

CHEMICAL KINETICS  
AND CATALYSIS

## Radical Abstraction Reactions with Concerted Fragmentation in the Chain Decay of Nitroalkanes

E. T. Denisov\*<sup>†</sup> and A. F. Shestakov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

\*e-mail: as@icp.ac.ru

Received June 8, 2017

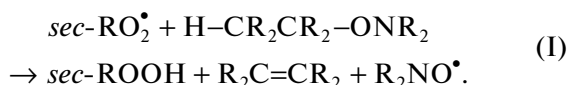
**Abstract**—Reactions of the type  $X^\bullet + \text{HCR}_2\text{CH}_2\text{NO}_2 \rightarrow \text{XH} + \text{R}_2\text{C}=\text{CH}_2 + \text{N}^\bullet\text{O}_2$  are exothermic, due to the breaking of weak C–N bonds and the formation of energy-intensive C=C bonds. Quantum chemistry calculations of the transition state using the reactions of  $\text{Et}^\bullet$  and  $\text{EtO}^\bullet$  with 2-nitrobutane shows that such reactions can be categorized as one-step, due to the extreme instability of the intermediate nitrobutyl radical toward decay with the formation of  $\text{N}^\bullet\text{O}_2$ . Kinetic parameters that allow us to calculate the energy of activation and rate constant of such a reaction from its enthalpy are estimated using a model of intersecting parabolas. Enthalpies, energies of activation, and rate constants are calculated for a series of reactions with the participation of  $\text{Et}^\bullet$ ,  $\text{EtO}^\bullet$ ,  $\text{RO}_2^\bullet$ ,  $\text{N}^\bullet\text{O}_2$  radicals on the one hand and a series of nitroalkanes on the other. A new kinetic scheme of the chain decay of nitroalkanes with the participation of abstraction reactions with concerted fragmentation is proposed on the basis of the obtained data.

**Keywords:** rate constant, density functional method, model of intersecting parabolas, nitroalkane, abstraction with fragmentation, free radicals, energy of activation, enthalpy of reaction, chain decay of nitroalkanes

**DOI:** 10.1134/S0036024418050072

### INTRODUCTION

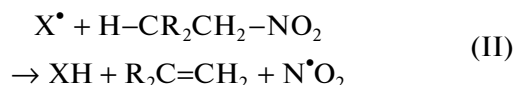
Compounds containing nitro groups find wide application in engineering and military as explosives [1]. Large amounts of energy are released as a result of their decay and are widely used in practice. The mechanism of the decay of such compounds includes both molecular and radical steps, and was discussed in detail in [2]. In [3–7], we showed there are highly exothermic reactions of a new type among radical reactions: *abstraction reactions with concerted fragmentation*. These reactions occur when the molecule under attack has a weak bond, the opening of which is compensated for by the formation of a fairly stable  $\pi$  bond. For example, in the reaction of  $\text{RO}_2^\bullet$  with an alkoxyamine, its weak C–O bond breaks along with the C–H bond, and the stronger C=C bond of an olefin is formed [6]:



Such a reaction is exothermic, its enthalpy  $\Delta H = -57.6$  kJ/mol ( $\text{sec-RO}_2^\bullet + 2,2,6,6\text{-tetramethylpiperidine-}N\text{-oxy-2'-propane}$ , [6]), while simple abstrac-

tion of an H atom from  $\text{HCR}_2\text{CH}_2\text{ONR}_2$  by a peroxide radical is endothermic ( $\Delta H = 25.0$  kJ/mol [6]). The high exothermicity of abstraction reactions with fragmentation is observed when the energy consumption for the breaking of a weak bond is overcompensated for by energy  $D_\pi$  of the  $\pi$  bond being formed. The occurrence of a radical reaction according to the mechanism of abstraction of an H atom with fragmentation therefore depends on the structure of the molecule being attacked, and it can be predicted on the basis of its structure.

Nitroalkanes have weak N–C bonds (for nitroalkanes,  $D_{\text{N-C}} = 230\text{--}242$  kJ/mol [8]). Because of this, the occurrence of radical abstraction reactions with concerted fragmentation of the type



can be expected for them.

To solve this problem, a quantum chemistry analysis of the transition state (TS) of abstraction reactions with fragmentation with the participation of nitroalkanes is performed in this work, the enthalpies of such

<sup>†</sup> Deceased.

reactions with the participation of various radicals are calculated, and the energies of activation and rate constants of the corresponding reactions are estimated using a model of intersecting parabolas (MIP).

## CALCULATION PROCEDURE

### *Quantum Chemistry Methods*

The PBE density functional method [9] using an SBK pseudopotential [10] and an extended basis for valence electrons was used for our theoretical study of the reactions of concerted abstraction of an H atom with fragmentation. The calculations were performed using the PRIRODA software package [11] at the Joint Supercomputer Center, Russian Academy of Sciences. The type of stationary points of the potential energy surface was determined from an analysis of Hessians during the analytical calculation of second derivatives. Thermodynamic functions were calculated in the harmonic oscillator–rigid rotor approximation. To verify the type of the TS, the coordinates of the reaction were calculated using an intrinsic reaction coordinate. The Hirshfeld method [12] was used for the analysis of the distribution of the electron and spin density by the atoms.

