Bond energies and formation enthalpies of mono- and polyradicals in nitroalkanes
1. Nitromethanes

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The enthalpies of formation of nitromethane derivatives were obtained on the basis of experimental and literature data. The procedure for the calculation of the bond dissociation energies in nitromethanes from the atomization enthalpies and energies of nonvalent interactions of nitro groups was proposed. The calculated values were compared with the data on the thermal decomposition kinetics. The atomization enthalpies and energies of nonvalent interactions of nitro groups were also used for the calculation of the bond dissociation energies in radicals.

Key words: thermochemical properties, bond dissociation energy, nonvalent interactions, formation enthalpy of radical, atomization enthalpy, substitution energy.

The bond dissociation energies and formation enthalpies of radicals are most important energy characteristics of molecules and intermediate reaction products (intermediates). These values determine stability of compounds and affect the mechanism and kinetics of conversion of substances, including the intensity of chain processes.[1] The bond dissociation energies and enthalpies of formation of radicals and substances in the gas phase are related by the equation

$$D(R^1—R^2) = \Delta H^\circ_f(R^1) + \Delta H^\circ_f(R^2) - \Delta H^\circ_f(R^1R^2)_g, \qquad (1)$$

where $D(R^1—R^2)$ is the dissociation energy of compound R^1R^2 to radicals R^1 and R^2; $\Delta H^\circ_f(R^1)$, $\Delta H^\circ_f(R^2)$, and $\Delta H^\circ_f(R^1R^2)_g$ are the formation enthalpies of radicals R^1, R^2, and compound R^1R^2 in the gas phase under standard conditions. It follows from Eq. (1) that the dissociation energy of bond is equal to the energy that should be tranferred to the molecule (radical) for its dissociation to radicals R^1 and R^2. The dissociation energies of bonds are usually determined by using the kinetic data on the activation energies (E_a) of monomolecular radical reactions of thermal decomposition. It is assumed[1] that the enthalpy of backward process (formation of a molecule from radicals) is zero. For such compounds as polynitroalkanes, nitrates, and secondary nitroamines, thermal decomposition proceeds as the monomolecular radical reaction with the dissociation of the $C—NO_2$, $O—NO_2$, or $N—NO_2$ radicals.[2,3] If the enthalpy of the backward reaction of radical association is considered equal to zero, then the dissociation energy of the $R—NO_2$ bond is equal to the activation energy of thermal decomposition

$$D(R—NO_2) = E_a. \qquad (2)$$

It was concluded[4] on the basis of the theory of absolute reaction rates that the difference between D and E_a includes RT and depends on the differences between the heat capacities of the products and reactants in the dissociation reaction and on the differences of the heat capacities of the transition state and initial radicals in recombination. The integrals taken of the heat capacity differences have different signs, and various molecules at certain temperatures exactly obey Eq. (2).The differences between D and E_a can be estimated from the statistical mechanics equations if the parameters of geometric structures, internal rotation barriers, and vibration frequencies of polyatomic particles are known. These calculations are rather difficult for the classes of compounds studied in this work and, hence, we will use Eq. (2).

Equations (1) and (2) are used for the determination of unknown formation enthalpies of radicals and dissociation energies of bonds. However, inaccuracies of the data on the thermal decomposition kinetics, as well as on other reactions, can vary in a wide range depending on the conditions of the reactions and analytical methods used.

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In many cases, the determination of the primary act of decomposition to radicals is impeded by secondary reactions or reaction proceeding *via* other mechanisms,[2,3] which results in discrepancy of data obtained by independent authors. In these cases, the method for determination of most reliable values is Eq. (1) in which experimental values of formation enthalpies of compounds in the gas phase and tabulated values of formation enthalpies of radicals are used. The formation enthalpies of radicals usually have maximum inaccuracy (≥2 kcal mol^{-1}). For example, an analysis of the simplest methylamine radicals[5] showed that for the $^{\cdot}NMe_2$ radical the formation enthalpy values obtained by independent authors ranged from 29.4 to 39.0 kcal mol^{-1}, and those for $^{\cdot}NHMe$ range from 29.4 to 45.4 kcal mol^{-1}. None of the studies propose objective quantitative criteria that would allow one to choose the most reliable values. The calculations by Eq. (1) provide reliable values of the formation enthalpies of radicals and dissociation energies of bonds only if the corresponding kinetic and thermochemical reference data are available.

