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Physicochemical aspects of isomerisation of free radicals

E T Denisov, T G Denisova

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Abstract. Kinetic data on intramolecular abstraction of hydrogen atoms in alkyl, alkoxyl and peroxyl radicals are generalised and analysed. It is shown that the activation energies of these reactions are affected by ring strain. The kinetic parameters of mono- and bimolecular elimination reactions are compared. The difference between the activation energies of these reactions is interpreted using the model of intersecting parabolas. The same model is used to discuss the results of analysis of cyclisation of alkyl radicals; the ring strain energy is shown to play an important role in the activation of these reactions. It is noted that the difference between the electron affinities of the C, N and O atoms is clearly manifested in the cyclisation of aminyl and ω-formylalkyl radicals. The kinetic parameters of cyclisation and bimolecular radical addition reactions are compared. The experimental data on the transfer of the vinyl and aryl groups in alkyl radicals are analysed. The bibliography includes 146 references.

I. Introduction

The possible mechanisms of isomerisation of free radicals were discussed by N N Semenov back in 1958;[1] however, no quantitative kinetic data for these reactions were available at that time. The kinetics of these reactions has been studied rather intensively since the late 1970s.[2–4] Radical isomerisation reactions can be classified into (i) hydrogen atom migrations from one position to another; (ii) cyclisation reactions in radicals; (iii) ring opening reactions; (iv) cleavage of a peroxide bridge and epoxide formation; (v) migrations of aryl and vinyl groups in alkyl radicals.[2]

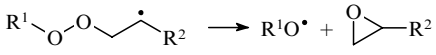
The isomerisation of alkyl radicals, for example

$$R^1C^{\bullet}H(CH_2)_nCH_2R^2 \longrightarrow R^1CH_2(CH_2)_nC^{\bullet}HR^2,$$

accompanied by migration of a hydrogen atom from one carbon to another is involved in chain processes of hydrocarbon cracking, photolysis and radiolysis,[5] radical polymerisation and oligomerisation of monomers,[6] and thermal and thermooxidative destruction of polymers.[7] These reactions affect appreciably both the overall process rates and the composition of products. The isomerisation of peroxyl radicals

$$R^1CH(OO^{\bullet})(CH_2)_nCH_2R^2 \longrightarrow R^1CH(OOH)(CH_2)_nC^{\bullet}HR^2$$

takes place during oxidation of hydrocarbons and yields bifunctional products (dihydroperoxides, dihydric alcohols, and so on) even at early oxidation steps.[8–10] These reactions play an important role in the oxidation of carbochain polymers.[7,11] Decomposition of peroxoalkyl radicals takes place during the oxidation of monomers[8,12] and is accompanied by cyclisation to give epoxides.



Alkyl radicals containing double bonds rapidly undergo intraradical cyclisation,[3] giving rise to cyclic radicals. The rings thus formed contain $n + 2$ or $n + 3$ carbon atoms.

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

These reactions have been studied intensively during the last two decades. They are used in physical chemistry, for example, as a clock reaction in the method of competing reactions. For synthetic purposes, such reactions are employed to prepare diverse cyclic and spirocyclic compounds.[13–15]

Recently, we have analysed a number of classes of radical isomerisation reactions using the method of intersecting parabolas (MIP)[16–19] and have revealed some new features. Note that analysis of radical isomerisation reactions in terms of the MIP allows one to compare them with one another and with analogous bimolecular reactions involving radicals. This review presents the experimental kinetic parameters for radical isomerisation processes and the results of their analysis and comparison with reactions of other classes.

E T Denisov, T G Denisova Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 54 20. Tel. (7-096) 522 19 14. E-mail: edenisov@icp.ac.ru (E T Denisov), denisova@icp.ac.ru (T G Denisova)

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II. Parabolic model of radical reactions

The isomerisation reactions of free radicals

$$R^1C^{\bullet}H(CH_2)_nCH_2R^2 \longrightarrow R^1CH_2(CH_2)_nC^{\bullet}HR^2,$$

$$R^1CH(O^{\bullet})(CH_2)_nCH_2R^2 \longrightarrow R^1CH(OH)(CH_2)_nC^{\bullet}HR^2,$$

$$R^1CH(OO^{\bullet})(CH_2)_nCH_2R^2 \longrightarrow R^1CH(OOH)(CH_2)_nC^{\bullet}HR^2$$

are represented, within the framework of the MIP, as an intersection of the potential energy curves of the stretching vibrations of the reacting bonds, *i.e.*, the bond being cleaved and the bond being formed.[16, 20–23] The *y*-coordinate of the intersection point of these curves in the 'bond vibration amplitude–potential energy' coordinate system corresponds to the activation energy. The stretching vibration of the bond is taken to be harmonic.

