Bond energies and the enthalpies of formation of mono- and polyradicals in nitroalkanes

2*. Nitro derivatives of ethane and propane

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Based on the experimental results and the published data, the enthalpies of formation of ethane and propane nitro derivatives were obtained for both the standard state and gas phase. The bond dissociation energies of the ethane and propane nitro derivatives were calculated using the enthalpies of atomization and the energies of nonvalent interactions of nitro groups. The calculated values were compared with the kinetic data on thermal decomposition. The bond dissociation energies in radicals of the ethane and propane nitro derivatives were also calculated using the enthalpies of atomization and the energies of nonvalent interactions of nitro groups. Regularities of changes in the bond dissociation energies of the ethane and propane nitro derivatives and their radicals were established.

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

Nitroalkyl radicals are intermediates of many reactions of synthesis and decomposition of high-energy compounds. Knowledge of the enthalpies of radical formation is necessary for calculations of enthalpies of chemical reactions and for prediction of the most probable reaction mechanisms. The bond dissociation energies and the enthalpies of formation of radicals and molecules are related by the following equation

$$D(\mathrm{R}^1\text{—}\mathrm{R}^2) = \Delta H_f^\circ(\mathrm{R}^1) + \Delta H_f^\circ(\mathrm{R}^2) - \Delta H_f^\circ(\mathrm{R}^1\mathrm{R}^2), \qquad (1)$$

where $D(\mathrm{R}^1\text{—}\mathrm{R}^2)$ is the dissociation energy of the compound $\mathrm{R}^1\mathrm{R}^2$ to the radicals R^1 and R^2; $\Delta H_f^\circ(\mathrm{R}^1)$, $\Delta H_f^\circ(\mathrm{R}^2)$, and $\Delta H_f^\circ(\mathrm{R}^1\mathrm{R}^2)$ are the enthalpies of formation of the radicals R^1 and R^2, and compound $\mathrm{R}^1\mathrm{R}^2$ in the gas phase under standard conditions, respectively. In the present work, it is assumed that the dissociation energy of the $\mathrm{R—NO_2}$ bond is equal to the activation energy of monomolecular thermal decomposition of nitrogen-containing compounds proceeding by a radical mechanism (E_a).[1] Equation (1) is used for determining unknown enthalpies of formation of radicals and bond dissociation energies. The enthalpies of formation of radicals are usually determined with the largest error (≥2 kcal $\mathrm{mol^{-1}}$). Calculations using Eq. (1) give reliable values of ΔH_f° and D if the corresponding kinetic and thermodynamic data are available.

Previously,[1] it was proposed to calculate changes in $\mathrm{R—NO_2}$ bond dissociation energies in polyfunctional compounds using the changes in the contributions of nitro groups to the enthalpy of atomization relative to the corresponding contributions in mononitroalkane, in particular, nitromethane. The term "contribution of nitro group to the enthalpy of atomization" means the energy (enthalpy) of replacement of hydrogen atoms in an alkane by nitro groups rather than the contributions of nitro groups to the enthalpy of atomization, which are determined from calculations. In this case, only the experimental data for the same molecular structure are used, what permits minimization of the calculation error. For the nitro derivatives of methane, the kinetic data are in reasonable agreement with the values calculated in Ref. 1. The results of similar calculations for radicals also agree with the enthalpies of formation of methane polyradicals.[1] In the present work, the procedure used for $D(\mathrm{R—NO_2})$ calculations for molecules and radicals of the nitro derivatives of ethane and propane is similar to that described earlier.[1] The dissociation energies of $\mathrm{R—NO_2}$ bonds in mononitroalkanes are determined from Eq. (1) using the experimental values of the enthalpies of formation of these substances in the gas phase and the reference data on the

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* For Part 1, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 870—874, May, 2010.

