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

3.* Nitroalkanes C_4—C_7

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Based on the experimentally determined values and published data, the enthalpies of formation of nitroalkanes C_4—C_7 in the standard state and in the gas phase were recommended. The dissociation energies of bonds in these compounds were determined taking into account the enthalpies of atomization and the energies of nonvalent interactions of nitro groups with one another. The calculated values were compared with the available thermal decomposition kinetic data. The dissociation energies of bonds in C_4—C_7 nitroalkane radicals 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 nitroalkanes C_1—C_7 and their radicals are established.

Key words: thermochemical properties, bond dissociation energies, nonvalent interactions, enthalpies of formation of radicals, enthalpy of atomization, substitution energy, C_4—C_7 nitroalkanes.

Nitroalkyl radicals are intermediates of many synthesis or decomposition reactions of high-energy compounds. The enthalpies of formation of radicals are required to calculate the enthalpies of reactions and, therefore, to predict the most plausible reaction mechanisms. The bond dissociation energies and the enthalpies of formation of radicals and molecules are related by the following equation:

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

where $D(\mathrm{R^1—R^2})$ is the energy of dissociation of the compound R^1R^2 to the radicals R^1 and R^2; $\Delta H^\circ_f(\mathrm{R^1})$, $\Delta H^\circ_f(R^2)$, and $\Delta H^\circ_f(\mathrm{R^1R^2})$ are the enthalpies of formation of the radicals R^1 and R^2 and of compound R^1R^2 in the gas phase under standard conditions. In the present work, it is assumed that the dissociation energy of the R—NO_2 bond in the molecule of a nitro compound, $D(\mathrm{R—NO_2})$, is equal to the activation energy of radical monomolecular decomposition of this nitro compound (E_a).[2] Equation (1) is used for the determination of unknown enthalpies of formation of radicals and bond dissociation energies. The enthalpies of formation of radicals are usually determined with the largest error (at least 2 kcal mol^{-1}). Calculations using Eq. (1) give reliable values of ΔH°_f and D if the corresponding kinetic and thermochemical reference data are available.

Earlier,[1,3] it was proposed to calculate changes in R—NO_2 bond dissociation energies in nitroalkanes using the changes in the contributions of nitro groups to the enthalpy of atomization relative to the corresponding contribution in a mononitroalkane, in particular, nitromethane. In the present work, the contributions of nitro groups to the enthalpy of atomization are meant the energies (enthalpies) 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 within the framework of certain computational schemes. In this case, only the experimental data for the same molecular structure are used; this allows one to minimize the calculation error. Calculations for the nitro derivatives of methane,[3] ethane, and propane[1] led to reasonable agreement between the kinetic data and the values calculated using the method we have proposed. The results of similar calculations for radicals agree with the enthalpies of formation of methane polyradicals.[3]

The method used in the present work to calculate the $D(\mathrm{R—NO_2})$ values for molecules and radicals of nitroalkanes C_4—C_7 is analogous to that used earlier.[1,3] The dissociation energies of R—NO_2 bond in mononitroalkanes are determined from Eq. (1) using the enthalpies of formation of these substances in the gas phase and the tabulated enthalpies of formation of NO_2 and alkyl radicals; these values are reported with the corresponding errors.

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* For Part 2, see Ref. 1.

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The determination of the bond dissociation energies by analyzing the thermochemical properties (enthalpies of replacement of hydrogen atoms by nitro groups in the enthalpies of atomization and the energies of nonvalent interaction of nitro groups) is followed by calculating the enthalpies of formation of corresponding radicals for polynitroalkanes C_4—C_7 using Eq. (1). The *D* values obtained from thermochemical calculations are compared with the kinetic data, *viz.*, the activation energies of monomolecular radical decomposition of nitro compounds with elimination of NO_2 radicals in the first stage. There are not many compounds that decompose by the monomolecular radical mechanism. These include nitroalkanes, nitrates, secondary nitramines, peroxides, and some other substances whose molecules contain certain chemical bonds significantly differing from other bonds in energy characteristics. Unfortunately, the molecular mechanism involving a nitro-nitrite rearrangement also usually contributes to the decomposition of nitro compounds.[4,5] In addition, the reaction rate can be affected by catalysis by the decomposition products. The minimum error in the kinetic measurements is about 5% (more often, it is 10% and larger). The kinetics of thermal decomposition of nitroalkanes was studied in the temperature range from 250 to 600 and even to 900 °C, and reduction of the data obtained at such temperatures to 298 K is a severe problem due to the lack of the temperature dependences of the heat capacities of radicals and molecules in the gas phase.[2] Therefore, a comparison of the bond dissociation energies with the activation energies[2] of thermal decomposition is semiquantitative. These parameters can differ by 2—3 kcal mol^{-1}, which can be treated as reasonable agreement.

