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# Kinetic Parameters of the Cyclization and Decyclization Reactions of Nitrogen- and Oxygen-Containing Radicals

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**Abstract**—The intersecting parabolas model is used to analyze experimental data for the following radical cyclization and decyclization reactions: $RCH{=}CH(CH_2)_nN^{\bullet}R^1 \longrightarrow$ *cyclo*-$[NR^1CH(CH_2)_n]C^{\bullet}HR$, $R(CH_2)_2OOCH_2C^{\bullet}HR \longrightarrow$ *cyclo*-[RCHOCH$_2$] + $RCH_2CH_2O^{\bullet}$, *cyclo*-$[(CH_2)_nOOCHC^{\bullet}HR] \longrightarrow$ *cyclo*-$[RCHOCH](CH_2)_nO^{\bullet}$, *cyclo*-$[(CH_2)_nOC^{\bullet}RO] \longrightarrow RC(O)O(CH_2)_{n-1}C^{\bullet}H_2$, and *cyclo*-$[(CH_2)_nCHO^{\bullet}] \longrightarrow CH(O)(CH_2)_{n-1}C^{\bullet}H_2$. The activation energy of the thermally neutral reaction ($E_{e,0}$) is calculated for each class of reactions. $E_{e,0}$ depends on the electronegativity of the heteroatom Y of the reaction center C···C…Y, the force constants of the reacting bonds, and the strain energy of the ring formed. For the cyclization and decyclization of six-membered rings, the empirical relationship between the elongation of the reacting bonds in the transition state ($r_e$) and the difference in electronegativity ($\Delta EA$) between the C and Y atoms (Y = C, N, O) has the form $r_e \times 10^{11}$, m = 3.83 – 0.0198($\Delta EA$, kJ/mol).

## INTRODUCTION

Radical cyclization and decyclization reactions are used in organic synthesis. The rate constants of these reactions, as shown experimentally, are solvent-independent and, therefore, find wide use as clock reactions in the kinetic method of competitive reactions [1, 2]. In our previous work [3], we analyzed the cyclization of hydrocarbon radicals and found that the activation energy depends strongly on the ring strain energy $E_{rcs}$ and the preexponential factor depends on the entropy of ring formation. Among the radical cyclization and decyclization reactions, only reactions involving radicals with a free valence at a nitrogen or oxygen atom and alkyl radicals containing peroxy and carbonyl groups were studied experimentally [4]. In this work, we analyze these reactions in terms of the intersecting parabolas model [3–7], as in a previous study [3].

## CALCULATION PROCEDURE

The enthalpy of cyclization, $\Delta H$, was calculated as the difference between the enthalpies of formation of the final ($R_f^{\bullet}$) and initial ($R_i^{\bullet}$) radicals:

$$\Delta H = \Delta H_f^0(R_f^{\bullet}) - \Delta H_f^0(R_i^{\bullet}). \quad (1)$$

The enthalpy of formation of $R^{\bullet}$ was calculated from the enthalpy of formation of the molecule RH and the dissociation energy of the R–H bond

$$\Delta H_f(R^{\bullet}) = \Delta H_f^0(RH) + D(R{-}H) - \Delta H_f^0(H), \quad (2)$$

and the enthalpy of the reaction was calculated using the thermochemical equation

$$\Delta H = \Delta H_f^0(R_fH) + D(R_f{-}H) - \Delta H_f^0(R_iH) - D(R_i{-}H). \quad (3)$$

The enthalpies of formation of molecules were taken from a database [8] or calculated using the group increment method [9]. Group increments were taken from [10]; C–H bond dissociation energies for hydrocarbons, from [4]. The activation energy of a reaction was calculated by the Arrhenius formula

$$E = RT\ln(A_n/k), \quad (4)$$

where $A_n$ is the preexponential factor of the cyclization reaction for a ring of $n$ carbon atoms, which is determined by averaging experimental $A$ data. The factor $A$ depends on ring size [3]:

| $n$ | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|
| log$A$ [$s^{-1}$] | 11.60 | 10.90 | 10.20 | 9.90 | 9.10 |

To calculate $\Delta H_e$, $E_e$, and the parameter $br_e$, we used the following formulas [6]:

