Influence of the size of the formed cycle on the reactivity of free radicals in cyclization reactions

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Numerous experimental data for the cyclization of free radicals $C^{\bullet}H_2(CH_2)_nCH{=}CH_2 \rightarrow$ *cyclo*-$[(CH_2)_{n+1}CH(C^{\bullet}H_2)]$, and $C^{\bullet}H_2(CH_2)_nCH{=}CHR \rightarrow$ *cyclo*-$[(CH_2)_{n+1}C^{\bullet}HCHR]$ were analyzed in the framework of the parabolic model. The activation energy of thermoneutral ($\Delta H_e = 0$) cyclization E_{e0} decreases linearly with an increase in the energy of cycle strain E_{rsc}: $E_{e0}(n)$ (kJ mol^{-1}) $= 85.5 - 0.44E_{rsc}(n)$ (n is the number of atoms in the cycle). The activation entropy of cyclization $\Delta S^{\neq}$ also depends on the cycle size: the larger the cycle, the lower $\Delta S^{\neq}$. A linear dependence of $\Delta S^{\neq}$ on the difference between the entropies of formation S° of cyclic hydrocarbon and the corresponding paraffin was found: $\Delta S^{\neq} = 1.00[S^{\circ}(\text{cycle}) - S^{\circ}(C_nH_{2n+2})]$. The E_{e0} values coincide for cyclization reactions with the formation of the six-membered cycle and the bimolecular addition of alkyl radicals to olefins.

Key words: reactivity, free radical, cyclization, parabolic model, reaction rate constant, activation energy, enthalpy of reaction, activation entropy.

Alkyl radicals containing double bonds undergo fast intraradical cyclization

$$C^{\bullet}H_2(CH_2)_nCH{=}CH_2 \longrightarrow \textit{cyclo}\text{-}[(CH_2)_{n+1}CH(C^{\bullet}H_2)],$$

$$C^{\bullet}H_2(CH_2)_nCH{=}CHR \longrightarrow \textit{cyclo}\text{-}[(CH_2)_{n+1}C^{\bullet}HCHR]$$

to form cyclic radicals containing $n + 2$ or $n + 3$ C atoms in the cycle. These reactions were studied intensely during the last two decades. They are widely used for studying the kinetics of radical reactions by the method of competing reactions as clock reaction and in the synthetic chemistry for syntheses of various cyclic compounds.[1—5] In this work, we analyzed the kinetic data for these reactions using the parabolic model of the radical reaction. Previously[6—10] we successfully applied this model for studying the bimolecular reactions of addition of atoms and radicals to multiple bonds. Now we used this approach to analyze the kinetic data on the intramolecular addition of the C atom bearing the free valence to the double bond of the same radical.

Calculation procedure

Cyclization reactions of free radicals are described in the parabolic model by the intersection of potential curves for the stretching vibration of the cleaved (i) and formed (f) bonds in the potential energy—amplitude of vibration coordinates.[9,10] The stretching vibration of the bond is taken as harmonic. The reaction is described by the following parameters.

1. The enthalpy of the reaction ΔH_e, which includes the difference between the zero-point vibrational energies of the reacting bonds

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f), \quad (1)$$

where D_i and D_f are the dissociation energies of the cleaved (initial) and formed bonds, ν_i and ν_f are the frequencies of the stretching vibration of these bonds, h is the Planck constant, and L is Avogadro´s number.

2. The activation energy E_e, which includes the zero-point vibrational energy of the cleaved bond and is related to the experimental activation energy E by the simple correlation

$$E_e = E + 0.5(hL\nu_i - RT), \quad (2)$$

where $0.5hL\nu_i$ is the zero-point vibrational energy of the cleaved bond, R is the gas constant ($R = 8.314$ J mol^{-1} K^{-1}), and T is the absolute temperature.

3. The sum of amplitudes of vibrations of reacting bonds r_e in the transition state (r_e is the distance between the vertices of two intersecting parabolas).

4. The parameters (for each class of radical reactions in the parabolic model) $\alpha = b_i/b_f$ ($2b_i^2$ is the force constant of the bond i, $b_i = \pi\nu_i(2\mu_i)^{0.5}$, $b_f = \pi\nu_f(2\mu_f)^{0.5}$); μ_i and μ_f are the reduced weights of the atoms involved in the formation of these bonds), and br_e ($b = b_i$). The br_e parameter was calculated for each individual reaction using the formula[10]

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

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5. The activation energy of the thermoneutral reaction E_{e0} and position of the transition state $r_0^{\neq}$ ($r_0^{\neq}/r_e = \alpha(1 + \alpha)^{-1}$) in the section r_e at $E_e = E_{e0}$

$$\sqrt{E_{e0}} = br_e/(1 + \alpha), \quad (4)$$

which also characterize each class of radical reactions.

The values of the parameters (α, b_i, $0.5hL\nu_i$, and $r_0^{\neq}/r_e$) for the cyclization reactions under discussion are presented below.

Radical reactions of the same series are characterized by the same pre-exponential factor per the C—H bond attacked.[10] Therefore, the activation energy was calculated from the experimental reaction rate constant using the Arrhenius formula

$$E = RT\ln(A_n/k), \quad (5)$$

where A_n is the pre-exponential factor of the reaction (n is the number of C atoms in the cycle) obtained by averaging of the experimental A values from the data of the works cited in Table 1.

