

$r = 0.975$, $s = 0.53$ eV, $IP_{i(max)} = 11.7$, $s\% = 4.5$, $n = 192$.

The results of the separate correlations of the data from Table 2 for different molecules are represented in Table 3. Some typical examples of this type of correlations are given in Fig. 6.

Table 3

Correlation Statistics of the Least Squares Analysis of PES in Terms of Eqn.(9).[a]

No	Compound	α'	β'	r^b	s^c	n^d
1.	H_2O	0.86(0.104)	-1.32(2.523)	0.986	1.82	4
2.	MeOH	0.65(0.10)	1.89(2.00)	0.964	0.31	5
3.	EtOH	0.77(0.07)	-0.18(1.25)	0.984	0.49	6
4.	FOH	0.30(0.18)	8.88(3.41)	0.859	1.09	3
5.	ClOH	0.84(0.10)	-0.78(1.77)	0.985	0.43	4
6.	$HC{\equiv}CCH_2OH$	0.85(0.08)	-2.02(1.44)	0.981	0.71	7
7.	CF_3CH_2OH	1.10(0.10)	-4.96(1.85)	0.984	0.48	6
8.	$(CF_3)_2CHOH$	1.04(0.05)	-3.68(1.00)	0.996	0.23	5
9.	$(CF_3)_3CCH_2OH$	1.16(0.18)	-5.78(3.17)	0.956	0.72	6
10.	$CF_3C(OH)_2H$	1.11(0.12)	-6.10(2.18)	0.982	0.54	5
11.	H_2O_2	0.57(0.08)	3.34(1.44)	0.983	0.60	4
12.	Me_2O	0.82(0.14)	-1.17(2.41)	0.960	0.78	5
13.	Et_2O	1.02(0.05)	-4.10(0.91)	0.996	0.42	5
14.	$t\text{-}Bu_2O$	0.93(0.05)	-2.68(0.74)	0.998	0.07	3
15.	$MeOSiMe_3$	0.85(0.14)	-1.90(2.18)	0.975	0.48	4
16.	$(Me_3Si)_2O$	1.27(0.39)	-7.05(5.65)	0.919	0.89	4
17.	F_2O	0.67(0.05)	2.66(1.12)	0.991	0.43	5
18.	Cl_2O	1.04(0.08)	-3.68(1.36)	0.986	0.47	7
19.	CF_3OF	1.06(0.15)	-4.39(3.06)	0.961	0.73	6
20.	CF_3CH_2OMe	0.96(0.05)	-3.98(0.91)	0.994	0.28	7
21.	CF_3CH_2OEt	1.18(0.11)	-7.30(1.95)	0.977	0.62	7
22.	Me_2SO	0.76(0.13)	-0.03(2.18)	0.944	0.88	6
23.	F_2SO	0.89(0.06)	-1.90(1.25)	0.987	0.34	7
24.	Cl_2SO	0.96(0.10)	-2.36(1.71)	0.967	0.60	8
25.	HCOOH	0.65(0.10)	2.50(1.81)	0.960	0.79	6
26.	MeCOOH	0.70(0.02)	0.94(0.44)	0.998	0.18	6
27.	EtCOOH	0.58(0.04)	3.56(0.68)	0.986	0.37	9
28.	CF_3COOH	0.90(0.10)	-4.60(1.93)	0.966	0.72	8
29.	$HCOOCH_2CF_3$	1.06(0.06)	-4.17(1.10)	0.992	0.38	7
30.	H_2CO	0.56(0.19)	3.63(3.63)	0.903	1.35	4

31. MeCHO	0.69(0.13)	1.71(2.43)	0.937	1.17	6
32. t-BuCHO	0.77(0.08)	0.48(1.38)	0.973	0.57	7
33. CF_3CHO	0.98(0.07)	-3.07(1.27)	0.989	0.39	7
34. CCl_3CHO	0.73(0.04)	1.30(0.62)	0.991	0.35	10
35. Me_2CO	0.87(0.06)	-1.40(1.09)	0.990	0.45	6
36. F_2CO	0.81(0.06)	0.16(1.31)	0.985	0.63	8
37. Cl_2CO	0.63(0.05)	3.24(0.92)	0.982	0.55	8
38. $(CF_3)_2CO$	0.91(0.05)	-1.19(0.98)	0.994	0.28	6
39. FCH_2COMe	1.14(0.05)	-5.20(0.95)	0.995	0.36	7
40. CF_3COMe	0.94(0.07)	-2.15(1.28)	0.987	0.43	7
41. $(F_2CH)_2CO$	1.08(0.08)	-4.26(1.57)	0.991	0.50	5
42. CCl_3COCF_3	0.88(0.03)	-1.02(0.57)	0.995	0.27	10
43. CO	0.81(0.08)	0.03(1.59)	0.996	0.38	3
44. NH_3	1.51(0.13)	-13.41(2.38)	0.996)	0.38	3
45. $MeNH_2$	0.67(0.13)	1.03(2.41)	0.951	0.98	5
46. Me_2NH	0.55(0.09)	3.21(1.61)	0.952	0.81	6
47. Me_3N	1.06(0.21)	-4.09(3.31)	0.946	1.02	5
48. F_2NH	0.74(0.06)	1.20(1.22)	0.990	0.45	5
49. NF_3	0.91(0.09)	-1.73(1.79)	0.986	0.41	5
50. $CF_3CH_2NH_2$	1.29(0.12)	-7.92(2.33)	0.977	0.79	7
51. $(CF_3)_2NCl$	1.38(0.54)	-9.71(8.91)	0.931	0.74	3
52. $CNCH_2NMe_2$	0.95(0.05)	-2.63(0.88)	0.991	0.48	9
53. $ClNH_2$	0.93(0.08)	-1.94(1.36)	0.989	0.48	5
54. Cl_2NH	0.94(0.09)	-1.96(1.49)	0.978	0.56	7
55. NCl_3	0.96(0.08)	-2.31(1.31)	0.986	0.43	6
56. MeNHCl	0.79(0.10)	0.10(1.62)	0.972	0.71	6
57. Me_2NCl	0.69(0.11)	1.18(1.90)	0.951	0.81	6
58. $MeNCl_2$	0.65(0.06)	2.46(0.97)	0.976	0.48	8
59. HCN	0.76(0.01)	-0.11(0.17)	0.999	0.05	3
60. MeCN	0.56(0.15)	3.54(3.01)	0.932	1.03	4
61. FCN	0.93(0.17)	-2.82(3.81)	0.967	1.31	4
62. ClCN	0.88(0.20)	-1.41(3.76)	0.952	1.07	4
63. FCH_2CN	0.45(0.03)	5.81(0.59)	0.992	0.13	5
64. $ClCH_2CN$	0.75(0.22)	1.32(3.30)	0.961	0.30	3
65. Cl_2CHCN	0.93(0.04)	-1.05(0.59)	0.998	0.13	5
66. CCl_3CN	0.87(0.07)	-0.47(1.19)	0.984	0.49	7
67. $CNCH_2CN$	0.41(0.03)	6.50(0.63)	0.983	0.31	7

68. Me_2NCN	0.87(0.08)	-1.53(1.36)	0.977	0.25	8

a - The error limits of the regression coefficients are given in parentheses.
b - Correlation coefficient.
c - Standard deviation.
d - The number of points.

One can see that despite the general success of this approach there are some molecules (mostly carbonyl- and cyanogen-compounds) for which the slope α' is far from unity and the standard deviation   exceeds 1 eV. A possible reason for this devious behavior might be the use of not fully optimized geometries for these classes of compounds.

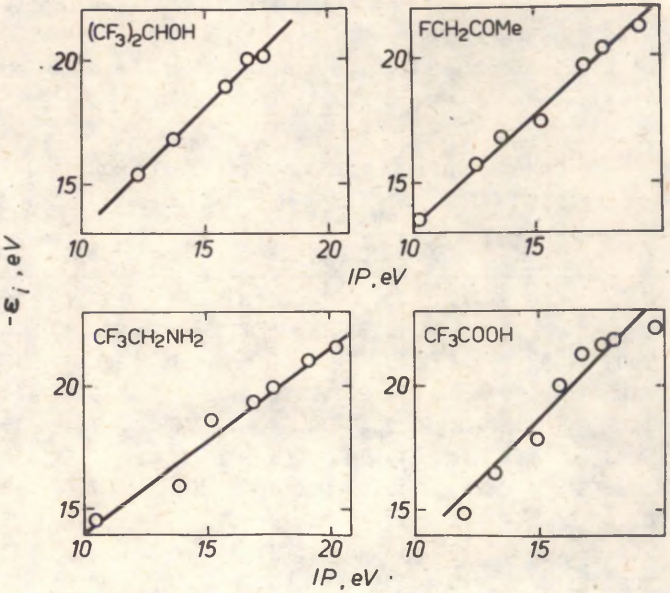


Fig. 6. Separate correlations of IP_i with the MO energies $\varepsilon_{i(calc)}$.

In general, the CNDO/2 based correlations by Eqn.(9) are not as accuarate as those using the results of ab initio calculations.[4] However, as evidenced by Table 4 in several cases the agreement between theory and experiment is more than satisfactory.

In the framework of this paper it is reasonable to try to clarify the nature of the relationship[10] between proton affinities (PA) and IP of molecules using the CNDO/2 calculated values for both of these quantities. As far as **PAs** refer only to the protonization center, the Koopmans' theorem was used to determine the energies of the MOs localized on the basicity center of the base. In the case of several equivalent ionization centers it is necessary to take into account the splitting of the corresponding orbitals. The averaged values of the energies of these orbitals were used for comparisons with the **PAs**.

The statistical analysis was done using the data on CNDO/2 calculated **PAs** and ε_{CNDO} from Table 4.

Table 4.

The CNDO/2 Proton Affinities (in kcal/mol) and Energies of HOMO ε_{CNDO} (in eV) of the Basicity Center.

	PA_{CNDO}	ε_{CNDO}		PA_{CNDO}	ε_{CNDO}
1. O	173.3	20.35	14. CF_3CH_2OMe	284.7	15.18
2. OH	219.8	18.83	15. $MeOSiMe_3$	276.9	14.69
3. MeOH	262.4	15.13	16. $(CF_3)_2O$	217.8	18.80
4. EtOH	271.8	14.80	17. Me_3NO	353.7	11.01
5. LiOH	384.4	12.40	18. F_3NO	287.1	15.57
6. NaOH	409.4	10.54	19. H_2SO_4	244.2	15.95
7. FCH_2OH	242.1	15.35	20. CF_3SO_3H	307.8	15.35
8. CF_3CH_2OH	245.4	16.11	21. FSO_3H	301.4	15.84
9. CCl_3CH_2OH	252.9	16.48	22. $HClO_4$	234.9	18.08
10. FCH_2CH_2OH	259.6	14.96	23. O_2	182.8	20.35[b]
11. F_2CHCH_2OH	247.6	15.99	24. H_2CO	245.3	14.82
12. CF_3OH	228.1	18.33	25. MeCHO	302.6	13.70
13. Me_2O	265.1	14.44	26. CF_3CHO	255.4	15.09

27. Me_2CO	321.0	13.25	64. Cl_2CHCN	302.3	14.19
28. F_2CO	246.9	17.28	65. Cll_3CN	298.0	14.26
29. $(FCH_2)_2CO$	298.8	13.82	66. FCH_2CN	303.1	15.85
30. $(F_2HC)_2CO$	261.4	14.27	67. H_2NCN	298.5	14.10
31. FCH_2COMe	312.5	13.49	68. Me_2NCN	309.4	13.20
32. $HCONH_2$	309.0	13.31	69. MeSCN	304.4	14.40
33. CF_3CONH_2	260.1	16.82	70. H_2O	249.3	17.80
34. $(Me_2N)_2CO$	334.3	12.94	71. NH_3	300.8	16.14
35. HCOOH	297.3	14.88	72. OH^-	607.0	0.02
36. CF_3COOH	305.7	14.93	73. OF^-	577.2	1.02
37. FCH_2COOH	300.8	14.46	74. ClO^-	529.0	4.43[b]
38. HCOOMe	316.3	14.52	75. MeO^-	569.0	1.96
39. CF_3COOEt	296.9	14.20	76. CF_3O^-	516.8	4.93
40. $HCOOCH_2CF_3$	291.5	15.01	77. $HOCH_2O^-$	560.5	2.26
41. NCCOOEt	280.4	14.45	78. HSO_4^-	472.6	6.76
42. N	236.1	16.91	79. SO_4^{2-}	665.0	-1.86
43. NH	225.2	16.32	80. $CF_3SO_3^-$	457.7	7.07
44. NH_2	278.7	15.85	81. FSO_3^-	480.4	6.32
45. $MeNH_2$	308.7	14.26	82. NO_2^-	490.4	5.64[b]
46. CF_3NH_2	277.4	16.59	83. NO_3^-	450.2	6.50
47. $MeONH_2$	295.8	13.87	84. FCH_2O^-	548.1	2.64
48. $H_2N(CH_2)_4NH_2$	322.7	13.62	85. $CF_3CH_2O^-$	534.4	3.53
49. $CF_3CH_2NH_2$	306.9	14.59	86. $CCl_3CH_2O^-$	535.5	4.07
50. Me_3N	315.0	12.11	87. $(CF_3)_2CHO^-$	512.8	4.68
51. $Me_2N(CH_2)_2NMe_2$	344.5	12.14	88. $(CF_3)_3CCH_2O^-$	523.3	4.48
52. $Me_2N(CH_2)_4NMe_2$	330.4	12.27	89. $(CF_3)_2C(OH)O^-$	510.5	4.97
53. Me_2NCF_3	292.2	13.62	90. $(CF_3)_3CO^-$	501.0	5.19
54. NF_3	201.7	16.72	91. ClO_4^-	437.5	9.15[b]
55. $(CF_3)_3N$	238.8	17.52	92. $(CF_3)_2C\genfrac{}{}{0pt}{}{O^-}{O^-}$	678.2	-2.39
56. Me_2NCH_2CN	316.3	13.13	93. HOO^-	580.2	2.02[b]
57. N_2H_4	271.7	14.19	94. FCH_2COO^-	510.0	3.58
58. N_2	231.6	18.51	95. $(CF_3)_3CCOO^-$	471.1	5.26
59. CN	263.4	15.94	96. $(CF_3)_2CHCOO^-$	480.9	4.68
60. MeCN	305.2	15.85	97. $MeNH^-$	596.9	0.99
61. ClCN	290.2	14.98	98. CF_3NH^-	555.1	3.55
62. CF_3CN	273.0	17.35	99. $(CF_3)_2N^-$	492.0	5.90
63. $ClCH_2CN$	285.7	14.55	100. N^{3-}	1603.2	-40.91

101. $CF_3CH_2^-$	580.8	2.30	106. $-OCH_2O^-$	763.6	-6.55[b]
102. $(CF_3)_3C^-$	498.3	6.83	107. $HOOH_2^+$	38.5	26.43
103. CN^-	593.0	2.59	108. $HOCH_2OH_2^+$	115.2	22.09
104. $NCCH_2^-$	583.9	1.04[b]	109. $H_3\overset{+}{N}(CH_2)_4NH_2$	230.0	17.68
105. O_2^{2-}	925.7	-13.05	110. Pyridine	218.3	13.05

a - PA values are taken from Ref. 2, ε_{CNDO}- values are from this work

b - Arithmetic mean value from the energies of MO localized on the protonization center.

