Some peculiarities of the effect of molecular structure on the activation energy of radical gas-phase decay of aromatic nitro compounds

G. M. Khrapkovskii,[a] E. A. Ermakova,[a] and V. A. Rafeev[b]*

[a]*State Scientific Research Institute of Chemical Products, 420033 Kazan'*
[b]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (096) 515 3588

The relation of parameters of geometric and electronic structures to the activation energies of the radical gas-phase decomposition of nitro compounds is shown. A sufficiently simple and precise method for calculation of the activation energy is suggested.

Key words: aromatic nitro compounds; thermal decomposition; quantum chemical calculation; activation energy; correlation dependence.

Presently the kinetics of thermal decomposition of aromatic nitro compounds are sufficiently well studied.[1–4] Some important specific features of the reaction mechanism have been elucidated.[5–7] At the same time, the use of only experimental data does not allow one to follow fine details of the effect of the molecular structure, to elucidate the changes in kinetic parameters in the series of nitro compounds, and to justify one or another mechanism of the primary act.

Poorly studied geometry, electronic structures, and vibrational spectra of nitro compounds were for a long time one of the main reasons that prevented understanding the main regularities of the effects of molecular structures on kinetic parameters of thermal decomposition. Recently the situation has changed substantially. In addition to experimental studies, different classes of nitro compounds have been studied by the methods of quantum chemistry and molecular mechanics. However, despite great possibilities of these methods in the comparative analysis of reactivity of various organic compounds, as a rule they were not systematically used for consideration of problems of chemical stability.

The kinetics of thermal decomposition was studied in the majority of cases without taking into account the results obtained in the studies of molecular structures. We attempted to compensate in part for this deficiency by the example of aliphatic nitro compounds.[8] In this work, the analogous approach was used to consider the peculiarities of the effect of molecular structure on the activation energy of the radical gas-phase decomposition of aromatic nitro compounds.

The systematic study of geometry of aromatic nitro compounds was begun in sixties.[9] Presently, geometric parameters for more than 100 molecular crystals have been determined by X-ray analysis.[10] The number of compounds studied in the gas-phase state is significantly smaller.[10,11] Considerable errors of experimental values of length of valence bonds and angles preclude identification of the structures of nitro compounds on the geometric parameters of the C—NO_2 group. Additional difficulties arise in the analysis of experimental data because the geometry of nitrobenzene was determined by microwave spectroscopy while other molecules were studied by gas electronography (GE),[10] and divergences in the values of lengths of C—N bonds determined by different methods exceed errors of experimental measurements.

In order to obtain comparable data on molecular geometry in the gaseous state, which can be useful for the further consideration of the effect of the molecular structure on the change in kinetic parameters of the primary act of the radical gas-phase decomposition, we determined equilibrium values of bond lengths and valence angles for 15 of the simplest aromatic nitro compounds by the MINDO/3 method. In particular, we studied the compounds for which experimental data on the kinetics of the radical decomposition are obtained in the gaseous state[1–4] (except chloro- and bromonitrobenzenes, because MINDO/3 has no corresponding reliable parametrization).

The calculations were performed with complete optimization of geometric parameters, and accuracy for C—N bond lengths was ±0.05 pm. Ionization potentials were calculated by the same method based on the Koupmans theorem. The distribution of the electronic density for equilibrium conformations of molecules was studied using the CNDO/2 approach, which, compared

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2118—2122, December, 1994.

Table 1. Geometric parameters of aromatic nitro compounds

Compound	*r*(C—N)	*r*(N=O)	*r*(C—H)	Angle ONO
	/pm			/deg
Nitrobenzene	143.8	122.8	110.5	128.6
o-Dinitrobenzene	144.6	122.4	110.6	133.1
m-Dinitrobenzene	144.4	122.5	110.5	130.8
p-Dinitrobenzene	144.3	122.7	110.3	129.9
1,2,3-Trinitrobenzene	144.8; 145.1	122.4	110.6	133.4
1,2,4-Trinitrobenzene	144.6; 144.9	122.4	110.6	133.1
1,3,5-Trinitrobenzene	144.6	122.4	110.6	130.6
m-Fluoronitrobenzene	143.8	122.8	110.4	130.0
p-Fluoronitrobenzene	143.6	122.8	110.8	129.4
m-Nitrotoluene	143.8	122.8	110.6	129.4
p-Nitrotoluene	143.7	122.8	110.6	129.4
m-Nitroaniline	143.6	122.9	110.5	129.3
p-Nitroaniline	143.2	122.9	110.6	129.6
m-Nitrophenol	143.7	122.5	110.2	129.7
p-Nitrophenol	143.5	122.5	110.3	129.6