We will try to reveal what properties of molecules and their functional groups make it possible to calculate the bond dissociation energies with allowance for reliable experimental data. These energy characteristics of compounds can be precision experimental thermochemical properties. Presently there is a large database of experimental data (more than 100 substances) on formation enthalpies of the compounds with energy-saturated groups, including those with C—NO_2 groups, in the standard state and in the gas phase for which inaccuracies do not exceed 1—2 kcal mol^{-1}.

In our studies, we propose the procedure of calculation of the bond dissociation energies and formation enthalpies of radicals, including polyradicals. The procedure is based on the determination of the energy properties of functional groups: substitution enthalpies of hydrogen atoms in the molecule or radical and for functional groups and energies of nonvalent interaction of the functional groups. The background for calculations are the precision experimental data (combustion and formation enthalpies in the standard state and in the gas phase and atomization enthalpies). The bond dissociation energies are determined from the analysis of the thermochemical characteristics, and the formation enthalpies of the corresponding radicals are calculated by Eq. (1). The bond dissociation energies obtained from the thermochemical calculation are compared with the results of kinetic experiments.

Enthalpic properties of nitromethanes

Nitro derivatives of methane are parent compounds of the class of alkane nitro derivatives. Particular carbon atoms with different numbers of nitro groups are introduced into the composition of energy-saturated compounds, because the introduction of nitro groups enhances the oxygen balance of the molecules. Nitromethyl radicals are intermediates of many reactions of synthesis or decomposition of components of explosives, blasting powders, and rocket fuels. Formation enthalpies of radicals are necessary for calculations of reaction enthalpies and, correspondingly, prediction of the most probable mechanisms of these reactions. Evidently, the thermochemical values for these compounds and radicals should be determined with minimum errors, accessible by the modern calorimetric technique, which is developed for studies of energy-saturated compounds. Therefore, in spite of many earlier works, including our studies,[6—8] on thermochemistry of nitromethane derivatives, additional measurements of the characteristics of these substances were performed in the present study.

Control experiments were carried out for the samples in which, according to the data of cryometric analysis of the melting curves,[8] the total content of impurities does not exceed 0.07 mol.%. The combustion energies were determined on a precision microcalorimeter designed at the Institute of Chemical Physics of the Russian Academy of Sciences.[9] The vapor formation enthalpies were measured on a Calvet microcalorimeter using our procedure,[10] which minimizes the influence of moisture and solvent traces to the utmost extent. Based on the analysis of the obtained and available published data, the average weighed values of enthalpies of combustion, formation, vapor formation, and formation in the gas phase were recommended (Table 1).

Thermochemical calculation

The bond dissociation energies in the nitromethane derivatives and nitromethyl radicals were calculated on the basis of the energies of nonvalent interactions of the functional groups, which were obtained from a comparison of the contributions of the nitro groups to the atomization enthalpies of polysubstituted compounds with the

Table 1. Thermochemical characteristics of the nitromethane derivatives (kcal mol^{-1})*

Compound	$-\Delta H^\circ_c$(c)	ΔH°_f(c)	ΔH_v	ΔH°_f(g)
Nitromethane (liquid)	169.5±0.2	−27.0±0.2	9.2±0.1	−17.8±0.2
Dinitromethane (liquid)	137.3±0.2	−25.1±0.2	15.9±0.2	−9.2±0.3
Trinitromethane (crystal)	117.4±0.2	−10.8±0.2	16.5±0.2	5.7±0.3
Tetranitromethane (liquid)	103.2±0.4	9.1±0.4	10.6±0.1	19.7±0.4

* The enthalpies of combustion in the standard state (ΔH°_c(c)), enthalpies of formation in the standard state (ΔH°_f(c)), enthalpies of vaporization (ΔH_v), and enthalpies of formation in the gas phase (ΔH°_f(g)) are presented.

contribution of the nitro group to the atomization enthalpy of monosubstituted molecules or radicals. The results obtained for the dissociation energy of bonds were compared with the available kinetic data. The formation enthalpies of radicals were further determined by Eq. (1).