### *Method of Intersecting Parabolas*

The method of intersecting parabolas (MIP) was also used to calculate the energies of activation and rate constants of radical reactions. According to this method, a radical abstraction reaction of the type



is characterized by a number of parameters [13–15]: (1) classic enthalpy ( $\Delta H_e$ ) associated with the enthalpy of the reaction  $\Delta H$  by the correlation

$$\Delta H_e = \Delta H + 0.5hN_A(v_{C-H} - v_{X-H}), \quad (1)$$

where  $v_{X-H}$  and  $v_{C-H}$  are the frequencies of valence vibrations of the reacting bonds,  $h$  is the Plank constant, and  $N_A$  is the Avogadro number; (2) the classic potential energy barrier of the reaction  $E_e$  which includes the energy of the zero-point vibration of a breaking bond ( $0.5hN_A v_{C-H}$ ) and the average kinetic energy of the movement of the H atom along the reaction coordinate ( $0.5RT$ ) and is associated with the experimental energy of activation  $E$  by the correlation

$$E_e = E + 0.5hN_A v_{C-H} - 0.5RT; \quad (2)$$

(3) distance  $r_e$ , which characterizes the elongation of the reacting bonds (in this case, the R–H and H–X bonds) in the TS; (4) parameter  $b$  ( $2b^2$  is the force constant of the breaking R–H bond), parameter  $b_f$  ( $2b_f^2$  is the force constant of the forming X–H bond), and coefficient  $\alpha = b/b_f$ ; (5) preexponential factor  $A_{C-H}$

per one C–H bond being attacked. The values of the above parameters and the coefficients for a number of the classes of reactions under discussion can be found in [13, 14].

In the MIP, classic potential energy barrier  $E_e$  and classic enthalpy of a reaction  $\Delta H_e$  are associated by the equation [14]

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \quad (3)$$

This allows us, on one hand, to calculate parameter  $br_e$  for a selected class of reactions using the experimental data ( $\Delta H$  and  $E$ ) and, on the other hand, in the case of known parameters  $br_e$  and  $\alpha$ , to calculate the energy of activation for any reaction of this class through its enthalpy according to the equation

$$E = B^2 \left\{ 1 - \alpha \sqrt{1 - \frac{\Delta H_e}{Bbr_e}} \right\}^2 - 0.5(hN_A v_{C-H} - RT), \quad (4)$$

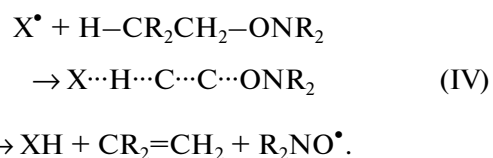
where  $B = br_e/(1 - \alpha^2)$ . Parameter  $br_e$  also allows us to calculate the characteristics of an entire class of reactions such as the classic potential energy barrier of a thermally neutral ( $\Delta H_e = 0$ ) reaction [14]:

$$E_{e0} = \left\{ \frac{br_e}{1 + \alpha} \right\}^2. \quad (5)$$

When the coefficient  $\alpha = 1$ , the equation for the energy of activation takes a simpler form:

$$\sqrt{E} = \sqrt{E_{e0}} + \frac{\Delta H}{2br_e}. \quad (6)$$

Note there is an analogy between the TSEs in reactions between  $X^\bullet$  and a nitroalkane (II) or an alkoxyamine (I) [6]:



Because of this, the kinetic parameters of the MIP that describe the reactions between radicals and the C–H bonds of alkoxyamines [6] can be used for the calculation of the energies of activation of such reactions. Table 1 presents the values of these parameters.

In the case of a concerted abstraction reaction with fragmentation of the molecule, the probability of the concentration of the energy of activation on the breaking bonds depends on their number. We must then consider that the excess (activation) energy is concentrated on a larger number of bonds than with simple abstraction. In the oscillation model of the reacting molecule [16], in which the molecule is considered as a sum of interrelated oscillators, the preexponential factor of reaction  $A$  depends on the number of bonds  $n$

**Table 1.** Kinetic parameters of the MIP of abstraction reactions of H with concerted fragmentation of radicals of different types with the C–H bonds of nitro compounds [6, 13]

Reaction	$\alpha$	$br_e$ , (kJ/mol) <sup>1/2</sup>	$0.5h(v - v_f) N_A$ , kJ/mol	$A$ , L/(mol s)
$R^\bullet + R_1H \rightarrow RH + R_1^\bullet$	1.00	17.30		
$RO^\bullet + R_1H \rightarrow ROH + R_1^\bullet$	0.796	13.10	–4.3	$1.0 \times 10^9$
$RO_2^\bullet + R_1H \rightarrow ROOH + R_1^\bullet$	0.814	13.61	–3.8	$1.0 \times 10^8$
$R^\bullet + RNO_2$	1.00	20.79	0.0	$1.0 \times 10^9$
$R^\bullet + PhCH_2CH_2NO_2$	1.00	21.21	0.0	$1.0 \times 10^8$
$RO^\bullet + RNO_2$	0.796	16.77	–4.3	$1.0 \times 10^9$
$RO^\bullet + PhCH_2CH_2NO_2$	0.796	17.08	–4.3	$1.0 \times 10^8$
$RO_2^\bullet + RNO_2$	0.814	17.17	–3.8	$1.0 \times 10^8$
$RO_2^\bullet + PhCH_2CH_2NO_2$	0.814	17.73	–3.8	$1.0 \times 10^7$
$N^\bullet O_2 + RCH_2NO_2$	0.802	16.08	–4.1	$2.0 \times 10^9$
$N^\bullet O_2 + PhCH_2CH_2NO_2$	0.802	16.56	–4.1	$2.0 \times 10^8$