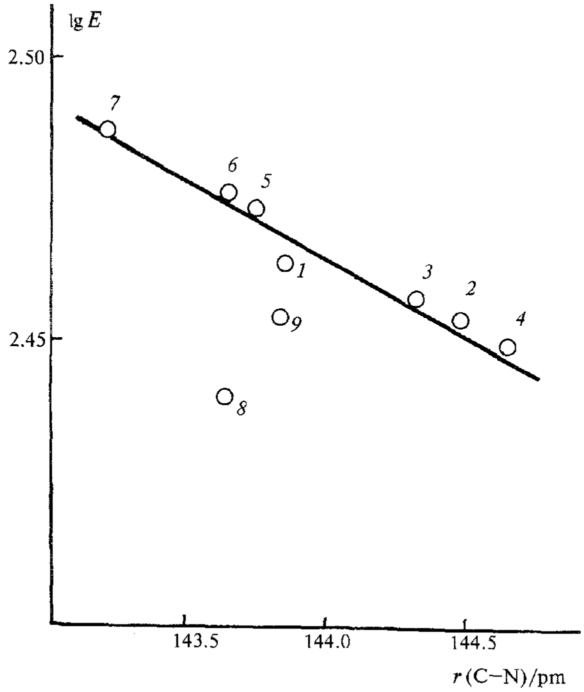

Fig. 1. Dependence of the logarithm of the activation energy of the thermal decomposition (E/kJ mol^{-1}) on the C—N bond length (r(C—N)/pm) for nitrobenzene (*1*), *m*-dinitrobenzene (*2*), *p*-dinitrobenzene (*3*), 1,3,5-trinitrobenzene (*4*), *m*-nitrophenol (*5*), *m*-nitroaniline (*6*), *p*-nitroaniline (*7*), *p*-nitrotoluene (*8*), and *m*-nitrotoluene (*9*).

with MINDO/3, better reflects the charge distribution over atoms and population densities of bonds.

Some of the results are presented in Table 1. The calculations show that the changes in geometric parameters in the nitrobenzene series are comparatively small, at least, they are considerably lower than those observed for the accumulation of NO_2 groups in nitroalkanes, for example, in the series nitromethane, dinitromethane, and trinitromethane.[8]

At the same time, on the basis of the resulting data, one can establish some regularities in the change in bond lengths and valence angles of the C—NO_2 group. The C—NO_2 bond lengthens when the hydrogen atom is replaced by the NO_2 group in nitrobenzene. In this case, the *r*(NO) value slightly decreases. Unlike polynitroalkanes, the *r*(C—H) values are almost unchanged in the series considered. No clear tendency is observed for the changes in other valence bonds. As for valence angles, a monotonic increase in the ONO angle as NO_2 groups are accumulated in the molecule is observed.

The results of the calculation allow one to observe the changes in *r*(C—N) depending on the mutual arrangement of NO_2 groups in the molecule for the example of isomeric dinitro- and trinitrobenzenes. The maximum *r*(C—N) are observed for the compounds with the 1,2-arrangement of nitro groups (*o*-dinitrobenzene, 1,2,3-, and 1,2,4-trinitrobenzenes). The calculation predicts different values of *r*(C—N) in the same molecule depending on positions of NO_2 groups. For example, the value of *r*(C—N) is higher for the central (for C(2)) C—N bond in 1,2,3-trinitrobenzene than in C—NO_2 groups for C(1) and C(3). A similar effect is observed for 1,2,4-trinitrobenzene.