Experimental

In the present work, we report the results of the measurements for nitroalkanes C_4—C_7. The samples used in the experiments were purified by fractional sublimation *in vacuo* (10^{-3} Pa) following distillation or recrystallization. The overall concentration of impurities was at most 0.05—0.07 mol.% according to data of cryometric analysis of the melting curves using the ampoule method.[6] The energy of combustion and the enthalpy of vaporization of 1,1,1-trinitrobutane were measured for the first time. The purity of the sample determined from the melting curves was 99.96±0.05 mol.%. The measurement procedure has been described in detail earlier.[1,3] It is noteworthy that the combustion calorimeter[7] is characterized by an energy equivalent of (531.14±0.02 cal deg^{-1}), which is about six times smaller than

Table 1. Thermochemical properties[a] of nitroalkanes C_4—C_7 (kcal mol^{-1})

Compound	Phase[b]	$-\Delta_f H°$	$\Delta_v H$	$-\Delta_f H°(g)$
1-Nitrobutane	l	46.1±0.2	11.5±0.1	34.6±0.2
2-Nitrobutane	l	49.7±0.3	11.1±0.2	38.6±0.4
2-Methyl-2-nitropropane	l[c]	52.1±0.4	10.2±0.1	41.9±0.5
	c	55.1±0.3	13.2±0.1	
1,1-Dinitrobutane	l	47.0±0.2	15.5±0.2	31.5±0.3
1,4-Dinitrobutane	l[d]	56.6±0.4	18.5±0.2	38.1±0.5
	c	59.4±0.3		
1,1,1-Trinitrobutane	l	35.2±0.3	15.9±0.2	19.3±0.4
1,1,1,4-Tetranitrobutane	c	45.7±0.4	24.5±0.3	21.2±0.5
1,1,1,3-Tetranitro-2-methylpropane	c	42.1±0.4	22.5±0.2	19.6±0.5
1,1,3,3-Tetranitrobutane	c	53.4±0.4	23.2±0.3	30.4±0.5
2,2,3,3-Tetranitrobutane	c	43.6±0.3	19.0±0.2	24.6±0.4
1-Nitropentane	l	51.4±0.3	12.2±0.1	39.2±0.3
1,1-Dinitropentane	l	51.6±0.3	15.4±0.2	36.2±0.4
1,1,1-Trinitropentane	l	41.2±0.3	17.2±0.2	24.0±0.4
1,1,1,3,5,5,5-Heptanitropentane	c	37.7±0.4	27.3±0.3	10.4±0.5
2,3-Dimethyl-2,3-dinitrobutane	c	75.0±0.3	18.0±0.2	57.0±0.4
2-Methyl-2,3,3-trinitropentane	c	69.6±0.3	22.0±0.2	47.6±0.4
2,2-Dimethyl-1,1,1,4,4-pentanitrobutane	c	37.7±0.4	27.3±0.3	10.4±0.5

[a] $\Delta_f H°$ is the enthalpy of formation under standard conditions; $\Delta_v H$ is the enthalpy of vaporization; $\Delta_f H°(g)$ is the enthalpy of formation in the gas phase. The standard enthalpies of formation of the compounds under study were calculated using the following numerical values of the enthalpies of formation of combustion products[9]: $\Delta_f H°[CO_2](g) = -94.051 \pm 0.031$ kcal mol^{-1} and $\Delta_f H°[H_2O](l) = -68.315 \pm 0.010$ kcal mol^{-1}.

[b] "l" and "c" denote the liquid and crystalline phase, respectively.