The enthalpy of radical cyclization ΔH was calculated as a difference between the enthalpies of the final ($R_f^{\bullet}$) and initial ($R_i^{\bullet}$) radicals

$$\Delta H = \Delta H(R_f^{\bullet}) - \Delta H(R_i^{\bullet}). \quad (6)$$

In turn, the enthalpy of the $R^{\bullet}$ radical was calculated from the enthalpy of formation of the RH molecule and the dissociation energy of the corresponding bond

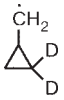
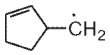
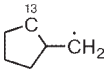
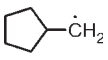
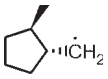
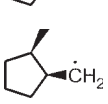
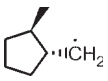
$$\Delta H(R^{\bullet}) = \Delta H(RH) + D(R—H) - \Delta H(H^{\bullet}),$$

so that the enthalpy of the reaction was determined using the thermochemical equation

$$\Delta H = \Delta H(R_fH) + D(R_f—H) - \Delta H(R_iH) - D(R_i—H). \quad (7)$$

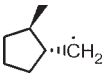
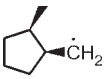
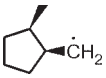
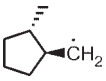
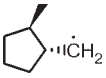
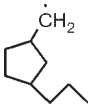
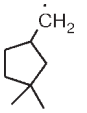
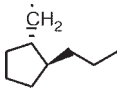
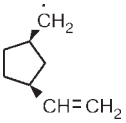
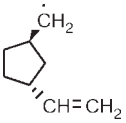
The enthalpies of formation of molecules were taken from the database[45] or calculated by the method of group increments,[46] using the published values of increments[47] and bond

Table 1. Rate constants at 298 K (k) and activation energies (E) of alkyl radical cyclization

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
		$n = 3$, $\log(A/s^{-1}) = 11.6$						
1	CH_2=CHCHMeC$^{\bullet}$H$_2$		23.0	333—379	$4.94 \cdot 10^4$	39.4	12.69	11
2	CH_2=CHCH$_2$C$^{\bullet}$D$_2$		23.4	252—276	$5.37 \cdot 10^3$	44.9	13.87	12
		$n = 4$, $\log(A/s^{-1}) = 11.3$						
3			−104.8	338	$8.3 \cdot 10^4$	34.8	21.11	13
		$n = 5$, $\log(A/s^{-1}) = 10.2$						
4	CH_2=CH(CH$_2$)$_3$C$^{\bullet}$H$_2$		−64.4	313	$1.8 \cdot 10^5$	29.7	18.44	14
5	CH_2=CH(CH$_2$)$_3$C$^{\bullet}$H$_2$		−64.4	188—373	$3.75 \cdot 10^4$	32.1	18.77	15—18
6	CH_2=CH(CH$_2$)$_2$CHMeC$^{\bullet}$H$_2$		−66.7	318—373	$4.57 \cdot 10^5$	25.9	18.04	19—21
7	CH_2=CHCMe(CH$_2$)C$^{\bullet}$H$_2$		−66.3	298—373	$7.74 \cdot 10^4$	30.3	18.45	19—21
8	CH_2=CHCHMe(CH$_2$)$_2$C$^{\bullet}$H$_2$		−69.8	298—373	$3.74 \cdot 10^5$	26.4	18.29	19—21

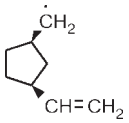
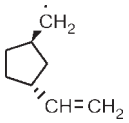
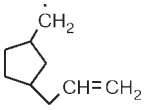
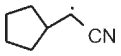
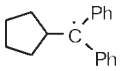
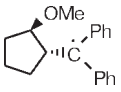
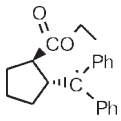
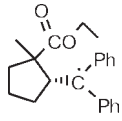
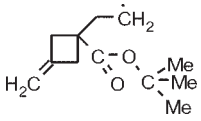
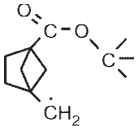
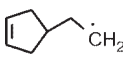
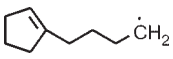
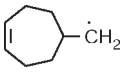
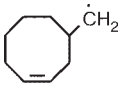
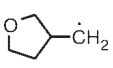
(*to be continued*)

Table 1 (*continued*)

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
9	$CH_2{=}CHCH_2CHMeCH_2C^{\bullet}H_2$		−66.7	318—373	$2.40 \cdot 10^5$	27.5	18.27	19—21
10	$CH_2{=}CHCH_2CHMeCH_2C^{\bullet}H_2$		−63.2	318—373	$2.40 \cdot 10^5$	27.5	17.87	19—21
11	$CH_2{=}CH(CH_2)_2CHMeC^{\bullet}H_2$		−63.2	318—373	$2.40 \cdot 10^5$	27.5	17.87	19—21
12	$CH_2{=}CMe(CH_2)_3C^{\bullet}H_2$		−65.3	298—338	$2.22 \cdot 10^4$	33.4	19.00	15, 21, 22
13	$CH_2{=}CH(CH_2)_3C^{\bullet}HMe$		−66.8	298—338	$1.03 \cdot 10^5$	29.6	18.57	15, 21
14	$MeCH{=}CMe(CH_2)_3C^{\bullet}H_2$		−61.7	338	$3.3 \cdot 10^5$	30.3	18.37	15
15	$CH_2{=}CMe(CH_2)_3C^{\bullet}Me_2$		−43.8	313	$6.2 \cdot 10^4$	32.4	17.55	22
16	$CH_2{=}CHCH_2CH(CH_2C^{\bullet}H_2)Pr$		−64.4	353	$6.6 \cdot 10^6$	22.8	17.44	19, 23
17	$CH_2{=}C(CHMe_2)(CH_2)_3C^{\bullet}H_2$		−61.6	338	$2.5 \cdot 10^4$	37.5	19.34	19
18	$CH_2{=}CH(CH_2)_2CMe_2C^{\bullet}H_2$		−64.4	298—353	$2.81 \cdot 10^6$	21.4	17.23	23—25
19	$Me_2C{=}CH(CH_2)_3C^{\bullet}H_2$		−69.3	338	$2.6 \cdot 10^6$	24.5	17.99	15
20	$CH_2{=}CH(CH_2)_3C^{\bullet}HPr$		−66.8	338	$8.5 \cdot 10^5$	27.6	18.29	15
21	$CH_2{=}CH(CH_2)_2CH(C^{\bullet}H_2)CH{=}CH_2$		−60.9	353	$7.8 \cdot 10^5$	29.1	18.16	19
22	$CH_2{=}CH(CH_2)_2CH(C^{\bullet}H_2)CH{=}CH_2$		−64.4	353	$1.4 \cdot 10^6$	27.3	18.10	19