The dissociation energy of the C—NO_2 bond in nitromethane calculated by Eq. (1) from the formation enthalpy of the radical $^{\cdot}CH_3$ (34.9±0.2 kcal mol^{-1}),[4] NO_2 (7.9±0.1 kcal mol^{-1}),[11] and nitromethane (−17.8±0.2 kcal mol^{-1}) is 60.6±0.3 kcal mol^{-1} (Table 2). The error of the dissociation energy of bond is indicated in this work when this value is calculated with allowance for the tabulated data and experimental formation energy. The activation energy of the thermal decomposition with NO_2 elimination at the first stage is 54.2—59.7 kcal mol^{-1} according to the kinetic data of different authors.[2,3] The most thorough kinetic measurements agree satisfactorily with the value obtained by Eq. (1).

The energy of substitution of the hydrogen atom for the nitro group was calculated from the equation

$$P_1(1) = \Delta H_{at}(MeNO_2) - \Delta H_{at}(CH_4), \quad (3)$$

where $P_1(1)$ is the energy of substitution of the hydrogen atom for the nitro group in methane, and $\Delta H_{at}(MeNO_2)$ and $\Delta H_{at}(CH_4)$ are the enthalpies of atomization of nitromethane and methane. The enthalpies of atomization are the values inverse to the formation enthalpies of compounds from atoms and are equal to the sum of the enthalpies of formation of elements comprising the molecule and the enthalpy of formation of the substance in the gas phase. For the enthalpies of formation of elements C, H, N, and O in the gas phase 171.30±0.11, 52.10±0.001, 113.0±0.1, 59.56±0.02 kcal mol^{-1}, respectively, were accepted.[12] With allowance for these values and formation enthalpies in the gas phase of nitromethane (−17.8±0.2 kcal mol^{-1}) and methane (−17.8±0.1 kcal mol^{-1}),[13] the effect of hydrogen atom substitution for the nitro group in nitromethane was 180.0 kcal mol^{-1}.

Table 2. The bond dissociation energies in nitromethanes and nitromethyl radicals (kcal mol^{-1})

Compound	D/kcal mol^{-1}	
	C—H	C—NO_2
CH_4	104.8	—
CH_3NO_2	104.8	60.6
$CH_2(NO_2)_2$	104.0	52.0
$CH(NO_2)_3$	100.0	44.6
$C(NO_2)_4$	—	41.8
$^{\cdot}CH_3$	110.5	—
$^{\cdot}CH_2NO_2$	110.3	66.3
$^{\cdot}CH(NO_2)_2$	109.0	58.3 (58.5)*
$^{\cdot}C(NO_2)_3$	—	53.9 (55.4)*
$^{\cdot\cdot}CHNO_2$	101.4	56.8
$^{\cdot\cdot}CH_2$	100.8	—
$^{\cdot\cdot}C(NO_2)_2$	—	50.7 (48.8)*
$^{\cdot\cdot\cdot}CNO_2$	—	36.8 (37.2)*

* Calculated under assumption that the presence of the nitro group exerts no effect on the dissociation energies of C—H bonds in nitromethyl radicals.