[c] The enthalpy of melting was calculated as the difference between the enthalpy of vaporization and the enthalpy of sublimation.

[d] The numerical value of the enthalpy of melting was taken from Ref. 10.

those of conventional calorimeters, and that the reproducibility of the calibration experiments with a benzoic acid reference sample is 8—10 times higher than that of the domestic and foreign laboratory equipment. This is of great importance in the studies of high-energy or hardly accessible compounds, as well as the small experimental error, which allows one to combust small weighs in the presence of auxiliary substances and to obtain results with a reasonable error. The root-mean-square (RMS) deviation was about 0.004%; multiplication by the Student coefficient for a 95% confidence level gives a value of 0.01% when calibrating with the benzoic acid reference sample in the certification of the instrument at the D. I. Mendeleev Research Institute of Metrology.

The enthalpies of vaporization were measured on a Kalve microcalorimeter using the ampoule method,[8] which allows one to minimize the effect of trace amounts of water, solvents, as well as low-volatile and non-volatile impurities present in the sample. In addition to 1,1,1-trinitrobutane, the enthalpies of sublimation of five other low-volatile polynitroalkanes were measured for the first time (Table 1).

Two to four experiments on combustion and vaporization of samples were carried out for each compound. For 1,1,1-trinitrobutane and five polynitroalkanes mentioned above, six experiments were performed. The results obtained were added to the available data array[6] and joint processing of these data gave the recommended weight-averaged enthalpies of formation in the standard state and in the gas phase. A handbook[11] includes the numerical values of the enthalpies of formation of nitroalkanes in the standard state that have been determined before 1970, but it does not contain our data on the enthalpies of formation in the standard state and on the enthalpies of vaporization and sublimation of nitroalkanes reported in Refs 6 and 12.

The thermochemical properties of nitroalkanes C_4—C_7 are listed in Table 1.

Thermochemical Calculations

Earlier,[1,3] we have proposed a method for calculations of bond dissociation energies in polyfunctional nitro compounds and their radicals using the enthalpies of replacement of hydrogen atoms by functional (nitro) groups in the enthalpies of atomization, the energies of nonvalent interactions in these groups, and the dissociation energies of the C—NO_2 bond in the corresponding mononitroalkanes. These parameters are determined directly from experimental thermochemical data (enthalpies of formation of compounds and atoms in the gas phase) that have some errors. The energies of replacement of a hydrogen atom by a nitro group in, *e.g.*, 1-nitropentane molecule are calculated from the following equation

$$P_1(1) = \Delta_{\text{at}}H(C_5H_{11}NO_2) - \Delta_{\text{at}}H(C_5H_{12}), \qquad (2)$$

where $P_1(1)$ is the energy of replacement of a hydrogen atom by a nitro group in the *n*-pentane molecule, $\Delta_{\text{at}}H(C_5H_{11}NO_2)$ and $\Delta_{\text{at}}H(C_5H_{12})$ are the enthalpies of atomization of 1-nitropentane and *n*-pentane, respectively.

The energies of nonvalent interaction of functional groups are determined by comparing the energies of replacement of a hydrogen atom by a nitro group in the mononitroalkane and corresponding polynitroalkane molecules using Eq. (3). For instance, for 1,1-dinitropentane one has:

$$P_1(2) = \Delta_{\text{at}}H(C_5H_{10}(NO_2)_2) - \Delta_{\text{at}}H(C_5H_{12}), \qquad (3)$$

where $P_1(2)$ is the energy of replacement of two hydrogen atoms by two nitro groups in the 1,1-dinitropentane molecule and $\Delta_{\text{at}}H(C_5H_{10}(NO_2)_2)$ is the enthalpy of atomization of 1,1-dinitropentane.