The cyclisation reaction

$$Y^{\bullet}(CH_2)_nCH{=}CHR \longrightarrow \text{cyclo-}[(CH_2)_nYCH(C^{\bullet}HR)]$$

is represented, within the framework of the MIP, as an intersection of the potential energy curves of the stretching vibrations of the reacting bonds, *i.e.*, the C=C double bond to which the addition takes place and the C–Y bond that forms upon the addition of the Y atom having a free valence to a double-bond C atom.

The isomerisation reaction is described in terms of the MIP by the following parameters: the enthalpy (ΔH_e), the activation energy (E_e), the coefficients b and b_f ($2b^2$ is the force constant of the bond being cleaved, $2b_f^2$ is that of the bond being formed) and the overall elongation (r_e) of the bonds in the transition state. The reaction enthalpy (ΔH_e) includes the difference between the zero-point vibration energies of the reacting bonds

$$\Delta H_e = D_i - D_f + 0.5\,hN_A(v_i - v_f), \tag{1}$$

where D_i and D_f are the dissociation energies of the bond being cleaved (i) and the bond being formed (f), v_i and v_f are the stretching vibration frequencies of these bonds, respectively, h is the Planck constant, and N_A is Avogadro's number. The activation energy (E_e) also involves the zero-point vibration energy of the bond being cleaved and is related to the Arrhenius activation energy (E_a) as follows:

$$E_e = E_a + 0.5\,(hN_Av_i - RT). \tag{2}$$

Radical reactions of one class are described by equal pre-exponential factors A_{C-H} per C–H bond being attacked (n_i is the number of these bonds).[20] Therefore, from a known experimental rate constant of the reaction, one can calculate the activation energy

$$E_a = -RT\ln\left(\frac{k}{n_iA_{C-H}}\right). \tag{3}$$

Each class of radical reactions is described according to the MIP by the parameters $\alpha = b/b_f$ and br_e. The br_e parameter is related to the reaction enthalpy (ΔH_e) and the activation energy (E_e) by the equation

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \tag{4}$$

This equation has been used to calculate the br_e parameter from experimental data. In addition to the α and br_e parameters, each class of radical reactions is characterised in terms of the MIP by a classical potential barrier (the activation energy which includes the zero-point vibration energy of the bond being attacked) to the thermally neutral reaction (E_{e0}) and the position ($r_0^{\neq}$) of the hydrogen atom in the transition state (TS) in the r_e segment at $E_e = E_{e0}$:

$$\sqrt{E_{e0}} = \frac{br_e}{1+\alpha}, \tag{5}$$

$$r_0^{\neq} = r_e(1+\alpha)^{-1}. \tag{6}$$

The values of α and b [measured in (kJ mol^{-1})$^{1/2}$ m^{-1}], $0.5\,hN_Av_i$ and $0.5\,hN_A(v_i - v_f)$ (both in kJ mol^{-1}) for different classes of radical isomerisation reactions accompanied by hydrogen migration are given below.

Reaction	α	$10^{-10}\,b$	$0.5\,hN_Av_i$	$0.5\,hN_A(v_i-v_f)$
$R^{\bullet}+H-C$	1.000	37.43	17.4	0.0
$RO^{\bullet}+H-C$	0.796	37.43	17.4	−4.3
$ROO^{\bullet}+H-C$	0.814	37.43	17.4	−3.8

The α and E_{e0} parameters can be used to calculate the activation energies of reactions of one class from their enthalpies. When α is close to 1 and the inequality $\Delta H_e(1-\alpha^2) \ll (br_e)^2$ holds, the dependence of the activation energy E_e on the enthalpy ΔH_e assumes the form

$$\sqrt{E_e} = \sqrt{E_{e0}} + \frac{\alpha\Delta H_e}{2(1+\alpha)\sqrt{E_{e0}}}. \tag{7}$$

For hydrogen transfer in alkyl radicals, the force constants of the outgoing and incoming bonds are equal; therefore, $\alpha = 1$. Thus, Eqn (7) assumes the form

$$\sqrt{E_e} = \sqrt{E_{e0}} + \frac{\Delta H_e}{4\sqrt{E_{e0}}}. \tag{8}$$

The contribution ΔE_H of the enthalpy to the activation energy of an individual reaction can be readily estimated from the formula

$$\Delta E_H = E_e - E_{e0}. \tag{9}$$

An important advantage of the MIP is the possibility to compare reactions of different classes through comparison of their characteristics such as the activation energy of the thermally neutral reaction (E_{e0}) and bond elongation (r_e) in the TS.