The energy of substitution of two hydrogen atoms for the nitro group ($P_1(2)$) for dinitromethane relative to methane calculated from the equation of type (3) was 351.4 kcal mol^{-1}. This value is 8.6 kcal mol^{-1} lower than $2P_1(1)$. We believe that this difference in substitution energies is due to the nonvalent interaction (repulsion) of the nitro groups and changes the bonds in the dinitromethane molecule compared to those in the nitromethane molecule. The substitution energy changed because of the nonvalent interaction of the bulky electronegative nitro groups, which weakens their bond with the carbon atom. In this case, the detachment of one nitro group from the dinitromethane molecule should occur with the energy 8.6 kcal mol^{-1} lower than that of the nitro group elimination from the nitromethane molecule. Based on this assumption, the bond dissociation energy for C—NO_2 in dinitromethane can be estimated as 52.0 kcal mol^{-1} (see Table 2). This value corresponds to the kinetic data[2] (52.8 kcal mol^{-1}). Using the bond dissociation energy for C—NO_2 (52.0 kcal mol^{-1}), one can calculate the formation enthalpy of the nitromethyl radical $CH_2NO_2^{\cdot}$ (34.9 kcal mol^{-1}) by Eq. (1), and then the bond dissociation energy for C—H in nitromethane can be calculated (104.8 kcal mol^{-1}). The latter coincides with the dissociation energy of the C—H bond in methane (104.8 kcal mol^{-1}).

The enthalpy of atomization of trinitromethane is 914.0 kcal mol^{-1}. The substitution enthalpy of three hydrogen atoms in methane for the nitro groups ($P_1(3)$) was obtained as equal to 516.5 kcal mol^{-1}. The energy of nonvalent interactions in trinitromethane calculated by the expression $3P_1(1) - P_1(3)$ was 23.5 kcal mol^{-1}. Three pair interactions of the nitro groups in trinitromethane contribute to this energy, and then 2/3 of this value or 15.7 kcal mol^{-1} accounts for the interaction of one nitro group with two adjacent nitro groups. This value should be the difference between the bond dissociation energy for C—NO_2 in trinitromethane and that in nitromethane. Thus, the bond dissociation energy for C—NO_2 in trinitromethane is equal to 44.6 kcal mol^{-1} (see Table 2), which is satisfactorily consistent with the kinetic data by the activation energy of thermal decomposition of trinitromethane (42.3 kcal mol^{-1}).[2,3] The bond dissociation energy for C—NO_2 in trinitromethane (44.6 kcal mol^{-1}) was used to calculate the formation enthalpy of the $CH(NO_2)_2^{\cdot}$ radical (42.7 kcal mol^{-1}) by Eq. (1). According to Eq. (1), the bond dissociation energy for C—H in dinitromethane is 104.0 kcal mol^{-1}, which is well consis-

tent with the bond dissociation energies for C—H in nitromethane and methane (104.8 kcal mol^{-1}).

For tetranitromethane the formation enthalpy in the gas phase is 19.7±0.4 kcal mol^{-1} (see Table 1) and the substitution enthalpy of four nitro groups ($P_1(4)$) is 682.4 kcal mol^{-1}, which is 37.6 kcal mol^{-1} lower than $4P_1(1)$ (720.0 kcal mol^{-1}). The value of 37.6 kcal mol^{-1} is obtained due to six pairs of NO_2—C—NO_2 interactions in tetranitromethane. Each nitro group interacts with three adjacent groups with an energy of 18.8 kcal mol^{-1} and, hence, the bond dissociation energy for C—NO_2 in tetranitromethane should be 18.8 kcal mol^{-1} lower than that in nitromethane, that is, 41.8 kcal mol^{-1}. The activation energy of tetranitromethane thermal decomposition ranges from 38.2 to 40.9 kcal mol^{-1},[2,3] which satisfactorily agrees with a value of 41.8 kcal mol^{-1}. The formation enthalpy of $C(NO_2)_3^{\cdot}$ calculated by Eq. (1) is 53.6 kcal mol^{-1}, and the bond dissociation energy for C—H in trinitromethane is 100.0 kcal mol^{-1}.