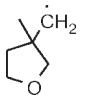
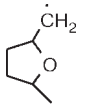
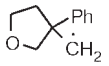
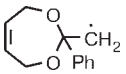
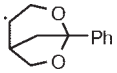
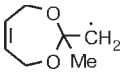
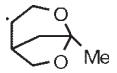
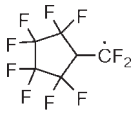
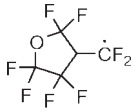
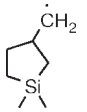
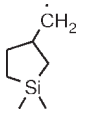
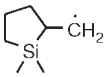
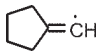
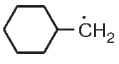
(*to be continued*)

Table 1 (*continued*)

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
23	$CH_2{=}CHCH_2CH(CH{=}CH_2)CH_2C^{\bullet}H_2$		−60.9	353	$2.2 \cdot 10^6$	26.1	17.52	19
24	$CH_2{=}CHCH_2CH(CH{=}CH_2)CH_2C^{\bullet}H_2$		−64.4	353	$6.6 \cdot 10^5$	29.6	18.43	19
25	$C^{\bullet}H_2CH_2CH(CH_2CH{=}CH_2)_2$		−65.4	303—357	$1.88 \cdot 10^6$	22.4	17.23	26
26	$N{\equiv}CCH{=}CH(CH_2)_3C^{\bullet}H_2$		−107.4	223—324	$1.72 \cdot 10^8$	11.2	18.06	27
27	$Ph_2C{=}CH(CH_2)_3C^{\bullet}H_2$		−112.5	226—317	$5.35 \cdot 10^7$	14.1	18.80	28
28	$Ph_2C{=}CH(CH_2)_3C^{\bullet}HOMe$		−106.7	273—313	$3.87 \cdot 10^7$	14.9	18.62	29
29	$Ph_2C{=}CH(CH_2)_3C^{\bullet}HC(O)OEt$		−98.1	273—313	$6.55 \cdot 10^7$	13.6	17.96	30
30	$Ph_2C{=}CH(CH_2)_3CMeC(O)OEt$		−87.6	273—333	$4.39 \cdot 10^5$	26.0	19.23	30
31			−61.6	274—383	$2.71 \cdot 10^5$	27.2	17.92	31
32			−51.2	366—403	$3.91 \cdot 10^3$	37.7	18.75	32
33			−61.9	338	$1.2 \cdot 10^5$	33.0	18.75	15
34			−53.8	280—470	$1.67 \cdot 10^5$	28.4	17.61	33
35			−56.4	280—470	$6.86 \cdot 10^4$	30.6	18.09	33
36	$CH_2{=}CH(CH_2)_2OC^{\bullet}H_2$		−65.7	180—220	$3.32 \cdot 10^4$	32.4	18.89	24, 34

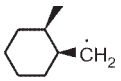
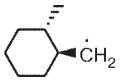
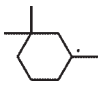
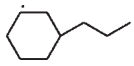
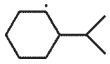
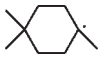
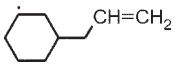
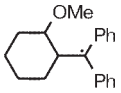
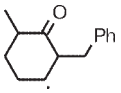
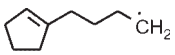
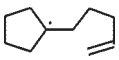
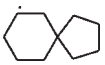
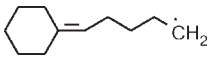
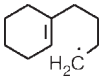
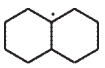
(*to be continued*)

Table 1 (*continued*)

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
37	$CH_2{=}CMeCH_2OCH_2C^{\bullet}H_2$		−62.9	313	$2.0 \cdot 10^5$	29.3	18.30	35
38	$CH_2{=}CHCH_2OCH_2C^{\bullet}HMe$		−96.1	338	$8.8 \cdot 10^6$	21.1	18.99	36
39	$CH_2{=}CPhCH_2OCH_2C^{\bullet}H_2$		−61.6	313	$1.7 \cdot 10^5$	29.7	18.28	35
40			−92.7	298—423	$4.96 \cdot 10^5$	25.7	19.47	37
41			−92.7	272—394	$8.38 \cdot 10^5$	24.4	19.28	37
42	$F_2C{=}CF(CF_2)_3C^{\bullet}F_2^{\bullet}$		−136.8	231—353	$4.22 \cdot 10^5$	26.1	21.68	38
43	$F_2C{=}CFO(CF_2)_2C^{\bullet}F_2$		−137.9	303	$3.5 \cdot 10^6$	21.2	21.08	39
44	$CH_2{=}CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−64.4	298	$1.0 \cdot 10^3$	36.6	19.38	17
45	$CH_2{=}CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−64.4	298	$7.5 \cdot 10^3$	38.7	19.65	17
46	$CH_2{=}CHSiMe_2(CH_2)_2C^{\bullet}H_2$		−64.4	298	$7.5 \cdot 10^4$	34.9	19.15	17, 25, 40
47	$HC{\equiv}C(CH_2)_3C^{\bullet}H_2$		−75.9	298	$2.8 \cdot 10^4$	32.8	22.98	21
		$n = 6$, $\log(A/s^{-1}) = 9.7$						
48	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$		−75.3	188—396	$1.78 \cdot 10^2$	42.5	20.73	15—17, 20, 24
49	$CH_2{=}CH(CH_2)_4C^{\bullet}H_2$		−92.5	338	$2.5 \cdot 10^4$	34.3	20.60	41
50	$CH_2{=}CMe(CH_2)_3C^{\bullet}H_2$		−108.3	298—338	$8.57 \cdot 10^3$	32.9	21.21	15, 21

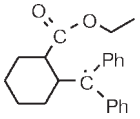
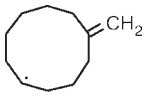
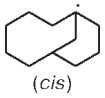
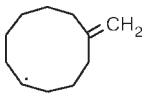
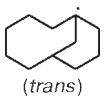
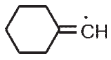
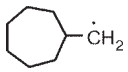
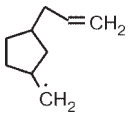
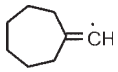
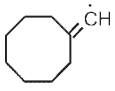
(*to be continued*)

