Some peculiarities of the influence of molecular structure on the activation energy of radical gas-phase decomposition of aliphatic nitro compounds

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Geometric parameters of nitro and fluoronitro derivatives of nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane (for which experimental data on kinetics of radical gas-phase decomposition are available) have been determined by the MINDO/3 method. Correlations between changes in logarithm of the activation energy and those in the lengths of C—N and C—H bonds as well as in the ionization potentials have been found. The major changes in the C—N— and C—H— bonds occur when bulky atoms and groups (NO_2, Cl, Br, and I) are introduced into the molecules. Nonempirical calculations of energies of dissociation of the C—N bonds in the molecules of nitromethane and its halogen derivatives have been carried out. An equation was proposed which allows one to perform a high-accuracy determination of the activation energy for radical gas-phase decomposition of nitroalkanes using the coefficients of steric interactions in the molecules calculated by the methods of molecular mechanics.

Key words: aliphatic nitro compounds; thermal decomposition; quantum-chemical calculations; activation energy; correlation dependence.

The kinetics and mechanism of thermal decomposition of aliphatic nitro compounds have been studied in detail. Several regularities of the effect of functional groups on kinetic parameters of the primary act of the reaction have been established.[1,2] At the same time, based on experimental data only, one fails to trace some fine details of the effect of molecular structure, to explain changes in the activation energies and those in pre-exponential factors of monomolecular decomposition, and to validate the possibility of realization of one or another mechanism of the primary act.

When thermal decomposition proceeds *via* a radical mechanism, the activation energy (E) of the reaction virtually coincides with the dissociation energy (D) of the cleaved bond.

$$E = D + RT$$

Hence, it is necessary to ascertain which molecular parameters affect the dissociation energy of the C—NO_2 bond for understanding major regularities of changes in the activation energy of radical gas-phase decomposition of nitro compounds. Correlations between changes in the bond lengths, populations, and bond strengths have been found[3,4] for hydrocarbons and some other classes of organic compounds.

The use of similar dependences in studies of nitro compounds was hampered by the absence of a sufficient amount of reliable data on the molecular geometry in the gaseous state.[5,6] Previously,[7] we attempted to investigate aromatic nitro compounds in a similar way. In this work, an analogous approach was applied to aliphatic nitro compounds whose gas-phase radical decomposition has been well studied experimentally. The main parameters of both geometric and electronic structures for a considerable number of nitro compounds were obtained at the first stage. They were further used in consideration of regularities of the behavior of the activation energy of the radical gas-phase decomposition.

The geometric and electronic structure of the molecules were investigated by the semiempirical quantum-chemical method MINDO/3 with full optimization of geometric parameters. Bond lengths and bond angles were optimized with an accuracy of 0.1 pm and 0.1°, respectively. The ionization potentials of molecules were determined on the basis of Koopmans' theorem.

Nonempirical calculations have been carried out using the GAMESS program.[8] Relativistic core potentials of Stevenst type and a split basis set of 31GF type with addition of polarization d-functions[9] were used for heavy atoms. Full optimization of the geometry was performed

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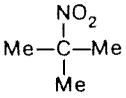
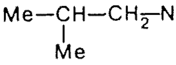
Table 1. The C—N bond lengths (pm) in aliphatic nitro compounds

Compound	*r*(C—N)	Compound	*r*(C—N)
$MeNO_2$	145.2 (148.9)	$MeFC(NO_2)_2$	149.0
$CH_2(NO_2)_2$	147.8	$FH_2C—C(NO_2)_3$	152.2
$CH(NO_2)_3$	149.0 (150.5)	1-$PrNO_2$	146.7
		2-$PrNO_2$	148.1
$C(NO_2)_4$	153.3 (152.6)	1-$BuNO_2$	146.7
CH_2FNO_2	145.3	2-$BuNO_2$	148.1
CHF_2NO_2	145.2		
$MeNO_2$	146.5 (149.0)	 $Me-\overset{NO_2}{\underset{Me}{C}}-Me$	150.1
$CHF(NO_2)_2$	147.9	 $Me-\underset{Me}{CH}-CH_2-NO_2$	146.6
$CF_2(NO_{2/2}$	148.0		
$CF(NO_2)_3$	149.9	1,1-$C_3H_6—(NO_2)_2$	149.5
$EtNO_2$	146.7 (150.5)	1,1,1-$C_3H_5(NO_2)_3$	152.4
$MeCH(NO_2)_2$	149.2	1,1-$C_4H_8(NO_2)_2$	149.5
$MeC(NO_2)_3$	152.3	1,1,1-$C_4H_7(NO_2)_3$	152.4