An analysis of the bond dissociation energies for C—H in mono-, di-, and trisubstituted halides and the C—H bonds in methylhalide mono- and biradicals[4] showed that for both the mono- and disubstituted molecules and mono- or biradicals the dissociation energies of the C—H bonds are similar to the bond dissociation energy for C—H in methane and its radicals within the error range. It follows from the results of the present study that the dissociation energies of the C—H bonds in mono- and dinitromethane derivatives coincide with the bond dissociation energy for C—H in methane. It can be assumed that the bond dissociation for C—H in mono- and dinitro derivatives of methyl mono- and biradicals is also equal to the dissociation energy of the C—H bonds in the methyl mono- and biradicals. The bond dissociation energies for C—H in the radicals $^{\cdot}CH_3$, $^{\cdot\cdot}CH_2$, and $^{\cdot\cdot\cdot}CH$ are 110.5, 100.8 (see Ref. 4), and 81.4 kcal mol^{-1} (see Ref. 14), respectively. Let us assume that the presence of nitro groups (as well as halogen atoms) exerts no effect on the dissociation energies of the C—H bonds in the nitromethyl radicals. Then, based on the dissociation energies for the nitromethyl mono- and biradicals, one can calculate the formation enthalpies of the radicals $^{\cdot\cdot}CHNO_2$, $^{\cdot\cdot}C(NO_2)_2$, and $^{\cdot\cdot\cdot}CNO_2$: 93.3, 101.1, and 142.0 kcal mol^{-1}. In this case, the dissociation energies of the C—NO_2 bonds in the radicals $^{\cdot}CH(NO_2)_2$, $^{\cdot}C(NO_2)_3$, $^{\cdot\cdot}C(NO_2)_2$, and $^{\cdot\cdot\cdot}CNO_2$ were obtained equal to 58.5, 55.4, 48.8, and 37.2 kcal mol^{-1}, respectively (see Table 2).

In another variant, the bond dissociation energies in the nitromethyl radicals and the formation enthalpies of the radicals can be calculated (as in the case of the nitromethyl monoradicals) only from the tabulated values of the enthalpies of formation in the gas phase of the methyl mono-, bi-, and triradicals and the carbon atoms and the energies of nonvalent interaction of nitro groups in the nitromethyl radicals.

According to Eq. (1) and published data,[4] the dissociation energy of C—NO_2 in $^{\cdot}CH_2NO_2$ is 66.3±2.0 kcal mol^{-1} (see Table 2). The enthalpy of atomization of the $^{\cdot}CH_2NO_2$ radical is 472.7 kcal mol^{-1}, and that of the $^{\cdot}CH_3$ radical is 292.7 kcal mol^{-1}. The substitution energy of the hydrogen atom for the nitro group in the nitromethyl radical is determined using the equation of type (3): 180.0 kcal mol^{-1}. In the radical $^{\cdot}CH(NO_2)_2$ the substitution energy of two hydrogen atoms for the nitro groups relative to the methyl radical is 352.0 kcal mol^{-1}, whereas the doubled substitution energy of hydrogen for the nitro group in the $^{\cdot}CH_2NO_2$ radical is 360 kcal mol^{-1}. Thus, the energy of nonvalent interaction of the nitro groups in the radical $^{\cdot}CH(NO_2)_2$ is 8.0 kcal mol^{-1}. This value is the difference between the dissociation energies of the C—NO_2 bond in $^{\cdot}CH(NO_2)_2$ and $^{\cdot}CH_2NO_2$. The bond dissociation energy for C—NO_2 in $^{\cdot}CH_2NO_2$ (58.3 kcal mol^{-1}) is similar to a value of 58.5 kcal mol^{-1} obtained by the calculation by the first variant. According to Eq. (1), the formation enthalpy of the $^{\cdot\cdot}CHNO_2$ radical is 93.1 kcal mol^{-1} rather than 93.3 kcal mol^{-1}, as it follows from the calculation assuming no effect of the nitro groups on the dissociation energy of the C—H bond.