Table 1 (*continued*)

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
51	$CH_2{=}CH(CH_2)_3C^{\bullet}HMe$		−97.6	338	$9.7 \cdot 10^3$	36.9	21.18	15
52	$CH_2{=}CH(CH_2)_3C^{\bullet}Me_2$		−87.6	298—338	$9.68 \cdot 10^3$	32.6	20.13	15, 21, 42
53	$CH_2{=}CH(CH_2)_4C^{\bullet}HMe$		−82.7	298	$2.1 \cdot 10^3$	33.9	20.03	21
54	$CH_2{=}CH(CH_2)_4C^{\bullet}HMe$		−90.5	298	$5.7 \cdot 10^3$	36.4	20.76	21
55	$CH_2{=}CMe(CH_2)_3C^{\bullet}Me_2$		−105.1	313	$5.4 \cdot 10^4$	29.7	20.64	15, 22
56	$MeCH{=}CMe(CH_2)_3C^{\bullet}H_2$		−92.2	338	$6.0 \cdot 10^4$	31.8	20.26	15
57	$CH_2{=}CH(CH_2)_3C^{\bullet}H(CH_2)_2Me$		−97.6	338	$4.1 \cdot 10^3$	39.4	21.49	15
58	$CH_2{=}C(CHMe_2)(CH_2)_3C^{\bullet}H_2$		−103.9	338	$8.0 \cdot 10^4$	31.0	20.75	19
59	$CH_2{=}CMe(CH_2)_2CMe_2C^{\bullet}H_2$		−105.0	318—373	$2.17 \cdot 10^4$	30.6	20.75	23
60	$(CH_2{=}CHCH_2)_2CHCH_2C^{\bullet}H_2$		−95.3	333	$2.3 \cdot 10^5$	27.6	19.86	26
61	$Ph_2C{=}CH(CH_2)_4C^{\bullet}HOMe$		−133.0	283—323	$1.51 \cdot 10^5$	25.8	21.47	29
62	$PhCH_2CH{=}CH(CH_2)_2CHMeC^{\bullet}(O)$		−84.8	353	$2.0 \cdot 10^5$	29.7	19.59	43
63			−89.3	338	$3.0 \cdot 10^4$	33.7	20.36	15
64			−76.8	338	$6.7 \cdot 10^4$	31.5	19.40	15
65			−89.5	338	$1.0 \cdot 10^6$	23.8	19.03	15
66			−89.4	338	$5.3 \cdot 10^4$	32.2	20.17	15

(*to be continued*)

Table 1 (*continued*)

Entry	$R_i^{\bullet}$ (reactant)	$R_f^{\bullet}$ (product)	ΔH /kJ mol^{-1}	T /K	k /s^{-1}	E^a	br_e^b	Reference
67	$Ph_2C{=}CH(CH_2)_4C^{\bullet}HC(O)OEt$		−124.5	273—313	$1.99 \cdot 10^7$	13.7	19.34	30
68	$CH_2{=}CMeCH_2OCH_2C^{\bullet}H_2$		−80.0	313	$4.6 \cdot 10^3$	36.2	20.19	35
69	$CH_2{=}CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−95.3	298	$1.6 \cdot 10^4$	34.0	20.70	17
70	$CH_2{=}CHSiMe_2(CH_2)_2C^{\bullet}H_2$		−95.3	298	$7.5 \cdot 10^4$	34.7	20.62	17
71	$CH_2{=}CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−95.3	298	$1.4 \cdot 10^4$	34.9	20.82	25
72		 (*cis*)	−136.2	313—396	$9.97 \cdot 10^8$	4.0	18.09	44
73		 (*trans*)	−149.6	313—396	$3.21 \cdot 10^9$	1.1	18.16	44
74	$HC{\equiv}C(CH_2)_4C^{\bullet}H_2$		−58.9	333	$4.6 \cdot 10^4$	32.1	21.79	18
		$n = 7$, $\log(A/s^{-1}) = 9.1$						
75	$CH_2{=}CH(CH_2)_4C^{\bullet}H_2$		−53.5	338	$4.8 \cdot 10^3$	35.0	18.52	41
76	$CH_2{=}CH(CH_2)_5C^{\bullet}H_2$		−64.6	338	$8.3 \cdot 10^2$	39.9	19.82	41
77			−73.4	338	$3.0 \cdot 10^3$	37.7	20.02	26
78	$HC{\equiv}C(CH_2)_5C^{\bullet}H_2$		−85.3	333	$2.5 \cdot 10^3$	36.3	24.37	18
		$n = 8$, $\log(A/s^{-1}) = 8.8$						
79	$HC{\equiv}C(CH_2)_6C^{\bullet}H_2$		−58.5	333	$1.2 \cdot 10^2$	42.8	23.39	18

[a] In kJ mol^{-1}.
[b] In kJ$^{0.5}$ mol$^{-0.5}$.

energies of C—H in hydrocarbons.[48] The activation energy of the reaction was calculated by formula (5). The pre-exponential factor of cyclization A_n depends on the number of atoms (n) in the cycle, and the corresponding values are presented below.

n	3	5	6	7
$\log(A/s^{-1})$	11.60±0.86	10.20±0.45	9.90±0.52	9.10

To calculate ΔH_e, E_e, and br_e, we used the following values of the parameters.[10]

Bond	α	$b \cdot 10^{-11}$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$0.5hLv_i$ kJ mol^{-1}	$0.5hL(v_i - v_f)$ kJ mol^{-1}
C=C	1.202	5.389	9.9	1.7
C≡C	1.542	6.912	12.7	4.5

The original experimental data are presented in Table 1.