The formal general Eqn. (11) was found to describe the data for 110 compounds of various chemical nature, charge type and multiplicity over a very wide range (more than 1600 kcal/mol in a PA scale) of changing the quantities compared:

$$PA_{CNDO} = -0.99(0.01)\,\varepsilon_{CNDO} + 626(3) \qquad (11)$$

$r = 0.993$, $s = 20$ kcal/mol, $PA_{max} = 1600$ kcal/mol, $s\% = 1.3$

The data for 13 sulfur compounds does not fit Eqn. (11) and are better described by Eqn. (12) which differs from the previous one mostly by its intercept:

$$PA_{CNDO} = -1.04(0.04)\,\varepsilon_{CNDO} + 496(11) \qquad (12)$$

$r = 0.992$, $s = 20$ kcal/mol, $PA_{max} = 465$ kcal/mol, $s\% = 4.3$

The compounds (OF, FOH, F_2O, FSH, F_2S) containing the fluorine atom in the immediate vicinity of the protonization center were also found to display a certain devious behavior. Eqns. (11) and (12) happen to predict the nearly ideal picture of the dependence of PAs, on the corresponding IP values of the series of bases B. On the grounds of the thermodynamical cycle[10] those values are interconnected by the following relationship:

$$PA(B) = -IP(B) + HA(B^{+\cdot}) + IP(H^{\cdot}) \qquad (13)$$

where $HA(B^{+\cdot})$ is the hydrogen affinity and $IP(H^{\cdot}) = 13.598$ eV

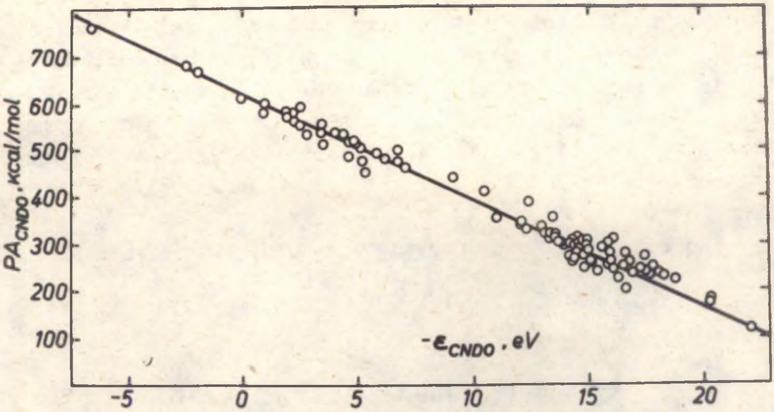


Fig. 7. Plot of the CNDO/2 calculated proton affinities on the energies of MO localized on the protonation centre.

One can see that the linearity between PA and IP could be observed either in the case of invariability of the hydrogen affinity values (slope - 1) or in the case of the existence of the additional linear relationship between IP and HA values (the slope should be different from -1)[10]. The analysis of the corresponding experimental data as well as PAs and IPs calculated on the ab initio level[4] shows that most probably the latter variant better corresponds to reality. It was evidenced[10] by the splitting of the "experimentally" found general formal near-to-ideal pseudo relationship* bet-

---

* One of the indirect reasons for the observance of such seemingly ideal relationships might be the lack of the unified and general scale of the basicity of compounds of various charge type and multiplicity determined from the direct equilibrium measurement of the PA. Up to now the different parts of equilibrium PA scales are interconnected by means of several reference PA values (NH_3, F^-, Cl^-, etc.) derived from thermochemical calculations using quantities (e.g. electron affinities) which are afterwords used in verifying the linearities of type (11) for compounds of different charge type.

tween **PAs** and **IPs** for compounds of various classes, charge type and multiplicity into several subfamily relationships with the average slope -0.65 ± 0.15. Actually the same behavior is characteristic also of the CNDO/2 calculated quantities of PA and $\mathcal{E}_{CNDO}$: within the separate classes of compounds Eqn.(11) splits into statistically distinguishable subfamily relationships with the slopes definitely different from (-1).

So Eqn. (14) holds for the alcohols, ethers, and DMSO:

$$PA_{CNDO} = -0.52(0.06)\,\mathcal{E}_{CNDO} + 446(20) \qquad (14)$$

r= 0.925, s= 9.9 kcal/mol, s%= 10.2, n= 16

Eqn. (15) describes the behavior of 11 amines.

$$PA_{CNDO} = -0.71(0.07)\,\mathcal{E}_{CNDO} + 537(26) \qquad (15)$$

r= 0.949, s= 9.5 kcal/mol, s%= 9.0, n= 11.

One can conclude that in general features CNDO/2 approximation describes adequately the experimentally observed relationships between proton affinities and ionization potentials.

References

1. J.A. Pople, D.L. Beveridge, Approximate Molecular Orbital Theory, Mc. Grow-Hill Book Co., 1970.
2. I.A. Koppel, U.H. Mölder, Organic Reactivity , 18, 42(1981).
3. I.A. Koppel, M.B. Comisarow, Organic Reactivity, 17, 498 (1980).
4. I.A. Koppel, U.H. Mölder, M.B. Comisarow, Organic Reactivity, 18, I9 (1981).
5. T. Koopmans, Physica, 1, 104(1933).
6. J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxle, F.H. Field, Ionization Potentials, Appearance Potentials and Heats of Formations of Gaseous Positive Ions, NSRDS-NBS, 26, U.S. Government Printing Office, Washington, D.C., 1969.

7. A.D. Baker and D.Betteridge, Photo-electron Spectroscopy, Chemical and Analytical Aspects, Pergamon Press, Oxford, 1972.

8. P. Baybutt, M.F. Guest, I.H. Hillier, Mol. Phys., 25, I025 (I973).

9. a) W.G. Richards, Int. J. Mass Sp. Ion Phys., 2, 419 (1969); b) D.C. Calabaro and D.L. Lichtenberger, Inorg.Chem., 19, 1732(1980); T. Minato and D.P. Chong, Chem. Phys. Lett., 72, 252(1980).

10. I.A. Koppel, U.H. Mölder, R.I. Pikver, Organic Reactivity, 17, 457(1980).

11. D.W. Turner, C. Baker, A.D. Baker, C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley-Interscience, London, 1970.

12. M.B. Robin, N.A. Kuebler, J. Electron Spectrosc. and Relat. Phenomena, 1, 13 (1972).

13. J.B. Peel, G.P. Willett, Austr. J. Chem., 28, 2357(1975).

14. J.Berkowitz, J.L. Dehmer, E.H. Appelman, Chem. Phys. Lett., 19, 334(1973).

15. D. Colbourne, D.C. Frost, C.A. Mc Dowell, N.P.C. Westwood, J. Chem. Phys., 68, 3574(1978).

16. This Work; experimental details and full spectra will be published.

17. R.S. Brown, Can. J. Chem., 53, 3439(1975).

18. S. Cradock, R.A. Whiteford, Farad. Trans. II, 68, 281 (1972).

19. M.J. Al-Joboury, D.W. Turner, J. Chem. Soc., 4434(1964).

20. C.R. Brundle, M.B. Robin, N.A. Kuebler, H. Basch, J. Am. Chem. Soc., 94, 1451(1972).

21. A.B. Cornford, D.C. Frost, F.G. Herring, C.A. Mc Dowell, J. Chem. Phys., 55, 2820(1971).

22. H. Bock, B. Solouki, Angew, Chem. 84, 436(1972).

23. H. Bock, M. Solouki, Chem. Ber., 107, 2299 (1974).

24. R.K. Thomas, Proc. R. Soc., A331, 249(1972).

25. D.A. Sweigart, D.W. Turner, J. Am. Chem. Soc., 94, 5592 (1972).

26. K. Kimura, S. Katsumata, T. Yamazaki, H. Wakabayashi, J. Electron Spectrosc. and Relat. Phenomena, 6, 41(1975).
27. W.C. Tam, D. Yee, C.E. Brion, J. Electron Spectrosc. and Relat. Phenomena, 4, 77(1974).
28. D. Chadwick, Can. J. Chem., 50, 737(1972).
29. J.W. Rabalais, L. Karlsson, L.O. Werme, J. Chem. Phys., 58, 3370(1973).
30. S. Katsumata, T. Iwai, K. Kimura, Bull. Chem. Soc. Jap., 46, 3391(1973).
31. V.I. Vovna and F.I. Vilesov, Optics and Spectr. (in Russian), 36, 436(1974).
32. D.R. Lloyd, N. Lynaugh, J. Chem. Soc. Faraday Trans. II, 68, 947(1972).
33. D. Colbourne, D.C. Frost, C.A. Mc Dowell, Chem. Phys. Lett., 72, 247(1980).
34. P.J. Bassett, D.R. Lloyd, J. Chem. Soc. Dalton Trans., 248(1972).
35. B.T. Wilkins, D. Phil. Thesis, Uni. of Sussex, 1973.
36. D. Colbourne, D.C. Frost, C.A. Mc Dowell, N.P.C. Westwood, J. Chem. Phys., 69, 1078(1978).
37. C. Baker, D.W. Turner, Proc. R. Soc., A308, 19(1968).
38. D.C. Frost, F.G. Herring, C.A. Mc Dowell, Chem. Phys. Lett., 4, 533(1970).
39. G. Bieri, Chem. Phys. Lett., 46, 107(1977).
40. E. Heilbronner, V. Hornung, K.A. Muszkat, Helv. Chim. Acta, 53, 347(1970).
41. R.F. Lake, H. Thompson, Proc. R. Soc., A317.187(1970).
42. H. Stafast, H. Bock, Z. Nafurfschg., B28, 746(1973).
43. H. Stafast, H. Bock, Chem. Ber., 107, 1882(1974).

Organic Reactivity
Vol.18,1(65),1981

Structure and Reactivity Correlations

I. On the Problem of Steric Effect

V. Galkin and R. Cherkasov
Dept. of Chemistry, Kazan State University,
Kazan

Received June 23, 1981

On the basis of the kinetic theory of active collisions the steric model has been suggested which allows to calculate steric substituent effects in terms of their structure and conformation. The scale of steric constants is suggested and compared with the steric scales available. The suggested model is shown to describe steric interactions with a high degree of accuracy and has proved to be effective when analyzing such questions as separation of steric and electronic effects, the isostericity principle, dependence of steric effect on substituent conformation, and other subjects connected with the problem of steric effect.

Correlation of organic structure and reactivity is one of the fundamental problems of modern chemistry. At present it has been accepted to subdivide the over-all interaction of substituent with the reaction center into inductive, resonance, and steric components, the latter in its essence should be the most related to the steric molecular structure. The attempts of quantitative isolation of steric effect from the over-all interaction are of long standing and are mainly connected with the works of Taft, Hancock, Palm, and Charton who introduced the corresponding scales of steric constants: E_S, E_S^c, E_S^o, and V.

The detailed characteristics of these scales are not necessary here as far as they were given, e.g., in Ref.1. It should be just noted that these scales are all obtained within the framework of the LFER principle and their application to the correlation analysis is often fruitful though has some restrictions. The latters involve both difficulty and unreliability of estimating namely the steric component with formal separation of various types of unhomogenous interactions[1] and also the restrictions imposed by standard reaction series used to derive constants. For example, in the E_s scale (and its derivatives E_s^e and E_s^o) the standard series (hydrolysis of esters) does not allow to determine steric constants of heteroatomic substituents of the type OR, SR, NR_2, etc. The isostericity principle used in such a case is effective only within narrow limits of similar substituents and does not compensate the above drawback.

Meanwhile, the experimental data collected up to the present indicate that the role of steric effect in the reactivity is much more significant than imagined earlier. Suffice it to note such examples as detection of considerable steric effect at the phosphorus atom[2], i.e. where it was absolutely neglected, or the latest opinion[3] that alkyl substituents possess at all no other effects than steric, not speaking already about dozens of works with purely qualitative reference to considerable steric interactions.

At the same time, in spite of clear understanding of steric effect and its, would seem, evident correlation with steric molecular structure, no satisfactory physical model of steric interactions (as noted by Palm[1]), has been proposed up to now, though many authors tried, and not unsuccessfully to elucidate, the nature of steric constants. The most strict approach to determining the energy component of steric interactions was in general form formulated by Becker[4]. However, due to hardly determinable parameters the use of his method in practice is much hindered at present. The work of Bohle[5] concerned with developing optimization programs on the basis of the Becker approach should be also noted. In this work at some assumptions satisfactory description of alkyl steric effects has been obtained. However, also this modification will hardly be a practical success in the nearest future. The most of other studies in this direction (see,e.g.Refs.6,12,14),among which the undoubtedly interesting topological model of Dubois and coworkers should be noted, is restricted by revealing formal regularities for narrow sets of similar, mainly alkyl, substituents. It should be admitted that the most simple and reasonable is at present the approach of Charton[7] who has reduced substituent steric effects to their Van der Waals radia. However, also this approach possesses the predictive power only for a limited number of monatomic substituents and spherical symmetry substituents of the type A_3B_1 for which more or less unambiguous determination of the r_v values is possible. Steric constants for other substituents have to be estimated from the reference reaction series[1].

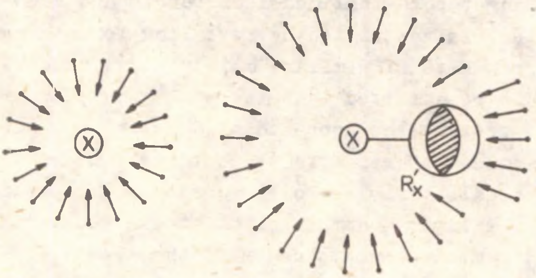
We have tried to design a simple steric model which allows to calculate the steric effect of any substituent at any reaction center in terms of its structure and conformation only.

Model of Frontal Steric Effect.

The suggested model is based on the concept about simple mechanical screening of a reaction center by a substituent, i.e. about the frontal nature of steric effect. Let us consider a tentative reaction center X which has no substituents and undergoes an attack of molecules of the second reagent (Fig. 1 a). It is natural that without substituents all radially attacking molecules reach the reaction center. According to the collision theory the reaction rate is proportional to the frequency of pairwise collisions:

$$k_o = Z e^{-E/RT} \qquad (1)$$

where Z is frequency of pairwise collisions and E is activation energy. Let us introduce substituent R_X to the reaction center (see Fig. 1b). Now not all of the attacking species reach the reaction center as some part of them are repelled by the substituent. This part is evidently proportional to the square occupied by the substituent R on the sphere isolating it from the reaction center.



(a) (b)

Fig.1. On the model of steric effect:
a) attack on the unsubstituted reaction center;
b) attack on the reaction center with a substituent.

Let r be a substituent radius and R a sphere radius i.e. the distance between the substituent and the reaction center. If for a time unit the reaction center is attacked by Z particles, statistically a square unit of the sphere accounts for $Z/4\pi R^2$ particles and the number of repelled particles Q, equals, respectively:

$$Q = \frac{Z}{4\pi R^2} \cdot \pi r^2 = Z \frac{r^2}{4R^2}$$

Then the number of particles reaching the reaction center is $Z-Q = (1-\frac{r^2}{4R^2})\, Z$ and the reaction rate constant equals

$$k_R = (1 - \frac{r^2}{4R^2}\; Ze^{-E/RT} \qquad (2)$$

In the polyatomic substituent each atom can be treated as an independent screening unit (i.e. as an independent substituent within the framework of this model) and then the rate constant is calculated from:

$$K_o = (1 - \sum\frac{r^2}{4R^2})\, Ze^{-E/RT} \qquad (3)$$

where r is the radius of each individual atom in the polyatomic substituents,and R is the distance between this atom and the reaction center.By the reasons given below it is expedient to choose atomic radii as r.

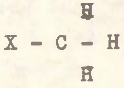
The parameter $(1 - \sum\frac{r^2}{4R^2})$ in Eq. (3) has the sense of the so called "steric" or "probability" factor P from the theory of active collisions, where the bimolecular reaction rate equals[8]:

$$k = PZe^{-E/RT} \qquad (4)$$

The theory of collisions itself gives neither distinct interpretation nor methods of calculation of the factor P, but just considers it as a measure of disagreement between experimental and theoretical rate constants, accounting this qualitatively for the fact that colliding molecules have a certain orientation [8,9]. In the light of the model discussed this orientation means that particles mutually approximate in such a way that the reaction center of a particle collides with the reaction center of another one, i.e. appears in the space free from screening by substituents.The factor P is actually the measure of probability within the framework of this model,as Eq.(3) can be obtained on the basis of the probability law. Since the probability of a radially attacking particle to reach the unsubstituted reaction center equals unity, it is easy to show that when introducing a substituent this probability is just $(1 - \sum\frac{r^2}{4R^2})$. When analyzing this parameter one can easily see that it will be less (and steric effect will be stronger) the more the substituent size (r) is and the nearer it is to the reaction center If $\sum\frac{r^2}{4R^2} = 1$ (conforms with the complete screening of the reaction center), $k_o = 0$, and the reaction does not take place at all. Thus, the obtained parameter $(1-\sum\frac{r^2}{4R^2})$ possessed a distinct physical sense and i is a space measure around the reaction center free from screening by substituents.