enthalpies of formation of the $^{\bullet}NO_2$ and alkyl radicals. The bond dissociation energies are determined by analyzing the thermochemical characteristics (enthalpies of replacement of hydrogen atoms by nitro groups in the enthalpies of atomization and the energies of nonvalent interaction of nitro groups) and then the enthalpies of formation of the corresponding radicals in polynitro derivatives of ethane and propane are calculated using Eq. (1). The D values obtained from thermochemical calculations are compared with the data of kinetic studies, *viz.*, E_a values. There are a few compounds which decompose by the monomolecular radical mechanism. These are nitroalkanes, nitrates, secondary nitramines, peroxides, and some other compounds containing bonds whose energies are considerably different from those of other bonds. Unfortunately, the decomposition of nitro compounds usually partially proceeds by the molecular mechanism involving the nitro-nitrite rearrangement;[2] the reaction rate can also be influenced by catalysis by the decomposition products. The minimum error in kinetics measurements is approximately 5%; however, more often it is 10% and higher. The kinetics of thermal decomposition of nitroalkanes is studied in the temperature interval from 250 to 600 and even 900 °C, and reduction of the data obtained at such temperatures to the standard values (at 25 °C) is a complicated problem due to the absence of the temperature dependences of the corresponding heat capacities of radicals and molecules in the gas phase. Therefore, a comparison of the bond dissociation energies with the activation energies of thermal decomposition is semiquntitative in character. If these values differ by 2—3 kcal mol^{-1}, they can be considered as being in satisfactory agreement.

The enthalpy properties of nitroethanes and nitropropanes

In the present work, additional measurements for ethane and propane nitro derivatives were performed using samples with the total impurity content of at most 0.05 mol.% (according to the data of cryometric analysis of the melting curves by the ampoule method) (see Ref. 3). Additional measurements of combustion energies were performed on a modified high-precision semi-microcalorimeter designed at the Institute of Chemical Physics, Russian Academy of Sciences (see Ref. 4) and certified at the D. I. Mendeleev Scientific and Research Institute for Metrology (VNIIM). The instrument has a reduced energy equivalent (531.14±0.02 cal deg^{-1}), which is important for studies of high-energy compounds or compounds available only in small amounts. In addition, the small experimental error allows combustion of small weighs in the presence of additional substances and obtaining the results with satisfactory measurement error. The root-mean-square deviation (RMSD) is approximately 0.004%; multiplication by the Student coefficient for a 95% probability gives a value of ~0.01% (calibration with a benzoic acid reference sample on certification at the VNIIM). Usually, when performing combustion experiments, the combustion products are analyzed for CO_2 content. This is a necessary step in calorimetric experiments on combustion of gases because the weight of the burned substance is calculated from the weight of carbon dioxide formed. When the liquids and solids are burned, analysis for CO_2 content is performed to confirm the completeness of combustion and the purity of the substance on the qualitative level. When additional

Table 1. Thermochemical characteristics of the ethane and propane nitro derivatives*

Compound	$\Delta H_f°$(st)	ΔH_v	$\Delta H_f°$(g)
		kcal mol^{-1}	
Nitroethane (liquid)	−34.4±0.1	9.9±0.1	−24.5±0.2
1,1-Dinitroethane (liquid)	−35.7±0.1	14.6±0.1	−21.1±0.2
1,2-Dinitroethane (liquid)	−42.6±0.1	19.5±0.2	−23.1±0.3
1,1,1-Trinitroethane(crystal)	−27.0±0.2	17.2±0.1	−9.8±0.3
Hexanitroethane (crystal)	19.2±0.1	14.8±0.1	34.0±0.2
1-Nitropropane (liquid)	−40.1±0.2	10.2±0.1	−29.7±0.3
2-Nitropropane (liquid)	−43.1±0.1	9.8±0.1	−33.3±0.2
1,3-Dinitropropane (liquid)	−49.5±0.1	17.1±0.1	−32.4±0.2
1,1-Dinitropropane (liquid)	−40.2±0.1	14.2±0.1	−26.0±0.2
2,2-Dinitropropane (amorphous)	−45.7±0.1	13.7±0.1	−32.1±0.2
1,1,1-Trinitropropane (liquid)	−28.9±0.1	14.8±0.1	−14.1±0.2
1,1,1,2,2-Pentanitropropane (crystal)	−13.7±0.1	18.5±0.2	4.8±0.3