Results and Discussion

Analysis of the br_e parameters calculated from the experimental data suggests that the decisive factor influencing the br_e (and E_{e0}) values in radical cyclization is the type of cyclization (Table 2). A comparison of the br_e parameters led us to the following conclusions: the br_e parameter depends in the sizes of the formed cycle; this parameter is independent (or depends slightly) on the position and number of substituents in the radical; the br_e parameter is the same for the cyclization of radicals with the same cycle size and chain consisting of C atoms only or including O and Si atoms; the cyclization of perfluorinated radicals occurs with a higher br_e parameter; and cyclization with the attack of the radical at the triple bond is characterized by a higher br_e parameter.

Influence of the energy of cycle strain on the activation energy. The data in Table 2 and Fig. 1 show that, depending on the cycle size, the activation energy of the thermoneutral reaction passes through a maximum E_{e0} = 86 kJ mol^{-1}, which is achieved in reactions producing the six-membered cycle. The minimum value E_{e0} = 36.4 kJ mol^{-1} is observed for the three-membered cycle (see Table 2). When a linear hydrocarbon molecule transforms into a cycloalkene, the energy of cycle strain appears. This is caused by the fact that the optimum for sp^3-hybridization C—C—C angle of 109° is transformed upon cyclization to another angle, *e.g.*, 60° in cyclopropane, and this enhances the energy of the cyclic molecule. Perhaps, this is precisely the strain in the formed cycle that changes the E_{e0} value. The strain energies E_{rsc} in the corresponding cycles[47] are presented in Table 2, and the E_{e0} values are compared with E_{rsc} in Fig. 2. A linear dependence between E_{e0} and E_{rsc} is expressed by the formula

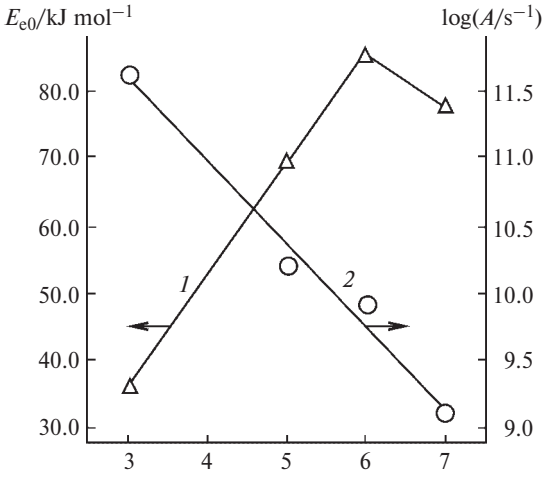


Fig. 1. Plots of the activation energy of thermoneutral radical cyclization E_{e0} (*1*) and logarithm of pre-exponential factor A (*2*) *vs.* number (n) of C atoms in the formed cycle.

$$E_{e0}/\text{kJ mol}^{-1} = 85.5 - (0.44 \pm 0.12)E_{rsc}, \quad (8)$$

i.e., the higher the energy of cycle strain, the lower the activation energy of the thermoneutral reaction. At the same time, the higher E_{rsc}, the higher the enthalpy of the reaction and, correspondingly, the higher the activation energy of cyclization, which depends on ΔH_e (formula (1)) as follows[10]:

$$\sqrt{E_e} = \frac{\sqrt{E_{e0}}}{1-\alpha}\left(1 - \alpha\sqrt{1 - \frac{1-\alpha}{E_{e0}}\Lambda H_e}\right) \quad (9)$$

Table 2. Comparison of the activation energy and pre-exponential factor of the cyclization of alkyl radicals with the energy of cycle strain (E_{rsc}) and entropy

n	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0}	E_{rsc}	$E_{e0}(6) - E_{e0}(n)$	$\log(A/s^{-1})$	$\Delta S^{\neq}$	$S°(C_nH_{2n})$	$S°(C_nH_{2n+2})$	$\Delta S° = S°(C_nH_{2n}) - S°(C_nH_{2n+2})$
		kJ mol^{-1}				J mol^{-1} K^{-1}			
3	13.28±0.59	36.4	115.1	49.3	11.60	−32.5	237.4	270.0	−32.6
5	18.39±0.60	69.7	26.7	16.0	10.20	−59.3	293.1	348.9	−55.8
6	20.39±0.64	85.7	0.7	0	9.90	−65.2	298.6	388.1	−89.5
7	19.45±0.66	78.0	26.3	7.7	9.10	−80.5	342.6	427.9	−85.3

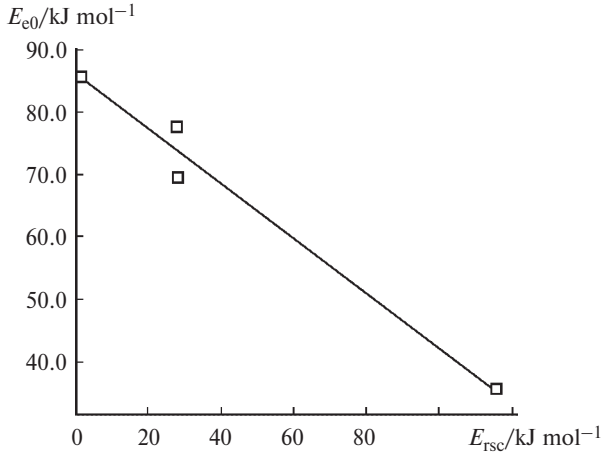


Fig. 2. Plot of the activation energy of thermoneutral radical cyclization (E_{e0}) *vs.* strain energy (E_{rsc}) in the formed cycle.

The insertion of formula (8) and coefficient α into Eq. (9) gives the formula for the calculation of E_e

$$\sqrt{E_e} = 3.28\sqrt{194.4 - E_{rsc}}\left(1.202\sqrt{1 + \frac{0.208\Delta H_e}{194.5 - E_{rsc}}} - 1\right) \qquad (10)$$

which allows the calculation of E (Eq. (2)) through the enthalpy of the reaction $\Delta H = \Delta H_e - 1.7$ and energy E_{rsc}. Table 3 contains the results of calculation of the energy at 298 K (E_{calc}) for the reaction

$$CH_2{=}CH(CH_2)_nC^{\bullet}HR \longrightarrow \textit{cyclo}\text{-}[CHR(CH_2)_nCH(C^{\bullet}H_2)].$$

It can be seen that ΔH_e and E_{rsc}, affecting in combination the activation energy, compensate, to a great extent, the opposite action. The E values calculated by formulas (1), (2), and (10) are close to the experimental values: $E_{calc} - E_{exp} = 1.14 \pm 3.48$ kJ mol^{-1} (see Table 3).