that break in the TS. In the reactions considered in this work, C–H and C–N bonds break,  $n = 2$ , and factor  $A$  is [16]

$$A = n_{C-H} A_{C-H} \sqrt{\frac{2RT}{\pi E}} \quad (7)$$

If rate constant  $k$  of such a reaction is expressed in Arrhenius form and we allow for the dependence of  $A$  on  $T$  (see Eq. (7)),  $E = RT^2(d \ln k/dT) = E_{\text{exp}} - 0.5RT$ , and the expression for  $k$  acquires the form

$$\begin{aligned} k &= n_{C-H} A \exp(-E/RT) \\ &= n_{C-H} A_{C-H} \sqrt{\frac{2RT}{\pi E}} \exp(-E/RT), \end{aligned} \quad (8)$$

where  $n_{C-H}$  is the number of equireactive C–H bonds under attack in the molecule.

#### Calculating the Enthalpy of Radical Reactions

To calculate the energy of activation of radical reactions in the MIP, we must know the enthalpy of the reaction (see Eq. (4)). For reactions of type (III) under discussion, this quantity was calculated according to the equation

$$\begin{aligned} \Delta H(\text{III}), \text{ kJ/mol} &= -D_{X-H} + \Delta H(R_2C=CH_2) \\ &\quad - \Delta H(R_2CHCH_2NO_2) + 251.2, \end{aligned}$$

where  $251.2 \text{ kJ/mol} = \Delta H(H^\bullet) + \Delta H(N^\bullet O_2)$ . The enthalpies of formation of the olefins are taken from [17]; the enthalpies of formation of nitroalkanes, from [8]; and the values of  $D_{X-H}$ , from [18]. The results from

calculating the enthalpy of reaction (III) and the energy of activation of the reactions between  $X^\bullet = EtO^\bullet, N^\bullet O_2, Et^\bullet, EtO_2^\bullet$  and a series of nitroalkanes are presented in Table 2.

## RESULTS AND DISCUSSION

### Radical Abstraction Reactions Involving Fragmentation with the Participation of Nitroalkanes

According to preliminary analysis, we would expect that the radical reactions of abstraction of H atoms from nitroalkanes to be accompanied by the fragmentation of these molecules. For our theoretical study of the mechanism of the above reactions, quantum-chemistry calculations of the energy of activation were performed for the systems

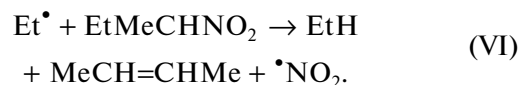
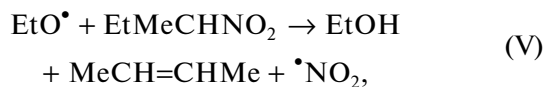


Table 3 presents the results from calculating the standard enthalpies and energies of activation of these reactions. The comparison to the experimental data and data of the MIP is indicative of the underestimated values of the energies of activation for reactions (V) and (VI) but satisfactory agreement between the enthalpies of the reactions.

**Table 2.** Enthalpies, energies of activation, and rate constants of abstraction reactions with fragmentation of the type  $X^\bullet + RNO_2 \rightarrow XH + >C=C< + N^\bullet O_2$ 