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_i - \nu_f), \quad (5)$$

where $\nu_i$ and $\nu_f$ are the stretching vibration frequencies of the attacked (initial) and forming bonds, respectively, and $h$ and $N_A$ are Planck's constant and Avogadro's number, respectively;

$$E_e = E + 0.5(hN_A\nu_i - RT) \quad (6)$$

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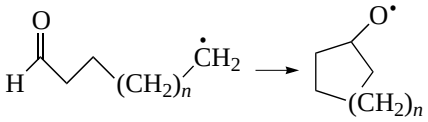
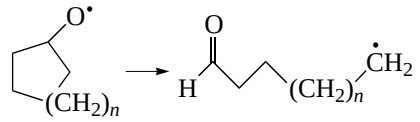
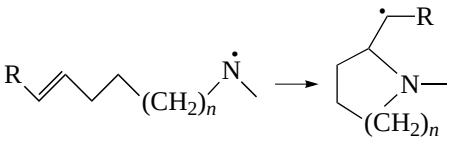
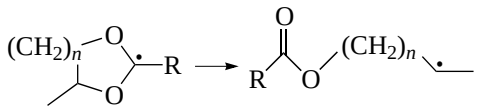
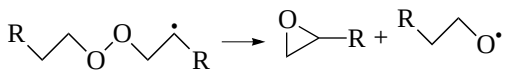
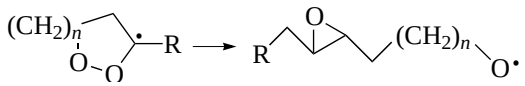
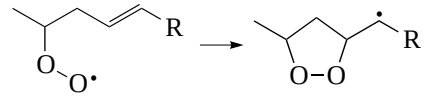
**Table 1.** Parameters of the intersecting parabolas model for radical cyclization and decyclization reactions [6]

| Reaction | α | $b \times 10^{-11}$, $(kJ/mol)^{1/2}$ $m^{-1}$ | $0.5hN_A\nu$, kJ/mol | $0.5hN_A(\nu_i - \nu_f)$, kJ/mol |
|---|---|---|---|---|
|  | 1.336 | 5.991 | 10.3 | 2.1 |
|  | 0.748 | 4.483 | 8.2 | –2.1 |
|  | 1.410 | 5.389 | 9.9 | 3.1 |
|  | 0.655 | 3.922 | 6.7 | –3.6 |
|  | 0.826 | 3.238 | 5.1 | –1.6 |
|  | 0.826 | 3.238 | 5.1 | –1.6 |
|  | 1.737 | 5.389 | 9.9 | 4.6 |

and

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}, \quad (7)$$

where $\alpha = b_i/b_f$, $b = b_i$, $b_i$ and $b_f$ are the dynamic characteristics of the breaking and forming bonds ($2b_i^2$ and $2b_f^2$ are the force constants of the corresponding bonds), and $r_e$ is the elongation of the reacting bonds in the transition state. The values of α, $b$, and $0.5hN_A\nu_i$ are presented in Table 1.

The activation energy of the thermally neutral reaction, $E_{e,0}$ was calculated using the formula [5]

$$E_{e,0} = \frac{(br_e)^2}{(1+\alpha)^2}. \quad (8)$$

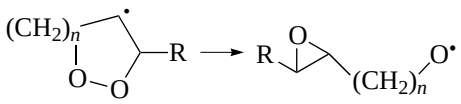
## RESULTS AND DISCUSSION

The starting data and $br_e$ parameters calculated by formula (7) for different cyclization and decyclization reactions of radicals containing nitrogen and oxygen atoms are presented in Tables 2–4.

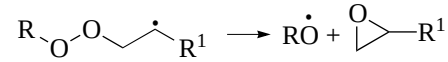
The data listed in Tables 2–4 allow the reactions to be grouped into 12 classes. The kinetic parameters α, $br_e$, and $E_{e,0}$ for these 12 classes are presented in Table 5.