Influence of the cycle size on the pre-exponential factor of cyclization. As mentioned above (see Calculation procedure), the pre-exponential factor of radical cyclization depends on the cycle size. The plot of log$A$ *vs.* number of atoms n in the formed cycle (see Fig. 1)

$$\log(A/s^{-1}) = (13.10 \pm 0.12) - 0.55n \qquad (11)$$

is linear.

What is the origin of such a relation? The formation of a cyclic transition state from a linear radical, for example, $CH_2{=}CH(CH_2)_nC^{\bullet}H_2$, is accompanied by the disappearance of the free rotation of the radical fragments about the corresponding C—C bonds (or C—O and C—Si bonds if any in the molecule). The entropy of the transition state decreases compared to that of the initial radical. The value of such a change can be estimated by the comparison of $S°$ of the linear (C_nH_{2n+2}) and cyclic (C_nH_{2n}) hydrocarbon molecules (see Table 2). It can be seen from the last column that the larger the cycle size, the higher the difference $\Delta S° = S°(C_nH_{2n}) - S°(C_nH_{2n+2})$ (for n = 3, 5, 7). This regularity is due to the fact that the greater the number of the C—C bonds in the cycle around which the groups rotate, the higher the entropy losses accompanying the cyclization of the molecule or radical. The only exception is the cyclohexane ring ($\Delta S°$(at $n = 6$) < $\Delta S°$(at $n = 7$)) likely due to the occurrence of two conformations (chair and bath), so

Table 3. Energies of cycle strain (E_{rsc}), enthalpies (ΔH_e), experimental (E_{exp}) and calculated (E_{calc}) activation energies of alkyl radical cyclization

Entry[a]	ΔH_e[b]	E_{rsc}[c]	E_{calc}[d]	E_{exp}[e]	$E_{calc} - E_{exp}$
	kJ mol^{-1}				
	$n = 3$, log(A/s^{-1}) = 11.6				
1	24.7	115.1	040.6	39.4	1.2
	$n = 5$, log(A/s^{-1}) = 10.2				
5	−62.7	26.7	34.3	32.1	2.2
7	−64.6	26.7	33.5	30.3	3.2
8	−68.1	26.7	32.0	26.4	5.6
9	−65.0	26.7	33.3	27.5	5.8
12	−63.6	26.7	33.9	33.4	0.5
13	−65.1	26.7	33.2	29.6	3.6
14	−60.0	26.7	35.5	30.3	5.2
17	−59.9	26.7	35.5	37.5	−2.0
20	−65.1	26.7	33.2	27.6	5.6
24	−62.7	26.7	34.3	29.6	4.7
27	−110.8	26.7	15.7	14.1	1.6
28	−105.0	26.7	17.7	14.9	2.8
30	−85.9	26.7	24.8	26.0	−1.2
36	−64.0	26.7	33.7	32.4	1.3
37	−61.2	26.7	34.9	29.3	5.6
	$n = 6$, log(A/s^{-1}) = 9.7				
48	−73.6	0.7	40.4	42.5	−2.1
49	−90.8	0.7	33.3	34.3	−1.0
50	−106.6	0.7	27.1	32.9	−5.8
51	−95.9	0.7	31.3	36.9	−5.6
52	−85.9	0.7	35.3	32.6	2.7
53	−81.0	0.7	37.3	33.9	3.4
54	−88.8	0.7	34.1	36.4	−2.3
55	−103.4	0.7	28.4	29.7	−1.3
56	−90.5	0.7	33.4	31.8	1.6
58	−102.2	0.7	28.8	31.0	−2.2
59	−103.3	0.7	28.4	30.6	−2.2
60	−93.6	0.7	32.2	27.6	4.6
	$n = 7$, log(A/s^{-1}) = 9.1				
75	−51.8	26.3	39.3	35.0	4.3
76	−62.9	26.3	34.4	39.9	−5.5

[a] See Table 1.
[b] Calculation by formula (1).
[c] See Ref. 47.
[d] Calculation by formulas (1), (2), and (10).
[e] For cited experimental works, see Table 1.

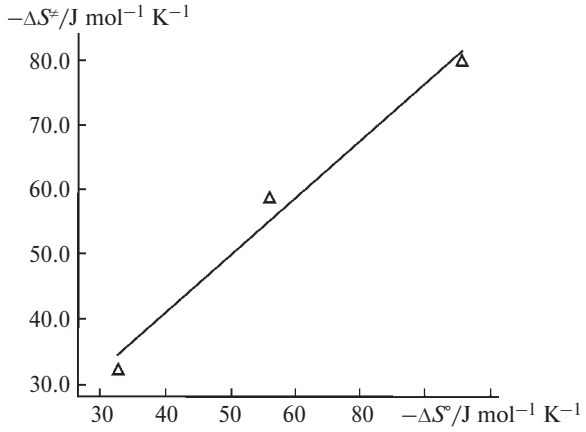


Fig. 3. Comparison of the activation entropy of radical cyclization ($-\Delta S^{\neq}$) with the difference between entropies of formation of alicyclic (C_nH_{2n}) and linear (C_nH_{2n+2}) paraffinic hydrocarbons ($\Delta S°$).