* The enthalpies of formation in the standard state ($\Delta H_f°$(st)), the enthalpies of vaporization (ΔH_v), and the enthalpies of formation in the gas phase ($\Delta H_f°$(g)) are listed.

substances are used (cotton thread for ignition, a polyethylene or lavsan film for combustion of liquids, benzoic acid, Nujol, dimethyl phthalate), analysis for CO_2 content as an indicator of the completeness of combustion and qualitative confirmation of purity of the product becomes not informative. Calorimeters at the ICP RAS are characterized by a RMS deviation of $(3-5) \cdot 10^{-3}\%$ in a series of five or six runs; therefore, traces of incomplete combustion in some runs will be detected immediately. In this connection, is not necessary to perform analysis for CO_2 content (the error is $(3-5) \cdot 10^{-2}\%$) in the experiments on modern combustion calorimeters at the ICP RAS, which are certified at the VNIIM.

The enthalpies of vaporization were measured on a Calve microcalorimeter by the ampoule method,[5] which allows one to minimize the influence of traces of water, solvents, low-volatile, and nonvolatile admixtures present in the sample.

The results of these measurements (two or three experiments on combustion and vaporization for each sample) were added to the previously obtained results.[3,6] Treatment of the combined data array gave the weighted mean values of the enthalpies of formation in the standard state and in the gas phase. A handbook[7] includes the enthalpies of formation of nitroalkanes obtained before 1970; unfortunately, our data on the enthalpies of formation in the standard state and the enthalpies of vaporization and sublimation of nitroalkanes published in a monograph[8] and a review[3] were not included in that book.

The thermochemical data for the ethane and propane nitro derivatives are listed in Table 1.

Thermochemical calculation

In the present paper, the bond dissociation energies in polyfunctional nitro compounds and their radicals were calculated based on the enthalpies of replacement of hydrogen atoms by functional (nitro) groups and the energies of nonvalent interactions of nitro groups. These values are determined directly from thermochemical data with the corresponding errors. The energy of replacement of a hydrogen atom by a nitro group in, for example, ethane is calculated from the equation

$$P_1(1) = \Delta H_{at}(C_2H_5NO_2) - \Delta H_{at}(C_2H_6), \qquad (2)$$

where $P_1(1)$ is the energy of replacement of hydrogen atom by a nitro group in ethane and $\Delta H_{at}(C_2H_5NO_2)$ and $\Delta H_{at}(C_2H_6)$ are the enthalpies of atomization of nitroethane and ethane, respectively.

The energies of nonvalent interactions of functional groups are obtained by comparing the energy of replacement of hydrogen atom by a nitro group in ethane (propane) with the same value for polynitroethane (polynitropropane) using equations of the type

$$P_1(2) = \Delta H_{at}(C_2H_4(NO_2)_2) - \Delta H_{at}(C_2H_6), \qquad (3)$$

where $P_1(2)$ is the energy of replacement of two hydrogen atoms by two nitro groups in ethane, $\Delta H_{at}(C_2H_4(NO_2)_2)$ and $\Delta H_{at}(C_2H_6)$ is the enthalpies of atomization of dinitroethane and ethane, respectively.

The energies of replacement of hydrogen atoms by nitro groups in radicals of nitroethanes (nitropropanes) and the energies of nonvalent interactions of nitro groups in radicals are calculated using equations of the types

$$P_1(1)^{\bullet} = \Delta H_{at}({}^{\bullet}C_2H_4NO_2) - \Delta H_{at}({}^{\bullet}C_2H_5), \qquad (4)$$

$$P_1(2)^{\bullet} = \Delta H_{at}({}^{\bullet}C_2H_3(NO_2)_2) - \Delta H_{at}({}^{\bullet}C_2H_5), \qquad (5)$$

where $P_1(1)^{\bullet}$ and $P_1(2)^{\bullet}$ are the energies of replacement of one and two hydrogen atoms by nitro groups, respectively; and $\Delta H_{at}({}^{\bullet}C_2H_4NO_2)$, $\Delta H_{at}({}^{\bullet}C_2H_5)$, and $\Delta H_{at}({}^{\bullet}C_2H_3(NO_2)_2)$ are the enthalpies of atomization of the radicals ${}^{\bullet}C_2H_4NO_2$, ${}^{\bullet}C_2H_5$, and ${}^{\bullet}C_2H_3(NO_2)_2$, respectively.