$RNO_2$	$\Delta H$ , kJ/mol	$E$ , kJ/mol	$A \times 10^{-8}$ , L/(mol s)	$k$ (350 K), L/(mol s)
$X^\bullet = Et$ ( $D_{Et-H} = 420.5$ kJ/mol)				
EtNO <sub>2</sub>	-16.7	84.0	4.44	$1.30 \times 10^{-4}$
PrNO <sub>2</sub>	-24.2	80.4	3.03	$4.57 \times 10^{-4}$
Me <sub>2</sub> CHNO <sub>2</sub>	-9.5	87.5	8.72	$3.86 \times 10^{-5}$
MeEtCHNO <sub>2</sub>	-18.7	83.0	2.98	$1.83 \times 10^{-4}$
Me <sub>3</sub> CNO <sub>2</sub>	-8.3	88.0	13.0	$9.57 \times 10^{-5}$
<i>cyclo</i> -C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	-20.9	82.0	6.00	$2.64 \times 10^{-4}$
<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>	-16.3	100.5	5.43	$5.45 \times 10^{-7}$
PhCH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	-17.7	87.8	2.90	$2.29 \times 10^{-5}$
PhCHMeCH <sub>2</sub> NO <sub>2</sub>	-31.3	81.4	1.51	$1.07 \times 10^{-4}$
EtCH(NO <sub>2</sub> ) <sub>2</sub>	-26.7	79.2	3.06	$4.63 \times 10^{-4}$
EtC(NO <sub>2</sub> ) <sub>3</sub>	-59.2	64.5	3.39	$8.02 \times 10^{-2}$
$X^\bullet = EtO^\bullet$ ( $D_{EtO-H} = 441.0$ kJ/mol)				
EtNO <sub>2</sub>	-37.2	54.0	5.55	4.84
PrNO <sub>2</sub>	-44.7	51.1	3.80	9.00
Me <sub>2</sub> CHNO <sub>2</sub>	-30.0	57.0	12.2	3.80
MeEtCHNO <sub>2</sub>	-39.2	53.2	3.73	4.29
Me <sub>3</sub> CNO <sub>2</sub>	-28.8	57.3	16.2	4.55
<i>cyclo</i> -C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	-41.4	52.4	7.52	11.4
<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>	-36.8	54.1	7.40	6.24
PhCH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	-38.2	56.4	3.62	1.38
PhCHMeCH <sub>2</sub> NO <sub>2</sub>	-51.8	51.2	1.90	4.34
EtCH(NO <sub>2</sub> ) <sub>2</sub>	-47.2	50.2	5.76	18.6
EtC(NO <sub>2</sub> ) <sub>3</sub>	-79.7	38.7	6.56	$1.10 \times 10^3$
$X^\bullet = N^\bullet O_2$ ( $D_{ONO-H} = 330.7$ kJ/mol)				
EtNO <sub>2</sub>	73.1	98.2	8.24	$1.82 \times 10^{-6}$
PrNO <sub>2</sub>	65.6	94.1	5.61	$5.08 \times 10^{-6}$
Me <sub>2</sub> CHNO <sub>2</sub>	80.3	102.3	$1.61 \times 10$	$9.32 \times 10^{-7}$
MeEtCHNO <sub>2</sub>	71.1	97.1	5.52	$1.78 \times 10^{-6}$
Me <sub>3</sub> CNO <sub>2</sub>	81.5	103.0	$2.41 \times 10$	$1.02 \times 10^{-6}$
<i>cyclo</i> -C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	68.9	95.9	$1.11 \times 10$	$5.41 \times 10^{-6}$
<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>	73.5	98.4	$1.10 \times 10$	$2.27 \times 10^{-6}$
PhCH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	72.1	102.3	5.38	$2.91 \times 10^{-7}$
PhCHMeCH <sub>2</sub> NO <sub>2</sub>	58.5	94.9	2.79	$1.92 \times 10^{-6}$
EtCH(NO <sub>2</sub> ) <sub>2</sub>	63.1	92.7	5.65	$8.27 \times 10^{-6}$
EtC(NO <sub>2</sub> ) <sub>3</sub>	30.6	76.0	6.24	$2.84 \times 10^{-3}$
$X^\bullet = RO_2^\bullet$ ( $D_{ROO-H} = 365.5$ kJ/mol)				
EtNO <sub>2</sub>	38.3	90.0	$8.60 \times 10^{-1}$	$3.18 \times 10^{-6}$
PrNO <sub>2</sub>	30.8	86.3	$5.86 \times 10^{-1}$	$7.74 \times 10^{-6}$
Me <sub>2</sub> CHNO <sub>2</sub>	45.5	93.6	$8.44 \times 10^{-1}$	$9.06 \times 10^{-7}$
MeEtCHNO <sub>2</sub>	36.3	89.0	$2.89 \times 10^{-1}$	$1.51 \times 10^{-6}$
Me <sub>3</sub> CNO <sub>2</sub>	46.7	94.2	1.26	$1.10 \times 10^{-6}$
<i>cyclo</i> -C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	34.1	87.9	$5.81 \times 10^{-1}$	$4.42 \times 10^{-6}$
<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>	38.7	90.2	$5.71 \times 10^{-1}$	$1.97 \times 10^{-6}$
PhCH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	37.3	95.4	$2.78 \times 10^{-2}$	$1.61 \times 10^{-8}$
PhCHMeCH <sub>2</sub> NO <sub>2</sub>	23.7	88.8	$1.44 \times 10^{-2}$	$8.05 \times 10^{-8}$
EtCH(NO <sub>2</sub> ) <sub>2</sub>	28.3	85.0	$2.95 \times 10^{-1}$	$6.09 \times 10^{-6}$
EtC(NO <sub>2</sub> ) <sub>3</sub>	-4.2	79.1	$3.06 \times 10^{-1}$	$4.80 \times 10^{-5}$

With the abstraction of the H atom from the  $\beta$ -C–H bonds of 2-nitrobutane, C2 and C3 postreaction complexes (see Figs. 1 and 2) with the participation of the intermediate unstable  $\text{MeCH}^{\bullet}\text{CHMeNO}_2$  radical are formed. In this radical, elongation of the C–N bond by 0.05 Å is observed. However, as is shown by the analysis of the distribution of the spin density, its total value on the nitro group is already 0.12, while ~0.60 remains on the C atom of the reaction site. Despite the moderate energy gain from the abstraction of the H atom by radicals  $\text{EtO}^{\bullet}$  and  $\text{Et}^{\bullet}$ , the TS1 and TS3 transition states occur early. The decay of the C2 and C3 intermediate complexes with the breaking of the C–N bond is not only energetically advantageous but also has a negligibly low energy barrier of ~10 kJ/mol. Considering the substantial increase in the entropy as a result of the formation of additional molecules, equilibrium is strongly shifted toward the C2 and C3 decay products. The corresponding change in the free energy in the gas phase is –84.7 and –83.3 kJ/mol, which yields equilibrium constant of decay of  $\sim 10^{15}$ .

The alternative channel for the decay of C2 and C3 to an intermediate radical and EtOH or EtH requires energy consumption of 10.1 and 1.0 kJ/mol, respectively. The somewhat higher stability toward decay into components with C2 in comparison to C1 is reflected in the shortening of the distance between an H atom and a radical center from 2.57 to 2.31 Å.