Note. Experimental values[6] are given in parentheses.

by using the modified Baker's method at the ROHF level[8] (a standard component for the GAMESS program). Correlation corrections to the energy for optimized geometries were calculated at the second-order Møller—Plesset level of perturbation theory (MP2).[10]

Steric strains in the molecules were evaluated by the methods of molecular mechanics. The interaction between nonbonded atoms was calculated on the basis of the Buckingham "6—12" potentials using the Dashevskii parametrization.[11]

Results and Discussion

The electronic structure of aliphatic nitro compounds has been studied in detail.[12—21] However, calculations by modern quantum-chemical methods were carried out in many cases without optimization of the main geometric parameters. Therefore, the results published by different authors can hardly be compared to one another.

Some of the results we obtained by the MINDO/3 method for nitro and fluoronitro derivatives of methane, ethane, propane, and butane are given in Table 1. Calculated and experimental values of the bond lengths in the molecules are in good agreement. Maximum differences do not exceed 3.8 pm (0.038 Å)*. Both experimentally observed and calculated changes in geometric parameters are in agreement in most cases. Thus, for instance, increasing the number of nitro groups in the molecule leads to an increase in *r*(C—N) and *r*(C—H) and some decrease in *r*(N—O). The lengths of valent bonds in the $C—NO_2$ fragment are slightly affected by fluorine atoms. At the same time, the values of *r*(C—F) decrease monotonously in the series CH_2FNO_2, CHF_2NO_2, CF_3NO_2. A similar tendency has also been observed for fluoromethanes.[8] The replacement of hydrogen atoms by a nitro group and a fluorine atom in the nitromethane molecule leads to a pronounced increase in the O—N—O angle. In addition, a lengthening of the $C—NO_2$ bond in nitroethane is predicted by calculations, in agreement with experimental data.

The geometric parameters of dinitromethane are also presented in Table 1. In spite of repeated attempts, they were not determined experimentally due to the extremely low chemical stability of dinitromethane. Taking into account that the values of geometric parameters of nitroalkanes (obtained by MINDO/3 method) are in fairly good agreement with experimental data and that the values of bond lengths and bond angles in dinitromethane do not violate the general tendency of their changes in the series (nitromethane, trinitromethane, tetranitromethane), one can assume that the calculated values are fairly close to real ones.

According to the MINDO/3 calculations, the values of N—O bond lengths in nitromethane and those in nitroethane are very close. Distances *r*(C—N) and *r*(C—H) in nitroethane, 1-nitropropane, and 1-nitrobutane are somewhat longer than those in nitromethane. A similar tendency also persists for *gem*-polynitro derivatives of nitromethane and nitroethane as well as for 1-nitropropane and 1-nitrobutane containing equal numbers of NO_2 groups.

Attention should be drawn to the fact that the lengthening of the C—N bonds (Δ*r*(C—N)) with increasing number of nitro groups in dinitro and trinitro derivatives of methane, ethane, nitropropane, and nitrobutane is nearly the same. Thus, the value of Δ*r*(C—N) is equal to 2.6 pm on going from nitromethane to dinitromethane (147.8—145.2) while that for nitroethane and 1,1-dinitroethane is equal to 2.5 pm (149.2—146.7). Similar tendency is also observed for trinitro compounds.

The calculations showed that the values of *r*(C—N) and *r*(N—O) for nitro- and fluoronitro derivatives of methane and ethane, containing equal numbers of NO_2 groups, nearly coincide. It can also be noted that an insignificant decrease in the C—N—O angle and an increase in the O—N—O angle is observed with increasing number of NO_2 groups in derivatives of nitromethane, nitroethane, nitropropane, and nitrobutane. It is essential that the changes in values of those angles in the series (nitromethane, dinitromethane, trinitromethane) and (nitroethane, 1,1-dinitroethane, 1,1,1-trinitroethane) are virtually the same.