III. Migration of a hydrogen atom in alkyl radicals

The kinetic and thermodynamic parameters of hydrogen migration in alkyl radicals are summarised in Table 1.

The enthalpies of such reactions vary from −65 to +26 kJ mol^{-1} and the activation energies, from 12 to 40 kJ mol^{-1}. The transition states of these reactions are cyclic. The configuration of atoms in the TS of 1–4- and 1–5-migrations of a hydrogen atom calculated by the density functional theory (B3LYP)[17] is shown in Fig. 1.

Activation entropy of hydrogen migration. The formation of a cyclic TS eliminates the free rotation of alkyl fragments around the C–C bond. This results in a negative activation entropy ($\Delta S^{\neq}$). Comparison of the experimental pre-exponential factors A with the theoretical value [32] calculated from the formula

$$A = \frac{RT}{N_Ah}\exp\left(\frac{\Delta S^{\neq}}{R}\right), \tag{10}$$

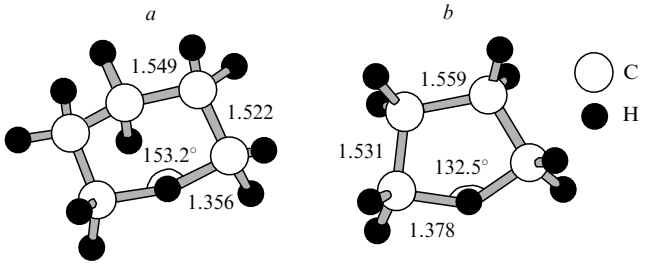


Figure 1. Geometric structure of the TS for hydrogen migration in the pentyl (*a*) and butyl (*b*) radicals based on quantum-chemical calculations (B3LYP).[17]
The bond lengths are in Å.

Table 1. Thermodynamic (D_i, D_f, ΔH) and kinetic (E_a) parameters of hydrogen migration in alkyl radicals.

Radical [a]	D_i (see [b])	D_f (see [b])	ΔH (see [b])	E_a (see [b])	Ref.
Six-membered ring					
$C^{\bullet}Cl_2(CH_2)_3(C-H)HMe$	413.0	388.7	24.3	39.9	24
$C^{\bullet}Cl_2(CH_2)_3(C-H)HEt$	414.5	388.7	25.8	39.0	24
$C^{\bullet}Cl_2(CH_2)_2SiEt_2(C-H)HMe$	413.0	388.7	24.3	44.8	25, 26
$C^{\bullet}H_2(CH_2)_3(C-H)HC(O)OMe$	398.8	422.0	−23.2	25.1	27
$(C-H)(O)CH_2CHBu^tCH_2C^{\bullet}H_2$	385.6	422.0	−36.4	12.5	28
$CH(O)(C-H)HCH_2CHBu^tCH_2C^{\bullet}H_2$	397.8	422.0	−24.2	17.1	28
Five-membered ring					
$C^{\bullet}H_2(CH_2)_2(C-H)HC(O)OMe$	398.8	422.0	−23.2	32.4	27
2-$[Me_2C(C-H)H_2]$-4,6-$Bu^t_2C_6H^{\bullet}_2$	422.0	474.0	−52.0	19.0	29–31
2,4,6-$Ad_3C_6H^{\bullet}_2$ (see [c])	408.8	474.0	−65.2	18.0	29, 31

[a] Here and in Tables 2, 3, 6, 7 and 8, the bond being attacked is designated by C—H; [b] in kJ mol^{-1}; [c] AdH is adamantane.

has shown that the $\Delta S^{\neq}$ value is exactly equal to the difference between the entropies of the linear and cyclic hydrocarbons:[18]

$$\Delta S^{\neq} = S(\text{cyclo-}C_nH_{2n}) - S(C_nH_{2n+2}).$$

The logarithms of the pre-exponential factors calculated from relation (10) are listed in Table 2.