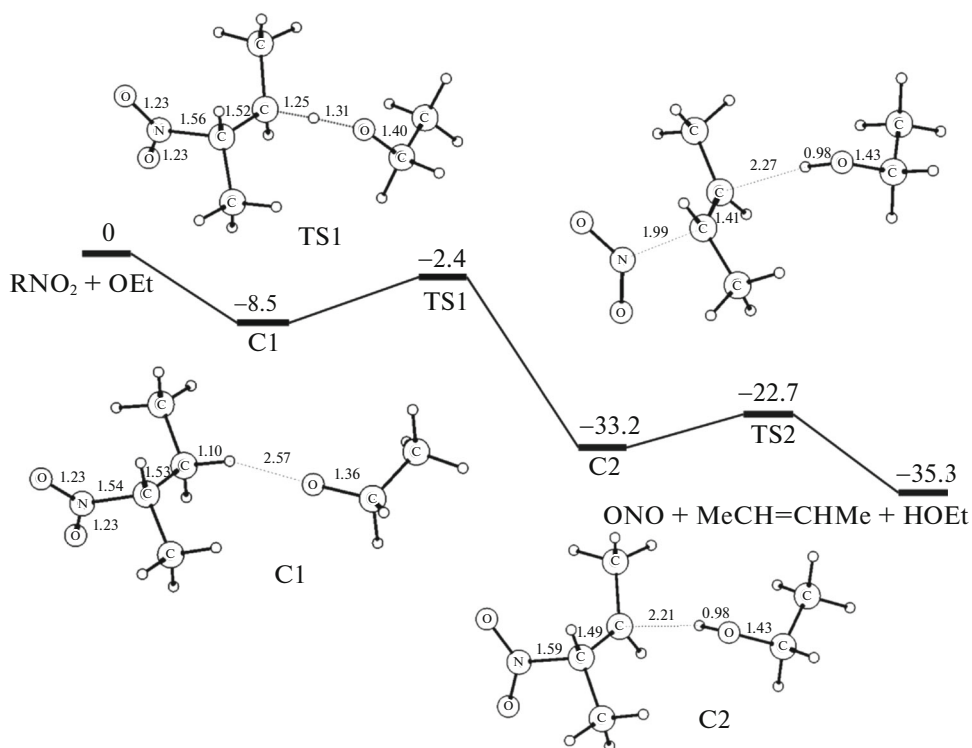
**Table 3.** Comparison of the calculated standard enthalpies and energies of activation of the reactions with the experimental data (kJ/mol)

Reaction	$\Delta H_{298}$		$E$	
	calculations	experiment	calculations*	MIP
(VIII)	–32.4	–39.2	1.9**	53.2
(IX)	–29.6	–18.7	27.7	83.0
(X)	83.3	71.1	88.2	97.1

\* Allowing for thermal corrections at 298 K.

\*\* Relative to the pre-reaction complex.

Considering the low value of the energy of activation of the decay of the  $\text{MeCH}^{\bullet}\text{CHMeNO}_2$  radical to  $\text{MeCH}=\text{CHMe}$  and  $\text{NO}_2$  (9.5 kJ/mol), its lifetime is very short. This radical therefore decays as soon as it forms, and it is not an independent particle. Although a comparison of the energy data leads to the conclusion that for reaction (V), joint and two-step processes are equally probable, while the two-step process predominates for reaction (VI), and these processes are practically indiscernible. The abstraction of the H atom from the  $\text{EtMeCHNO}_2$  molecule followed by its fragmentation may therefore be considered as one elementary step.



**Fig. 1.** Energy diagram of the reaction between  $\text{EtO}^{\bullet}$  and 2-nitrobutane. Energies are in kJ/mol; distances, in Å.

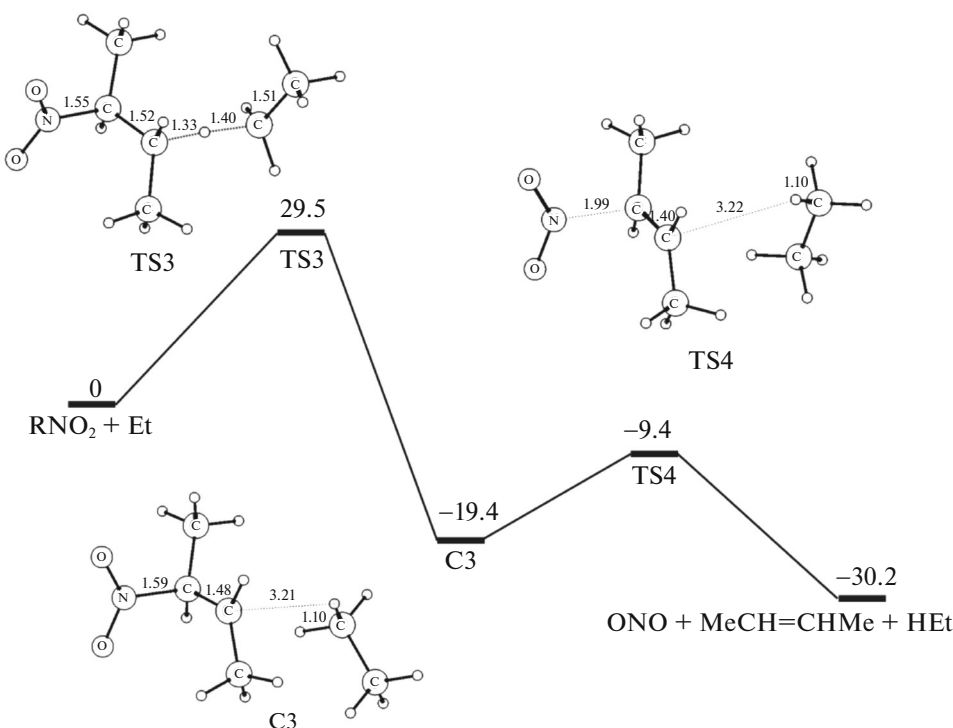
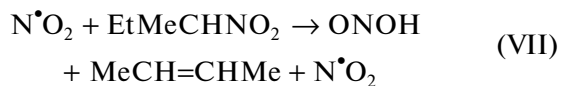


Fig. 2. Energy diagram of the reaction between Et<sup>•</sup> and 2-nitrobutane. Energies are in kJ/mol; distances, in Å.