Let us consider the ratio of the reaction rate constants of substituted and unsubstituted compounds described accordingly, by Eqns.(3) and (1). For simplicity's sake, let us suppose that the substitution does not influence significantly the activation energy. Then $k_R/k_o=(1-\sum\frac{r^2}{4R^2})$, and the logarithm of this ratio is the measure of changes in activation free energy when introducing a substituent. But lg(k_r/k_o) in the reaction series with steric control equals (if a standard series) or is, at least, proportional to the steric constant, $E_S(E_S^o)$. Thus, provided that the suggested model is correct a good linearity should be observed in the coordinates of lg$(1-\sum\frac{r^2}{4R^2})$ - $E_s(E_s^o)$. We have calculated the $\sum\frac{r^2}{4R^2}$ values for a wide enough set of substituents in terms of a standard series (hydrolysis of esters R-C(O)OC$_2$H$_5$) where the carbon atom of the carbonyl group is the reaction center X. The calculation was carried out using atomic radii (r), standard bondlengths and bond angles. For the sake of simplicity and uniformity the bondlength can be estimated without a great error via the sum of covalent radia of the elements which form it. This is especially convenient with heteroatomic substituents where the precise values of bondlengths are not always known. There are some examples of calculating the $\sum\frac{r^2}{4R^2}$ values:

methyl group:

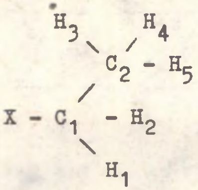


$$X-\overset{H}{\underset{H}{C}}-H$$

the distance of X-C=1.54 Å; the distance of X-H is calculated from the values of bond lengths C-C(1.54 Å) and C-H(1.07 Å) and bond angle 109° and is 2.0 Å. Atomic radia of carbon and hydrogen equal 0.77 and 0.46 Å [10], respectively, Hence,

$$\sum\frac{r^2}{4R^2} = \frac{0.77^2}{4\cdot 1.54^2} + 3\,\frac{0.46^2}{4\cdot 2.0^2} = 0.102$$

ethyl group:



$R_{X-C_1} = 1.54$ Å , $R_{X-C_2} = 2.5$ Å, $R_{X-H_{1,2}} = 2.0$ Å , $R_{X-H_{3-5}}$ averages 3.0 Å. $\sum \frac{r^2}{4R^2} = 0.130$

and so on.

In all the cases less gauche transoid conformations were chosen. The distance to the hydrogen atoms of the terminal methyl groups was averaged. The error in determining $\sum \frac{r^2}{4R^2}$ resulting from the taken assumptions is within ±0.003. The $\sum \frac{r^2}{4R^2}$ values calculated in such a way for different substituents are listed in Table 1. For these values to be more correct a contribution of invariable within the reaction series substituents (carbonyl oxygen and ethoxy group) should be added. The sum of their contributions equals 0.199.

Table 1

Steric Substituent Parameters at Carbon Atom

No	Substituent	$\sum \frac{r^2}{4R^2}$	$-E_s^a$	$-E_s^{o\,a}$	$-R_s$
1.	H	0.046	-1.24	-0.25	0.62
2.	CH_3	0.102	0	0	1.40
3.	C_2H_5	0.130	0.07	0.27	1.82
4.	C_3H_7	0.143	0.36	0.56	2.01
5.	C_4H_9	0.152	0.39	0.59	2.15
6.	C_5H_{11}	0.157	0.40	0.60	2.23
7.	$(CH_3)_2CH$	0.158	0.47	0.85	2.24
8.	$(CH_3)_2CHCH_2$	0.166	0.93	1.13	2.36
9.	$C_2H_5(CH_3)CHCH_2$	0.175	0.97	1.17	2.51

Table 1 continued

No	Substituent	$\sum \frac{r^2}{4R^2}$	$-E_s^a$	$-E_s^{o\,a}$	$-R_s$
10.	$C_2H_5(CH_3)CH$	0.178	1.13	1.53	2.55
11.	$(CH_3)_3C$	0.193	1.54	2.14	2.79
12.	$(CH_3)_3CCH_2$	0.189	1.74	1.94	2.73
13.	$(CH_3)_3CCH_2(CH_3)CH$	0.213	1.85	2.25	3.13
14.	$(C_2H_5)_2CH$	0.215	1,98	2.38	3.15
15.	$(C_3H_7)_2CH$	0.223	2.11	2.51	3.29
16.	$(CH_3)_3CCH_2(CH_3)_2C$	0.248	2.57	3.17	3.71
17.	$(CH_3)_3C(CH_3)CH$	0.269	3.33	3.73	4.08
18.	$(C_2H_5)_3C$	0.287	3.80	4.40	4.40
19.	$(CH_3)_3C(CH_3)_2C$	0.297	3.90	4.50	4.59
20.	CH_2Cl	0.123	0.24	0.57	1.71
21.	CH_2Br	0.133	0.27	0.60	1.86
22.	CH_2I	0.141	0.37	0.70	1.98
23.	$CHClCH_3$	0.151	0.86	1.19	2.13
24.	$CHBrCH_3$	0.161	1.00	1.33	2.28
25.	CH_2CH_2Cl	0.160	0.90	1.10	2.27
26.	CH_2CH_2Br	0.168	1.12	1.32	2.40
27.	CH_2CH_2I	0.178	1.00	1.20	2.55
28.	CH_2OH	0.119	0.07	0.40	1.65
29.	$CH(OH)CH_3$	0.147	0.31	0.64	2.07
30.	$CH(OH)C_2H_5$	0.160	0.69	1.02	2.27
31.	$CH(OH)C_3H_7$	0.169	0.68	1.01	2.41
32.	$C(OH)(CH_3)_2$	0.175	1.32	1.65	2.51
33.	C_6H_5	0.145	0.20	-0.25	2.04

34. F	0.051	-	-	0.68
35. Cl	0.079	-	-	1.07
36. Br	0.089	-	-	1.22
37. I	0.100	-	-	1.37
38. CH_2F	0.111	0.24	0.57	1.53
39. $CHCl_2$	0.143	1.54	2.20	2.01
40. CCl_3	0.163	2.06	3.05	2.32
41. CH_2CN	0.128	1.21	1.41	1.79
42. o-F-C_6H_4	0.152	-	-	2.13
43. o-Cl-C_6H_4	0.163	-	-	2.31
44. o-Br-C_6H_4	0.169	-	-	2.40
45. o-I-C_6H_4	0.177	-	-	2.52
46. o-CH_3-C_6H_4	0.171	-	-	2.43

---

[a] Steric constants E_S and E_S^o are taken from Refs. 1,11, and 12.

Thus, it is more correct to check the $E_S(E_S^o)$ scale with not $\lg(1 - \sum \frac{r^2}{4R^2})$ but $\lg(1 - \sum \frac{r^2}{4R^2} - 0.199) = \lg(0.801 - \sum \frac{r^2}{4R^2})$.

In the first place, we have checked the obtained values of $\lg(0.801 - \sum \frac{r^2}{4R^2})$ with the E_S and E_S^o scales for alkyl substituents which are not apt to strong electron interactions, in consequence of which their steric constants seem to be the most reliable. As one can see from Figs. 2 and 3, for hydrocarbon substituents over the whole range of the E_S and E_S^o scales a strict enough linearity with the calculated parameter $\lg(0.801) - \sum \frac{r^2}{4R^2})$ is observed. This is expressed in excellent correlation dependences:

$$\lg(0.801-\sum\frac{r^2}{4R^2})=(-0.1684\pm0.0020)+(0.0325\pm0.0011)E_s \quad (5)^{*}$$

$$n = 19,\ r = 0.9913,\ s = 0.0060$$

$$\lg(0.801-\sum\frac{r^2}{4R^2})=(-0.1649\pm0.0021)+(0.0287\pm0.0009)E_s^o \quad (6)^{**}$$

$$n = 18,\ r = 0.9920,\ s = 0.0052$$

The correlation with the Charton ν scale is also good:

$$\lg(0.801-\sum\frac{r^2}{4R^2})=(0.1331\pm0.0037)-(0.0674\pm0.0027\ \nu \quad (7)^{***}$$

$$n = 16,\ r = 0.9889,\ s = 0.0074$$

The high correlation coefficient in Eqns.(5)-(7) indicates that the descriptipn of the steric coefficient within the suggested model is correct enough and allows to elucidate the nature of steric constants to some extent. As to the E_S and E_S^o scales themselves the difference between them is reduced mainly, as noted by V. Palm[1], to the relative value of the steric constant for a hydrogen atom.Figs.2 and 3 also illustrate this. If in the correlation of $\lg(0.801-\sum\frac{r^2}{4R^2})-E_S$ the point for the hydrogen atom yields well to the general dependence,its E_S^o constant is evidently overestimated from the view of the above model.

When analysing Eqns. (5) and (6), it is noteworthy that the value of the δ (~ 0.03) parameter is relatively low. A simple enough explanation, however, can be given. First, for the sake of simplification of the model, the size of an attacking species is neglected,i.e.the proton is actually taken as an attacking species.Since within the reaction series the attacking species remains the same, such neglect of its

---

* Points 1-19 from Table 1 are included

** Points 2-19 from Table 1 are included

*** Points 1-14 from Table 1 are included size is evidently possible. However, it somewhat underestimates the value of the δ parameter, as a species of a greater (than proton) size will be, naturally, more sensitive to steric substituent effects. The second and more important consideration which underestimates the δ value is the above assumption that introduction of a substituent does not influence the reaction activation energy. Strictly speaking, this is not so. In the common case, it follows from Eqns. (1) and (3) that:

$$\lg(k_R/k_o) = \lg\left(1 - \sum\frac{r^2}{4R^2}\right) + \frac{1}{2.3RT}\Delta E \quad (8) \quad \text{where } \Delta E = E_o - E_R.$$

At the same time, it is known that within the reaction series, linear relationship between the activation energy, E, and lgPZ (isokinetic dependence in the theory of collisions) should be held. Thus, it follows with necessity that the Δ E parameter in Eqn. (8) should be related linearly to $\lg(1 - \sum\frac{r^2}{4R^2})$. Let us assume that $\Delta E = \lg(1-\sum\frac{r^2}{4R^2})$. Then:

$$\lg(k_R/k_o) = \left(\frac{\alpha}{2.3RT} + 1\right)\lg\left(1 - \sum\frac{r^2}{4R^2}\right) = A\lg\left(1 - \sum\frac{r^2}{4R^2}\right) \quad (9)$$

where A is a constant with arbitrary but constant value within the reaction series. Neglecting changes in the activation energy, this affects neither the accuracy of the given calculations, nor the correctness of the consequent conclusions, though the true value of the δ parameter in Eqns.(5) and (6) should be higher by factor A i.e. 0.03 A. If A is a value of the order of several dozens (which is quite possible), the δ value will be close to unity. Thus, the δ value in correlation eqns.(5) and (6) is just related to the choice of a scale and should not be given more important meaning to.

Critical Analysis of the Model.

Some assumptions used as the basis for the described model should be paid special attention to, as they may lead,

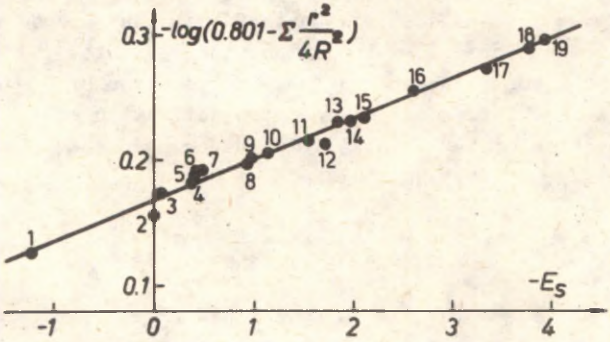


Fig. 2. Plot of the parameter lg(0.801- $\sum\frac{r^2}{4R^2}$) vs. steric constants E_S (point numbers are as listed in Table 1)

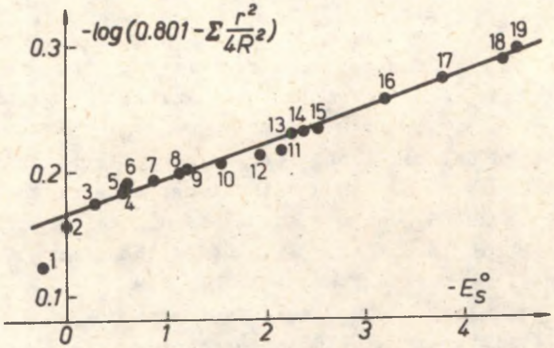


Fig. 3. Plot of the parameter lg(0.801- $\sum\frac{r^2}{4R^2}$) vs. steric constants E_S^o (point numbers are as listed in Table 1).

in principle, to some errors when estimating screening substituent effects. In the first place, this concerns the fact that in calculations atomic (but not van der Waals`) radii of substituent forming elements were used and the size and structure of the attacking reagent were not taken into account. The following should be noted in this connection.

The use of van der Waals radii within the framework of this model is impossible, as within the same composite substituent van der Waals radii of separate elements are markedly overlapped. This is in contradiction with the screening effect principle used in this model as leading to the overlapping of the screened areas represented by responding space angles is physically senseless. The above shortcoming is essentially eliminated by using atomic radii, as in this case the overlapping area does not exceed 5% of the total screening area which allows to apply the additive approach. Since atomic radii still reflect actual atom sizes (though ignore their heat vibrations to a considerable extent) and within the framework of this approach describe the space angle based for the second reagent accurately enough, we have found it to be expedient to use namely these values.

Not taking into account the size and structure of an attacking reagent is, undoubtedly, a shortcoming of this variant of the model, as in this case energy contributions of other types of steric interactions (up to the strain of valence angles) which can occur with the reaction center attack by bulky enough species are completely ignored. For this reason the suggested model is rather formal than physical. Despite the fact that the good quality of correlations (5)-(7) seems to justify the assumed assumptions, steric substituent effect cannot, undoubtedly, be reduced just to the screening of the reaction center. The latter should, evidently, be treated just as a component of steric effect which in virtue of some reasons (may be just formal) is related linearly to the over-all effect. Thus the actual physical sense of the regularities resulting from this approach should be considered cautiously.

Estimating Scale for Steric Constants, R_S

Since the suggested model permits the steric substituent effect to be estimated simply and reliably enough in terms of their structure and confirmation, it can also be used to estimate unknown steric constants, E_S, E_S^0, and V on the basis of correlation equations (5), (6), and (7). Besides, we consider it to be expedient to suggest together with the operating empirical scale a purely estimating scale also, based on this model only. Being free from experimental restrictions, such a scale would allow, (without making confusion into the operating scales) to compare from the same viewpoint steric effects of any substituent (including heteroatomic ones) which, in turn, enables to solve many problems unsolvable or hardly solvable within the framework of experimental operating scales.

This allows also to eliminate the errors caused by statistical scattering in correlations (5), (6), and (7) which will undoubtedly appear with converting parameter $\lg(0.801 - \sum \frac{r^2}{4R^2})$ into the corresponding constants E_S, E_S^0, and V.

Besides, for some electronegative substituents the results given by the model are not in accord with their E_S constants, which may be due to the presence of the electron component in the latter . Also for this reason, it seems to be more expedient to consider and check the substituent steric effect resulting from the suggested screening model within the framework of the estimating scale constructed on the basis of this model.

Finally, the estimating scale compensates possible systematic errors in determining screening effects to a maximum extent.

Since in this model energy measure of steric effect is, as shown above, parameter $A\lg(1 - \sum \frac{r^2}{4R^2})$, it should be, evidently, taken as the basis of such a scale, which may be denoted via, say, R_S (substituent R steric effects).