One can compare the values of geometric parameters of mononitroalkanes containing primary and secondary

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* Similar discrepancies between calculated and experimental values are comparable with the distinction in determination of the geometric parameters of molecules by gas electron diffraction and microwave spectroscopy, which exceeds 6—7 pm for a number of aliphatic nitro compounds.[5]

NO_2 groups by the example of isomeric nitropropanes and nitrobutanes, whereas the isomeric nitrobutanes allow one to consider the effect of branched structure of the carbon skeleton. According to calculations, the r(C—N) distances in 2-nitropropane and 2-nitrobutane are longer than those in the corresponding 1-nitro compounds. The most significant changes in geometric parameters are observed in nitro derivatives of isobutane. Thus, the values of r(C—N) in 1-nitro-2-methylpropane and in 1-nitrobutane are virtually the same. At the same time, calculations predict a pronounced lengthening of the C—N bond in 2-nitro-2-methylpropane. It has been established by gas electron diffraction study[5] that appreciable lengthening of the C—C bonds formed with the participation of the tertiary carbon atom can be observed in iso-hydrocarbons due to the increasing energy of interaction between nonbonded atoms. An increase in r(C—N) in *tert*-nitrobutane might also be due to a similar reason.

It is of interest to compare the obtained data on geometry of some nitro- and fluoronitro derivatives of methane, ethane, propane, and butane and the data on the distribution of the electron density (Table 2). When considering the charge distribution in the molecules of nitroethane, nitropropane, nitrobutane, and their nitro derivatives, attention is drawn to the fact that the carbon atom directly bonded to the nitro group is negatively charged. At the same time, the adjacent carbon atom has a small positive charge. The absolute values of the charges on the carbon atom in nitromethane and nitroethane, as well as those in their nitro derivatives differ significantly. However, subtraction of the value of the charge on the carbon atom in the first representative of the series (nitromethane and nitroethane, respectively) from that on the carbon atom in polynitro compounds results (in the case of compounds containing equal numbers of NO_2 groups) in very close values of the differences. An analogous tendency is also observed for the values of charges on the carbon atoms of C—NO_2 fragments in nitro derivatives of 1-nitropropane and 1-nitrobutane.

The results reported in this work allow one to draw some conclusions on the effect of molecular structure (branched or nonbranched) on the geometric and electronic structures of molecules in the series of nitro and fluoronitroalkanes. The most significant changes in geometric parameters and charges on the carbon atoms occur when hydrogen atoms are replaced by nitro groups. A pronounced lengthening of the C—N bonds is observed as the number of nitro groups increases. On the contrary, the N—O bonds are slightly shortened. The lengths of C—N, N—O, and C—H bonds for all fluoronitroalkanes studied hardly differ from those calculated for the corresponding unsubstituted nitroalkanes. Increasing the number of carbon atoms in the alkyl radical also affects slightly the parameters of the C—NO_2 fragment.

Table 2. Charges (units of the electron charge, *e*) on carbon atoms in the molecules of nitro derivatives of methane, ethane, propane, and butane

Compound	$-q_{C(1)}$	Compound	$-q_{C(1)}$
$MeNO_2$	0.159	Me—CH_2—CH_2NO_2	0.118
$CH_2(NO_2)_2$	0.349	Me—$CHNO_2$—Me	0.081
$CH(NO_2)_3$	0.550	Me—$CH(NO_2)_2$	0.292
$C(NO_2)_4$	0.729	Me—$C(NO_2)_3$	0.492
CFH_2NO_2	−0.287	Me—CH_2—CH_2—CH_2NO_2	0.116
CF_2HNO_2	−0.757	Me—CH_2—$CHNO_2$—Me	0.091
CF_3NO_2	−1.153	Me—CH_2—CH_2—$CH(NO_2)_2$	0.300
Me—CH_2NO_2	0.107	Me—CH_2—CH_2—$C(NO_2)_3$	0.498

Hence, the observed changes in geometric parameters can be related mainly to steric strains caused by the bulky C—NO_2 fragments. One can assume that analogous tendencies for changes in geometric parameters also remain for chloro- and bromonitroalkanes. The MINDO/3 method we used has no reliable parametrization for chloro- and bromonitro compounds. However, the gas electron diffraction data[5,6] on the geometry for a number of chloro- and bromonitroalkanes are available. It follows from these data that although the errors in determination of bond lengths can be fairly large (up to 1.2 pm), the fact of essential lengthening of r(C—N) in chloro- and bromotrinitromethanes as compared to trinitromethane and tetranitromethane is beyond question.