The observed changes in geometric parameters in the series of nitrobenzenes can be explained by two main factors: the electron-acceptor character of the NO_2 group and steric effects. An increase in *r*(C—N) in the series nitrobenzene, *m*-dinitrobenzene, and 1,3,5-trinitrobenzene is related to the appearance of acceptor properties of nitro groups. At the same time, there is an additional increase in *r*(C—N) caused by steric strains for molecules with 1,2-arrangement of NO_2 groups.[12]

The effect of donor substituents on geometric parameters of the C—NO_2 group was studied by the examples of nitroalkanes, nitrotoluenes, nitrophenols, and fluoronitrobenzenes. The substitution of the hydrogen atom in nitrobenzene by the NH_2 or OH group or by the fluorine atom results, as should be expected, in a small decrease in *r*(C—N). This effect is expressed relatively stronger for *p*-isomers, which can be related to the manifestation of the direct polar conjugation impossible for the *m*-arrangement of the NO_2 group and the donor acceptor. Geometric parameters of isomeric nitrotoluenes are almost the same as those of nitrobenzene, which corresponds to the weakest donor properties of the CH_3 group.[13]

It is interesting to compare the changes in geometry of the NO_2 group with the values of the activation energy of the radical gas-phase decomposition. In the series of nitroalkanes, a decrease in this energy is shown[8] to be symbatic with an increase in r(C—N). It follows from the data presented in Fig. 1 that a similar dependence is also observed for the majority of aromatic nitro compounds studied. The experimental values of the activation energies[1,2,4] are determined under the conditions when thermal decomposition of aromatic nitro compounds in the gaseous phase was homogeneous and monomolecular, and the kinetics was determined by the rate of its first elementary stage. The error of the values obtained ranged from ±4 to ±12 kJ mol^{-1}.

As has been already mentioned, the C—N bond length increases and the activation energy of the radical decomposition decreases, when the hydrogen atom is replaced in nitrobenzene by the NO_2 group. At the same time, the introduction of the donor substituents F, NH_2, and OH results in a decrease in r(C—N) with a corresponding increase in the activation energy. The activation energy almost coincides with the dissociation energy of the cleaved bond for the radical mechanism of the primary act of the thermal decomposition. In particular, the following correlation is valid for nitro compounds:

$$D(\mathrm{C—N}) = E - RT\,. \qquad (1)$$

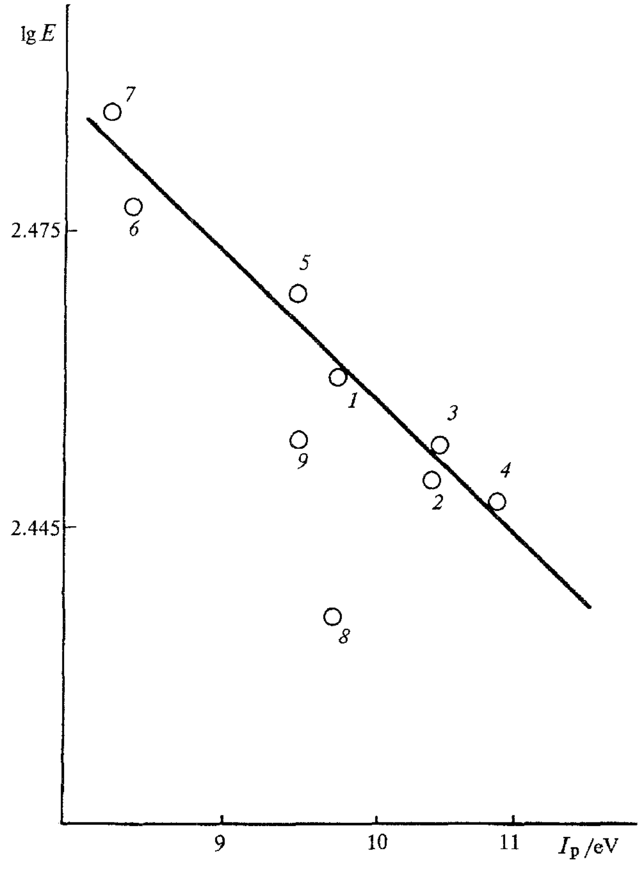

Fig. 2. Dependence of the logarithm of the activation energy of the thermal decomposition (E/kJ mol^{-1}) on the ionization potential (I_p/eV) for nitrobenzene and its derivatives. See Fig. 1 for numeration of points.

Therefore, the change in the activation energy in the series considered is explained by the influence of donor or acceptor substituents on the strength of the C—N bond.