The $C-NO_2$ bond dissociation energy in nitroethane calculated by Eq. (1) using the enthalpies of formation of the ${}^{\bullet}C_2H_5$ radical (27.0±2.0 kcal mol^{-1} (see Ref. 10)), NO_2 (7.9±0.1 kcal mol^{-1} (see Ref. 7)), and nitroethane (−24.5±0.2 kcal mol^{-1}) is 59.4±2.1 kcal mol^{-1}. The error in determination of a bond dissociation energy is listed when this energy is calculated using the reference data and the experimental enthalpies of formation. According to kinetic data, the activation energy of thermal decom-

Table 2. The $C-NO_2$ bond dissociation energies (D) in ethane and propane nitro derivatives and in their radicals*

Compound	D/kcal mol^{-1}
$CH_3CH_2-NO_2$	59.4±2.0 (55.6)
$CH_3CHNO_2-NO_2$	51.6 (47.1)
$CH_3C(NO_2)_2-NO_2$	43.8 (43.2)
$NO_2CH_2CH_2-NO_2$	53.6
$(NO_2)_3CC(NO_2)_2-NO_2$	32.6 (35.8)
$CH_3C^{\bullet}H-NO_2$	72.8
$CH_3C^{\bullet}NO_2-NO_2$	64.9
${}^{\bullet}CH_2CH_2-NO_2$	57.0
$CH_3C^{\bullet\bullet}-NO_2$	61.8
$CH_3CH_2CH_2-NO_2$	58.6±2.0 (58.5)
$(CH_3)_2CH-NO_2$	60.3±2.6 (54.0)
$CH_3CH_2CHNO_2-NO_2$	50.2 (48.0)
$(CH_3)_2CNO_2-NO_2$	50.8 (50.5)
$CH_3CH_2C(NO_2)_2-NO_2$	42.0 (42.3)
$NO_2CH_2CH_2CH_2-NO_2$	56.6
$CH_3CH_2C^{\bullet}H-NO_2$	73.1
$(CH_3)_2C^{\bullet}-NO_2$	76.7
$CH_3CH_2C^{\bullet}NO_2-NO_2$	64.7
$CH_3CH_2C^{\bullet\bullet}-NO_2$	63.1

* The activation energies of thermal decomposition (E_a) of corresponding ethane and propane nitro derivatives by the radical mechanism are given in parentheses (see Ref. 2).

position with abstraction of NO_2 in the first stage is 55.6 kcal mol^{-1} (see Ref. 2); this satisfactorily agrees with the value obtained from Eq. (1). The $\Delta H_f°$ values for ethane (-20.1 ± 0.05 kcal mol^{-1}) and propane (-25.0 ± 0.1 kcal mol^{-1}), which are necessary for calculations, were taken from Ref. 10, those for atoms were taken from Ref. 1.

The C—NO_2 bond dissociation energy in 1-nitropropane with inclusion of the enthalpy of formation of $^{\bullet}C_3H_7$ radical (21.0 ± 2.0 kcal mol^{-1} (see Ref. 10)) is 58.6 ± 2.1 kcal mol^{-1} while the activation energy of thermal decomposition is 58.5 kcal mol^{-1} (see Ref. 2). The C—NO_2 bond dissociation energies in the ethane and propane nitro derivatives and in their radicals are listed in Table 2.