Constant A should be chosen in such a way that the obtained scale would be convenient to work with. In this sense it is expedient to standardize it (at least approximately) to the scales E_S and E_S^o, i.e. to take A as equal, e.g. 30 Then

$$R_S = 30\ \lg(1 - \sum\frac{r^2}{4R^2}) \qquad (10)$$

The last column of Table 1 lists constants R_S for different substituents at the carbon atom calculated by Eq. (10).

The R_S scale constructed on the basis of the maximum simplified formal model cannot, undoubtedly, be of little importance for the operating empirical scales whose high reliability is proved by perennial experimental practice. Its function should be, evidently, restricted to the special problems which cannot be solved for the present within the framework of the operating scales. Statistically for alkyl substituents, this scale will hardly describe the steric effect better than the experimental scales.Moreover,for the series with varied lowest alkyls only, the correlations with R_S will be obviously worse than with E_S or E_S^o. This conclusion can be drawn from Figs. 2 and 3 where for lowest alkyls the greatest point scattering is observed. This may be caused by the above simplifications taken as a basis of the model.

However, despite these shortcomings the R_S scale has also some advantages. In its sense it describes the steric effect only and does not include contributions of other interactions. Constant R_S can be successfully determined both for alkyl and heteroatomic substituents of the OR, SR, NR_2 type and for other ones whose steric effects have not yet been estimated by the empirical scales.The determination of constant R_S requires no special experimental technique.It can be easily estimated for any substituent. This permits the analysis of steric interactions to be correct enough in those cases when steric substituent effects are not estimated reliably by the basic empirical scales.

The fact that this scale is based on the concrete model allows to operate with constants R_S themselves more correctly. Thus, e.g., the steric effect of two substituents equals not $\sum R_S$, but $30\lg\left[1-\left(\sum \frac{r^2}{4R^2}\right)_1 - \left(\sum \frac{r^2}{4R^2}\right)_2\right]$, i.e. addition of effects should be carried out under the logarithm sign. It is evident that for two equal substituents:

$$\sum R_S = 2R_S = 60\lg\left(1 - \sum \frac{r^2}{4R^2}\right) \neq 30\lg\left(1 - 2\sum \frac{r^2}{4R^2}\right) \quad (11)$$

The linearity between $2R_S$ and parameter $30\lg(1-2\sum\frac{r^2}{4R^2})$ is, in principle, good, however, the points corresponding to bulky substituents deviate markedly. With a greater number of substituents the deviation is more significant.

The over-all effect of two or several substituents is not always, as known, a pure sum of the effects of each of them. In the correlation analysis this was taken into account in the form of the so called cross term. In the light of this model the nature of such a cross term (at any rate for steric effects) can be interpreted in some cases as a compensation of inequality (11).

It follows also from the suggested model that in analysing the steric effect the contribution of not only varied but also all other substituents at the reaction center should be taken into account as it was done, in particular, in correlations (5)-(7). However, the attentive study of this problem shows that in most cases for the sake of simplicity and convenience the contribution of constant substituents may be neglected without a great error, which is usually done in the correlation analysis. A good correlation between constants E_S and R_S, in particular, speaks in favour of this, though they describe the screening effect of one variable substituent only:

$$R_S = (-1.710 \pm 0.048) + (0.733 \pm 0.025)E_S \quad (12)^*$$

$$n = 19,\ r = 0.9903,\ S = 0.144$$

---

[*] Points NN 1-19 from Table 1 were included

Using the R_S scale one can, as noted above, determine and check steric effects of any substituents (including heteroatomic), which allows to analyse some interesting problems concerned with the problem of steric effect. One of such problems is the isostericity principle widely used in practice.

The Isostericity Principle

This principle occupies a special place in estimating steric constants of non-hydrocarbon substituents and lies in,as known,that the steric effect on any heteroatomic substituent is set equal to the corresponding (isosteric) substituent effects which is obtained from the initial one with replacing all hetero atoms by carbon atoms each of which is bound to a certain number of hydrogen atoms to obtain eventually a saturated alkyl[1].

Since the considered model permits the direct estimation of the steric effect of any heteroatomic substituent,it was of interest to verify to what extent the above principle is observed within the framework of this model. With this purpose we have calculated the constants R_S of a series of alcoxy and thioalkyl substituents (Table 2) and checked them with those for isosteric hydrocarbon analogues.

Table 2.

Steric Constants, R_S, of Alkoxy and Thioalkyl Substituents at Carbon Atom

NN	Substituent	$\sum \frac{r^2}{4R^2}$	$-R_S$
1.	OH	0.064	0.86
2.	CH_3O	0.113	1.56
3.	C_2H_5O	0.126	1.76
4.	C_3H_7O	0.136	1.91
5.	C_4H_9O	0.141	1.98
6.	$(CH_3)_2CHO$	0.153	2.16
7.	$C_2H_5(CH_3)CHO$	0.162	2.30
8.	$(CH_3)_3CO$	0.180	2.59

Table 2

NN	Substituent	$\sum \frac{r^2}{4R^2}$	$-R_S$
9.	SH	0.132	1.84
10.	CH_3S	0.158	2.24
11.	C_2H_5S	0.169	2.41
12.	C_3H_7S	0.177	2.54
13.	C_4H_9S	0.182	2.62
14.	$(CH_3)_2CHS$	0.192	2.78
15.	$C_2H_5(CH_3)CHS$	0.199	2.89
16.	$(CH_3)_3CS$	0.215	3.15

In the calculations the C-O-C angle was taken as equal 110° and C-S-C as equal 100°, respectively. As in the case of alkyl substituents the less screened transoid confirmations were calculated.

Excellent linear relationships have proved to work in each series:

$$R_S(OR)=(0.812\pm0.115) + (1.256\pm0.053)R_S(CH_2R) \qquad (13)$$
$$n = 8,\ r = 0.995,\ S = 0.058$$

$$R_S(SR)=(-0.459\pm0.039)+(0.976\pm0.018)R_S(CH_2R) \qquad (14)$$
$$n = 8,\ r = 0.999,\ S = 0.019$$

Combining equations (13) and (14) with (12) one can obtain the corresponding expressions in the E_S scale:

$$E_S(OR) = 0.376 + 1.256\ E_S\ (CH_2R) \qquad (15)$$

$$E_S(SR) = -0.418 + 0.976\ E_S\ (CH_2R) \qquad (16)$$

As follows from correlations equations (13)-(16), substituent OR and SR steric constants are related linearly to the CH_2R group constants but not equalled to them. Thus, it is evident that the isostericity principle should work well in the series of substituents of the same type (e.g., OR or SR only), but is not effective in mixed series.

The analysis of angular coefficients in regressions (13-(16) indicates that the substituent OR steric effect is more intensive and that of SR less intensive than the corresponding influence of the CH_2R group. An analogous conclusion was drawn elsewhere[13].

Thus, within the framework of the present model the isostericity principle is mathematically substantiated and at the same time its restrictions are clearly seen. On the other hand, since direct estimation of the R_S constant for any heteroatomic substituent is possible, the isostericity principle loses its importance in this scale altogether.

Steric Effect and Substituent Conformation

It is evident that within the framework of the discussed model there is a direct and strong connection between the steric substituent effect and the substituent conformation. In particular, in the expression $\sum \frac{r^2}{4R^2}$ parameter R corresponding to the distance from each substituent forming atom to the center is sensitive to the conformation. On one hand, this speaks in favor of the suggested model, since the steric effect actually depends on the conformation[14]. On the other hand, such sensitivity to the conformation seems to be, at first glance, an undesirable factor, as not each substituent has the exactly known conformation. However, one can easily see that in real series the number of such substituents is not great. In the series of hydrocarbon substituents e.g., the problem of undetermined conformation appears mainly with normal propyl, butyl, and anyl. For the rest of others it is either absent at all or the realization of a certain conformation among several possible is evident. But in such a case, leaning against this majority of substituents, one can turn to the opposite procedure, i.e. determine which conformation is realized with those substituents where the extent of conformational uncertainty is high.

For this purpose it will do to calculate the steric effect (R_S) for each possible conformation (as a rule, their number does not exceed two) and to compare the obtained values with the experimental parameter (lg k) to choose that one whose accordance with the total series is the best. Table 3 lists an example of such conformational analysis for substituents CH_2OCH_3 and CH_2SCH_3. We have calculated the R_S constants for two possible types of orientation of these substituents (transoid conformation and that with free rotation around the C - E bond) and compared them with the R_S values calculated by correlation equation (12) from the experimental E_S values (Table 3).

Table 3.

Theoretical and Experimental* R_S Values for Metoxymethyl and Methylthiomethyl Substituents

N	Substituent	$-R_S$ theor.		$-E_S$	$-R_S$ exp. (±0.14)
		trans. orient.	free rotation		
1.	CH_2OCH_3	1.77	1.96	0.19	1.85
2.	CH_2SCH_3	2.11	2.46	0.34	1.96

* Experimental values of R_S are calculated from Eq. (12)

From Table 3 one can see that the methylthiomethyl substituent has well-defined transoid orientation. In the case of the metoxymethyl substituent the difference in the $R_{S\ theor.}$ values is not so great and does not permit a reliable choice between them. In this case, one can evidently speak about the realization of the non-cisoid form only.

The same analysis can be carried out also for those alkyl substituents for which the postulated transoid conformation is not evident. As has been noted above, these are in the first place, normal alkyls beginning with the propyl group. Figs. 2 and 3 illustrate that even suggesting the less in steric effect transoid conformation, the points corresponding to these substituents deviate somewhat to the side of the effects overestimated by the scale R_S. For other conformations this deviation should be even more significant. From this point of view the choice of transoid conformations is quite justified.

Thus the above analysis shows that the conformational sensitivity of the suggested model is not a shortcoming but, on the contrary, makes it more elastic and useful in practice.

Other Aspects of the Use of the Steric Model.

Since the present model permits the estimation of purely steric interactions, it can be used to isolate these interactions from the over-all effect which allows to carry out more correct analysis of electronic and steric factors. Thus, e.g., the majority of monohalide - oxy, -alkthio, and alkoxyalkyl substituents are satisfactorily described in the coordinates of R_S - E_S by the same dependence as for alkyls:

$$R_S = (-1.702 \pm 0.032) + (0.730 \pm 0.022) E_S \qquad (17)^*$$

$$n = 35, \; r = 0.9854, \; S = 0.141$$

This indicates the absence of any significant contribution of electronic effect to their E_S constants.

At the same time, the substituents containing more than one halide atom or other strongly negative groups (such as $CHCl_2$, $CHBr_2$, CCl_3, CH_2CN, CH_2NO_2, etc.) deviate markedly from correlation eqns. (5), (6), (12), and (17) to the side of greater effect (by the E_S (E_S^0) scale). The E_S(E_S^0) constants of these substituents contain, evidently, a considerable contribution of electronic component which can be interpreted either as polar interaction with the reaction center (+M or α-effect) or as repulsing electrostatic interaction with the identically charged attacking nucleophile. Palm[1] also notes the significant contribution of electronic effects for such substituents.

---

[*] Points NN 1-33 from Table 1 and NN 1,2 from Table 3 are included

It should be also noted that the suggested model has proved to be rather effective when analysing such problems as steric substituent effects at other (non-carbon) atoms, prediction of reactivity and other problems concerned with that of steric effect.

Thus, the described model being ultimately simplified as any other model preserves, nevertheless, correct description of steric interactions elucidating to some extent also their nature. Leaning against the real and reasonable mathematical apparatus, it permits the estimation of steric effect of any substituent at any reaction center on the basis of its structure and conformation only and may be helpful for elucidating and predicting the interaction between organic structure and reactivity.

Acknowledgement.

Our thanks are due to V. Palm and B. Istomin for valuable advice.

References.

1. V. Palm, "Fundamentals of Quantitative Theory of Organic Reactions", L. "Khimiya", 1977
2. B. Istomin, V. Baransky, A. Lobanov, and E. Grechkin, Organic Reactivity, 12, 69 (1975)
3. Ritchic C.D. and Sager W.F. in "Progres in Physical Organic Chemistry" (Rus. transl), M, "Mir", 1967
   B. Istomin and V. Palm , Reakts. sposobn. organ.soedin., 9, 423 (1972)
   DeTar D.F., J. Am. Chem. Soc., 102.7988 (1980).
4. Becker F., Z. Naturforsch., 14a. 547 (1959); 15b 251 (1960); 16b, 236 (1961).
5. Bohle M., Z. Chem., 17, 229 (1977).
6. I. Koppel, Reakts. sposobn. organ. soedin., 2, 26 (1965)
   Panaye A., MacPhee J.A., and Dubois J.E., Tetrah., 36, 759 (1980);
   DeTar D.F., and Tenpas C.J., J. Am. Chem. Soc., 98, 4567, 7903 (1976):

7. Charton M., J. Am. Chem. Soc., 97, 1552 (1975).
8. E. Eremin, "Fundamentals of Chemical Kinetics", M., "Vysshaya shkola", 1976.
9. H.E. Avery "Basic reaction kinetics and mechanisms", (Rus.transl.), M, "Mir" 1978.
10. V. Rabinovich andZ. Khanin, Brief Handbook of Chemistry, L. "Khimiya", 1978
11. Taft, R.W., in: "Steric effects in Organic Chemistry" (Rus. transl), M, IL, 1960
12. MacPhee J.A., Panaye A. and Dubois J.E., Tetrah., 34, 3553 (1978).
13. B. Istomin, B. Finkelstein, and G. Eliseyeva, Organic Reactivity, 16, 450 (1979)
14. Dubois J.E., MacPhee J.A., and Panaye A., Tetrah., 36, 919 (1980).

Organic Reactivity
Vol.18,1(65),1981

ALKYL AND ALKENYL ESTERS OF SULFOACIDS
26. ULTRAVIOLET SPECTRA AND INTEGRAL INTENSITIES OF SULFOGROUP VALENT FREQUENCIES BONDS. IN SULFOESTERS

Sendega R.V., Gorbatenko N.G., and Visgert R.V.
Polytechnical institute, Odessa

Received July 30, 1981

The UV-spectra of propargylbenzenesulfoesters of the summaric formula $XC_6H_4SO_2OCH_2C{\equiv}CH$ (X=H,3-Cl, 4-Me,4-Cl,4-Br,4-OMe,3-NO_2,4-NO_2,4-NH_2,4-NMe_2) have been investigated. Para-substituents lead to a batochromic displacement of K-bands, the degree of change is in accordance with the donor ability of group X. There exist two bands in propargylbenzenesulfoesters spectra: an intensive short-wave K-band ($A_{1g}\rightarrow B_{1u}$ transition) and a weaker long-wave B-band ($A_{1g}\rightarrow B_{2u}$ transition). The role of sulfur atom vacant d-orbitals for the studied propargylbenzenesulfonates is very significant in conjugation with benzene ring π-electrons. The IR-absorbance spectra are measured for the substituted benzene-and benzylsulfoacid esters in the region of the symmetric and asymmetric valent frequencies of the sulfogroup. Dependence is studied between the displacement and form of bands and the influence of substituents in sulfoacids, the aggregate condition, temperature and polarity of solvents. The integral intensities of symmetric and asymmetric valent frequencies of the sulfogroup are measured. One may suppose that their splitting is caused by the Fermi resonance.

Much valuable information about the distribution of electron density in sulfogroup containing compounds may be obtained from UV- and IR-spectroscopy data. The study of sulfocompounds UV-spectra is of great interest for the investigation of the SO_2R group microstructure (R=Cl, Br, F, Alk, OAlk, NH_2, $NHNH_2$, CF_3 etc.). Both the structure of the sulfogroup itself and the mechanism of the SO_2R group interaction with an aromatic ring are at present sub iudice. There exist three points of view on the mechanism of interaction of the SO_2R group with a cochromofore. The authors of Ref.[1,2] hold that the influence of the SO_2R group on a cochromofore is limited to the inductive effect. It is established for benzenesulfochlorides[3-5], sulfones,[6] and benzenesulfoamides[7] that the above cited interaction is realized by sharing the vacant 3-d-orbitals of sulfur atoms. The authors of Ref.[8,9] suppose a combinative interaction between the SO_2 group and connected atoms R in $C_6H_5SO_2R$ by means of both the inductive effect and the conjugation.