The energies of replacement of hydrogen atoms by nitro groups in nitroalkane radicals and the energies of nonvalent interaction of nitro groups in radicals are calculated using Eqs (4) and (5) For instance, for *n*-nitropentane radicals one has:

$$P_1(1)^{\cdot} = \Delta_{\text{at}}H(C_5H_{10}NO_2^{\cdot}) - \Delta_{\text{at}}H(C_5H_{11}^{\cdot}), \qquad (4)$$

$$P_1(2)^{\cdot} = \Delta_{\text{at}}H(C_5H_9(NO_2)_2^{\cdot}) - \Delta_{\text{at}}H(C_5H_{11}^{\cdot}), \qquad (5)$$

where $P_1(1)^{\cdot}$ is the energy (enthalpy) of replacement of a hydrogen atom by a nitro group in radicals,

Table 2. Enthalpies of formation of atoms and auxiliary radicals (kcal mol^{-1})*

Radical	$\Delta_f H^\circ$	Radical	$\Delta_f H^\circ$
$Me^{\cdot}$	34.9±0.2	$NO_2CH_2C^{\cdot}H_2$	22.6
$^{\cdot}NO_2$	7.9±0.1	$(NO_2)_3CC^{\cdot}(NO_2)_2$	58.7
$C^{\cdot}$	171.3±0.11	$MeC^{\cdot\cdot}H$	87.5
$H^{\cdot}$	52.1±0.001	$MeC^{\cdot\cdot}NO_2$	82.8
$N^{\cdot}$	113.0±0.1	$C(NO_2)_3C^{\cdot\cdot}NO_2$	102.5
$O^{\cdot}$	59.56±0.02	$C^{\cdot}H_2C^{\cdot}HNO_2$	67.0
$C^{\cdot}H_2NO_2$	34.9	$C^{\cdot}HNO_2C^{\cdot}HNO_2$	68.6
$C^{\cdot}H(NO_2)_2$	42.8	$C^{\cdot}HNO_2C^{\cdot}(NO_2)_2$	77.0
$C^{\cdot}(NO_2)_3$	53.7	$C^{\cdot}(NO_2)_2C^{\cdot}(NO_2)_2$	85.9
$C^{\cdot\cdot}HNO_2$	93.3	$C(NO_2)_3C^{\cdot\cdot\cdot}$	147.4
$C^{\cdot\cdot}(NO_2)_2$	99.6	$C^{\cdot}(NO_2)_2C^{\cdot\cdot\cdot}$	183.3
$C^{\cdot\cdot}H_2$	93.3	$C^{\cdot\cdot}NO_2C^{\cdot\cdot\cdot}$	240.0
$C^{\cdot\cdot\cdot}H$	142.0	$C^{\cdot}H_2C^{\cdot}H_2$	71.7
$MeC^{\cdot}H_2$	27.0	$C^{\cdot}H_2CH_2C^{\cdot}H_2$	66.9
$C^{\cdot\cdot\cdot}NO_2$	142.0	$MeCH_2C^{\cdot}H_2$	21.0±2.0
$MeC^{\cdot\cdot\cdot}$	137.0	$Me_2C^{\cdot\cdot}$	79.6
$MeC^{\cdot}HNO_2$	22.6	$Me_2C^{\cdot}H$	19.1±2.6
$MeC^{\cdot}(NO_2)_2$	26.1	$Me(CH_2)_2C^{\cdot}H_2$	16.0±2.0
$MeCH_2C^{\cdot}HNO_2$	16.3	$Me_3C^{\cdot}$	9.5±2.9
$Me_2C^{\cdot}NO_2$	10.8	$MeCH_2C^{\cdot\cdot}NO_2$	76.8
$NO_2CH_2CH_2C^{\cdot}H_2$	16.3	$MeCH_2C^{\cdot}HMe$	14.1±3.1
$MeCH_2C^{\cdot}(NO_2)_2$	20.0	$MeC(NO_2)_2C^{\cdot}(NO_2)_2$	32.6
$MeCH_2C^{\cdot\cdot\cdot}$	132.0	$MeCH_2C^{\cdot\cdot}H$	81.5
$MeCH_2C^{\cdot\cdot}Me$	74.6	$Me(CH_2)_3C^{\cdot}H_2$	10.9±2.4
$Me(CH_2)_3C^{\cdot\cdot}H$	71.4	$Me(CH_2)_2C^{\cdot\cdot}H$	76.5
$Me(CH_2)_2C^{\cdot\cdot\cdot}$	127.0	$Me(CH_2)_3C^{\cdot\cdot\cdot}$	121.9
$Me_2C^{\cdot}C^{\cdot}Me_2$	37.5		