It has been established previously[14,15] that the changes in the activation energy of the radical gas-phase decomposition are symbatic with the population density of the C—N bond. The validity of this dependence is confirmed for the majority of the compounds studied. In addition, the changes in lengths and population densities of bonds are symbatic for all 15 compounds. As for nitroalkanes, the changes in the activation energy and ionization potential are monotonic for aromatic nitro compounds studied. The introduction of the nitro group to the molecule results in an increase in the ionization potential. The substituents, which exhibit donor properties in the aromatic system (NH_2, OH, F, and CH_3), decrease the ionization potential. The linear dependence lg$E$ *vs.* I_p (Fig. 2) is observed in the semilogarithmic coordinates. The character of the dependence is almost unchanged, if calculated values of I_p are used instead of experimental values. (Experimental and published data[16] for the values of I_p are presented in Fig. 2.)

Nitrotoluenes drop out of the dependences presented in Figs. 1 and 2. We believe that this may be related to the lowered experimental values of the activation energy of the gas-phase decomposition. The experimental activation energy for p-nitrotoluene (275 kJ mol^{-1}) is lower than those for m- and p-dinitrobenzenes and 1,3,5-trinitrobenzene.

It is very difficult to explain the substantial decrease in the activation energy of the radical decomposition for the substitution of the hydrogen atom in nitrobenzene by the methyl group. It has been reliably established by many independent methods that in the aromatic series, the CH_3 group manifests weak donor properties.[13,17] Therefore, it should be expected that the activation energy of the radical decomposition is somewhat higher for p-nitrotoluene than for nitrobenzene.

Using the calculated value of r(C—N) and the dependence presented in Fig. 1 and interpolating, we obtain an estimate for p-nitrotoluene within 292—295 kJ mol^{-1} that almost coincides with that from the dependence lg$E$ *vs.* I_p (see Fig. 2). For m-nitrotoluene one can expect a small (by 2—4 kJ mol^{-1}) decrease in the activation energy as compared with the p-isomer.

The results of the quantum chemical calculation of D(C—N) in nitrotoluenes agree well with the estimates presented.[12] It should be mentioned that there is a monotonic dependence between changes in length and the Mulliken population density of the C—N bond for all of the aromatic nitro compounds studied. In this case, *m*- and *p*-toluenes do not drop out of the general dependence. On the basis of analysis of all data available, we believe that the experimental values of the activation energy of the radical decomposition are lowered for *m*- and *p*-toluenes. This can be caused by unstable admixtures in the compounds, by the contribution of secondary reactions or faster heterogeneous processes on the walls of the reaction vessel, or by other things.[18]

Taking into account the results obtained, let us consider the problem of the theoretical estimation of the activation energy for the radical decomposition of aromatic nitro compounds. The analysis of the experimental data shows that, in the case of the gas-phase decomposition of these compounds, pre-exponential factors are determined with relatively low accuracy. In any case, the presented[1—4] errors in determination of lg *A* in some cases exceed the changes observed. Difficulties in describing rate constants of the thermal decomposition based on correlation dependences may be associated with this fact. The question arises as to whether linearity in the change in the activation enthaply is observed for the radical decomposition. The latter condition is considerably less rigid than the principle of linearity of the free energy underlying the Hammett—Taft equations.[13,18] It is shown below that the experimental values of the activation energies of the radical decomposition reactions of aromatic nitro compounds fall sufficiently well within the terms of the dependence of the activation enthalpies on constants of substituents, which makes it possible to perform rather simple theoretical estimation of *E*.

We have already mentioned that there are three factors for aromatic nitro compounds, which affect geometric parameters (r(C—N)), electronic structures ($P_{\text{C—N}}$, I_p), and activation energies of the radical gas-phase decomposition: 1) conjugation of substituents with the phenyl ring, 2) direct polar conjugation of the NO_2 group with donor substituents at *o*- and *p*-positions, and 3) steric effects in the case of the 1,2-arrangement of the nitro group and bulk substituents. Resonance constants of substituents σ_R can serve[13] as a measure of conjugation with the reaction center for derivatives of nitrobenzene. The values of ${\sigma^+}_R$ reflect donor properties of +R-substituents. All ${\sigma^+}_R$ are less than zero; their absolute values increase as donor properties increase. The ${\sigma^-}_R$ constants, which characterize acceptor properties of —R-substituents, are represented by positive numbers increasing as these properties enhance. It is natural to take the difference ${\sigma^+}_R - {\sigma^-}_R$ as a measure of the direct polar conjugation. In the case of steric strains, as has been shown for the example of nitroalkanes,[8] it is most convenient to use $\Delta\alpha = \alpha - \alpha_0$, where $\alpha = 100\Delta U_s/\Delta H_{at}$ is the ratio of the energy of strain to the enthalpy of atomization of the molecule, and α_0 is the corresponding value for the first representative of the series, nitrobenzene. The energy of strain and the enthalpy of atomization are easily calculated by the methods of molecular mechanics.