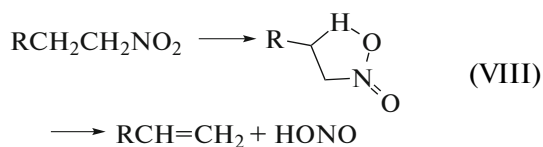
The considered decay reactions result in the formation of a N<sup>•</sup>O<sub>2</sub> radical that also can abstract an H atom from nitro compounds. The energy diagram for the reaction



is presented in Fig. 3. The abstraction of the H atom from the β-C–H bond of 2-nitrobutane requires a substantially lower energy of activation (97.1 kJ/mol) that the thermal decay of nitroalkanes with the breaking of the C–NO<sub>2</sub> bond (232.6 kJ/mol for EtNO<sub>2</sub> [2]) or removal of HNO<sub>2</sub> (187.5 kJ/mol for EtNO<sub>2</sub> [19]). It is interesting that for reaction (VII), the energies of the TS of the abstraction of the H atom, TS5, the C4 intermediate complex, the TS of its decay, TS6, and its products differ very little. In the TS5 transition state, most of the spin density (0.39) on the C atom of the radical center, while a smaller part (0.32) is concentrated on the attacking radical N<sup>•</sup>O<sub>2</sub>, and 0.10 is concentrated on the nitro group. In the C4 transition complex, there is an increase in the spin density on the C atom to 0.56 (and on the nitro group to 0.12) and a reduction of it on the NO<sub>2</sub> fragment of the NHO<sub>2</sub> molecule to 0.05. The energy of the decay of C4 to the intermediate MeCH<sup>•</sup>CHMeNO<sub>2</sub> radical and HNO<sub>2</sub> requires energy consumption of 10.6 kJ/mol.

#### Chain Decay Reaction of Nitroalkanes

Two fundamentally different mechanisms of decay are known for the decay of nitroalkanes: a free radical mechanism [2] and a molecular mechanism [2, 19]. Radicals are formed as a result of the decay of RNO<sub>2</sub> from the weak C–N bonds, followed by a cascade of different radical reactions [2]. Molecular decay occurs via a five-membered TS [19]:



and is characterized by a high energy of activation (187.5 kJ/mol for the decay of nitroethane [19]). The radical abstraction reaction with concerted fragmentation of type (II) corroborated in this work allow us to propose a new chain mechanism of the decay of nitroalkanes. The limiting step in the chain decay of an RNO<sub>2</sub> nitroalkane is its decay with the breaking of the weakest N–C bonds (230–242 kJ/mol [8]). For example, the decay of nitroethane



occurs quickly with a rate constant  $k = 8.0 \times 10^{15} \exp(-(232.6 \text{ kJ/mol})/RT) \text{ s}^{-1}$  [2]. With an increase in temperature, the rate of the decay of RNO<sub>2</sub> grows

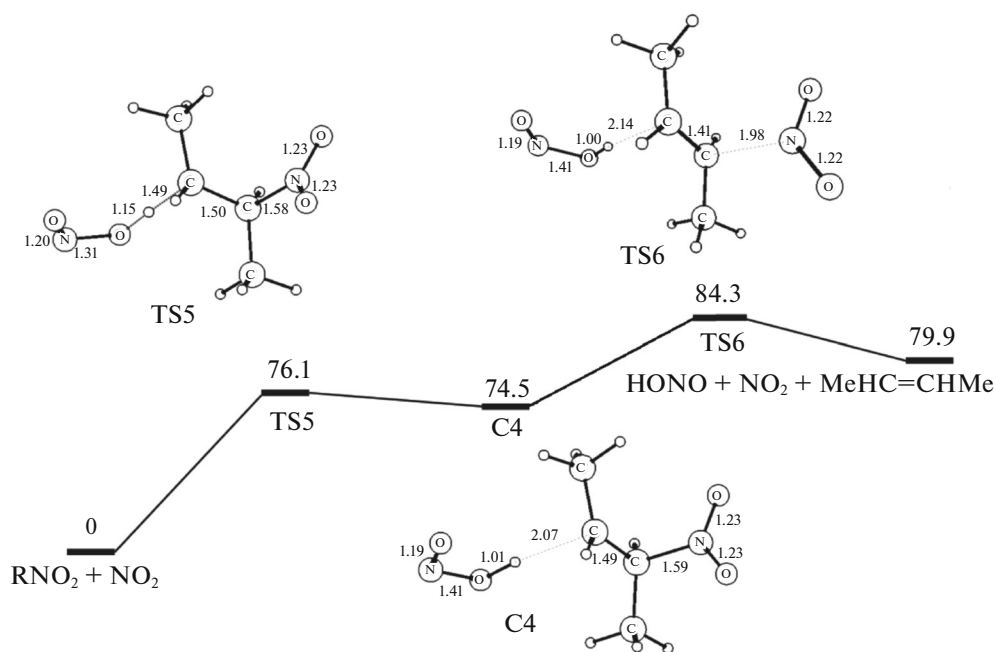
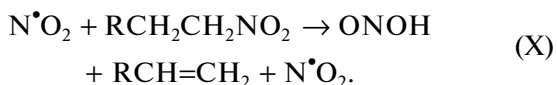
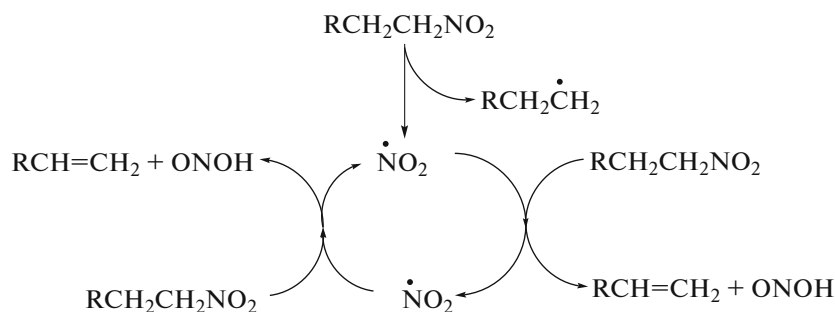