* The numerical values were taken from handbooks,[2,9,11,13] research articles,[1,3] and calculated using the published data.[2]

$\Delta_{at}H(C_5H_{10}NO_2{}^{\cdot})$ and $\Delta_{at}H(C_5H_{11}{}^{\cdot})$ are the enthalpies of atomization of the radicals $C_5H_{10}NO_2{}^{\cdot}$ and $C_5H_{11}{}^{\cdot}$, respectively, $P_1(2)^{\cdot}$ is the energy of replacement of two hydrogen atoms by two nitro groups, and $\Delta_{at}H(C_5H_9(NO_2)_2{}^{\cdot})$ is the enthalpy of atomization of the radical $C_5H_9(NO_2)_2{}^{\cdot}$.

The dissociation energies of the C—NO_2 bond in nitroalkanes were calculated using the enthalpies of formation of atoms and radicals listed in Table 2. The enthalpies of formation of alkanes in the gas phase necessary to calculate the D(C—NO_2) values for mononitroalkanes were taken from Ref. 14:

Compound	$-\Delta_f H$/kcal mol^{-1}
n-Butane	30.0±0.2
2-Methylpropane	32.1±0.2
n-Pentane	35.1±0.2
2-Methylpentane	41.8±0.24
2,2-Dimethylpentane	49.2±0.36

The procedure for calculations of D(C—NO_2) for molecules and radicals has been reported in detail elsewhere.[1,3]

According to calculations of the C—NO_2 bond dissociation energies for the nitroalkanes C_2—C_7, the energies of long-range interactions of the nitro groups at carbon atoms in positions C_1—C_2, C_1—C_3, and C_1—C_4 are in reasonable agreement (within 0.1—0.2 kcal mol^{-1} for different compounds) with the published data.[6] Therefore, for the long-range interactions we used the averaged values taken from Ref. 6 rather than the values calculated for each substance. The energies of longe-range interactions of nitro groups (kcal mol^{-1}) for the nitroalkanes C_1—C_2 were set to be equal to $[7.3 - 0.6(m + n)]$, where m and n are the numbers of nitro groups at neighboring carbon atoms; for C_1—C_3 one has (2.0) while for C_1—C_4 one has (0.95).

The enthalpies of formation of radicals of the nitroalkanes C_4—C_7 calculated using our method are listed in Table 3. Using the data presented in Tables 2 and 3, one can calculate the dissociation energies of the C—NO_2, C—C, and C—H bonds in the nitroalkane molecules and radicals. Tables 4 and 5 list the D(C—NO_2) and D(C—C) values for some molecules and radicals of nitro compounds. For comparison, we also list the C—C bond energies in the nonnitrated compounds. The C—H bond dissociation energies (in kcal mol^{-1}) for the molecules and radicals are equal to the C—H bond dissociation energies for the corresponding nonnitrated compounds, *e.g.*, one has 98.1 for butane and nitrobutane, 112.6 for the butyl and nitrobutyl radicals, 112.9 for amyl and 112.6 for nitroamyl. A characteristic feature is that these bond energies for radicals are much higher than for the corresponding molecules.

From Table 4 it follows that the energies D(C—NO_2) are in reasonable agreement with the published activation energies of thermal decomposition (values in parentheses) of butane nitro derivatives.[4,5] Unfortunately, we failed to find any published kinetic data for other nitroalkanes and thus to make a corresponding comparison. As for the C—H bonds, the energies D(C—NO_2) for radicals are much higher than for molecules. Interestingly, the dissociation energies of the N—NO_2 bonds in the secondary nitramines are about 46 kcal mol^{-1} lower than in the radicals $R^{\cdot}N$—NO_2.[15]

As an example, Table 5 presents a number of D(C—C) values for molecules and radicals including, for comparison, some compounds containing no nitro groups. The

Table 3. Enthalpies of formation of C_4—C_7 nitroalkane radicals (kcal mol^{-1})