The results of the study of the electron density distribution also point to the existence of pronounced steric strains in chloronitroalkanes. It should be noted[13] that the oxygen atoms of chloronitroalkanes have significantly smaller negative charges as compared to compounds containing equal numbers of the NO_2 groups among the series of nitro- and halogen nitro substituted methanes. This is in good agreement with the regularities established in studies of conformations of aliphatic nitro compounds by the methods of molecular mechanics. It has been shown previously[22] that introduction of a chlorine atom to the α-position of the molecule causes a rotation of functional groups by a larger angle than that of an additional nitro group. On the contrary, fluorine atoms slightly affect changes in the angle of rotation of the NO_2 group though fluorine has a higher electronegativity than the other halogens. Using these data, one can draw the conclusion that introduction of bulky halogen atoms (for instance, chlorine) into the molecules of aliphatic nitro compounds causes stronger steric strains than that of the NO_2 groups.

Having considered some regularities in the change in geometric and electronic structure of nitroalkanes, one can directly discuss the effrect of these factors on the activation energy of the radical gas-phase decomposition of nitroalkanes.

It has been reliably established that a large group of aliphatic nitro compounds in the gaseous state decomposes by the radical mechanism.[1] Analysis of experimental data[1,2] allowed one to reveal the main regularities of the effect of molecular structure on the activation energy of the radical decomposition of nitroalkanes and the C—N bond strength. It was noted, for instance, that the value of *D*(C—N) is independent of the length of alkyl radical R in the series $RCH_n(NO_2)_{3-n}$. The value of *D*(C—N) is affected by the substituents NO_2, Cl, Br, and I approximately to the same extent (Br and I decrease the value of *D*(C—N) somewhat more strongly than Cl and NO_2).[5] The value of *D*(C—N) remains nearly constant when an H atom is replaced by a F atom in α-position relative to the nitro group. The abovementioned regularities in the change in activation energy are valid for a large number of nitroalkanes and can serve as a good basis for reliable estimations of *E* and *D*(C—N). At the same time, the question of the reasons for these changes and of their relation with the structure of aliphatic nitro compounds was little understood up to present.

Experimental data on the kinetics of thermal decomposition as well as the above results of the studies of geometric and electronic structure of nitroalkanes allow one to discuss these problems. Since the value of the difference between the C—N bond length for a given compound and that for the first representative of the series (nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane), Δ*r*(C—N), remains nearly constant for compounds containing equal numbers of NO_2 groups, the replacement of hydrogen atoms by fluorine atoms or alkyl groups has virtually no effect on the C—N bond length (see Table 1) in polynitro and fluoronitroalkanes.

Thus, lengthening of the *r*(C—N) in the series of nitroalkanes occurs under the action of the same structural factors which cause a decrease in the activation energy of the radical gas-phase decomposition. Main changes in the *r*(C—N) and *E* values in nitro and fluoronitroalkanes can only be due to an increase in the number of NO_2 groups. Therefore, the question on the relationship between changes in the *r*(C—N) value and those in the activation energy of the radical gas-phase decomposition naturally arises.

Analysis of both the data listed in Table 1 and the data on the kinetics of the gas-phase decomposition[1—5] showed that an increase in *r*(C—N) for the compounds studied is accompanied by a monotonous decrease in *E*. This tendency in the case of nitro and fluoronitro derivatives of nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane can be described by Eq. (1):

$$\log E = 2.337 - 0.0158\Delta r(\mathrm{C{-}N}) \qquad (1)$$

(the correlation coefficient is 0.967),

where Δ*r*(C—N) is the difference between the C—H bond length in a given compound and that of the first representative of the series. Equation (1) can be used for approximate estimate of the activation energy in the absence of experimental data on the kinetics of the thermal decomposition. After determining the geometric parameters of a molecule by the MINDO/3 method and calculating the Δ*r*(C—N) value, one can make an estimate of *E*. For instance, the value of the activation energy for dinitromethane is 198 kJ mol^{-1}.

The choice of the logarithmic dependence for *E* in (1) is based on the fact that the changes in the equilibrium bond lengths in the series of related compounds are determined mainly by the repulsive part of the Morse curve (*i.e.*, by the contribution of the A exp(−Br) term to the empirical potentials of the molecular mechanics). The linear dependence between the bond orders, bond lengths, and ionization potentials in the series of related compounds has been discussed repeatedly.[3] It was found that quantitative allowance for the repulsion of nonbonded atoms in the molecules allows one to calcutate various physico-chemical properties of aliphatic nitro compounds: the atomization enthalpies, vibrational spectra, *etc.*[21—24] It will be shown below that the activation energies of the radical gas-phase decomposition can be estimated analogously with good accuracy.