Fig. 3. Energy diagram of the reaction between  $\text{N}^\bullet\text{O}_2$  and 2-nitrobutane. Energies are in kJ/mol; distances, in Å.

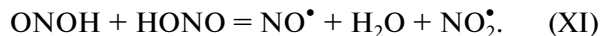
rapidly, due to the high energy of activation, so  $k$  (300 K) =  $2.5 \times 10^{-25} \text{ s}^{-1}$ ,  $k$  (400 K) =  $3.4 \times 10^{-15} \text{ s}^{-1}$ , and  $k$  (500 K) =  $4.0 \times 10^{-9} \text{ s}^{-1}$ . Chain propagation occurs via the abstraction reaction with fragmentation of  $\text{N}^\bullet\text{O}_2$  by the  $\beta\text{-C-H}$  bonds of a nitroalkane; e.g.,



This reaction is remarkable due to  $\text{N}^\bullet\text{O}_2$  being both a reagent and a product of it. Formally, it can be considered the nitrogen dioxide-catalyzed transformation of a nitroalkane into an olefin and nitrous acid. The values of  $\Delta H$ ,  $E$ , and  $k$  (350 K) for such reactions are presented in Table 3. The chain decay reaction of a nitroalkane can in this case be presented as

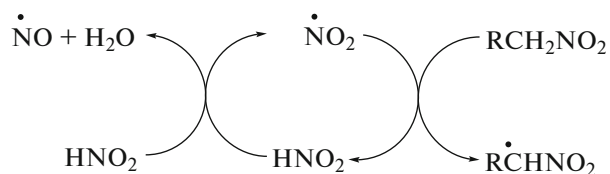


The attack of  $\text{N}^\bullet\text{O}_2$  on the  $\alpha\text{-C-H}$  bond of a nitroalkane also leads to the formation of nitrous acid. As a result of the decay of nitrous acid, the regeneration of  $\text{NO}_2^\bullet$  occurs in turn, according to the reaction [20]



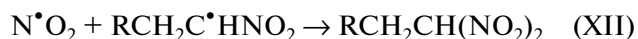
This reaction proceeds with a high rate constant whose experimental values vary from  $k = 5.7 \times 10^2 \text{ L}/(\text{mol s})$

(296 K) [21] to  $k = 1.8 \times 10^6 \text{ L}/(\text{mol s})$  (300 K) [22]. The alternating of the reactions  $\text{NO}_2^\bullet + \text{RNO}_2$  and  $\text{ONOH} + \text{HONO}$  starts a parallel chain reaction:



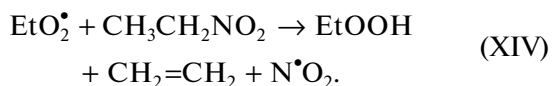
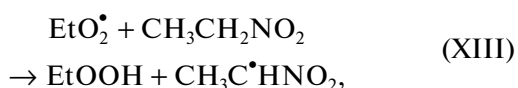
The chain decay of nitroalkanes therefore takes the form of two concerted chain reactions with the involvement of one particle, nitrogen dioxide, in the chain propagation. With the accumulation of  $\text{N}^{\bullet}\text{O}_2$ , the self-acceleration of the decay of a nitroalkane is observed. The chains are terminated as a result of both the reversible dimerization of  $\text{N}^{\bullet}\text{O}_2$  and the addition of  $\text{N}^{\bullet}\text{O}_2$  to alkyl radicals of the types  $\text{RCH}_2\text{C}^{\bullet}\text{H}_2$ ,  $\text{RCH}_2\text{C}^{\bullet}\text{HNO}_2$ , and  $\text{RCH}^{\bullet}\text{CH}=\text{CH}_2$ . The reversible dimerization of  $\text{N}^{\bullet}\text{O}_2$  is negligible at elevated temperatures, and its influence is apparent only in the form of a slight reduction in the active concentration of nitrogen dioxide.

Polynitroalkanes formed according to the reaction



decay into radicals faster than mononitroalkanes. Thus, for example, the decay of nitroethane occurs with  $k = 8.0 \times 10^{15} \exp(-232.6/RT \text{ kJ/mol}) = 3.4 \times 10^{-15} \text{ s}^{-1}$  (400 K),  $\text{CH}_3\text{CH}(\text{NO}_2)_2$ , with  $k = 2.4 \times 10^{15} \exp(-199.6/RT \text{ kJ/mol}) = 2.06 \times 10^{-11} \text{ s}^{-1}$  (400 K), and  $\text{CH}_3\text{C}(\text{NO}_2)_3$ , with  $k = 1.25 \times 10^{17} \exp(-182.4/RT \text{ kJ/mol}) = 1.89 \times 10^{-7} \text{ s}^{-1}$  (400 K) [2]. Because of this, the chain decay of a nitroalkane accelerates with the accumulation of polynitroalkanes, and the mode of the reaction changes from an unbranched chain to a degenerate branched chain.