Effect of the size of the ring formed in the transition state on the activation energy. The activation energy of hydrogen migration in an alkyl radical obviously depends on the reaction enthalpy.[20] What other factors influence the rate of migration of the hydrogen atom? This issue has been addressed in a study [16] where the br_e, r_e and E_{e0} parameters were calculated by the method of intersecting parabolas on the basis of experimental data. The activation energy for hydrogen migration in an alkyl radical was found to depend on the size of the ring formed in the TS. The reactions whose TS contain rings with equal numbers of carbon atoms are characterised by the same set of parameters ($\alpha = 1$, br_e, r_e and E_{e0}) and differ only in their activation enthalpies and energies. These parameters for the reactions

$$R^1C^{\bullet}H(CH_2)_nCH_2R^2 \longrightarrow R^1CH_2(CH_2)_nC^{\bullet}HR^2$$

are shown in Table 2. Below the classical potential barriers (E_{e0}) for such reactions are juxtaposed with the ring strain energies (E_{rsc}) in cycloalkanes (n is the number of carbon atoms in the TS ring).[33]

n	5	6	7
E_{e0} /kJ mol^{-1}	72.5 ± 0.9	52.0 ± 1.7	72.2
E_{rsc} /kJ mol^{-1}	26.7	0.7	26.8
$10^{10}\, r_e$ /m	0.455	0.385	0.454

It can be seen that the classical potential barriers to the reactions whose TS contain five- (72.5 kJ mol^{-1}) or seven-membered rings (72.2 kJ mol^{-1}) are markely higher than those for TS with six-membered rings (52.0 kJ mol^{-1}). Obviously, this is due to the difference between the ring strain: the higher the strain, the higher the activation energy. An empirical dependence between the E_{e0} and E_{rsc} values (expressed in kJ mol^{-1}) is as follows:

$$E_{e0} = 51.5 + 0.788\, E_{rsc}. \quad (11)$$

Thus, the dependence of the activation energy E_e on the ΔH and E_{rsc} values has the form [18]

$$\sqrt{E_e} = \sqrt{51.5 + 0.788E_{rsc}} + \frac{\Delta H}{4\sqrt{51.5 + 0.788E_{rsc}}}. \quad (12)$$

Table 2. MIP parameters for hydrogen migration in alkyl radicals.[16]

Radical $(R^1)^{\bullet}$	br_e /(kJ mol^{-1})$^{1/2}$	E_{e0}(m) [a] /kJ mol^{-1}	$10^{10}\, r_e$ /m	logA_{C-H} (s^{-1})	E_{e0}(b) [a] /kJ mol^{-1}
$(R^1)^{\bullet} \longrightarrow (R^2)^{\bullet}$ (Four-membered TS)					
$RC^{\bullet}H(CH_2)_3(C-H)HY$	23.85	142.2	0.637	11.16	74.8
$RC^{\bullet}H(CH_2)_3(C-H)HPh$	24.16	145.9	0.646	10.16	79.2
$RC^{\bullet}H(CH_2)_3(C-H)HCH=CH_2$	24.68	152.3	0.659	10.16	86.5
$(R^1)^{\bullet} \longrightarrow (R^2)^{\bullet}$ (Five-membered TS)					
$RC^{\bullet}H(CH_2)_2(C-H)HY$	17.03	72.5	0.455	10.55	74.8
$RC^{\bullet}H(CH_2)_2(C-H)HPh$	17.46	76.2	0.466	9.55	79.2
$RC^{\bullet}H(CH_2)_2(C-H)HCH=CH_2$	18.18	82.6	0.486	9.55	86.5
$(R^1)^{\bullet} \longrightarrow (R^2)^{\bullet}$ (Six-membered TS)					
$RC^{\bullet}H(CH_2)_3(C-H)HY$	14.42	52.0	0.385	9.95	74.8
$RC^{\bullet}H(CH_2)_3(C-H)HPh$	14.93	55.7	0.399	8.95	79.2
$RC^{\bullet}H(CH_2)_3(C-H)HCH=CH_2$	15.73	61.9	0.420	8.95	86.5
$(R^1)^{\bullet} \longrightarrow (R^2)^{\bullet}$ (Seven-membered TS)					
$RC^{\bullet}H(CH_2)_4(C-H)HY$	16.99	72.2	0.454	8.20	74.8
$RC^{\bullet}H(CH_2)_4(C-H)HPh$	17.42	75.9	0.465	7.20	79.2
$RC^{\bullet}H(CH_2)_4(C-H)HCH=CH_2$	18.14	82.3	0.485	7.20	86.5

[a] E_{e0}(m) and E_{e0}(b) are the classical potential barriers for the monomolecular cyclisation and bimolecular hydrogen abstraction, respectively.