As an example, we will calculate the D(C—NO_2) values for 1,1,1-trinitroethane and hexanitroethane which bears the maximum possible number of nitro groups for ethane. The necessary data and the enthalpies of formation of the radicals taken from Ref. 1 are listed in Table 3. In hexanitroethane, one deals with not only short-range nonvalent interactions of nitro groups (NO_2 groups at the same carbon atom), but also long-range ones (NO_2 groups at neighboring carbon atoms). The most reliable kinetics studies were also performed for hexanitroethane. We need the data for 1,1,1-trinitroethane as an intermediate. In accordance to Eq. (2) the energy of replacement of hydrogen atom in ethane by a nitro group is 184.4 kcal mol^{-1}. Next, using Eq. (3), the energy of replacement of three hydrogen atoms by three nitro groups ($P_1(3)$), is found to be equal to 529.8 kcal mol^{-1}. The tripled energy of replacement of hydrogen atom by a nitro group in nitroethane ($3P_1(1)$) is 553.2 kcal mol^{-1} or 23.4 kcal mol^{-1} higher than 529.8 kcal mol^{-1}. The value 23.4 kcal mol^{-1} corresponds to the energy of three nonvalent interactions NO_2—C—NO_2 in 1,1,1-trinitroethane. Each nitro group participates in two such interactions (energy is 15.6 kcal mol^{-1}). This is the difference between D(C—NO_2) for 1,1,1-trinitroethane and nitroethane; thus, the C—NO_2 bond dissociation energy in 1,1,1-trinitroethane is 43.8 kcal mol^{-1}. The activation energy of thermal decomposition is 43.2 kcal mol^{-1} for the gas phase and 42.6 kcal mol^{-1} for the molten state,[2] which is also in good agreement with the value 43.8 kcal mol^{-1}. Using the last value and Eq. (1), one gets $\Delta H_f°(CH_3{}^{\bullet}C(NO_2)_2)$ = 26.1 kcal mol^{-1}. Hence D(C—H) is 99.3 kcal mol^{-1} for 1,1-dinitroethane, which agrees with the data for ethane (99.2 kcal mol^{-1}) and nitroethane (99.2 kcal mol^{-1}).

Table 3. Enthalpies of formation of radicals ($\Delta H_f°$)

Radical	$\Delta H_f°$/kcal mol^{-1}	Radical	$\Delta H_f°$/kcal mol^{-1}
$CH_2NO_2^{\bullet}$	34.9	$CH_3CNO_2^{\bullet\bullet}$	83.1
$CH(NO_2)_2^{\bullet}$	42.8	$CH_3C^{\bullet\bullet\bullet}$	137.0
$C(NO_2)_3^{\bullet}$	53.7	$C(NO_2)_3CNO_2^{\bullet\bullet}$	89.4
$CHNO_2^{\bullet\bullet}$	93.3	$^{\bullet}CH_2CHNO_2^{\bullet}$	67.0
$C(NO_2)_2^{\bullet\bullet}$	99.6	$^{\bullet}CHNO_2CHNO_2^{\bullet}$	68.2
$CNO_2^{\bullet\bullet\bullet}$	142.0	$^{\bullet}CHNO_2C(NO_2)_2^{\bullet}$	76.3
$(NO_2)_3CC(NO_2)_2^{\bullet}$	58.7	$^{\bullet}C(NO_2)_2C(NO_2)_2^{\bullet}$	87.9
$NO_2CH_2CH_2^{\bullet}$	22.6	$C(NO_2)_3C^{\bullet\bullet\bullet}$	126.2
$CH_3CH_2C^{\bullet\bullet}H$	81.5	$^{\bullet}C(NO_2)_2C^{\bullet\bullet\bullet}$	162.1
$CH_3CHNO_2^{\bullet}$	22.6	$^{\bullet\bullet}CNO_2C^{\bullet\bullet\bullet}$	219.1
$CH_3C(NO_2)_2^{\bullet}$	26.1	$(CH_3)_2C^{\bullet}NO_2$	10.7
$CH_3CH_2C^{\bullet}HNO_2$	16.3	$CH_3C(NO_2)_2C^{\bullet}(NO_2)_2$	32.6
$NO_2CH_2CH_2CH_2^{\bullet}$	16.3	$CH_3CH_2C^{\bullet\bullet}NO_2$	76.8
$CH_3CH_2C^{\bullet}(NO_2)_2$	20.0	$CH_3CH_2C^{\bullet\bullet\bullet}$	132.0