Lengthening of the C—H bonds formed by the carbon atom of the CNO_2 fragment is also observed in nitro compounds with increasing number of nitro groups. The dependence between *r*(C—H) and *E* (analogous to Eq. (1)) is described by the formula:

$$\log E = 2.342 - 0.0277\Delta r(\mathrm{C{-}H}) \qquad (2)$$

(the correlation coefficient is 0.984),

where Δ*r*(C—H) is the difference between the C—H bond length in a given compound and that of the first representative of the series (nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane). It should be noted that the values of *r*(C—H) for nitro and fluoronitro compounds containing equal numbers of NO_2 groups nearly coincide. It is also essential that the values of the actvation energy of thermal decomposition calculated using Eqs. (1) and (2) are fairly close (198 and 197 kJ mol^{-1}, respectively, for dinitromethane).

According to the gas electron diffraction data, the introduction of the chlorine and bromine atoms to the α-position results in a pronounced lengthening of the C—N bond*. For instance, the value of *r*(C—N) in trinitromethane is 1.3—1.4 pm less than those in chloro and bromotrinitromethanes[9]. For instance, the activation energy of the gas-phase decomposition of trinitromethane is higher than those of chloro and bromotrinitromethanes. A substantial increase in *r*(C—N) is observed for trichloronitromethane as compared to that for nitromethane. The experimental value of the activation energy of the radical gas-phase decomposition for this compound is more than 80 kJ mol^{-1} lower than that for nitromethane. Hence, lengthening of the C—N bond and decreasing of the activation energy of thermal decomposition in the gaseous state are found to be symbatic also for the molecules containing bulky halogen atoms.

As follows from the analysis of structural data (experimental and calculated), no simple dependence between changes in the bond angles of the NO_2 group and the activation energy of the radical decomposition was

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* The values of *r*(C—H) are usually not reported in experimental works due to difficulties in precise determination of coordinates of hydrogen atoms.

observed for free molecules of aliphatic nitro compounds. Despite the fact that in the series of nitromethane, dinitromethane, and trinitromethane a monotonous increase in the O—N—O angle is observed, which corresponds to weakening of the C—NO_2 bond, the results obtained for tetranitromethane and halogen nitroalkanes are not described by a monotonous dependence. Thus, for instance, the O—N—O angle in trichloronitromethane is significantly larger than that in nitromethane (125.4 and 131.7°, respectively), but its value for chlorotrinitromethane is somewhat smaller.

No simple dependence between the deformation of the bond angles and steric strains in the molecule is observed. The largest (among nitroalkanes) values of the O—N—O angle are observed in fluoromononitro compounds where steric strains are insignificant. Based on the experimental and calculated data, analysis of the geometry of nitroalkanes in the gaseous state showed that steric strains in the molecules manifest itself primarily as deformations of the valent bonds. The angles in the C—NO_2 fragment can also change when nonbonded atoms interact with essentially lower energies, in particular, under the action of redistribution of the electron density caused by highly electronegative atoms or groups (when they are introduced into the molecule).

It is also of interest to trace whether changes in the charges on H, C, N, and O atoms are related to a decrease in the activation energy of the radical decomposition. No monotonous dependences were observed between changes in the activation energy and those in charges on the atoms of the NO_2 group. At the same time, for most compounds studied, a decrease in this energy is accompanied by an increase in the negative charge on the carbon atom of the C—NO_2 group. However, the charge on the C atom in nitroalkanes is known to be determined primarily by electronegativity of the substituents.[13] Therefore, fluorine and chlorine atoms cause stronger changes in this charge as compared to NO_2 groups. Hence, fluoronitroalkanes drop out of the above-mentioned dependence since substantial (the largest in the series) changes in the charge on the carbon atom for corresponding molecules, containing equal numbers of NO_2 groups, are only accompanied by an insignificant change in the activation energy of the radical gas-phase decomposition.