Radical	$\Delta_f H^\circ$	Radical	$\Delta_f H^\circ$
$NO_2CH_2(CH_2)_2CH_2{}^{\cdot}$	11.4	$Me(CH_2)_2C^{\cdot}(NO_2)_2$	15.0
$MeC^{\cdot}NO_2CH_2CH(NO_2)_2$	8.5	$NO_2CH_2(CH)_2C^{\cdot}HNO_2$	7.9
$MeC^{\cdot}NO_2CH_2C^{\cdot}HNO_2$	44.8	$MeC^{\cdot}NO_2CH_2Me$	5.2
$MeC^{\cdot}NO_2C^{\cdot}NO_2Me$	45.9	$Me(CH_2)_2C^{\cdot}HNO_2$	11.4
$(NO_2)_3C(CH_2)_2C^{\cdot}H_2$	26.7	$NO_2CH_2(CH_2)_2C^{\cdot}(NO_2)_2$	12.4
$NO_2CH_2(Me)CHC^{\cdot}H_2$	9.5	$NO_2CH_2(Me)CHC^{\cdot}(NO_2)_2$	12.7
$NO_2CH_2(Me)CHC^{\cdot}HNO_2$	7.1	$MeC(NO_2)_2CH_2C^{\cdot}H_2{}^{*}$	11.8
$Me(CH_2)_2C^{\cdot\cdot}NO_2$	71.9	$MeC(NO_2)_2CH_2C^{\cdot}HNO_2$	7.9
$NO_2CH_2(CH_2)_2C^{\cdot\cdot}H$	71.8	$MeC(NO_2)_2C^{\cdot}NO_2Me$	8.2
$NO_2CH_2(CH_2)_2C^{\cdot\cdot}NO_2$	68.4	$NO_2CH_2(Me)CHC^{\cdot\cdot}H$	69.9
$MeC(NO_2)_2C^{\cdot\cdot}Me$	64.9	$NO_2CH_2(Me)CHC^{\cdot\cdot}NO_2$	67.6
$MeC^{\cdot}NO_2C^{\cdot\cdot}Me$	107.8	$MeC(NO_2)_2CH_2C^{\cdot\cdot}H$	72.3
$NO_2CH_2(CH_2)_2C^{\cdot\cdot\cdot}$	123.7	$NO_2CH_2(Me)CHC^{\cdot\cdot\cdot}$	120.4
$Me(CH_2)_3C^{\cdot}HNO_2$	6.8	$Me(CH_2)_3C^{\cdot}(NO_2)_2$	10.6
$Me(CH_2)_3C^{\cdot\cdot}NO_2$	67.3	$(NO_2)_3CCH_2C^{\cdot}HCH_2C(NO_2)_3$	30.3
$Me_2CNO_2C^{\cdot}Me_2$	−10.4	$(NO_2)_3CCH_2CH\ NO_2CH_2C^{\cdot}(NO_2)_2$	22.2
$C_2H_5C(NO_2)_2C^{\cdot}Me_2$	−0.4	$C_2H_5C^{\cdot}NO_2CMe_2NO_2$	−6.5
$MeC(NO_2)_2CH_2CMe_2C^{\cdot}(NO_2)_2$	−8.2	$MeC(NO_2)_2CH_2CMe_2C^{\cdot\cdot}NO_2$	49.5
$MeC(NO_2)_2CH_2CMe_2C^{\cdot\cdot\cdot}$	99.3	$MeC^{\cdot}NO_2CH_2CMe_2C^{\cdot\cdot\cdot}$	142.2

Table 4. $C-NO_2$ bond dissociation energies (kcal mol^{-1})