The literature also does not give an uniform opinion on the nature of splitting of bands in the region of symmetric (ν_s) and antisymmetric (ν_{as}) valent sulfogroup oscillations[10-18]. Thus the splitting of both ν_s and ν_{as} bands may be observed in IR spectra of alkanesulfohalides[10-12], arylsulfohalides[13-15], and sulfones[16-18]. The interpretation of the obtained spectra is contradictory and is often caused by the conditions of IR-spectra study. The authors of Ref.[10] observed two bands in the ν_s region of liquid alkanesulfohalogenides IR-spectra. However in a gazeous phase they discovered in the same region a unity band only which was attributed to symmetric oscillations of the sulfogroup. The authors of Ref.[14] report that one of the doublet bands is benzoic but do not define more exactly which of them. Other authors[16,17] suppose on the basis of IR-spectra study of sulfones that the splittering of ν_{as} bands is caused by superposition of bands of flat deformation vibrations of CH-groups[16] or by interaction with C-S-C vibrations[17]. The authors of Ref.[18] assume that both bands of the doublet correspond to sulfogroup vibrations. Recently the papers Ref.[19-22] were published in which the doublet structure of ν_s and ν_{as} bands was explained by the Fermi type resonance interaction of two vibrations of near frequence and identical symmetry. Apparently this problem is complex enough. One may conclude from the literature that the doublet structure of bands may be expected either for ν_s or ν_{as} or for both bands depending on the substituents X and Y in the XSO_2Y compounds, on the conditions of the experiment and on the aggregate state.

In the present paper we give the results of the study of UV-spectra of propargylic esters of substituted benzene sulfonic acids $X\text{-}C_6H_4\text{-}SO_2OCH_2\text{-}C\equiv CH$; X=H, p-OMe, 4-Me, 4-Cl, 4-Br, 3-Cl, 3-NO_2, 4-NO_2, 4-NH_2, 4-NMe_2. Our purpose was to estimate these substituents and the $SO_2\text{-}O\text{-}CH_2\text{-}C{=}CH$ fragment influence on the electron accepting properties of the sulfogroup and to compare this influence with the previously studied one in other sulfocompounds of total structure $X\text{-}C_6H_4\text{-}SO_2Y$. We have studied the nature of the ν_s and ν_{as} bands splittering for propyl esters of benzene- and benzylsulfoacides too. These compounds were chosen for the investigation as for propyl-p-tolyl sulfoester both ν_s and ν_{as} splittering may be observed and for propyl-4-methylbenzylsulfoester the splittering exists only for ν_{as}.

EXPERIMENTAL

The studied esters were obtained according to Ref.[23,24] The purity was established chromatographically on the level of 99, 8-99.9%.

The UV-spectra of substituted propargyl esters of benzenesulfoacid were taken on the SF-16 spectrophotometer in dioxane solutions of 10^{-3}-10^{-5} mole/1 concentration. The molecular extinction coefficient is equal to ε = DxMW/10xC; D=optical density, C=concentration mole/1, MW=molecular weight, and 10 - the thickness of layer in mm.

The IR-spectra were obtained in CCl_4 solutions onIKS-14a spectrophotometer with a NaCl prism with thickness of layer 0.104mm. The solvents were purified by well known methods. As symmetrical and antisymmetrical valent vibration bands of the sulfogroup overlap we undertook their graphical subdivision. The area under the curve was calculated at an interval equal to 2-4 halfwidths of bands. We obtained for each substance in the same solvent not less than 4-5 curves. The values of band halfwidths given in Tables mean. The integral intensities of bands were calculated on a Minsk-22 computer according to the Yohansen method[25].

RESULTS AND DISCUSSION

Electronic spectra of substituted propargylbenzenesulfonates contain two bands of unequal intensity - one intensive K-band at shorter waves and the other B-band of less intensity at longer waves. In accordance with Ref.[6] one may consider the K-band as the displaced K-band of benzene (λ_{max}203.5nm, ε_{max}7400) $A_{Ig} \rightarrow B_{In}$ transition, and the less intensive long wave B-band as the displaced B-band of benzene $A_{Ig} \rightarrow B_{2u}$ transition (λ_{max}254nm, ε_{max}230)..

The p-substituents X in propargyl ester if benzenesulfoacid give a batochromic displacement of K-band symbatic to the increase of their $_+$M-effect. The growth of band intensity is observed in the same order excluding Cl - and Br- substituents. An analogic influence of Cl and Br atoms may be observed for UV-spectra of benzenesulfochlorides or sulfobromides[5,26] but it did not take place for $X\text{-}C_6H_4SO_2R$ compounds with R=F[27], CH_3[28], NH_2[7], $NHNH_2$[9], CF_3[6]. The B-band of low intensity is either overlapped in general or depends on the character of X-substituent in compounds $X\text{-}C_6H_4SO_2R$ very insignificantly[6,7,9,26-28]. K-bands batochromic displacement for propargyl ester of benzenesulfoacid increases symbatically with the increase of the $_+$M-effect of substituents X. There exists a linear dependence between these displacements values $\Delta\lambda$ and the σ_c^+ constants of substituents (Fig.1) as these constants which in accordance with V.A. Palm[29] characterizes the ability of substituents for immediate polar conjugation. This linear dependence points

Table I

UV SPECTRA OF PROPARGYL ESTERS OF BENZENESULFOACIDS $XC_6H_4SO_2OCH_2C{\equiv}CH$

N°	X	K-band		B-band	
		λ_{max} nm	$\varepsilon_{max}\cdot IO^5$	λ_{max} nm	$\varepsilon_{max}\cdot IO^4$
I	H	220	2.48	265	I.96
2	3-Cl	22I	3.IO	overlapped	
3	4-Me	227	3.34	262	I.I8
4	4-Cl	229	5.07	overlapped	
5	4-Br	234	4.88	overlapped	
6	4-OMe	240	3.69	overlapped	
7	$3\text{-}NO_2$	248	3.52	overlapped	
8	$4\text{-}NO_2$	250	6.89	overlapped	
9	$4\text{-}NH_2$	268	7.23	overlapped	
IO	$4\text{-}NMe_2$	282	7.85	overlapped	

Table 2

INTERATOMIC DISTANCES, VALENT ANGLES, POWER CONSTANTS AND ORDER OF BONDS OF SO_2 GROUP IN $R_I\text{-}SO_2\text{-}R_2$ COMPOUNDS

R_I	R_2	r_{SO}, A°	OSO°	$k_{SO}\cdot IO^5$ dyn/cm	n_{SO}
C_6H_5	C_3H_7O	I.42	II8	IO.39	I.85
C_2H_5	C_3H_7O	I.43	II7	IO.I8	I.83
$C_6H_5CH_2$	C_3H_7O	I.43	II7	IO.2I	I.83
C_3H_7	C_3H_7	I.45	II5	9.28	I.73
C_6H_5	Cl	I.42	II9	IO.50	I.87
CH_3	F	I.42	II9	IO.66	I.88
C_6H_5	NH_2	I.44	II7	9.78	I.78
CH_3	NHC_6H_5	I.44	II7	9.86	I.79
CH_3	CH_3	I.44	II6	9.72	I.78
C_6H_5	C_6H_5	I.44	II6	9.72	I.78

but the existence of an appreciable-M-effect of the sulfopropargylic group $SO_2-O-CH_2-C{\equiv}CH$. The influence of the substituent X character in $XC_6H_4-SO_2-OCH_2C{\equiv}CH$ on the displacement of the K-band may be presented by the equation (1):

$$\lambda_{max}=220 + (0.793 \pm 0.088)\sigma_c^+ \quad ; r=0.987$$

On the other hand the correlation of λ_{max} of propargyl esters of benzenesulfoacids with λ_{max} of benzenesulfochlorids[27] and benzenesulfohydrazids[9] may be expressed by following linear dependencies (2) and (3);

$$\lambda_{max}=210 + (1.278 \pm 0.156)\Delta\lambda \quad ; r=0.953 \qquad (2)$$

$$\lambda_{max}=213 + (1.012 \pm 0.239)\Delta\lambda \quad ; r=0.960 \qquad (3)$$

Analogous dependencies are established for the other sulfogroup containing compounds too which indicate similarity of structure of their cochromoforic systems[9,30]. The nearer the correlation coefficient to unity the more similar is the influence of X and Y substituents in the compounds

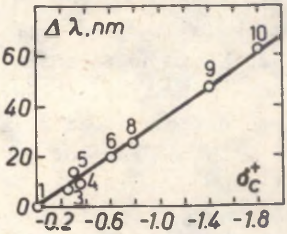


Fig. 1. Correlation of maximum displacement $\Delta\lambda$ with σ_c^+ of substituents for propargylesters of benzenesulfoacid. N°N° of points correspond to Table 1.

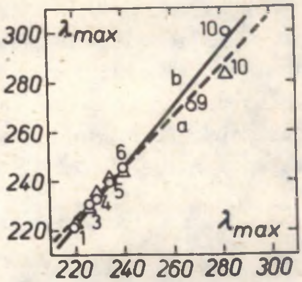


Fig. 2. Correlation between λ_{max} of compounds $XC_6H_4SO_2R$:

a) $-CH{\equiv}C-CH_2-O-NHNH_2$

b) $-CH{\equiv}C-CH_2-O-F$

N°N° of points correspond to Table 1.

X-SO_2-Y on the displacement of benzenic absorbance. In addition we may observe that the K-band of benzenic absorbance virtually does not depend on the character of the SO_2R group when R=F, Br, CF_3, $OCH_2C{\equiv}CH$, $NHNH_2$. The values λ_{max} of the K-band equal correspondingly to 220, 222, 220; 220, and 222nm in spite of the opposite directions of polarisation effects in bonds $S \rightarrow Br$, $S \rightarrow F$, $S \rightarrow CF_3$ and $S \leftarrow OCH_2C{\equiv}CH$ and $S \leftarrow NHNH_2$.

From the results obtained we can conclude that the interaction between the SO_2R group and the benzene nucleus is the consequence of the involvement of the sulfur atoms vacant d-orbitals rather than the S-O bond. If this is the case the oxygen atom is not involved in the chromofore system. In structures $X\text{-}C_6H_4SO_2R^{31}$ the sulfur atom is the+ last one belonging to the respective conjugated system playng the role of a "buffer" - electron acceptor, and as a result the p-π-conjugation of X and R substituents is only negligible for the S=O, S-Hal, S-N, S-O,S-C bonds polarity.One may conclude from the identity of UV-spectra of the cited compounds that the sulfogroup possesses a significant autonomy and that no important interaction between S=O bonds and π -electron system of the benzene ring exists. The absence of considerable intramolecular interaction of S=O bonds with the rest of the molecule may be supported by the results of calculations of structure of sulfurcontaining compounds (Table 2) followed according to empirical formulas given in Ref[12]. One may see from Table 2 that the lengths of S=O bonds differ only negligibly ca. 1.42-1.45 A^{o} and the O-S-O angle is constant enough and oscillates in the range 110-115°. The discrepancies in SO group power constants and order of bonds are small too.

2. Position, form and integral intensity of sulfogroup valent oscillations ν_s and ν_{as}

The dependence between the position of ν_s and ν_{as} frequencies and the nature of substituents is given in

Table 3. As one may see from these two bands of absorbance are in the spectrum of propyl ester of p-toluenesulfonic acid both in the ν_s and ν_{as} regions. However the ν_s absorbance manifests itself as a distinctly expressed doublet and the ν_{as} is presented in the form of two bands; One of them manifests itself as a less intensive shoulder on the high-frequency part of the main one. The presence of the NO_2 group in the benzene ring leads to the manifestation of ν_s in the form of a single band and the high-frequency band ν_{as} displaces on $13 cm^{-1}$ with the simultaneous redistribution of absorbance bands intensities and the increase of frequencies interval between the absorbance maximum from $23 cm^{-1}$ for propyl-p-tolylsulfonate to $36 cm^{-1}$ for propyl-p-nitrobenzenesulfonate (Fig.3c). Propyl-p-methylbenzylsulfonate is characterized in the ν_s region by a single band and in the ν_{as} region by two bands (Fig. 3b). The introduction of a nitrogroup in the benzene ring changes the position of bands only negligibly but one may observe the redistribution of band intensities in the ν_{as} region (Fig. 3d).

Table 3

INFLUENCE OF SUBSTITUENTS ON THE FORM AND POSITION OF ν_s AND ν_{as} FREQUENCIES FOR PROPYL ESTERS OF SULFOACIDS $X-SO_2-OCH_2CH_2CH_3$

X	ν_{SO_2} cm^{-I}	
	ν_s	ν_{as}
$p-MeC_6H_4$	II84 II94	I353 s I376
$p-NO_2C_6H_4$	II92	I353 I389
$p-MeC_6H_4CH_2$	II84	I360 s I374
$p-NO_2C_6H_4CH_2$	II82	I362 I377 s

The investigation of the substituents influence on ν_s and ν_{as} bands shows that the character of substituent influences considerably the form, position and intensity of absorbance bands. In order to investigate the character of doublet structure of ν_s and ν_{as} bands we have studied the influence of the aggregate condition, the esters concentration, the nature of solvent and temperature.

We established that the variation of esters concentration for more the 100 times does not influence the absorbance bands position, interval of frequencies and redistribution of intensities of doublet components in the ν_s and ν_{as} region. The only negligible dependence of doublet components intensities from concentration and temperatures testifies that the presence of doublets in the ν_s and ν_{as} region is not connected with the existence of complexes or rotatory isomers. A characteristic phenomenon for doublets is the conservation of the summary integral intensity when intensities redistribute between the doublet components. Thus in the spectra of propyl p-toluenesulfonate and propyl-p-methylbenzylsulfonate the characteristic indications of Fermi-like resonance interaction are established in the regions 1160-1200 and 1340-1380 cm^{-1}.

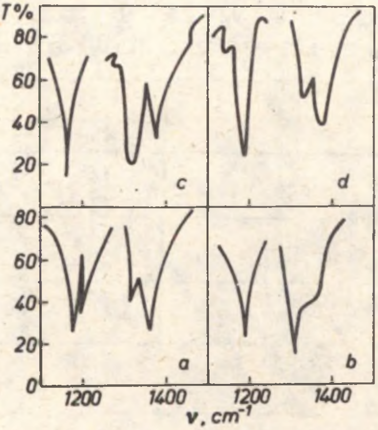


Fig. 3. IR-spectra of $XC_6H_4SO_2OR$ (a,c) and $XC_6H_4CH_2SO_2OR$ (b,d). X=p-Me(a,b) and p-NO_2(c,d); R = $CH_2CH_2CH_3$

The investigation of the influence of the character and polarity of solvents on the doublet structure of bands supports the presence of resonance interaction. One may expect that the influences of solvents should be different on the different bands. However we do not detect any significant change of bands position in the ν_s and ν_{as} region despite the variation of dielectric permeativity of solvents for more than 20 times. More sensible to the variation of solvent polarity are the intensities of doublet components at ν_s and ν_{as}. The ratio of component intensities remains constant in the solvents of low polarity. The growth of the polarity leads to a redistribution of the intensities in doublet components and to some displacement of the doublet bands to the lower frequencies region. However the summary integral intensity almost does not change at the transition from low polar hexane to high polar acetonitrile.

Thus the conservation of the practically constant summary integral intensity of doublets in the ν_s and ν_{as} region at the change of the aggregate state of sulfoesters and at the use of solvents of different polarity accompanied by considerable redistribution of intensities between the separate compounds of the doublet as well the only insignificant dependence on temperature and concentration are typical of intramolecular interaction of frequencies for which the necessary conditions are the same symmetry and near values of the energetic levels.

In accordance with the classical theory of resonance the intensity of basic tone or overtone cannot exceed the intensity of ground band of absorbance. However as one may see from Tables 4-6 in the polar solvents we observe a redistribution of intensities of doublet components at which the "weak" component intensity is larger than the "strong" one intensity.