### *Isomerization of Peroxoalkyl Radicals*

The isomerization reactions

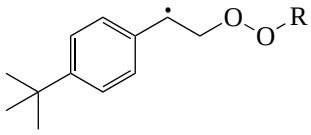
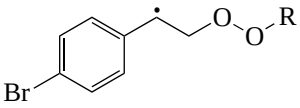
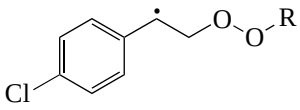
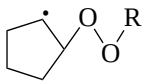
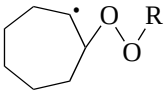


and

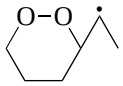
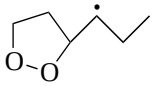


produce epoxides. Although the epoxide ring has a high strain energy (115 kJ/mol [10]), epoxide formation is an exothermic reaction (see Tables 2 and 3). This is due

**Table 2.** Kinetic parameters of peroxoalkyl radical decomposition reactions yielding epoxides [11, 12]

| Radical | $-\Delta H$, kJ/mol | $T$, K | $k$, $s^{-1}$ | $E$, kJ/mol | $br_e$, $(kJ/mol)^{1/2}$ |
|---|---|---|---|---|---|
| $ROOMeCHC^{\bullet}HMe$ | 76.6 | 363 | $9.1 \times 10^6$ | 38.3 | 15.55 |
| $ROOCH_2C^{\bullet}MePr$ | 70.3 | 343 | $9.1 \times 10^6$ | 36.2 | 15.06 |
| $ROOMe_2CC^{\bullet}HMe$ | 62.5 | 333 | $6.7 \times 10^6$ | 36.0 | 14.73 |
| $ROOCH_2C^{\bullet}HPh$ | 31.8 | 323 | $7.6 \times 10^3$ | 53.0 | 15.38 |
| $ROOCH_2MePh$ | 28.1 | 323 | $6.8 \times 10^4$ | 47.2 | 14.57 |
|  | 35.0 | 368 | $6.6 \times 10^4$ | 53.8 | 15.60 |
|  | 30.4 | 368 | $4.7 \times 10^4$ | 54.9 | 15.53 |
|  | 35.5 | 368 | $7.6 \times 10^4$ | 53.4 | 15.53 |
|  | 68.5 | 323 | $4.5 \times 10^6$ | 36.0 | 14.97 |
|  | 64.5 | 333 | $2.9 \times 10^7$ | 32.0 | 14.32 |

to the fact that, in this reaction, a weak O–O bond (162 kJ/mol [4]) is broken and a strong C–O bond (340–350 kJ/mol [27]) is formed. The activation energy of the thermally neutral reaction, $E_{e,0}$ depends on the ring size and increases from 60 to 100 kJ/mol in going from a six- to a five-membered ring:

| $R^{\bullet}$ |  | $ROOCH_2C^{\bullet}HR^1$ |  | $R^{\bullet} + R^1OOR^1$ |
|---|---|---|---|---|
| $E_{e,0}$, kJ/mol | 59.5 | 68.7 | 99.9 | 122.7 |
| $E_{rsc}$, kJ/mol | ~10 | 0 | 29 | 0 |

This dependence is probably due to the higher activation energy of the five-membered ring. Note that the isomerization of a linear peroxoalkyl radical is characterized by $E_{e,0} > E_{e,0}(\text{cyclo-}C_4O_2)$, while the bimolecular reaction between an alkyl radical and a peroxy group (which is similar in the structure of the reaction center to isomerization) is characterized by a very high $E_{e,0}$ value of 123 kJ/mol [28].

*Isomerization of Cycloalkoxyl Radicals*

The decyclization of cycloalkoxyl radicals occurs with a low activation energy $E_{e,0}$ (Tables 3, 5). The $E_{e,0}$ values for the cyclization and decyclization of each particular radical coincide within the measurement error (±2 kJ/mol). The activation energy of the thermally neutral isomerization of a cyclopentoxyl radical, $E_{e,0}(C_5H_9O^{\bullet})$, is somewhat higher than that of a cyclohexoxyl radical.