Compound	*D*
$Me(CH_2)_2CH_2-NO_2$	58.5±2.1
$MeCH_2MeCH-NO_2$	60.6±3.2
Me_3C-NO_2	59.3±3.0
$Me(Me)CHCH_2-NO_2$	58.5±2.1
$NO_2CH_2(CH_2)_3-NO_2$	57.4
$C(NO_2)_3(CH_2)_2CH_2-NO_2$	55.8
$Me(CH_2)_2CHNO_2-NO_2$	50.8 (48.1)
$Me(CH_2)_3CHNO_2-NO_2$	50.9
$Me(CH_2)_2C(NO_2)_2-NO_2$	42.2 (43.6)
$Me(CH_2)_3C(NO_2)_2-NO_2$	42.5
$NO_2CH_2(CH_2)_2C(NO_2)_2-NO_2$	40.4
$Me(CH_2)_2C^{\cdot}H-NO_2$	73.0
$Me(CH_2)_3C^{\cdot}H-NO_2$	72.5
$Me(CH_2)_3C^{\cdot}NO_2-NO_2$	67.5
$Me(CH_2)_3C^{\cdot\cdot}-NO_2$	59.6
$MeC(NO_2)_2CH_2C^{\cdot}H-NO_2$	72.3
$Me_2C^{\cdot}Me_2C-NO_2$	55.8
$NO_2CH_2(Me)CHC^{\cdot}NO_2-NO_2$	62.8
$MeC(NO_2)_2CH_2CMe_2C^{\cdot}NO_2-NO_2$	65.6
$NO_2CH_2(Me)CHC^{\cdot\cdot}-NO_2$	60.7
$MeC(NO_2)_2CH_2CMe_2C^{\cdot\cdot}-NO_2$	57.7
$C^{\cdot\cdot\cdot}Me_2CCH_2C(Me)NO_2-NO_2$	50.8

introduction of nitro groups at carbon atoms strengthens the nearest C—C bond while long-range interactions of nitro groups weaken this bond; this is consistent with the conclusions[1,3,4] about the effect of nitro groups on the energies of C—C bonds in molecules. The net effect depends on the number and positions of nitro groups in the molecule. The introduction of nitro groups into radical structures affects the C—C bond dissociation energies in the same manner as in the molecules.

Table 5. C—C bond dissociation energies (kcal mol^{-1})

Compound	*D*
C_3H_7-Me	85.9
C_4H_9-Me	86.0
$C_3H_7-C_2H_5$	83.1
$C_4H_9-CH_2NO_2$	90.1
$C_4H_9-CH(NO_2)_2$	95.0
$C_4H_9-C(NO_2)_3$	93.7
$NO_2CH_2CH_2CH_2-C(NO_2)_3$	91.2
$MeC(NO_2)_2-C(NO_2)_2Me$	76.8
$Me_2CNO_2-CNO_2Me_2$	78.6
$C_3H_7-C^{\cdot}H_2$	98.3
$C_3H_7-C^{\cdot\cdot}H$	86.5
$C_3H_7-C^{\cdot}HNO_2$	102.9
$C_4H_9-C^{\cdot}HNO_2$	102.5
$C_3H_7-C^{\cdot}(NO_2)_2$	105.6
$C_4H_9-C^{\cdot}(NO_2)_2$	105.0
$C_3H_7-C^{\cdot\cdot}NO_2$	91.1
$C_4H_9-C^{\cdot\cdot}NO_2$	90.5
$MeC(NO_2)_2-C^{\cdot}NO_2Me$	100.7

Summing up, we carried out an experimental study of the thermochemical properties (enthalpies of combustion, enthalpies of formation, and enthalpies of vaporization) of nitroalkanes C_4-C_7. The method for calculating the $C-NO_2$ bond dissociation energies using the experimentally determined enthalpies of formation of nitro compounds from atoms and energies of nonvalent interactions of nitro groups was proposed. The calculated bond dissociation energies are in reasonable agreement with the activation energies of monomolecular radical thermal decomposition at the $C-NO_2$ bond, which proves the applicability of the method proposed. This method was also used to calculate the dissociation energies of $C-NO_2$ bonds in nitroalkyl radicals. This allowed the enthalpies of formation of a large number of nitroalkyl radicals including bi- and triradicals to be determined. The data array thus obtained enables calculations and analysis of the dissociation energies of the $C-NO_2$, C—C, and C—H bonds in the nitroalkane molecules and radicals. The energies $D(C-NO_2)$ and $D(C-H)$ determined for radicals are appreciably higher than the corresponding values for molecules. The energies of C—H bonds in nitroalkanes and in unnitrated compounds are almost equal. The addition of nitro groups to alkyl structures causes an increase in the energy of the adjacent C—C bond, whereas their introduction at different carbon atoms leads to both an increase and a decrease in the energies of adjacent C—C bonds.

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