Such a redistribution of intensities between the doublet components in a crystalline phase and in solutions in polar solvents may be probabily explained by the conditionality of complex structure of bands in the region of ν_s and ν_{as}

Table 4

FREQUENCIES (ν_s cm^{-I}) AND INTEGRAL INTENSITIES (A.IO^{3}l.mole^{-I}.cm^{-2})

OF p-TOLUENESULFOACID PROPYL ESTER DOUBLET (II60 -I200)

Solvent	C, mole/l	ν_s	$\Delta\nu_{1/2}$	$A\nu_1$	ν_2	$\Delta\nu_{1/2}$	$A\nu_2$	$\nu_2-\nu_1$	$A\nu_1+A\nu_2$
CCl_4	0.005	II85	7.4	I2.3	II96	5.8	I0.2	II	22.5
CCl_4	0.050	II84	7.5	I2.2	II94	5.7	I0.4	I0	22.6
CCl_4	0.525	II83	7.6	I2.0	II94	5.7	I0.7	II	22.7
Hexane	0.05	II84	7.8	I2.4	II95	6.I	I0.0	II	22.4
Benzene	0.05	II83	7.3	I2.2	II94	6.4	I0.2	II	22.4
Dioxane	0.05	II84	8.2	I2.0	II94	6.7	II.I	I0	23.I
$CHCl_3$	0.05	II8I	8.3	II.8	II9I	6.I	I2.0	I0	22.7
Tetrachloroethane	0.05	II82	7.4	II.6	II93	6.8	II.9	II	23.5
Dichloroethane	0.05	II82	8.I	II.3	II92	6.3	I2.7	I0	24.0
Acetonitrile	0.05	II82	7.5	II.7	II9I	7.2	I2.0	9	23.7
Liquid sample		II75			II8I			7	
Crystal.sample		II74			II80			6	

Table 5

FREQUENCIES (ν_{as} cm^{-I}) AND INTEGRAL INTENSITIES (A.IO^{3} l.mole^{-I}cm^{-2})

OF p-TOLUE[illegible]SULFOACID PROPYL ESTER DOUBLET (I350 - I380)

Solvent	C, mole/l	ν_1	$\Delta\nu_{1/2}$	$A\nu_1$	ν_2	$\Delta\nu_{1/2}$	$A\nu_2$	$\nu_2-\nu_1$	$A\nu_1+A\nu_2$
CCl_4	0.005	I354	8.8	6.2	I377	9.7	8.4	23	I4.6
CCl_4	0.050	I354	9.0	6.4	I376	I0.0	8.6	23	I5.0
CCl_4	0.525	I352	9.I	6.5	I375	I0.2	7.7	23	I4.2
Hexane	0.05	I353	9.0	6.3	I375	I0.8	8.3	22	I4.6
Benzene	0.05	I353	9.8	7.2	I376	9.9	7.8	22	I5.0
Dioxane	0.05	I354	8.3	6.2	I375	II.2	8.9	2I	I5.I
$CHCl_3$	0.05	I352	7.4	9.3	I373	I0.3	6.2	2I	I5.5
Tetrachloroethane	0.05	I350	8.5	8.9	I372	II.4	7.I	22	I6.0
Dichloroethane	0.05	I35I	9.2	9.5	I372	I0.5	6.7	22	I6.2
Acetonitrile	0.05	I352	7.8	8.7	I372	II.2	6.2	20	I4.9
Liquid sample		I348			I362			I4	
Crystal.sample		I347			I358			II	

Table 6

FREQUENCIES (ν_{as} cm^{-I}) AND INTEGRAL INTENSITIES (A.IO^3 l.mole^{-I}.cm^{-2}) OF p-METHYLBEB7ŸLSULFOACID PROPYL ESTER DOUBLET (I350 - I380)

Solvent	C, mole/l	ν_1	$\Delta\nu_{1/2}$	$A\nu_1$	ν_2	$\Delta\nu_{1/2}$	$A\nu_2$	$\nu_2-\nu_1$	$A\nu_1+A\nu_2$	$\nu_s SO_2$
CCl_4	0.005	I36I	8.5	5.9	I376	II.0	I0.0	I5	I6.0	II83
CCl_4	0.050	I36I	8.7	5.8	I375	I0.5	I0.3	I4	I6.I	II84
CCl_4	0.525	I359	8.8	5.7	I373	I0.7	I0.2	I4	I5.9	II83
Hexane	0.05	I360	8.5	5.8	I377	II.3	II.0	I7	I6.8	II82
Benzene	0.05	I36I	8.7	5.3	I375	I2.0	I2.3	I4	I7.6	II83
Dioxane	0.05	I36I	8.9	6.I	I376	II.4	I0.2	I5	I6.3	II84
$CHCl_3$	0.05	I36I	7.8	9.7	I373	II.3	7.2	I2	I6.9	II84
Tetrachloroethane	0.05	I36I	9.I	I0.5	I372	I0.7	6.2	II	I6.7	II83
Dichloroethane	0.05	I362	8.4	II.3	I37I	I0.2	6.0	I0	I7.3	II83
Acetonitrile	0.05	I360	7.8	I0.2	I370	I2.3	7.I	I0	I7.3	II82
Liquid sample		I352			I360			8		
Cryst.sample		I352			I358			7		

of propyl esters of toluenesulfoacid and p-methylbenzylsulfoacid from resonance interaction of two oscillatory levels in contrast to the usually observed interaction of the basic tone with an overtone or a composite tone[32,33]. As a result one does not neglect the contribution of the "weak" component into a matrix element of the dipole moment of transition from the basic state[34].

On the basis of the study of integral IR-spectra intensities of benzene- and benzylsulfoacids esters, benzenesulfochlorides[19], sulfolane[20], di-, tri-, and tetrabutyl (or phenyl) sulfoalkanes[22] one may come to a conclusion that the observed splitting of sulfogroup absorbance bands in the symmetrical and antisymmetrical valent frequencies region should be caused by the Fermi-resonance for the other compounds too and is common for all compounds containing a sulfogroup.

REFERENCES

I. Kirsanov A.V., KirsanovaN.A. Sh.obsh.khim. 29,I802 (I96I).
2. Ghersetti S. Bull.scient.fac.chim.industr.Bologna, 2I, 228 (I963).
3. Neimisheva A.A., Savtshuk V.I., and Knunyants I.L., Isv. Acad.sci. USSR.ser.khim.,I968,n I2,2730.
4. Biryukov I.P., Deytsh A.Ya., Isv.Acad.sci.Latv.SSR,ser. khim.,I973, nI,35.
5. Naumov Yu.I., Ismailskij V.A., Dokl.Acad.sci.USSR, 203, n5,I082 (I972).
6. Lutskij A.E., Yagupolskij L.M., and Voltshenok S.A., Sh.obsh.khim., 34,n8,2726 (I963).
7. Momose T., Ueda Y., and Shuqiero G., Chem.and Pharm. Bull.Japan, 7,n8,858 (I959).
8. Lutskij A.e. and Ishtshenko I.K., Sh.obsh.khim.,38,n7, I6I8 (I967).
9. Naumov Yu.I. and Orlova T.I. In "Fiziko-khim.svojstva organ. veshtshestv i ikh svyaz so stroeniem i strukturoi",Moskva,I973,23I.
I0. Ham N.S. and Hambly A.N., Austral.J.Chem. 6,33 (I953).

II. Simon A. and Kriegsman H., Chem.Ber. 89,I883 (I956).
I2. Gillespie R.J. and Robinson E.A., Canad.J.Chem., 4I, 2074 (I963).
I3. Ham.N.S., and Hambly A.N., Austral.J.Chem. 6,I . (I953)
I4. Hirsjarvi P., and Tomilla E., Ann.Acad.Sci.Fennica. All.Chemica,S.all.,78,I (I957).
I5. Robinson E.A.,Canad.J.Chem.,39,247 (I96IO.
I6. Toyozo Uno, Katsunosuke Machida, Kazuhiko Hanai, Spectrochim.Acta,24 A, I705 (I968).
I7. Pinchas S., Samuel D., and Weis U., J.Chem.Soc. I962, 3968.
I8. Malewski G. and Weiqmann H.J., Spectrochim.Acta, I8, 725 (I962).
I9. Tsivileva I.M., Ukr.fiz.sh.,I3, Io93 (I968).
20. Shabalin I.I. and Kiva E.A., Sh.prikl.spektr.,I7, 495 (I972).
2I. Dathe K. and Doerffel K., J.prakt.Chem.,3I7,757 (I975).
22. Doerffel K. and Brunn J., J.prakt.Chem.,3I2,70I (I970).
23. Malinovskij M.S. and Prib O.A., Sh.obsh.khim., 32, I885 (I962).
24. Vizgert R.V. and Tutshapskij I.M., Sh.organ.khim., II, I886 (I975).
25. Yohansen A.V.,Optika i spektrosk.,I6,8I3 (I964).
26. Naumov Yu.I. and Magdeeva N.L., In "Fizitsh. svojstva organitsh. veshtshestv i ikh svyaz' so stroeniem i strukturoj",M.,I973, 206.
27. Naumov Yu.I. and Minkin V.I., Sh.fiz.khim.,40, nIO, 2560 (I966).
28. Bardvel F.G. and Cooper G.D., J.Amer.Chem.Soc., 74, I058 (I952).
29. Palm V.A., Usp.khimii,30,I092 (I96I).
30. Naumov Yu.I. and Ismailskij V.A., Dokl.Acad.Sci.USSR, I63,n6,I404 (I965).
3I. Nejmisheva A.A., Savtshuk V.I., and Knunyants I.L., Isv.Acad.Sci. USSR,ser.khim.,I968,nI2,2770.
32. Lisitsa I.P., Khalimonova I.N., and Stryshevski V.L., Dokl.Acad.Sci.USSR,I45,I262 (I962).

33. Lisitsa M.P. and Malinko V.N., Ukr.fiz.sh.,3,482(I958).

34. Malnev A.F. and Tsivileva I.M.,In "Spektroskopija. Metody i primenenije".M.,"Nauka",I973, I62.

Organic Reactivity
Vol.18, 1(65),1981

STRUCTURAL EFFECTS IN GAS PHASE HOMOLYSIS*

V.A. Palm, R.J. Hiob
Tartu State University, Department of Organic
Chemistry, Tartu, Estonian S.S.R.

Received 10 September, 1981

The main results of the statistical treatment of kinetic data for unimolecular gas phase homolytic dissociation according to the scheme

$$R_i-R_j \rightarrow R_i + R_j.$$

are presented.

The absence of the isokinetic relationship between logA and E values is observed. The applicability of the additivity rule for the formation enthalpies and entropies of the both radicals R_i and R_j has been proved. For activation energies (enthalpies) the relationship holds as follows:

$$E(\Delta H^{\neq}) = \Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - \Delta H^{o}_{OR_iR_j} .$$

By $\Delta H^{\neq}_{R\cdot}$ and $\Delta H^{o}_{OR_iR_j}$ the formation enthalpies for free radicals in activated state and for compound undergoing homolysis (at 0° K) are denoted, respectively. The procedure of the estimation of the formation enthalpies of free radicals is described using either the approximation of the effective mean value of the preexponential factor

---

[*] The lecture delivered on the XII Mendeleev Congress, Baku, September 1981

or the approach which takes into account the dependence of the entropy of activation on the nature of radicals R_i and R_j. The parametrization of equations reflecting the influence of the substituent effects on the formation enthalpies of free radicals is described. These equations are based on the analogy with those ones applicable for the formation enthalpies of compounds with covalent bonds. The parametrization of the equation representing the substituent effects on the additive terms of formation entropies of the substituted methyl radicals is presented as well.

There is also presented the calculation scheme for the estimation of the gas phase homolytic dissociation rate constants in dependence on the structure of the compound undergoing homolytic fission represented as two structural units, connected with the bond broken, and on the temperature.

One of the simplest chemical processes is represented by the gas phase homolysis according to the scheme:

$$R_i - R_j \xrightarrow{k} R_i\cdot + R_j\cdot \qquad (1)$$

This reaction may play a role of the initial stage in more complicated chain processes. The complete quantitative description of the last ones may require the knowledge of the rate constants for reactions belonging to the type (1). At pressures high enough these reactions are the unimolecular ones and each of them may be characterized by the first order rate constant which depends on the temperature.[1,2] This dependence is usually presented by listing the activation parameters related to the Arrhenius equation.

The experimental estimation of the mentioned above rate constants k is usually connected with rather complicated technique and may cause considerable errors[3]. Up to date the rate constants and activation parameters for a few hundreds of different combinations of R_i and R_j have been reported. The total number of radicals-substituents R involved equals, approximately, 100. Even for that limited number of radicals the number of different combinations equals 4950. Therefore the actuality of the development of the respective calculation methods is quite obvious.

We investigated a possibility of the development and parametrization of the calculation scheme using the experimental data reported in literature (for 236 different reactions in total). The main body of this data set was extracted from the compilation by V.I. Vedeneev and A.A. Kibkalo[3] and the data from more recent publications were added. For a number of reactions the parallel independent experimental data are available what enables us to judge of the degree of experimental accuracy of the estimation of k-values and the activation parameters obtained proceeding from them. It is well understandable why comparably moderate inaccuracies in k-values lead to large uncertainties in respective activation parameters. As an example representative enough the corresponding figures for the decomposition of ethane with the formation of two methyl free radicals are listed in Table 1. One can conclude that it is highly probable that the independent parallel data are related to one and the same physical process, the mean values remain constant when the data set is considerably broadened and the deviations from mean values are consistent with the normal statistical distribution. Nevertheless even these values of logA and E which correspond to the most self-consistent data set when k-values are considered demonstrate large differences between parallel independent estimations. Therefore in all cases when parallel data are absent the values of activation parameters may appear to be rather uncertain. Unfortunately, those cases constitute the majority. One have to pay attention also to nonsatisfactory results of the simultaneous treatment of all existing data according to the Arrhenius equation (see line 3. in Table 1).

As the enough representative sets of parallel data are available only for a comparably limited number of reactions the statistical treatment of as large as possible set of data in accordance with different possible hypotheses about the quantitative representation of structural effects on the log A and E values was considered as the most correct approach. The exclusion of significantly deviating points was applied in all cases.

For E or $\Delta H^{\neq}$ values the formulation and verification of these hypotheses are not connected with significant difficulties. Unfortunately, this is not the case for logA values. The absence of parallel data for a large number of reactions leads to the situation when the uncertainty of these figures for a single reaction is comparable with the whole range of the variation of logA values observed. This covers mainly 6 logarythmic units beginning from 12 up to 18. The data from Table 1 demonstrate that for the ethane homolysis the parallel values of logA cover the range of 3 units and this is by no means the limit. E.g. for the homolysis of the nitrobenzene with the formation of phenyl and nitro free radicals the alternative values of 12.6 and 17.3 are reported corresponding to E-values of 53.4 and 69.7, respectively. Nevertheless these parallel data could be considered to be related to the same process cited above because the corresponding $\log k_{700^\circ}$ values, equaling -4.07 and -4.46, are not too different (see Table 1).

For the reason considered one can hardly hope to disclose the full real picture of the dependence of the logA values on the structure of compounds undergoing homolysis, proceeding from the data available.

In principle, one of the possibilities listed below can be the real case:

i. The true values of logA do not depend on the structure and the reaction type considered belongs to isoentropic ones.

ii. There is a linear dependence between logA and E values and the isokinetic behaviour is the case.

iii. The logA and E values are completely independent from each other and depend on the structure differently.

For the true activation energy or enthalpy D the relationship on the nature of R_i and R_j can be represented as follows:

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

This relationship assumes the absence of interaction between free radicals formed in the activated state (the additivity rule). $\Delta H^{\neq}_{R\cdot}$ denotes the formation enthalpy of the respective free radicals in activated state, by $\Delta H^{o}_{OR_iR_j}$ the standard formation enthalpy of the compound R_iR_j at 0° K. It means, that for the radical-substituents R_i and R_j the constancy of the intrinsic contributions into the temperature-dependent part of the formation enthalpy during the activation process is assumed.