**Table 3.** Kinetic parameters of radical cyclization and decyclization reactions

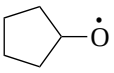
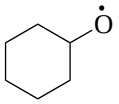
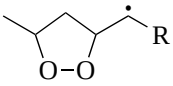
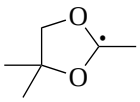
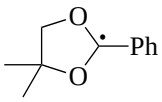
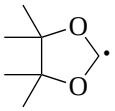
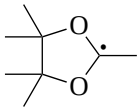
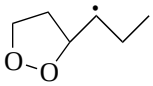
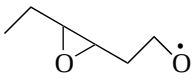
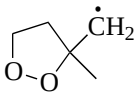
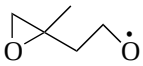
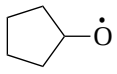
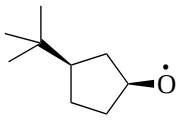
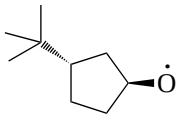
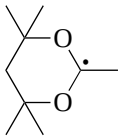
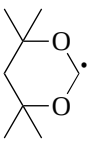
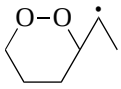
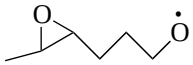
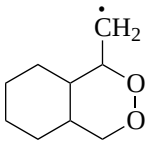
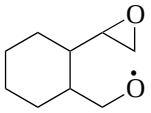
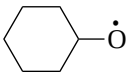
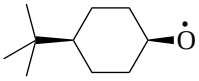
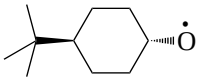
| $R_i^{\cdot}$ (Reactant) | $R_f^{\cdot}$ (Product) | $\Delta H$, kJ/mol | $E$, kJ/mol | $br_e$, $(kJ/mol)^{1/2}$ | References |
|---|---|---|---|---|---|
| Cyclization | | | | | |
| $HC(O)(CH_2)_3C^{\cdot}H_2$ |  | –2.3 | 28.8 | 14.51 | [13] |
| $HC(O)(CH_2)_4C^{\cdot}H_2$ |  | 33.2 | 8.3 | 13.83 | [13] |
| $MeCH(O_2^{\cdot})CH_2CH{=}CHR$ |  | –38.8 | 48.7 | 22.47 | [14] |
| Decyclization of a five-membered ring | | | | | |
|  | $MeC(O)OCH_2C^{\cdot}Me_2$ | 127.9 | 60.2 | 17.04 | [15, 16] |
|  | $PhC(O)OCH_2C^{\cdot}Me_2$ | 49.6 | 77.4 | 16.53 | [15] |
|  | $Me_2C^{\cdot}CMe_2OCH(O)$ | 93.0 | 58.7 | 16.08 | [16] |
|  | $Me_2C^{\cdot}CMe_2OCH(O)$ | 127.9 | 52.1 | 16.34 | [16] |
|  |  | 127.6 | 43.3 | 17.84 | [17] |
|  |  | 136.5 | 48.7 | 18.66 | [17] |
|  | $CH(O)(CH_2)_3C^{\cdot}H_2$ | –2.3 | 27.9 | 10.30 | [18] |
|  | $CH(O)(CH_2)_2CH(CMe_3)C^{\cdot}H_2$ | –2.3 | 33.5 | 11.11 | [19] |
|  | $CH(O)(CH_2)_2CH(CMe_3)C^{\cdot}H_2$ | –2.3 | 32.2 | 10.93 | [19] |
| Decyclization of a six-membered ring | | | | | |
|  | $MeC(O)OCMe_2CH_2C^{\cdot}Me_2$ | 35.3 | 35.1 | 12.04 | [16] |
|  | $CH(O)OCMe_2CH_2C^{\cdot}Me_2$ | 57.0 | 29.1 | 12.09 | [16] |

**Table 3.** (Contd.)

| $R_i^{\bullet}$ (Reactant) | $R_f^{\bullet}$ (Product) | $\Delta H$, kJ/mol | $E$, kJ/mol | $br_e$, $(kJ/mol)^{1/2}$ | References |
|---|---|---|---|---|---|
|  |  | 102.3 | 15.3 | 13.54 | [17] |
|  |  | 90.6 | 26.4 | 14.64 | [17] |
|  | $CH(O)(CH_2)_4C^{\bullet}H_2$ | –33.2 | 38.5 | 9.58 | [20] |
|  | $CH(O)(CH_2)_2CH(CMe_3)CH_2C^{\bullet}H_2$ | –33.2 | 39.4 | 9.74 | [19] |
|  | $CH(O)(CH_2)_2CH(CMe_3)CH_2C^{\bullet}H_2$ | –33.2 | 42.2 | 10.20 | [19] |

| Radical | $\Delta H$, kJ/mol | $E$, kJ/mol | $E_{e,0}$, kJ/mol | $E_{rsc}$, kJ/mol |
|---|---|---|---|---|
| $C_5H_9O^{\bullet}$ | 2.3 | 27.9 | 38.0 | 29 |
| $C_6H_{11}O^{\bullet}$ | 33.2 | 38.5 | 31.7 | 1 |

It is possible that the difference between the $E_{e,0}$ values for the $C_5H_9O^{\bullet}$ and $C_6H_{11}O^{\bullet}$ radicals is caused by the difference in strain energy between the five- and six-membered rings. Remarkably, the addition reaction

$$R^{\bullet} + O{=}CR^1R^2 \longrightarrow RR^1R^2CO^{\bullet},$$

which is similar to alkoxyl isomerization, occurs with a much higher activation energy of $E_{e,0}$ = 72.9 kJ/mol [6].