Quantum-chemical calculations have shown[17] that in the TS for isomerisation of the butyl radical, the angle between the C, H and C atoms of the ring is about 21° smaller than the corresponding angle in the TS for pentyl radical isomerisation (see Fig. 1). Hence, the activation energy (determined by quantum-chemical calculations) for isomerisation of the butyl radical is higher than that for the pentyl radical by 31 kJ mol^{-1}. The results of quantum-chemical calculations for the ω-isomerisation of the butyl and pentyl radicals are presented below (the activation energies are expressed in kJ mol^{-1}; φ is the C···H···C angle).[17]

Reaction	E_a	$10^{10}\,r$(C···H) /m	φ /deg
$C^{\bullet}H_2(CH_2)_2Me \rightarrow Me(CH_2)_2C^{\bullet}H_2$	96.8	1.378	132.5
$C^{\bullet}H_2(CH_2)_3Me \rightarrow Me(CH_2)_3C^{\bullet}H_2$	65.8	1.356	153.2

Thus, the calculated parameters are in good agreement with experimental data.

Effect of the α-π-bond on the activation energy. Analysis of the experimental data on bimolecular reactions

$$(R^1)^{\bullet} + R^2H \longrightarrow R^1H + (R^2)^{\bullet}$$

indicates that a double bond or an aromatic ring present in the α-position relative to the bond being attacked results in a higher E_{e0} value (see Ref. 20). This effect is illustrated in Table 2, which presents the MIP parameters characterising hydrogen migration reactions in radicals with different structures.[16] Table 3 summarises the results of calculations, using this method, of the rate constants for the migration of hydrogen atoms from the β-, γ-, δ- and ε-positions with respect to the carbon atom with a free valence in different radicals.

Comparison of mono- and bimolecular hydrogen abstraction. Bimolecular reactions of hydrogen abstraction from hydrocarbon molecules by alkyl radicals have been analysed.[20] This allowed one to compare the classical potential barriers to monomolecular and bimolecular hydrogen abstraction reactions. The difference between the structures of these TS is obvious. In the bimolecular reaction, the C···H···C atoms of the reaction centre are arranged in one straight line. In an intramolecular hydrogen migration to the δ-position, which is accompanied by the lowest ring strain, the C···H···C atoms form an angle of 153° (quantum-chemical calculations, see Fig. 1).[16] According to the absolute reaction rate theory, the minimum repulsion between the atoms in the TS is attained in the reaction centre with a linear atom configuration;[1,32] it can therefore be expected that $E_{e0}(m) > E_{e0}(b)$. However, analysis of the experimental data using the MIP provides the opposite result: $E_{e0}(m) = 52$ kJ mol^{-1}, $E_{e0}(b) = 74.8$ kJ mol^{-1}, *i.e.*, $E_{e0}(m) < E_{e0}(b)$.[16] As shown by quantum-chemical calculations of the activation energy of the reactions

$$C_2H_5^{\bullet} + C_2H_6 \longrightarrow C_2H_6 + C_2H_5^{\bullet}$$

and

$$C^{\bullet}H_2(CH_2)_3Me \longrightarrow Me(CH_2)_3C^{\bullet}H_2,$$

the bimolecular reaction of the ethyl radical with ethane is characterised by $E_{e0} = 62.5$ kJ mol^{-1}, and the monomolecular migration of the H atom in the pentyl radical has $E_{e0} = 65.8$ kJ mol^{-1}, *i.e.*, the calculated activation energies of these two thermally neutral reactions are approximately equal.[17]