Eq. (2) reflects the dependance of D_{ij} value on the nature of radicals-substituents and makes possible the calculation of $\Delta H^{\neq}_{R\cdot}$ values for free radicals in activated state. If the number of different combinations of radicals with the known values of D_{ij} considerably exceeds the number of different radicals involved in these combinations and the values of $\Delta H^{o}_{OR_iR_j}$ are either available or could be calculated the consistency of Eq. (2) can be proved and the values of $\Delta H^{\neq}_{R\cdot}$ and their standard deviations could be calculated using the technique of the multilinear regression analysis in coordinates of Eq. (2).

The isokinetic behaviour was investigated by means of linear regression analysis in coordinates $\log k_{T_2}$ and $\log k_{T_1}$ for different pairs of temperatures T_1 and T_2. In all cases the slope $\varkappa$ of the linear dependence of $\log k_{T_2}$ on $\log k_{T_1}$ is indistinguishable from the value of the ratio T_1/T_2. Formally this result corresponds to a special case of isoentropic behaviour. For $T_1 = 700°$ and $T_2 = 800°$ K for the set of 350 independent pairs of the values correlated $\varkappa = 0.877 \pm 0.002$ and $T_1/T_2 = 0.875$ while the standard deviation from the regression line $s = 0.21$. The mean effective value $\log A_o = 14.64 \pm 0.044$ by the range of the variation of $\log k$ values correlated reaching 30 logarythmic units.

From this result one can conclude that 95 per cent of logA values for the reactions involved in treatment lie in the range 14.64±3.4 i.e. beginning from 11.2 up to 18, and two thirds - in the range 14.64±1.7*. Nevertheless, for purely statistical and calculation purposes the preliminary recalculation of the primary data proceeding from the value of $\log A^{-}$ cited above may occur to be a useful procedure. The recalculation formula is as follows:

$$D = E + 2.3RT\,(\log A_{0} - \log A + \log n) \qquad (3)$$

n denotes the statistical factor.

This can be demonstrated by the following example. The parallel values for the 5 independent sources from Table 1 lead to the mean recalculated value $D_{mean} = 79.49 \pm 1.10$ while $E_{mean} = 86.3 \pm 4.5$. If in Eq.(3) the mean value $\log A_{mean}$ for this set of data is substituted for the value of $\log A_{0}$ one obtains a result $D_{mean} = 86.74 \pm 0.92$. One can conclude that with the use of the $\log A_{0}$ for a given data set instead of the $\log A_{mean}$ being significantly different the scatter of recalculated values of D is enhanced rather slightly although the corresponding change of the D_{mean} value is highly significant.

So the use of Eq. (3) for the recalculation of primary values of activation energies leads to the general increase of their statistical self-consistence. Therefore, even the purely formal acceptance of the isoentropic model may occur useful for calculation purposes.

More strict procedure for the detection of the isokinetic relationship proves the absence of the linearity or even of any tendency to that between the logA and E values.

The effective values of $\Delta H^{\neq}_{R\cdot}$ could be estimated by the use of the combination of Eqs. (2) and (3) as a result of

---

[*] Authors are indebted to G.B. Manelis for the realization that the "isoentropic" behaviour found out as it was described is compatible with the real and considerable variation of the logA value the last one being completely independent of the E value

the multilinear regression analysis in coordinates of the equation:

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

where D_{ij} is the value recalculated according to Eq. (3).

This kind of treatment has been applied to the complete data set for all available combinations of 98 different radicals as well as to the limited data set where the combinations of 15 radicals with the highest levels of the presentation were involved, only. In analogous way the original values of activation energies were treated substituting in Eq. (4) E_{ij} for D_{ij}. The obtained results are listed in Tables 2 and 3. One can see that the use of the recalculated according to Eq. (3) values of D_{ij} really results in some improvement of the statistical characteristics in comparison with the results for E_{ij} values.

According to the activated state theory for unimolecular reactions the relationship holds as follows:

$$\log k = \log(k'/h) + \log T + \Delta S^{\neq}/2.3R - \Delta H^{\neq}/2.3RT =$$

$$= \log(ek'/h) + \log T + \Delta S^{\neq}/2.3R - E/2.3RT \qquad (5)$$

k' denotes the Boltzmann and h - the Planck constant, E is an experimental activation energy calculated according to the Arrhenius equation, $\Delta H^{\neq} = E - RT$ represents the activation enthalpy and $\Delta S^{\neq}$ - the activation entropy.

For activation entropy the additivity hypothesis could be tested:

$$\Delta S^{\neq}_{ij} = \Delta S^{\neq}_{R_i^{\cdot}} + \Delta S^{\neq}_{R_j^{\cdot}} \qquad (6)$$

Here $\Delta S^{\neq}_{R\cdot} = S^{\neq}_{R\cdot} = S^{o}_{R}$ where $S^{\neq}_{R\cdot}$ is the entropy of a free radical in activated state and S^{o}_{R} denotes the additive contribution to the entropy of the initial state by a substituent R. For compounds of the type of R_iR_j the additivity of entropy holds with satisfactory accuracy[5].

For the statistical treatment of the primary data the equation can be written as follows:

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - T\,\Delta S^{\neq}_{o} - T\,\Delta S^{\neq}_{R_i\cdot} - T\,\Delta S^{\neq}_{R_j\cdot} = \Delta H^{o}_{OR_iR_j} + E_{ij} + 2.3RT(\log n_{ij} - \log A_{ij} + \log T) \qquad (7)$$

The multilinear regression analysis in coordinates of Eq. (7) of the data at three temperatures for each reaction involved (the minimum, mean and maximum temperatures of the range investigated for a given reaction) leads to relatively high accuracy of the description. For 14 radicals, 32(35) reactions and 199(300) independent equations $s = 0.54(2.05)$ kcal./mole (in parenthesis the values for the initial data set, before the beginning of the procedure of the exclusion of significantly deviating points, are presented). Unfortunately, the large "overpumping" effect between the obtained values of $\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$ is observed for a majority of radicals. This is a consequence of the limited ranges of the temperature variations for reactions involved. To avoid the simultaneous parametrization of $\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$ values the iterative approach has been used as a sequence of the following procedures:

i. Multilinear regression analysis in coordinates of the equation:

$$\Delta S^{\neq}_{R_i\cdot} + \Delta S^{\neq}_{R_j\cdot} = 2.3R(\log A_{ij} - \log n_{ij} - \log(ek'T_{mean}/h)) \qquad (8)$$

The $\Delta S^{\neq}_{R\cdot}$ values are evaluated.

ii. Calculation, proceeding from these $\Delta S^{\neq}_{R\cdot}$ values, corrected values of $\log A_{ij}$ and E_{ij} according to the equations:

$$\log A_{ij(corr)} = \log(ek'/h) + \log T_{mean} + (\Delta S^{\neq}_{R_i\cdot} + \Delta S^{\neq}_{R_j\cdot})/2.3R \qquad (9)$$

$$E_{ij(corr)} = E_{ij} + 2.3RT_{mean}(\log A_{ij(corr)} - \log A_{ij} + \log n_{ij}) \qquad (10)$$

iii. Multilinear regression analysis in coordinates of the equation (evaluation of $\Delta H^{\neq}_{R\cdot}$):

$$\Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} = E_{ij(corr)} - RT_{mean} + \Delta H^{o}_{OR_iR_j} \qquad (11)$$

iV. Calculation of new corrected values of E_{ij} and $\log A_{ij}$:

$$E_{ij(corr)} = \Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} = \Delta H^{o}_{OR_iR_j} - RT_{mean} \qquad (12)$$

$$\log A_{ij(corr)} = \log A_{ij} + (E_{ij(corr)} - E_{ij})/2.3RT_{mean} \qquad (13)$$

The completion of the first cycle of these calculations results in the estimation of first approximations of the $\Delta S^{\neq}_{R\cdot}$ and $\Delta H^{\neq}_{R\cdot}$ values.

To start the second cycle of calculations the values of $\log A_{ij}$ calculated by the use of Eq. (13) are substituted for $\log A_{ij}$ in Eq. (8) etc.

During the multiregression analysis procedure (steps i. and iii.) significantly deviating points are excluded.

The results of the exploiting of this iterative approach for 14 radicals presented by several independent combinations are reflected in Tables 2 and 3. The satisfactory self-consistency has been obtained after second cycle of calculations. The obtained values are reasonable. For halogen atoms the $\Delta S^{\neq}_{R\cdot}$ values are equal to zero and in case of Br and I represented by more than one equation the $\Delta H^{\neq}_{R\cdot}$ values are close to the figures estimated proceeding from ΔH^{o}_{0} for molecules Br_2 and I_2 and the dissociation energies D_o for these molecules. The estimates of $\Delta S^{\neq}_{R\cdot}$ for the mentioned 14 radicals different from the value of 2.25 e.u. corresponding to the $\log A_o = 14.64$ should be considered as statistically justified. Unfortunately, the large uncertainty of single logA values prevents the estimation of the real values of $\Delta S^{\neq}_{R\cdot}$ for radicals presented by a single combination R_iR_j , only.

In Table 4 some secondary values of $\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$

are listed for radicals not involved in the set of 14 ones. For these radicals the data related to several combinations with the radicals from the set of 14 (see Table 3) are available. One can see that for 7 radicals from Table 3 and for two ones from Table 4 (underlined) the estimates of $\Delta H^{\neq}_{R.}$ obtained as a result of iteration procedure differ from those obtained proceeding from the value $\log A_0 = 14.64$ more than 1 kcal/mole.

The logk values can be calculated using the values of $\Delta H^{\neq}_{R.}$ either based on the effective mean value of $\log A_0 = 14.64$ (let us denote them as $E_{R.}$) or on the "true" estimates and corresponding $\Delta S^{\neq}_{R.}$ values. Although the last approach should be considered as by no means, more preferable its applicability range is limited by the lack and unreliability of corresponding experimental data.

One can prove that the $E_{R.}$ and $\Delta H^{\neq}_{R.}$ values are related by the equation as follows:

$$E_{R.} = \Delta H^{\neq}_{R.} + T_e \cdot 10^{-3}(\Delta S^{o} - \Delta S^{\neq}_{R.}), \qquad (14)$$

where

$\Delta S^{o} = 2.3R(\log A_0 - \log(ek'/h) - \log T_e)/2$

equals the half value of the activation entropy corresponding to the effective mean value of $\log A_0$, T_e is some kind of averaged temperature for a data set used for the estimation of the given $\Delta S^{\neq}_{R.}$ value.

The values of $\Delta H^{o}_{OR_iR_j}$ may be estimated using the calculation scheme for the enthalpies of covalent compounds which takes into account the contributions caused by intramolecular interactions[5]. For tetrasubstituted methane the corresponding equation is as follows:

$$\Delta H^{o}_{OX_1X_2X_3X_4C} = \Delta H^{o}_{OCH_4} + \sum_i \Delta H^{o}_{OX_i} + \varphi_{CH_3} \sum_i \varphi_{X_i} +$$
$$+ A \sum_{i<j}\sum \left\{\varphi_{X_i}\ \varphi_{X_j}\right\} + B \sum_{i<j<k}\sum\sum \left\{\varphi_{X_i}\ \varphi_{X_j}\ \varphi_{X_k}\right\} + C\left\{\prod_i \varphi_{X_i}\right\} +$$
$$+ \alpha^{*} z^{*}_{C} \sum_{i<j}\sum \sigma^{*}_{X_i}\ \sigma^{*}_{X_j} - n_{FF}\cdot 5\ (\text{kcal/mol}), \qquad (15)$$

where by $\Delta H^{o}_{OX_i}$ the additive contributions for substituents X_i are denoted. φ_{CH_3} and φ_{X_i} denote the substituent constants reflecting their ability to the φ-interaction (the scaling factor is equalized to 1 kcal/mole), $A = -0.200$, $B = 0.0196$ and $C = -0.002$ are the constants enabling the calculation of the contributions of the coupling, triple and quarternary interactions via the C atom to the total energy of φ-interaction, $\sigma^{*}_{X_i}$, α^{*} and z^{*}_{C} denote the inductive substituent constants, scaling factor and transmission factor for a carbon atom, n_{FF} equals the number of coupling interactions between fluorine atoms connected with the same carbon atom.

For substituted methyls the substituent constants could be calculated as follows:

$$\varphi_{X_1X_2X_3C} = \varphi_{CH_3} + A\sum_{i}\varphi_{X_i} + B\sum_{i<j}\sum\varphi_{X_i}\varphi_{X_j} + C\prod_{i}\varphi_{X_i} \qquad (16)$$

$$\sigma^{*}_{X_1X_2X_3C} = z^{*}_{C}\sum_{i}\sigma^{*}_{X_i} \qquad (17)$$

The values of products in figure brackets have to be equalized to zero if all corresponding interacting substituents are halogen atoms. This is a reflection of the general rule that there is no interaction between halogen atoms connected with the same carbon atom. This rule should be also applied to σ^{*} and φ-values for substituted methyls if those are connected with a halogen atom.

In case of polysubstituted by halogen atoms methyls the correction term Δ_{Hal} should be added to the right part of Eq. (17) in order to take into account the lack of additivity:

$$\Delta_{Hal} = -\,0.0275(NHAL-1)\sum_i 2^{(4-n_{X_i})} \qquad (18)$$

By NHAL the number of halogen atoms among substituents X_i is denoted, n_{X_i} is a position number of halogen in the sequence of F, Cl, Br and I.

Combining Eqs. (15), (16) and (17) one can calculate the value of ΔH^o_0 for arbitrary polysubstituted alkane if the values of corresponding substituent constants and additive increments are available.

Using the term $I_{R_iR_j}$ of the interaction energy between substituents R_i and R_j in the initial state one can write:

$$\Delta H^o_{OR_iR_j} = \Delta H^o_{OR_i-} + \Delta H^o_{OR_j-} + I_{R_iR_j} \qquad (19)$$

and

$$I_{R_iR_j} = \psi_{R_i}\psi_{R_j} + \alpha^*\sigma^*_{R_i}\sigma^*_{R_j} . \qquad (20)$$

Instead of $\Delta H^{\neq}_{R.}$ the $\Delta\Delta H^{\neq}$ values can be estimated and used for calculations as follows:

$$\Delta\Delta H^{\neq}_{R.} = \Delta H^{\neq}_{R.} - \Delta H^o_{OR-} \qquad (21)$$

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

Then the Eq. (4) can be rewritten:

$$\Delta\Delta H^{\neq}_{R_i.} + \Delta\Delta H^{\neq}_{R_j.} = D_{ij} + I_{ij} \qquad (22)$$

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

Calculation of $\Delta H^{\neq}_{R.}$ or $\Delta\Delta H^{\neq}_{R.}$ and $\Delta S^{\neq}_{R.}$ values for the substituted methyl is a problem of major interest. Using the parameters and rules of the calculation scheme for ΔH^o_0 values of polysubstituted alkanes the corresponding statistical data treatment leads to the approvement of the equation for the quantitative description of $\Delta\Delta H^{\neq}_{R\cdot}$ values for radicals $X_1X_2X_3C\cdot$ as follows:

$$\begin{aligned}\Delta\Delta H^{\neq}_{X_1X_2X_3C\cdot} = {} & \Delta\Delta H^{\neq}_{CH_3\cdot} + (\varphi_{C\cdot} - \varphi_{CH_3}) \sum_i \varphi_{X_i} + \\ & + 0.200 \sum_i \sum_{<j} \left\{ \varphi_{X_i} \varphi_{X_j} \right\} - 0.0196 \left\{ \varphi_{X_1} \varphi_{X_2} \varphi_{X_3} \right\} + \\ & + \alpha^* \sigma^*_{C\cdot} \sum_i \sigma^*_{X_i} + N_= \Psi_= + N_{CN} \Psi_{CN} + N_{NO_2} \Psi_{NO_2}\end{aligned} \qquad (23)$$

$\varphi_{C\cdot}$ and $\sigma^*_{C\cdot}$ denote the corresponding substituent constants for the free radical centre $-\overset{|}{\underset{|}{C}}\cdot$; $\Psi_=$, Ψ_{CN} and Ψ_{NO_2} are the resonance energies for the interaction of π-electron systems (unsaturated and aromatic), cyano and nitro groups with that centre, respectively. By $N_=$, N_{CN} and N_{NO_2} the numbers of the π-electron systems, cyano and nitro groups connected with this centre are denoted. N_{NO_2} equals unity if one or several nitro groups are connected with the centre $-\overset{|}{\underset{|}{C}}\cdot$, otherwise it equals zero.