*Isomerization of N- and O-Containing Radicals: A Comparison*

Comparison of the activation energies of the thermally neutral decyclization reactions for six-membered ring radicals differing in structure shows that $E_{e,0}$ increases in the order cyclo-$C_6H_{11}O^{\bullet}$ < cyclo-$[(CH_2)_3OC^{\bullet}HRO]$ < cyclo-$[(CH_2)_3O_2C^{\bullet}HR]$ < cyclo-$[(CH_2)_4C^{\bullet}HRNR^1]$ < cyclo-$[(CH_2)_5C^{\bullet}HR]$. As follows from $E_{e,0}$ data for five- and six-membered rings (see below), $E_{e,0}(5)$ is always higher than $E_{e,0}(6)$.

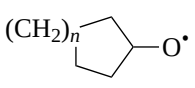
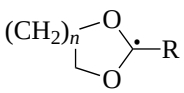
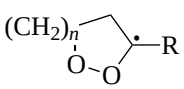
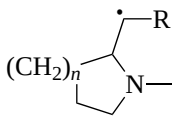
| Radical |  |  |  |  |
|---|---|---|---|---|
| $E_{e,0}$ ($n$ = 2), kJ/mol | 31.7 | 54.3 | 59.6 | 68.4 |
| $E_{e,0}$ ($n$ = 1), kJ/mol | 38.0 | 101.6 | 99.9 | 75.1 |