The decrease in the activation energy of the radical decomposition for most nitro and fluoronitro derivatives of methane, ethane, propane, and butane is accompanied by an increase in ionization potentials. The corresponding dependence can be described by Eq. (3):

$$\log E = 2.60 - 0.175\Delta I_p \quad (3)$$

(the correlation coefficient is 0.955),

where ΔI_p is the difference between the value of ionization potential for a given compound and that for the first representative of the series. We have also obtained analogous dependences in our studies of aromatic nitro compounds.[10] For instance, a lengthening of the C—N bond and an increase in the ionization potential of the molecule were shown to be followed by a monotonous decrease in E.

At the same time, essential distinctions were also observed due to peculiarities of the structure of these two classes of C-nitro compounds. The major changes in the geometric parameters of aromatic nitro compounds are determined mainly by the electronic effects of the substituents. However, the introduction of such a strong acceptor as a fluorine atom into nitroalkanes results only in insignificant changes in r(C—N), I_p, and E. The changes are due mainly to the steric strains appearing when hydrogen atoms are replaced by bulky atoms and groups (Cl, Br, I, NO_2).

Experimental data on the kinetics of thermal decomposition of nitroalkanes (see below) and independent quantum-chemical evaluations of the dissociation energy of the C—NO_2 bond obtained by a nonempirical method (Table 3) confirm the conclusion on the predominant role of steric interactions. Quantum-chemical calculations of the dissociation energies of the C—NO_2 bonds in nitromethane (NM) and its halogen derivatives are of special interest. In this simplest case one could expect the most pronounced effect of the substitution of a hydrogen atom by halogen atoms of steadily increasing size. The necessity of calculations also stems from the fact that no experimental data on the kinetics of thermal decomposition of monohalogen derivatives of NM as well as no thermochemical estimates of D(C—N) are available in the literature.[1,23]

Analysis of the results obtained showed that the calculated values of D(C—N) in NM exceed the experimental values (the most reliable thermochemical value is 251 kJ mol^{-1}).[23] At the same time, the kinetic estimates of D(C—N) reported by different authors lie in a fairly wide interval from 221 to 251 kJ mol^{-1}. It is believed that the calculated values of D(C—N) in NM and its derivatives remain slightly higher than the experimental values, due likely to inadequate allowance for electronic correlations which may result in increasing the energy of radicals. At the same time, based on the estimates of the dissociation energy for compounds belonging to various classes (including nitro compounds) reported in Refs. 18, 19, one can assume that the calculations adequately reflect the tendencies of changes in D(C—N) in the series. The results obtained are in good agreement with the experimental tendencies of

Table 3. Total energies (au) and dissociation energies of C—N bonds (kJ mol^{-1}).

Compound	$E_{MP2/ROHF}$	Radical	$E_{MP2/ROHF}$	D(C—N)
$MeNO_2$	−48.8064	Me	−7.2703	266.4
CH_2FNO_2	−72.2365	CH_2F	−30.7033	258.7
CH_2ClNO_2	−63.0307	CH_2Cl	−21.5053	238.0
CH_2BrNO_2	−61.4789	CH_2Br	−19.9538	237.6
CH_2INO_2	−59.5338	CH_2I	−18.0092	236.2
		NO_2	−41.4346	

changes in the activation energies of radical decomposition (and D(C—N)) for halogen polynitromethanes. In particular, the calculation has shown that the replacement of the hydrogen atom by the fluorine atom in nitromethane results in decreasing D(C—N) by ~8 kJ mol^{-1} while this effect exceeds 25 kJ mol^{-1} for chloronitromethane. A slight decrease in D(C—N is observed in the series chloro-, bromo-, and iodonitromethane. Thus, the results of nonempirical calculations of D(C—N) confirm the effect of steric factors on changes in the activation energy of the radical gas-phase decomposition of aliphatic nitro compounds.

The effect of steric strains on changes in the geometric parameters of aliphatic nitro compounds can be most conveniently traced in the studies of conformational transitions in *gem*-dinitro- and 1,1,1-trinitroalkanes (in particular, in the conformation of trinitromethane) by the MINDO/3 method. The difference between the values of r(C—N) for two conformations, the equilibrium conformation ($\varphi_1 = \varphi_2 = \varphi_3 = 37°$), and one of the energetically unfavorable ($\varphi_1 = \varphi_2 = \varphi_3 = 90°$), was found to be 4.4 pm (149.0 and 153.4 pm, respectively). The last value exceeds the value of r(C—N) for the equilibrium conformation of tetranitromethane (153.3 pm).[25]