Taking into account the above, we can write the equation for the activation energy of the radical gas-phase decomposition in the form:

$$E = E_0 - A\,\sigma_R - B({\sigma^+}_R - {\sigma^-}_{NO_2}) - C\Delta\alpha\ , \qquad (2)$$

where E_0 is the activation energy of the gas-phase decomposition of nitrobenzene.

The values of ${\sigma^+}_R$ and ${\sigma^-}_R$ determined previously[13] were used for the calculations, and the values of $\Delta\alpha$ were estimated from the published data.[12] The empirical constants *A*, *B*, and *C* found from the experimental data on the kinetics of the thermal decomposition are equal to 12.5, 7.0, and 29.0 kJ mol^{-1}, with accuracy of ±0.1 kJ mol^{-1}.

The results are presented in Table 2. The comparison of the calculated and experimental activation energies of the radical gas-phase decomposition shows that they agree rather well. The mean square deviation (7.3 kJ mol^{-1}) is comparable with the error of the experimental determination.

The agreement is improved if we exclude nitrotoluenes, whose great divergences are related, in our opinion, to a considerable understatement of ex-

Table 2. Calculated and experimental values of the activation energy of the radical decomposition of aromatic nitro compounds (E/kJ mol^{-1})

Compound	σ_R	$\Delta\sigma$*	$\Delta\alpha$	E_{exp}**	E_{calc}	ΔE***
Nitrobenzene	—	—	—	291	—	—
m-Nitrotoluene	−0.17	—	—	284	293	−9
p-Nitrotoluene	−0.17	−0.61	—	275	297	−22
m-Nitrophenol	−0.8	—	—	298	301	−3
p-Nitrophenol	−0.8	−1.24	—	—	310	—
m-Nitroaniline	−1.0	—	—	301	303	−2
p-Nitroaniline	−1.0	−1.44	—	308	314	−6
m-Fluoronitrobenzene	−0.24	—	—	—	294	—
p-Fluoronitrobenzene	−0.24	−0.68	—	—	299	—
o-Fluoronitrobenzene	−0.24	−0.68	—	—	299	—
m-Chloronitrobenzene	−0.15	—	—	293	293	0
p-Chloronitrobenzene	−0.15	−0.59	—	300	297	3
o-Chloronitrobenzene	−0.15	−0.59	0.55	281	281	0
m-Bromonitrobenzene	−0.11	—	—	297	292	5
p-Bromonitrobenzene	−0.11	−0.55	—	302	296	6
o-Bromonitrobenzene	−0.11	−0.55	0.59	—	279	—
m-Iodonitrobenzene	−0.13	—	—	299	293	6
p-Iodonitrobenzene	−0.13	−0.57	—	—	297	—
o-Iodonitrobenzene	−0.13	−0.57	0.62	—	279	—
m-Dinitrobenzene	+0.44	—	—	284	285	−1
p-Dinitrobenzene	+0.44	—	—	286	285	1
o-Dinitrobenzene	+0.44	—	0.50	—	271	—
1,2,5-Trinitrobenzene	0.88	—	—	281	280	1
1,2,3-Trinitrobenzene	0.88	—	1.25	—	244	—
1,2,4-Trinitrobenzene	0.88	—	1.04	—	250	—

* $\Delta\sigma = {\sigma^+}_R - {\sigma^-}_R$.