The $\Delta S^{\neq}_{R\cdot}$ values for substituted methyls could be represented by the equation:

$$\Delta S^{\neq}_{X_1X_2X_3C\cdot} = \Delta S^{\neq}_{CH_3\cdot} + Yp \qquad (24)$$

where Y is a parameter and by p the number of coupling interactions between substituents X_i is denoted.

It has to be mentioned that in consequence of the practical equality of the inductive transmission coefficients $z^*_{C\cdot}$ and z^*_C the corresponding term in Eq. (23) is omitted.

For the parametrization of the scheme with constant $\log A_0 = 14.64$ the data at the mean temperature T_{mean} for each independent combination of logA, E and $\Delta H^0_{R_iR_j}$ or $I_{R_iR_j}$ were used.

For the scheme with the variable activation entropy the data at T_{min}, T_{mean} and T_{max} i.e. minimum, mean and maximum temperatures for the range investigated experimentally were used. The results of the both parametrization procedures are listed in Table 5. One can see that the values of $\Delta\Delta H^{\neq}_{CH_3\cdot}$ and resonance parameters for those two schemes differ rather insignificantly. The differences in $\varphi_{C\cdot}$ and $\alpha^{*}\sigma^{*}_{C\cdot}$ values partly compensate each other. This closeness of the parameters for both alternative schemes is understandable for the reasons considered above.

The values of the standard deviations for these alternative schemes are not comparable because the first one was parametrizised using the data for a single temperature, only. In a broad temperature range the scheme which reflects the variation of the activation entropy shall demonstrate some advantages. This is illustrated by the comparison of the experimental and calculated values for the homolysis of tetranitromethane as represented in Table 6. One can see that the logk values for extreme temperatures calculated by the use of the scheme reflecting the variation of the activation entropy (6. in Table 6) are considerably better in agreement with the mean experimental values (3. and 4) than the corresponding figures related to the scheme based on $\log A_0$ = 14.64 value. For the middle of the investigated temperature range both schemes lead to close results.

In the terms of the scheme with constant $\log A_0$ = 14.64 it is possible to reflect the substituent effects for substituted alkoxy radicals, radicals RHg. and for the reactions of the homolytic dissociation of peroxides and azocompounds by the use of the following equations:

$$\Delta\Delta H^{\neq}_{XO\cdot} = 5.55 + 5.42\,\sigma^{*}_{X} - 21.3N_{=} \qquad (25)$$

$$D_{X_i O-OX_j} = 18{,}6 + 1.71(\varphi_{X_i} + \varphi_{X_j}) + 3.78(\sigma^{*}_{X_i} + \sigma^{*}_{X_j}) - $$

$$- 0{,}383\,\sigma^{*}_{X_i}\,\sigma^{*}_{X_j} - 21.3(N_{=X_i} + N_{=X_j}) \qquad (26)$$

$$\Delta\Delta H^{\neq}_{RHg\cdot} = -5.8 + 8.9\,\varphi_R \qquad (27)$$

$$D_{X_i-N=NX_j} = 11.5 + \Delta\Delta H^{\neq}_{X_i\cdot} + 2.17\gamma^{\rho}_{X_j} - 4.73\gamma_{X_i} +$$

$$+ 4.03(\sigma^*_{X_j} - \sigma^*_{X_i}) - 0.932\sigma^*_{X_j} - 0.38\sigma^*_{X_i}\sigma^*_{X_j} \qquad (28)$$

The value of $N_=$ equals one or zero for π-electron systems capable for the resonance interaction and for substituents lacking this capability, respectively.

The described calculation schemes are drawn up in a computer program designed for automatic calculation of the rate constants of homolytic dissociation depending on the structure of the radical-substituents and on the temperature.

The programs of multilinear regression analysis with automatic exclusion of points on different levels of significancy and nonsignificant parameters composed by us were used for the statistical treatment of the data.

More detail description of the methods of data processing and the obtained results will be published separately.

The approach described in this paper can be successfully applied to the gas phase radical substitution reactions.

Table 1

Data for reaction CH_3-$CH_3 \rightarrow 2CH_3$.

1. The set from 5 the most mutually consistent sources
2. The total set from all 11 sources available
3. The results of the simultaneous treatment of data from these 11 sources according to the Arrhenius equation
4. Proceeding from mean values of logA and E for 5 sources of data
5. Proceeding from mean values of $\log k_T$ for 5 sources of data

In parenthesis the variation ranges for parallel data are represented.

No.	Averaged values of 800°K	$-\log k_T$ 940°K	 1100°K	$\log A$ sec^{-1}	E kcal/mole
1.	7.33±0.25 (7.2 -7.6)	3.80±0.12 (3.7 -4.0)	0.92±0.16 (0.8 -1.1)	16.25± 1.04 (14.7 -17.5)	86.3± 4.5 (79.3-91.7)
2.	7.39±0.65 (6.2 -8.8)	3.90±0.62 (2.8 -5.2)	1.00±0.62 (-0.1-2.3)	16.05± 0.96 (14.7 -17.5)	85.8± 3.4 (79.3-91.7)
3.	7.61±0.42	4.24±0.42	1.44±0.42	15.01±0.60	82.8± 2.5
4.	7.3	3.8	0.9	-	-
5.	-	-	-	16.2	86.0

Table 2

Results of the data processing according to Eq. (4).

NE - the number of independent equations.

NRD- the number of different radicals-substituents.

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

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

s - standard deviation in kcal/mole.

Definition of D_{ij}	NE	NRD	NRN	s
Eq. (3), all data	231(281)	93(98)	125(138)	1.10(3.1)
The same for 15 most representative radicals	90(111)	15(15)	34(36)	1.30(2.6)
$D_{ij} = E_{ij}$	69(100)	14(14)	34(35)	1.34(3.8)
The iterative approach	74(100)	14(14)	31(35)	0.91(2.4)

Table 3

The values of $\Delta H^{\neq}_{R.}$ and $\Delta S^{\neq}_{R.}$ for free radicals. In parenthesis the number of independent equations used for the calculation of the respective value is given. For the hydrogen atom the values $\Delta H^{\neq}_{H.} = 51.6$[6] and $\Delta S^{\neq}_{H.} = 0$ are accepted.

R.	$\Delta H^{\neq}_{R.}$, kcal/mole				$\Delta S^{\neq}_{R.}$ e.u.
	From ΔH^{0}_{0} and D_{0} for diatomic molecules[6]	According to Eq.(4)		Iterative approach	
		D_{ij} according to Eq. (3)	$D_{ij}=E_{ij}$		
Cl	28.59	27.4±1.2	20.1±1.4(I)	24.4±1.0(I)*	-0.02±1.2
Br	28.18	30.0±0.7	23.5±0.8(4)	27.8±0.6(3)*	-0.06±0.7
I	25.63	29.3±0.5	24.9±0.6(7)	26.3±0.4(7)*	0.3 ±0.5
NH_2	-	44.8±0.3(7)	38.6±0.4(3)	37.1±0.3(3)	-3.2 ±0.3
NO_2	-	7.2±0.3(48)	8.6±9.4(6)	7.3±0.2(12)	3.6 ±0.3
SH	-	18.7±0.7(4)	13.3±0.7(4)	13.6±0.5(4)	-3.8 ±0.6
CH_3O	-	4.2±0.3(10)	4.4±0.3(6)	3.6±0.2(5)	2.9 ±0.3
C_2H_5O	-	-2.2±0.2(21)	-4.4±0.2(15)	-4.5±0.2(II)	-1.6±0.2
CH_3	-	31.9±0.2(81)	34.1±0.2(25)	32.0±0.1(28)	3.1±0.2
C_2H_5	-	25.2±0.4(21)	26.1±0.4(10)	25.7±0.3(II)	3.3±0.4
$(CH_3)_2CH$	-	17.1±0.3(14)	20.8±0.4(7)	19.3±0.3(6)	4.5±0.4
$(CH_3)_3C$	-	10.4±0.3(14)	13.1±0.4(7)	14.7±0.3(10)	7.5±0.3
$CH_2=CHCH_2$	-	40.9±0.5(8)	40.2±0.5(7)	37.4±0.4(8)	-0.9±0.5
$C_6H_5CH_2$	-	51.8±0.4(7)	49.6±0.5(12)	50.1±0.3(II)	1.9±0.4

* Calculated proceeding from the zero value of a respective $\Delta S^{\neq}_{R.}$

Table 4

The comparison of different evaluations of the $\Delta H^{\neq}_{R.}$ values for less represented radicals included in more than one combination like R_iR_j.

Statistically unreliable values are given in parenthesis.

No.	R.	Secondary values, obtained proceeding from the results of the iterative approach for most represented radicals from Table 3.		Eq.(4), Total set of data	D_{ij} from Eq.(3) Secondary values obtained proceeding from the results for 15 the most represented radicals
		$\Delta S^{\neq}_{R.}$ e.u.	$\Delta H^{\neq}_{R.}$, kcal/mole		
I	FO	4.8±1.4	28.3±0.1	28.2±0.8	28.3±0.16
2	C_3H_7O	0.8±0.1	-8.5±0.1	-8.0±0.7	-10.9±0.2
3	$(CH_3)_3CO$	5.8±0.4	-15.1±0.1	-15.9±0.1	-15.9±0.2
4	F_2N	3.9±1.0	8.7±0.2	8.6±0.4	8.6±0.0
5	C_6H_5NH	-4.7±0.2	55.0±1.5	60.0±0.65	59.8±1.4
6	NO	3.8±1.0	20.5±0.3	21.2±0.48	24.3±1.5
7	CH_3Cd	-11.5±1.3	41.7±0.6	53.8±0.65	53.7±1.37
8	CH_2Cl*	(-2.0)	(22.7)	28.3±1.3	28.0
9	C_6H_5	(2.9±9.1)	73.2±0.8	73.4±0.6	74.1±0.6
10	CH_3CO	(1.7±3.4)	(-8.8±3.4)	-5.8±0.4	77.7±3.5

---

* Represented by only a single combination of R_iR_j type.

Table 5

The parameters of Eqs. (23) and (24).

The values of $I_{R_iR_j}$ were calculated using Eq. (20).

The following values were used:

$\alpha^* = 1.37$ kcal/mole

$\sigma^*_{NO_2} = 4.5$

$\Delta H^o_{OCH_3^-} = \Delta H^o_{OCH_4} = -15.9$ kcal/mole

$\varphi_{CH_3} = 3.94$

The parameter		The value for the version with $\log A_{\sigma} = 14.64$	The value for the version with variable activation entropy
$\Delta\Delta H^{\neq}_{CH_3\cdot}$	(kcal/mole)	48.0 ± 0.2*	47.6 ± 0.2*
$\varphi_{C\cdot}$		2.19 ± 0.10*	2.55 ± 0.04*
$\alpha^*\sigma^*_{C\cdot}$		1.54 ± 0.05	1.34 ± 0.04
$\psi_{=}$	(kcal/mole)	-8.9 ± 0.2	-9.5 ± 0.2
ψ_{CN}	(kcal/mole)	-5.6 ± 0.7	-7.3 ± 0.7
ψ_{NO_2}	(kcal/mole)	-4.4 ± 0.5	-5.1 ± 0.3
$\Delta S^{\neq}_{CH_3\cdot}$	(e.u.)	-	3.2 ± 0.02*
Y	(e.u.)	-	1.19 ± 0.18
NE		64(97)	130(207)
NRN		51(62)	51(69)
s	(kcal/mole)	1.21	1.97

* Proceeding from the values of $\Delta\Delta H^{\neq}_{R\cdot}$ or $\Delta S^{\neq}_{R\cdot}$ for methyl, ethyl, isopropyl and t-butyl. The data for these radicals lead to the value $Y = 1.43 \pm 0.02$ e.u.

Table 6

The comparison of experimental and calculated values of logk and activation parameters for reaction

$$(NO_2)_3C\text{-}NO_2 \longrightarrow (NO_2)_3C\cdot + NO_2\cdot \qquad (n = 4)$$

1\. and 2. - the alternative independent experimental data.

3\. - Proceeding from the mean values of logA and E for these alternative data sets.

4\. - The simultaneous treatment of the data from both alternative sources.

5\. - The values calculated with the use of Eq. (23) according to the version with $\log A_0 = 14.64$.

6\. - The values calculated with the use of Eqs. (23) and (24) according to the version with variable activation entropy.

ΔT_{exp} - the range of temperature covered by experimental data (^{o}K).

Extrapolated logk values are given in parenthesis.

No.	logk 360°	450°	590°	logA	E kcal/mole	ΔT_{exp}
1.	(-7.30)	-2.34	2.38	17.53	40.90	443 - 596
2.	-7.14	-2.45	(2.00)	16.30	38.60	359 - 450
3.	-7.21	-2.39	2.19	16.90	39.70	-
4.	-7.17	-2.27	2.37	17.3±0.2	40.3±0.4	359 - 596
5.	-6.30	-2.01	2.08	14.64	35.52	-
6.	-6.78	-2.04	2.48	16.97*	39.12*	-

* Calculated according to the Arrhenius equation using the data for 360 and 590 ^{o}K. $\Delta S^{\neq} = 13.5$, $\Delta H^{\neq} = 38.23$.

REFERENCES

1. V.N. Kondratyev, Kinetics of Gas Phase Chemical reactions. Publ. House of Acad. Sci. U.S.S.R., Moscow, 1958. (in Rus.).
2. P.J. Robinson and K.A. Holbrook, Unimolecular reactions. Wiley-Interscience, London, New. York. Sydney. Toronto, 1972.
3. V.I. Vedeneev and A.A. Kibkalo, The Rate Constants of Gas Phase Unimolecular Reactions. "Nauka", Moscow, 1972 (in Rus.).
4. V.A. Kireev, Methods of Practical Calculations in Thermodynamics of Chemical Reactions. "Chimia", Moscow, 1970 (in Rus.).
5. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions. "Chimia", Leningrad, 1977 (in Rus.).
6. L.V. Gurvich, G.V. Karachevtsev, V.N. Kondratyev et. al. Energies of Bond Breaking. Ionization Potentials and Electron Affinities. "Nauka", Moscow, 1974 (in Rus.).

CONTENTS

I. Koppel, R. Pikver, A. Sügis, E. Suurmaa, and E. Lippmaa, FT ICR Study of Structure and Solvent Effects on Basicity of Some Anions in Gas Phase 3

I.A. Koppel, U.H. Mölder, and M.B. Comisarow, AB Initio SCF LCAO MO Calculations of Molecules. II. Ionization Potentials 19

I.A. Koppel and U.H. Mölder, CNDO/2 Calculations of Molecules. I. Proton Affinity. Comparison with Experiment. 42

I.A. Koppel, U.H. Mölder and R.I. Pikver, CNDO/2 Calculations of Molecules. II. Ionization Potentials 84

V. Galkin and R. Cherkasov, Structure and Reactivity Correlations I. On the Problem of Steric Effect 113

R.V. Sendega, N.G. Gorbatenko, and R.V. Visgert, Alkyl and Alkenyl Esters of Sulfoacids 26. Ultraviolet Spectra and Integral Intensities of Sulfogroup Valent Frequencies Bonds. In Sulfoesters 136

V.A. Palm, R.J. Hiob, Structural Effects in Gas Phase Homolysis 152

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том ХУIII. Вып. I(65). Сентябрь I98I.
На английском языке.
Тартуский государственный университет.
ЭССР, 202400, г.Тарту, ул.Юликооли, I8.
Ответственный редактор В.Пальм.
Подписано к печати 9.02.I982.
Формат 60x84/I6.
Бумага писчая.
Машинопись. Ротапринт.
Условно-печатных листов I0,23.
Учетно-издательских листов 9,I2.
Печатных листов II,0.
Тираж 400.
Заказ № I48.
Цена I руб. 40 коп.
Типография ТГУ, ЭССР, 202400, г.Тарту, ул.Пялсона, I4.