The data reported in this work allow one to evaluate steric strains in the molecules. The simplest way to do this is to use the methods of molecular mechanics.[11] In this connection one can use the total energy of interaction between nonbonded atoms (the energy of strain), E_s. However, by definition, E_s is an additive quantity: it increases monotonously as the number of atoms in the molecule increases. According to calculations, the values of E_s for nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane are equal to 108.0, 177.5, 267.0, and 351.5 kJ mol^{-1}, respectively. It is most convenient to use a dimensionless quantity, related to the energy of strain, that takes into account the number of atoms in the molecule for a comparative estimation of steric strains in a series of organic compounds. The coefficient of steric interactions in the molecule (α), *i.e.*, the ratio of the energy of strain to the enthalpy of atomization,[24,26] is appropriate for this purpose:

$$\alpha = \frac{E_s}{\Delta E^{\circ}_{at}} \cdot 100.$$

The enthalpy of atomization can easily be calculated by the methods of molecular mechanics.[11]

Known values of α calculated for the equilibrium conformations of nitro compounds[24,26,27] on the basis of the Dashevskii potentials are used below. An increase in α in most nitro- and halogen nitro derivatives of methane, ethane, propane, and butane was found to be followed by a decrease in the activation energy of the radical gas-phase decomposition. The value of E can be determined from Eq. (4):

$$\log E = 2.380 - 0.065\Delta\alpha, \tag{4}$$

where $\Delta\alpha$ is the difference between the value of the coefficient of steric strains for a given compound and that of the first representative of the series, *i.e.*, nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane.

Table 4. Activation energies (E/kJ mol^{-1}) of the radical decomposition of nitroalkanes

Compound	α	E_{exp}*	E_{calc}
$MeNO_2$	4.45	238	238
$EtNO_2$	5.19	—	—
$Me—CH_2—CH_2NO_2$	5.45	—	—
$Me—CH_2—CH_2—CH_2NO_2$	5.87	—	—
CCl_3NO_2	7.69	154	148
$CH_2(NO_2)_2$	5.74	—	197
$CHF(NO_2)_2$	5.75	199	197
$CF_2(NO_2)_2$	5.78	198	196
$CHCl(NO_2)_2$	6.85	—	167
$CCl_2(NO_2)_2$	7.94	143	142
$CH(NO_2)_3$	6.19	177	184
$CF(NO_2)_3$	6.25	175	183
$CCl(NO_2)_3$	7.62	152	149
$CBr(NO_2)_3$	7.76	152	146
$CI(NO_2)_3$	8.10	143	139
$C(NO_2)_4$	6.79	160	168
$FClC(NO_2)_2$	6.92	173	166
$FBrC(NO_2)_2$	6.99	165	163
$FIC(NO_2)_2$	7.12	165	161
$Me—CH(NO_2)_2$	6.07	197	209
$Me—C(NO_2)_3$	6.95	181	184
$Me—CH_2CH(NO_2)_2$	6.32	200	209
$Me—CH_2C(NO_2)_3$	7.14	177	186
$Me—CCl(NO_2)_2$	7.38	178	172
$Pr—C(NO_2)_3$	7.38	183	188

Note. The error in experimental determination of E is 4.8 kJ mol^{-1};[2] calculated and experimental estimates of E are rounded to 1 kJ mol^{-1}.

* Data from Refs. 1, 2.

Experimental and calculated values of E for 20 aliphatic nitro compounds (whose kinetic parameters were obtained) and α are given in Table 4. The value of the root-mean-square deviation of the calculated and experimental data is equal to 6.0 kJ mol^{-1}. This value is comparable with the error of experimental determination of the activation energy of the radical decomposition of nitroalkanes (4—8 kJ mol^{-1}).[1,2]

The ease and high accuracy of the method have drawn attention to the described procedure of calculation of E, which is based on the established dependence between the activation energy of the radical gas-phase decomposition and steric strains in aliphatic nitro compounds. The only variable used in the calculations has a clear physical meaning and can be easily determined by the methods of molecular mechanics. This advantageously distinguishes the approach developed in this work from the known methods of determination of the activation energy of thermal decomposition and D(C—N).[23,28] One can assume that quantitative estimates of the intramolecular interaction (α) will allow one to calculate the bond strengths for organic compounds belonging to the other classes. In this case, the presence of sufficiently strong steric interactions, which determine changes in the bond strengths for compounds of a given class, is essential.

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