that transition from one conformation to another enhances the entropy of the six-membered ring. As can be seen in Fig. 3, the activation entropy ($-\Delta S^{\neq}$) depends linearly on $\Delta S° = \Delta S°(C_nH_{2n}) - \Delta S°(C_nH_{2n+2})$ for $n = 3$, 5, and 7, and the reaction producing cyclohexane ring ($n = 6$) is an exception. The plot of $\Delta S^{\neq}$ *vs.* $\Delta S°$ is linear with the slope equal to unity, which indicates the purely entropic influence of the cycle size on the pre-exponential factor

$$\Delta S^{\neq} = (1.00\pm0.04)(S°(C_nH_{2n}) - S°(C_nH_{2n+2})). \qquad (12)$$

Role of the force constant in cyclization. The activation energy of the bimolecular elimination and addition reactions depend on the force constant of the reacting bonds.[10] The activation energy of the thermoneutral reaction E_{e0} is determined, according to the parabolic model, by three parameters: total amplitude of vibration of the reacting bonds r_e and force constants of the cleaved (b_i) and formed (b_f) bonds by formula (4). The triple carbon—carbon bond has a higher force constant than the double bond. Therefore, one should expect a higher activation energy E_{e0} for addition at the triple bond than that at the double carbon—carbon bond. This is confirmed by the results of studying the cyclization of the $H_2C{=}CH(CH_2)_3C^{\bullet}H_2$ and $HC{\equiv}CH(CH_2)_3C^{\bullet}H_2$ radicals (see Table 1). It is seen from the comparison of the corresponding parameters of radical cyclization producing the five-membered cycle, which are presented below.

Bond	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	$b\cdot10^{-11}$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}
C=C	18.39	69.7	5.389
C≡C	22.98	81.7	6.912

Note that the r_e parameters for these two classes of reactions are close: $r_e\cdot10^{11}$ is 3.41 and 3.32 m for addition at the C=C and C≡C bonds, respectively. This implies that the difference between the activation energies for reactions of these classes is caused only by different force constants of the double and triple bonds.

Polar interaction. The cyclization of perfluorinated radicals occurs with a higher activation energy of the thermoneutral reaction: $E_{e0} = 94.3$ kJ mol^{-1} ($n = 5$), while hydrocarbon radicals are cyclized with $E_{e0} = 69.7$ kJ mol^{-1} ($n = 5$). The difference between the activation energies $\Delta E_{e0} = E_{e0}(n = 5, F) - E_{e0}(n = 5, H) = 24.6$ kJ mol^{-1} is sufficiently high and characterizes the contribution of the polar influence of the C—F bonds to the energy of the transition state.

Comparison of cyclization with other reactions. Previously,[9,10] we analyzed bimolecular radical addition reactions in the framework of the parabolic model. It is of interest to compare the kinetic parameters of these very resembling reactions. Since in the bimolecular reaction the transition state has a noncyclic structure, it is reasonable to compare bimolecular reactions with cyclization resulting in the formation of the six-membered cycle without the bond strain upon the formation of the cyclic transition state. The parameters of reactions of these two types are presented below.

Reaction	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	$r_e\cdot10^{11}$ /m
Cyclization ($n = 6$)	20.39±0.64	85.6	3.78
Bimolecular addition	20.01±0.41	82.6	3.71

It is seen that these parameters coincide within the estimation error. Thus, the activation energies of bimolecular addition and six-membered cyclization are close at the same enthalpy of addition. Their rates are close at the concentration of the monomer equal to 16 mol L^{-1} when $A_{cycl} = 8\cdot10^9$ s^{-1} = ($A_{bim} = 5\cdot10^8$ L mol^{-1} s^{-1})[M], (A_{cycl} and A_{bim} are the pre-exponential factors of cyclization and bimolecular addition, respectively; M is the monomer).

We have recently[49] analyzed the intraradical abstraction of the H atom

$$RCH(CH_2)_nC^{\bullet}H_2 \longrightarrow RC^{\bullet}(CH_2)_nMe,$$

which allows the comparison of radical isomerization with the elimination of the H atom and addition at the double bond. Below we present the kinetic parameters characterizing these two types of reactions occurring through the five-, six-, and seven-membered cyclic transition states (data for addition at the double bond are top

figures, and data for isomerization with H atom abstraction are shown as bottom figures).

n	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	$r_e \cdot 10^{11}$ /m
5	18.39	69.7	3.41
	15.41	59.4	4.12
6	20.39	85.7	3.78
	13.66	46.6	3.65
7	19.45	78.0	3.61
	15.11	57.1	4.04

A comparison of the E_{e0} values shows that the abstraction of the H atom occurs with a lower E_{e0} energy than addition. The plots of E_{e0} *vs.* cycle size are opposite: for addition $E_{e0}(n = 6)$ is maximum and for abstraction, on the contrary, it is minimum. Thus, the cycle strain has different effects on the potential barrier E_{e0} in intramolecular addition and abstraction. The difference in E_{e0} is likely related to the following circumstance. For the addition reaction the cyclic transition state coincides with the cyclic structure of the product (cyclic radical) and differs from the initial linear structure of the reactant. In the intramolecular abstraction reaction only the transition state is cyclic and the reactant and product are linear. Intramolecular abstraction and addition with the formation of the six-membered cycle are characterized by a great difference in the E_{e0} values (47 and 86 kJ mol^{-1}, respectively) and, at the same time, the r_e parameters are very close ($3.78 \cdot 10^{-11}$ and $3.65 \cdot 10^{-11}$ m). This is a result, most likely, of different force constants of the reacting bonds: for H atom abstraction $\alpha = 1$ and $b = 3.743 \cdot 10^{11}$ kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}, whereas for addition $\alpha = 1.202$ and $b = 5.389 \cdot 10^{11}$ kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}.

Thus, the activation energy and rate constant of the cyclization of alkyl radical are determined by three main factors: enthalpy of the reaction, size of the formed cycle, and force constants of the reacting bonds. The size of the cycle influences on the enthalpy of the reaction and the activation energy of the thermoneutral reaction. The latter depends on the energy of cycle strain (see formula (8)). The dependence of the activation energy of cyclization on its enthalpy and energy of cycle strain is described by rather simple equation (10), which allows the estimation of E for cyclization with any size of the cycle. The activation entropy also depends on the cycle size: it is proportional to the entropy loss on going from the linear to cyclic structure (see formula (12)). Equations (10) and (11) allow the estimation of cyclization rate constants for any alkyl radicals containing the double bond. The important role of the force constant of the reacting multiple bond is shown for the cyclization of radicals with the attack at the double and triple bond. Cyclization reactions of perfluorinated radicals prove an important role of the polar effect.