With the decay of nitroalkanes in air in the presence of oxygen, alkyl radicals are quickly transformed into peroxy radicals, and chain propagation occurs with the participation of both  $\text{N}^{\bullet}\text{O}_2$  and  $\text{RO}_2^{\bullet}$  (see Table 3). A peroxy radical attacks both the  $\alpha\text{-C-H}$  and  $\beta\text{-C-H}$  bonds:



Which one of these two reactions predominates? Reaction (XIII) is characterized by the kinetic parameters  $\Delta H = 37.2 \text{ kJ/mol}$ ,  $E = 46.7 \text{ kJ/mol}$ ,  $A = 2.0 \times 10^8 \text{ L/(mol s)}$ , and  $k$  (350 K) =  $21.4 \text{ L/(mol s)}$ , while reaction (XIV) is characterized by  $\Delta H = 38.3 \text{ kJ/mol}$ ,  $E = 90.0 \text{ kJ/mol}$ ,  $A = 8.6 \times 10^7 \text{ L/(mol s)}$ , and  $k$  (350 K) =  $3.18 \times 10^{-6} \text{ L/(mol s)}$  (see Table 3); i.e., the abstraction of H from the  $\alpha\text{-C-H}$  bond predominates. As a result of adding oxygen, a thermally unstable per-

oxynitrate is formed that decomposes to radicals very rapidly (e.g., the dissociation energy of the O—O bond in  $\text{PrOONO}_2$  is just  $85 \text{ kJ/mol}$  [23]) and therefore raises the rate of their generation.

## CONCLUSIONS

We have considered abstraction reactions with fragmentation and the participation of nitrogen dioxide that play a crucial role in the chain decay of nitroalkanes. This reaction transforms  $\text{N}^{\bullet}\text{O}_2$  into an active intermediate particle of the chain decay reaction. Its concentration grows with the progress of the reaction. The accumulation of polynitro compounds that decay to radicals faster than  $\text{RNO}_2$  transforms the unbranched chain decay reaction of a nitroalkane into a degenerate branched chain reaction. The accumulation of an olefin accelerates the chain propagation reaction.

## ACKNOWLEDGMENTS

This work was supported by the OKhNM 1 program, and by the Russian Academy of Sciences.

## REFERENCES

1. Chemical Encyclopedia, *Explosives* (Sov. Entsiklopediya, Moscow, 1988), Vol. 1, p. 365 [in Russian].
2. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Thermal Decomposition and Combustion of Explosives and Powders* (Nauka, Moscow, 1996) [in Russian].
3. E. T. Denisov and A. F. Shestakov, *Russ. Chem. Bull.* **61**, 17 (2012).
4. E. T. Denisov and A. F. Shestakov, *Kinet. Catal.* **54**, 22 (2013).
5. E. T. Denisov, *Kinet. Catal.* **56**, 56 (2015).
6. E. T. Denisov and A. F. Shestakov, *Russ. J. Phys. Chem. A* **89**, 1343 (2015).
7. E. T. Denisov, A. F. Shestakov, and N. S. Emel'yanova, *Kinet. Catal.* **57**, 297 (2016).
8. Yu. A. Lebedev, E. A. Miroshnichenro, and Yu. A. Knobel, *Thermochemistry of Nitro Compounds* (Nauka, Moscow, 1970) [in Russian].
9. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
10. W. J. Stevens, H. Basch, and M. J. Krauss, *Chem. Phys.* **81**, 6026 (1984).
11. Yu. A. Ustynyuk and D. N. Laikov, *Russ. Chem. Bull.* **54**, 820 (2005).
12. F. L. Hirshfeld, *Theor. Chim. Acta* **44**, 129 (1977).
13. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants* (CRC, Boca Raton, FL, 2000).
14. E. T. Denisov, *Russ. Chem. Rev.* **66**, 859 (1997).



15. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Ed. by Z. B. Alfassi (Wiley, New York, 1999), p. 79.
16. I. V. Aleksandrov, *Teor. Eksp. Khim.* **12**, 299 (1976).
17. D. Lide, *Handbook of Chemistry and Physics* (CRC, Boca Raton, FL, 2007–2008).
18. E. T. Denisov and V. E. Tumanov, *Russ. Chem. Rev.* **74**, 825 (2005).
19. E. T. Denisov and T. C. Pokidova, *Russ. Chem. Rev.* **81**, 415 (2012).
20. A. M. Mebel and M. C. Lin, *J. Phys. Chem. A* **102**, 1803 (1998).
21. W. H. Chan, R. J. Nordstrom, J. G. Calvert, and J. H. Shaw, *Chem. Phys. Lett.* **37**, 441 (1976).
22. L. G. Wayne and D. M. Yost, *J. Chem. Phys.* **19**, 41 (1951).
23. V. L. Antonovskii and S. L. Khursan, *Physical Chemistry of Organic Peroxides* (Akademkniga, Moscow, 2003; Koninklijke Brill NV, Leiden, 2005).

*Translated by E. Boltukhina*