The enthalpy of replacement of six hydrogen atoms by nitro groups in ethane ($P_1(6)$) in the formation of hexanitroethane (1025.8 kcal mol^{-1}) is 80.6 kcal mol^{-1} lower than the sum of six values of the enthalpy of replacement of hydrogen atom by a nitro group in nitroethane ($6P_1(1)$). The difference $P_1(6) - 6P_1(1)$ is the sum of the energies of six interactions of nitro groups, which are similar to the interactions in 1,1,1-trinitroethane, and nine long-range interactions. Assuming that nitro groups at the same carbon atom in the hexanitroethane molecule interact with one another with the same energy as in 1,1,1-trinitroethane, one gets 3.76 kcal mol^{-1} for each long-range interaction in hexanitroethane. The total energy of nonvalent interactions of one nitro group with other nitro groups in the hexanitroethane molecule is 26.9 kcal mol^{-1}. The C—NO_2 bond dissociation energy in hexanitroethane should be 26.9 kcal mol^{-1} lower than in nitroethane, or 32.6 kcal mol^{-1}. This equals the C—NO_2 bond dissociation energy (32.7 kcal mol^{-1}) obtained from calculations of the energy of long-range interactions in hexanitroethane using the equation derived in the analysis of $\Delta H_f°$ and the enthalpies of atomization of nitroalkanes[3]

$$7.3 - 0.6(m + n)\ \text{kcal mol}^{-1},$$

where m and n are the numbers of nitro groups at neighbouring carbon atoms. The activation energy of thermal dissociation of hexanitroethane in the gas phase by the radical mechanism is 35.8 kcal mol^{-1} (see Ref. 2). Taking into account the complexity of kinetic experiments and the multistage character of thermochemical calculations (from the C—NO_2 bond dissociation energy in nitroethane), the difference of 3.2 kcal mol^{-1} can be considered as a good agreement for the values of D(C—NO_2) and E_a for hexanitroethane. In addition, the decomposition of hexanitroethane under conditions of pulsed vacuum pyrolysis is accompanied by the formation of tetranitroethylene in high yield.[11] The kinetic parameters of the decomposition correspond to abstraction of NO_2 group from the pentanitroethane radical rather than elimination of N_2O_4 group from hexanitroethane. As it is seen from the data of Table 2, the abstraction energy of NO_2 group from the radicals is considerably higher than from nitroalkanes. Obviously, the decomposition of hexanitroethane is accompanied by abstraction of NO_2

Table 4. The C—C bond dissociation energies (*D*) in ethane and propane nitro derivatives and their radicals

Compound	*D*/kcal mol^{-1}
H_3C-CH_3	89.9
$H_3C-CH_2NO_2$	94.3
$H_3C-CH(NO_2)_2$	98.8
$H_3C-C(NO_2)_3$	98.4
$NO_2H_2C-CH_2NO_2$	92.9
$(NO_2)_3C-C(NO_2)_3$	73.4
$H_3C-C^{\bullet}H_2$	101.2
$H_3C-C^{\bullet}HNO_2$	105.6
$H_3C-C^{\bullet}(NO_2)_2$	108.4
$NO_2H_2C-C^{\bullet}H_2$	105.6
$(NO_2)_3C-C^{\bullet}(NO_2)_2$	94.6
$C_2H_5-CH_3$	86.9
$C_2H_5-CH_2NO_2$	91.6
$C_2H_5-CH(NO_2)_2$	95.8
$C_2H_5-C(NO_2)_3$	94.8
$CH_3-CHNO_2CH_3$	90.8
$CH_3-C(NO_2)_2CH_3$	93.1
$NO_2CH_2-CH_2CH_2NO_2$	89.9
$CH_3-C(NO_2)_2C(NO_2)_3$	88.8
$C(NO_2)_3-C(NO_2)_2CH_3$	75.0
$H_3C-C^{\bullet\bullet}H$	89.4
$H_3C-C^{\bullet\bullet}NO_2$	93.8
$(NO_2)_3C-C^{\bullet\bullet}NO_2$	106.3
$(NO_2)_3C-C^{\bullet\bullet\bullet}$	98.8
$(NO_2)_2C^{\bullet}-C^{\bullet\bullet\bullet}$	108.8
$NO_2C^{\bullet\bullet}-C^{\bullet\bullet\bullet}$	75.5
$H_2C^{\bullet}-C^{\bullet}H_2$	114.9
$H_2C^{\bullet}-C^{\bullet}HNO_2$	119.6
$NO_2HC^{\bullet}-C^{\bullet}HNO_2$	118.4
$NO_2HC^{\bullet}-C^{\bullet}(NO_2)_2$	116.6
$(NO_2)_2C^{\bullet}-C^{\bullet}(NO_2)_2$	111.3
$C_2H_5-C^{\bullet}H_2$	99.3
$C^{\bullet}H_2-CH_2CH_2NO_2$	99.6
$C_2H_5-C^{\bullet}HNO_2$	104.0
$C_2H_5-C^{\bullet}(NO_2)_2$	106.6
$CH_3-C^{\bullet}NO_2CH_3$	107.3
$NO_2CH_2-CH_2C^{\bullet}H_2$	90.3
$C^{\bullet}(NO_2)_2-C(NO_2)_2CH_3$	93.1
$CH_3-C(NO_2)_2C^{\bullet}(NO_2)_2$	90.2
$C_2H_5-C^{\bullet\bullet}H$	87.5
$C_2H_5-C^{\bullet\bullet}NO_2$	92.2