**Table 4.** Kinetic parameters of the cyclization of aminyl radicals

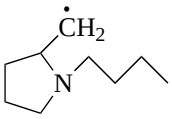
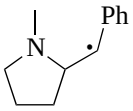
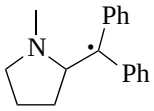
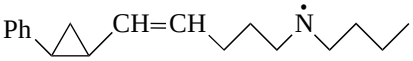
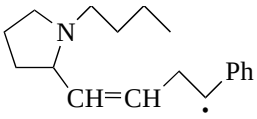
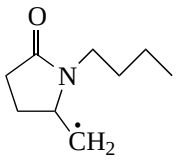
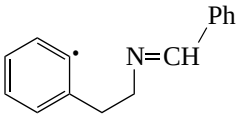
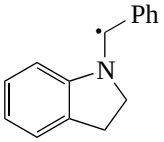
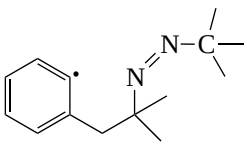
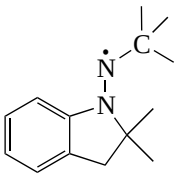
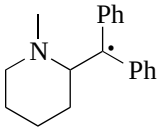
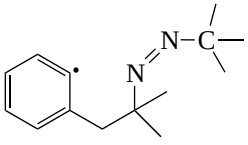
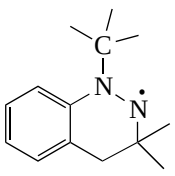
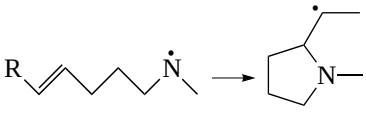
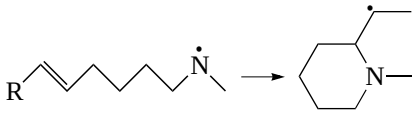
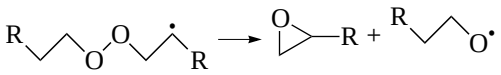
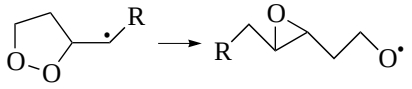
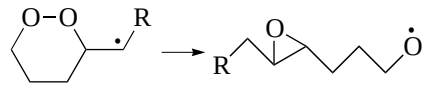
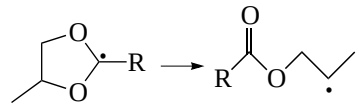
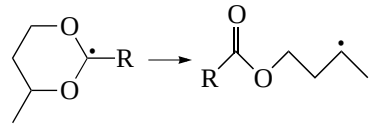
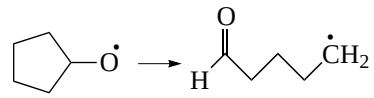
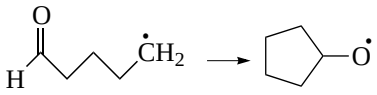
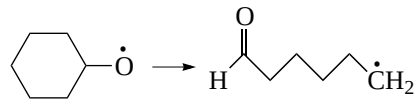
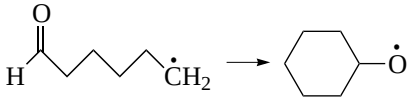
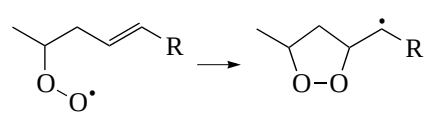
| $R_i^{\bullet}$ (Reactant) | $R_f^{\bullet}$ (Product) | $\Delta H$, kJ/mol | $E$, kJ/mol | $br_e$, $(kJ/mol)^{1/2}$ | References |
|---|---|---|---|---|---|
| Formation of a five-membered ring | | | | | |
| $CH_2{=}CH(CH_2)_3N^{\bullet}Bu$ |  | –49.0 | 34.0 | 19.78 | [21] |
| $PhCH{=}CH(CH_2)_3N^{\bullet}Me$ |  | –70.3 | 27.6 | 20.34 | [22] |
| $Ph_2C{=}CH(CH_2)_3N^{\bullet}Me$ |  | –90.9 | 26.3 | 21.51 | [22] |
|  |  | –73.0 | 38.3 | 22.47 | [23] |
| $CH_2{=}CH(CH_2)_2C(O)N^{\bullet}Bu$ |  | –49.0 | 38.3 | 20.42 | [24] |
|  |  | –114.1 | 17.7 | 22.00 | [20] |
|  |  | –131.2 | 6.9 | 21.18 | [25, 26] |
| Formation of a six-membered ring | | | | | |
| $Ph_2C{=}CH(CH_2)_4N^{\bullet}Me$ |  | –40.8 | 32.8 | 19.44 | [22] |
|  |  | –130.0 | 3.7 | 20.49 | [25, 26] |

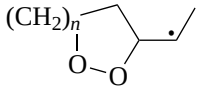
**Table 5.** Kinetic parameters for classes of cyclization and decyclization reactions of N- and O-containing radicals

| Reaction (class) | α | $br_e$, $(kJ/mol)^{1/2}$ | $E_{e,0}$, kJ/mol |
|---|---|---|---|
|  | 1.410 | 20.88 ± 0.75 | 75.1 ± 2.7 |
|  | 1.410 | 19.96 ± 0.52 | 68.4 ± 1.8 |
|  | 0.826 | 15.13 ± 0.44 | 68.7 ± 2.0 |
|  | 0.826 | 18.25 ± 0.41 | 99.9 ± 2.2 |
|  | 0.826 | 14.09 ± 0.55 | 59.5 ± 2.3 |
|  | 0.655 | 16.50 ± 0.35 | 101.6 ± 2.1 |
|  | 0.655 | 12.06 ± 0.55 | 54.3 ± 2.5 |
|  | 0.748 | 10.78 | 38.0 |
|  | 1.336 | 14.51 | 38.6 |
|  | 0.748 | 9.84 | 31.7 |
|  | 1.336 | 13.83 | 35.0 |
|  | 1.737 | 22.47 ± 0.40 | 67.4 ± 1.2 |

Evidently, this is due to the difference in strain energy between the five- and six-membered rings. The six-membered ring is characterized by a low (almost zero) ring strain energy. For the five-membered ring, this energy is much higher. For the three-membered ring, it exceeds 100 kJ/mol [10].

| Ring |  |  |  |  |  |
|---|---|---|---|---|---|
| $E_{rsc}$, kJ/mol | 0.68 | 26.7 | 29.0 | 114.6 | 115.1 |