The atomization enthalpy of the $^{\cdot}C(NO_2)_3$ radical is 814.1 kcal mol^{-1}. The substitution energy of three hydrogen atoms in the methyl radical for three nitro groups by the equation of type (3) is 521.4 kcal mol^{-1}. This value is 18.6 kcal mol^{-1} lower than the tripled values of the energy of hydrogen substitution for the nitro group in the $^{\cdot}CH_2NO_2$ radical and is due to three pair interaction energies of the nitro groups in the trinitromethyl radical. Each nitro group in the $^{\cdot}C(NO_2)_3$ radical interacts only with two nitro groups, *i.e.*, its interaction energy is 2/3 of the total value of 18.6 kcal mol^{-1}, being 12.4 kcal mol^{-1}. Due to this value, the dissociation energy of the C—NO_2 bond in the $^{\cdot}C(NO_2)_3$ radical (53.9 kcal mol^{-1}) is lower than that in the radical $^{\cdot}CH_2NO_2$. This value agrees satisfactorily with that calculated by the first variant (55.4 kcal mol^{-1}). Based on the energy of the C—NO_2 bond calculated by Eq. (1) (53.9 kcal mol^{-1}), we determined the enthalpy of formation of the biradical $^{\cdot\cdot}C(NO_2)_2$ (99.6 kcal mol^{-1}), which only slightly differs from the value 101.1 kcal mol^{-1}, obtained by the calculation according to the first variant.

The atomization enthalpy of the biradical $^{\cdot\cdot}CHNO_2$, obtained on the basis of its enthalpy of formation of 93.1 kcal mol^{-1}, is equal to 362.1 kcal mol^{-1}. The atomization enthalpy of the biradical $^{\cdot\cdot}CH_2$ is 182.2 kcal mol^{-1}. The substitution energy of the hydrogen atom in the methyl biradical for the nitro group by the equation of type (3) is obtained equal to 179.9 kcal mol^{-1}. The difference between the doubled substitution energy of the hydrogen atom for the nitro group in the methyl biradical and the substitution energy of two hydrogen atoms for the nitro groups to form the $^{\cdot\cdot}C(NO_2)_2$ biradical is 6.1 kcal mol^{-1}.

The enthalpies of formation of the radical $^{\cdot\cdot\cdot}CH$ (142.0±1.0 kcal mol^{-1})[14] and $^{\cdot\cdot}CHNO_2$ (93.1 kcal mol^{-1}) allow one to determine the energy of the C—NO_2 bond in $^{\cdot\cdot}CHNO_2$, which is equal to 56.8 kcal mol^{-1}. Based on this value and taking into account the interaction of the nitro groups, we found that the dissociation energy of the C—NO_2 bond in the $^{\cdot\cdot}C(NO_2)_2$ biradical is 50.7 kcal mol^{-1}, which agrees satisfactorily with the above obtained value of 48.8 kcal mol^{-1}. The formation enthalpy of the $^{\cdot\cdot\cdot}CNO_2$ radical is 142.4 kcal mol^{-1}, and the bond dissociation energy for C—NO_2 in the triradical $^{\cdot\cdot\cdot}CNO_2$ is 36.8 kcal mol^{-1}, which agrees well with the value of 37.2 kcal mol^{-1} calculated ignoring the effect of the nitro groups on the dissociation energy of the C—H bond.

The dissociation energies of the C—H and C—NO_2 bonds in the nitromethane derivatives and methyl and nitromethyl radicals are given in Table 2.

Thus, the calculations of the dissociation energies of the C—NO_2 bonds in the nitromethyl radicals and formation enthalpies of the nitromethyl bi- and triradicals by two independent methods showed good agreement between the obtained values and confirmed reliability of assumptions accepted in the calculations. We consider to be more reliable the bond dissociation energies and enthalpies of formation of radicals calculated by the variant that uses only the tabulated formation enthalpies of radicals and energies of nonvalent interactions of nitro groups. At the same time, good agreement between the calculated dissociation energies of bonds and formation enthalpies confirms that the presence of nitro groups and halogen atoms exerts no effect, in fact, on the bond dissociation energies for C—H in the nitromethyl radicals relative to the dissociation energies of these bonds in the methyl radicals.

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