group from both the molecule and pentanitroethane radical, which can result in overestimation of E_a relative to *D*, whereas in other examples the *D* values are somewhat higher than E_a.

The C—NO_2 bond dissociation energies in the ethane and propane nitro derivatives obtained from thermochemical calculations are in satisfactory agreement with the E_a values (see Ref. 2 and Table 2). For 2-nitropropane, the E_a value is 6.3 kcal mol^{-1} lower than *D*, which can be due to the fact that the molecular reaction resulting in HNO_2 and characterized by E_a = 43.5 kcal mol^{-1} (see Ref. 2) contributes largely to thermal decomposition. For *gem*- and 1,1,1-trinitroalkanes, which mainly decompose by the radical mechanism, the *D* and E_a values differ to a much lesser extent (*cf.* 50.8 and 50.5 kcal mol^{-1}, respectively, for 2,2-dinitropropane).

The *D*(C—NO_2) values for nitro radicals are considerably higher than for the corresponding molecules (see Table 2), as well as for the methane nitro derivatives and their radicals.[1]

The enthalpies of formation of radicals of the methane, ethane, and propane nitro derivatives obtained from Eqs (1)—(5) are listed in Table 3. Using these values and the enthalpies of formation of molecules and radicals, the C—C bond dissociation energies in the molecules and radicals of the ethane and propane nitro derivatives were determined (Table 4).

The *D*(C—C) values for the molecules and radicals containing no nitro groups are listed in Table 4 for comparison. The introduction of nitro groups into molecules or radicals strengthen the nearest C—C bond, whereas the long-range interaction of nitro groups weaken this bond; this corresponds to the conclusions concerning the influence of nitro groups on the C—C bond energies in molecules.[2] From the data of Tables 1 and 3 and Eq. (1) it follows that the *D*(C—H) values for the molecules and radicals containing nitrogroups are close to the *D* values of these bonds in the corresponding molecules and radicals having no nitro groups.

Our study of the C—NO_2 bonds in the nitro derivatives of methane, ethane, and propane revealed that the *D* values obtained from thermochemical calculations based on the energies of nonvalent interactions of nitro groups are in satisfactory agreement with the E_a values, which confirms the reliability of the proposed computational method. The *D*(C—NO_2) values for nitroradicals are considerably higher than for the corresponding molecules. The introduction of nitro groups at the carbon atom substantially strengthens the neighboring C—C bond in the molecules and radicals, whereas long-range interactions of nitro groups weaken this bond. The C—H bond dissociation energies in the molecules and radicals containing nitro groups and in the corresponding molecules and radicals having no nitro groups are equal to one another.

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Received January 20, 2009;
in revised form October 23, 2009