The following differences in $E_{e,0}$ ($\Delta E_{e,0} = E_{e,0}(5) - E_{e,0}(6)$) correspond to these $E_{rsc}$ data:

| Cyclizing radical | $C^{\bullet}H_2(CH_2)_nCHO$ | $CH_2=CH(CH_2)_nN^{\bullet}R$ |  | $RC(O)O(CH_2)_nO^{\bullet}$ |
|---|---|---|---|---|
| $\Delta E_{e,0}$, kJ/mol | 5.0 | 6.7 | 40.7 | 47.3 |

Another important factor in $E_{e,0}$ is the different electronegativities of the atoms forming the reaction center of the transition state. The electronegativity factor is very conspicuous in radical abstraction reactions [5]. In the radical cyclization and decyclization reactions considered here and in [3], we deal with reaction centers of the type C…C…Y, where Y = C, N, or O. What is the influence of the difference in electronegativity between the C and Y atoms on $E_{e,0}$ of cyclization? Let us compare the parameters of the reactions involving this reaction center for six-membered rings, in which the ring strain energy is the lowest. Since $E_{e,0}$ also depends on the force constants of the reacting bonds and the C=C, C=O, C–O, and C–N bonds are different in this respect, we will compare $r_e$ values, which are independent of the force constants [5]. The difference between Pauling's electronegativities [29] of the C and Y atoms ($\Delta EA$) was calculated by the formula

$$\Delta EA = D(\text{C–Y}) - 0.5[D(\text{C–C}) - D(\text{Y–Y})]. \quad (9)$$

$\Delta EA$ was calculated using the following reference bond dissociation energy data [27]:

| Compound | $CH_3$–$CH_3$ | $NH_2$–$NH_2$ | $CH_3O$–$OCH_3$ | $CH_3$–$NH_2$ | $CH_3$–$OCH_3$ |
|---|---|---|---|---|---|
| $D$, kJ/mol | 377 | 282 | 162 | 359 | 348 |

The calculated $r_e$ and $\Delta EA$ data are presented below:

| Radical | $CH_2=CH(CH_2)_3C^{\bullet}HR$ | $CH_2=CH(CH_2)_3N^{\bullet}R$ | $CH(O)(CH_2)_4C^{\bullet}H_2$ |
|---|---|---|---|
| Reaction center | C…C⋯C | N…C⋯C | O⋯C…C |
| $r_e \times 10^{11}$, m | 3.78 | 3.33 | 2.25 |
| $\Delta EA$, kJ/mol | 0 | 29.5 | 78.5 |

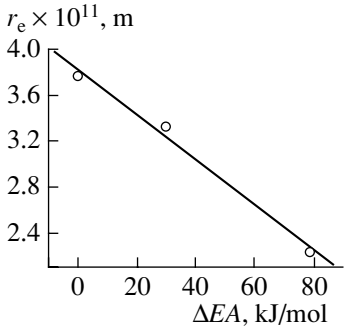
One can see that $r_e$ decreases in going from Y=C to Y=N and from Y=N to Y=O. This trend is correlated with the electron affinity ($EA$) of the N and O atoms exceeding that of carbon. For three classes of reactions examined, the relationship between $r_e$ and $\Delta EA$ is linear (figure) and is described by the equation

$$r_e \times 10^{11},\ \text{m} = 3.83 \pm 0.09 - (1.98 \pm 0.18) \times 10^{-2} \Delta EA, \quad (10)$$

where $\Delta EA$ is expressed in kJ/mol.

It is clear that the activation energy of the cyclization (and decyclization) reaction of a radical depends considerably on the electronegativity of the heteroatom (N, O): the higher $\Delta EA$, the lower $r_e$ and, accordingly, $E_{e,0}$ (see formula (8)).

Thus, the activation energy of the cyclization and decyclization reactions of radicals with a free valence at the C, N, and O atoms depends on the enthalpy of reaction, the force constants of the rearranging bonds (parameters $b$ and $\alpha$), the electronegativity of the atoms in the reaction center, and the strain energy of the forming ring. It is of interest that the strain energy reduced




Elongation of the reacting bonds, $r_e$, versus the difference between the electronegativities of the atoms in the reaction center, $\Delta EA$.

$E_{e,0}$ in the cyclization of hydrocarbon radicals [3] and increases $E_{e,0}$ in the cyclization of radicals involving heteroatoms. Undoubtedly, triplet repulsion also plays an important role in cyclization, although it acts in combination with other factors. Its particular contribution has been determined for bimolecular radical addition reactions [6].

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