References

1. J. W. Wilt, *Free Radicals*, Ed. J. K. Kochi, Wiley, New York, 1973, **1**, 333 pp.
2. D. P. Curran, N. A. Porter, and B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, 1995.
3. A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925.
4. D. C. Spellmeyer and K. N. Houk, *J. Org. Chem.*, 1987, **52**, 959.
5. C. Chatgilialoglu and P. Renaud, in *General Aspects of the Chemistry of Radicals*, Ed. Z. B. Alfassi, Wiley, New York, 1999, 501.
6. E. T. Denisov, *Kinet. Katal.*, 1992, **33**, 66 [*Kinet. Catal.*, 1992, **33**, 50 (Engl. Transl.)].
7. E. T. Denisov, *Kinet. Katal.*, 1999, **40**, 835 [*Kinet. Catal.*, 1999, **40**, 756 (Engl. Transl.)].
8. E. T. Denisov and T. G. Denisova, *Khim. Fiz.*, 1998, **17**, 83 [*Chem. Phys. Reports*, 1998, **17**, 2105 (Engl. Transl.)].
9. T. G. Denisova and E. T. Denisov, *Neftekhimiya*, 1998, **38**, 15 [*Petroleum Chem.*, 1998, **38**, 12 (Engl. Transl.)].
10. E. T. Denisov, *Usp. Khim.*, 2000, **69**, 166 [*Russ. Chem. Rev.*, 2000, **69**, 153 (Engl. Transl.)].
11. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.*, 1989, **54**, 2681.
12. A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *J. Am. Chem. Soc.*, 1980, **102**, 1734.
13. E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 1972, **37**, 2550.
14. P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, 1978, **100**, 2493.
15. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.*, 1974, **26**, 2251.
16. D. Lal, G. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6355.
17. J. W. Wilt, J. Lusztyk, M. Peeran, and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 281.
18. A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073.
19. A. L. J. Beckwith, T. Lawrence, and A. K. Serelis, *J. Chem. Soc., Chem. Commun.*, 1980, **11**, 484.
20. A. L. J. Beckwith, C. J. Easton, T. Lawrence, and A. K. Serelis, *Aust. J. Chem.*, 1983, **36**, 545.
21. A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925.
22. C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, 1972, **94**, 6064.
23. A. L. J. Beckwith and T. Lawrence, *J. Chem. Soc., Perkin Trans. 2*, 1979, **11**, 1535.
24. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.*, 1988, **53**, 1632.
25. J. W. Wilt, *Tetrahedron*, 1985, **41**, 3979.
26. A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1975, **15**, 1726.
27. M. Newcomb, T. R. Varick, C. Ha, M. B. Manek, and X. Yue, *J. Am. Chem. Soc.*, 1992, **114**, 8158.
28. C. Ha, J. H. Horner, M. Newcomb, T. R. Varick, B. R. Arnold, and J. Lusztyk, *J. Org. Chem.*, 1993, **58**, 1194.
29. C. C. Johnson, J. H. Horner, C. Tronche, and M. Newcomb, *J. Am. Chem. Soc.*, 1995, **117**, 1684.
30. M. Newcomb, J. H. Horner, M. A. Filipkowski, C. Ha, and Seung-Un Park, *J. Am. Chem. Soc.*, 1995, **117**, 3674.

31. P. E. Pigou, *J. Org. Chem.*, 1989, **54**, 4943.
32. J. W. Wilt, S. N. Massie, and R. B. Dabek, *J. Org. Chem.*, 1970, **35**, 2803.
33. F. MacCorquodale and J. C. Walton, *J. Chem. Soc.*, *Perkin Trans. 1*, 1989, **2**, 347.
34. A. L. J. Beckwith and S. A. Glover, *Aust. J. Chem.*, 1987, **40**, 157.
35. T. W. Smith and G. B. Butter, *J. Org. Chem.*, 1978, **43**, 6.
36. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, 1974, **96**, 1613.
37. A. C. Hindson, F. MacCorquodale, and J. C. Walton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, **5**, 871.
38. C. F. Sturino and A. G. Fallis, *J. Org. Chem.*, 1994, **59**, 6514.
39. W. R. Dolbier, *Chem. Rev.*, 1996, **96**, 1557.
40. J. W. Wilt, *J. Am. Chem. Soc.*, 1981, **103**, 5251.
41. A. L. J. Beckwith and G. Moad, *J. Chem. Soc.*, *Chem. Commun.*, 1974, **12**, 472.
42. J. Lusztyk, B. Maillard, S. Deycard, D. A. Lindsay, and K. U. Ingold, *J. Org. Chem.*, 1987, **52**, 3509.
43. C. Chatgilialoglu, C. Ferreri, and A. Sommazzi, *J. Am. Chem. Soc.*, 1996, **118**, 7223.
44. A. L. J. Beckwith, V. W. Bowry, and C. H. Schiesser, *Tetrahedron*, 1991, **47**, 121.
45. S. G. Lias, J. F. Liebman, R. D. Levin, S. A. Kafafi, and E. S. Stein, *NIST Positive Ion Energetics — Ver. 2.0. NIST Standard Reference Database 19A*, Gaithersburg, 1993.
46. S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1968.
47. E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data*, 1993, **22**, 805.
48. V. E. Tumanov and E. T. Denisov, *Neftekhimiya*, 2001, **41**, 109 [*Petroleum Chem.*, 2001, **41** (Engl. Transl.)].
49. T. G. Denisova and E. T. Denisov, *Kinet. Katal.*, 2001, **42**, 684 [*Kinet. Catal.*, 2001, **42**, No. 5 (Engl. Transl.)].

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