** See Refs. 1, 2, and 4.

*** $\Delta E = E_{exp} - E_{calc}$.

perimental values. In this case, the mean square deviation of the calculated values of E from the experimental values is 3.7 kJ mol^{-1}. Using formula (2), it is easy to calculate the activation energy of the thermal decomposition *via* the radical mechanism for any compound. The theoretical estimation of E for compounds decomposing *via* the molecular mechanism is of definite interest. For these compounds it is easy to find D(C—N) and to use the values obtained for discussion about the competition of different routes of the primary act of decomposition. The values used in the calculation of the activation energy have a sufficiently clear physical meaning and are related to electronic and steric effects in molecules of aromatic nitro compounds. All of the data necessary for the calculations are available.

Thus, on the basis of theoretical analysis of the substituent effects, one can find a correlation between the activation energy of the radical decomposition and geometry and electronic structures of aromatic nitro compounds. Using the resulting data, one can explain the observed changes in the activation energy and for some compounds, *e.g.*, for *m*- and *p*-nitrotoluenes, to improve the experimental estimates of E.

References

1. V. G. Matveev and G. M. Nazin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 774 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
2. V. G. Matveev, V. V. Dubikhin, and G. M. Nazin, *Kinet. Katal.*, 1976, **17,** 280 [*Kinet. Catal.*, 1976, **17** (Engl. Transl.)].
3. V. G. Matveev, V. V. Dubikhin, and G. M. Nazin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 474 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 456 (Engl. Transl.)].
4. V. G. Matveev, V. V. Dubikhin, and G. M. Nazin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 783 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 650 (Engl. Transl.)].
5. S. Meyerson, R. W. Haar, and E. K. Fields, *J. Org. Chem.*, 1972, **37**, 4114.
6. E. K. Fields and S. Meyerson, in *Adv. Free-Radic. Chem.*, London, 1975, **5**, 5.
7. V. D. Kolosov, Yu. A. Pankrushev, G. M. Khrapkovskii, G. A. Osipov, P. N. Stolyarov, and G. K. Klimenko, *Khimicheskaya fizika protsessov goreniya i vzryva. Kinetika khimicheskikh reaktsii* [*Chemical Physics of Burning and Explosion Processes. Kinetics of Chemical Reactions*], Chernogolovka, 1977, 54 (in Russian).
8. G. M. Khrapkovskii, V. A. Rafeev, Ju. I. Rubthov, G. N. Marchenko, and G. B. Manelis, *Proc. of the 17th International Pyrotechnics Seminar Combined with the 2nd Beijing International Symposium on Pyrotechnics and Explosives*, Beijing, China, 1991, **1**, 424.
9. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, *Opredelenie geometricheskogo stroeniya svobodnykh molekul* [*Determination of Geometrical Structure of Free Molecules*], Khimiya, Leningrad, 1978, 224 (in Russian).
10. N. I. Sadova and L. V. Vilkov, *Usp. Khim.*, 1982, **51**, 153 [*Russ. Chem. Rev.*, 1982, **51** (Engl. Transl.)].
11. N. I. Sadova, L. S. Khaikin, and L. V. Vilkov, *Usp. Khim.*, 1992, **61**, 2129 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
12. G. M. Khrapkovskii, A. G. Shamov, A. A. Levin, Yu. A. Pankrushev, and T. S. Pivina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2317 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
13. V. A. Pal'm, *Vvedenie v teoreticheskuyu organicheskuyu khimiyu* [*Introduction to Theoretical Organic Chemistry*], Vysshaya Shkola, Moscow, 1974, 445 pp. (in Russian).
14. V. V. Zverev, I. Sh. Saifullin, and G. P. Sharnin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 313 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 241 (Engl. Transl.)].
15. V. V. Zverev, I. Sh. Saifullin, and G. P. Sharnin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 521 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 368 (Engl. Transl.)].
16. *Energiya razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektrony* [*Energy of Dissociation of Chemical Bonds. Ionization Potentials and Electron Affinity*], Ed. V. N. Kondrat'ev, Nauka, Moscow, 1974, 352 pp. (in Russina).
17. A. M. Vereshchagin, *Induktivnyi effekt* [*Inductive Effect*], Nauka, Moscow, 1987, 325 pp. (in Russian).
18. Yu. Ya. Maksimov, S. B. Sorochkin, and S. I. Titov, *Trudy MKhTI im. D. I. Mendeleeva* [*Transactions of D. I. Mendeleev Moscow Chemical Technological Institute*], 1980, 26 (in Russian).

Received January 14, 1994;
in revised form June 20, 1994