What is the reason for the fact that $E_{e0}(b) \geqslant E_{e0}(m)$? The answer can be derived from MIP considerations. In attaining the TS of mono- and bimolecular hydrogen abstraction, the following factors are important. In a bimolecular reaction whose TS has a linear reaction centre, C···H···C, the crucial role in the activation is played by the stretching vibration of the C–H bond being attacked. In this case, the activation energy depends on the force constant of the stretching vibration of the C–H bond being cleaved [$b = 37.43 \times 10^{10}$ (kJ mol^{-1})$^{1/2}$ m^{-1}]. In the case of intraradical migration of hydrogen, the situation is more complicated. The angular configuration of the C···H···C fragment needed for TS formation is attained through excitation of both the stretching vibration of the C–H bond being cleaved and the angular bending vibrations of the C–C–C and C–C–H bonds, which form a cyclic TS. There are five such bonds in a pentyl radical. The frequencies and the force constants of bending vibrations of the C–C–C bonds are much smaller than these parameters for the C–H bond. Owing to these 'soft' vibrations, this TS is attained more easily (as regards the energy expenditure), despite its seemingly less favourable angular configuration. In this case, the br_e parameter is the sum of $b_j r_{ej}$, where every partial parameter present in the $\Sigma b_j r_{ej}$ sum reflects the shifts of atoms in the TS induced by activation of vibrations of the corresponding bonds. Since the force constants of bending vibrations are lower than those of stretching vibrations, $\Sigma b_j r_{ej} < br_e$(b).

Polar effect. The polar interaction in the TS of bimolecular reactions is manifested in the reactions of halide-containing radicals with haloalkanes. The introduction of a halogen atom into a molecule or a radical not only changes the reaction enthalpy but also decreases the activation energy of the thermally neutral reaction.[20] The role of polar effect in the activation energy can be judged from the difference between the E_{e0} values of the reactions of radicals with a haloalkane and the corresponding hydrocarbon

$$\Delta E_{\mu} = E_{e0}(RX) - E_{e0}(RH). \qquad (13)$$

The data illustrating this effect for reactions of trichloromethyl radicals with a number of chloroalkanes are presented below.[19]

Compound	ΔE_{μ} /kJ mol^{-1}
CH_2Cl_2	−8.0
$CH_2ClCH_2CCl_3$	−18.8
$EtCCl_3$	−17.9
Pr^nCCl_3	−16.0

The polar interaction also shows itself in hydrogen migration (see Table 1). The E_{e0} and ΔE_{μ} values (in kJ mol^{-1}) calculated from experimental data for the hydrogen migration processes that involve the formation of a six-membered transition state are presened below.[19]

Table 3. Enthalpies, activation energies, and rate constants (k) for hydrogen migration in alkyl radicals calculated using the MIP relations.[16]

Radical	ΔH_e (see [a])	E_e(m) [b]	$k_{350\,K}$ (see [c])	E_e(b) [b]
$C^{\bullet}H_2CH_2(C-H)HMe$	−10.0	121.2	2.49×10^{-7}	54.0
$C^{\bullet}H_2(CH_2)_2(C-H)HMe$	−10.0	51.6	1.41×10^{3}	54.0
$C^{\bullet}H_2(CH_2)_3(C-H)HMe$	−10.0	31.1	4.07×10^{5}	54.0
$C^{\bullet}H_2(CH_2)_4(C-H)HMe$	−10.0	51.2	7.24×10^{3}	54.0
$MeC^{\bullet}H(CH_2)_3(C-H)HMe$	0	36.0	7.56×10^{4}	58.9
$MeC^{\bullet}H(CH_2)_3(C-H)Me_2$	−12.0	30.2	2.77×10^{5}	53.0
$MeC^{\bullet}H(CH_2)_2NH(C-H)HMe$	−33.4	20.6	1.50×10^{7}	43.2
$MeC^{\bullet}H(CH_2)_2NMe(C-H)HMe$	−44.9	16.0	7.30×10^{7}	38.2
$Me_2C^{\bullet}(CH_2)_2NH(C-H)Me_2$	−43.0	16.7	2.87×10^{7}	39.0
$Me_2C^{\bullet}(CH_2)_2NMe(C-H)Me_2$	−54.5	12.3	1.30×10^{8}	34.2
$MeC^{\bullet}H(CH_2)_3(C-H)HOH$	−14.6	29.0	8.38×10^{5}	51.8
$MeC^{\bullet}H(CH_2)_3(C-H)MeOH$	−20.5	26.2	1.10×10^{6}	49.0
$MeC^{\bullet}H(CH_2)_2C(O)(C-H)H_2$	−2.0	35.0	1.60×10^{5}	57.9
$MeC^{\bullet}H(CH_2)_2C(O)(C-H)HMe$	−14.2	29.1	8.09×10^{5}	52.0
$MeC^{\bullet}H(CH_2)_2C(O)(C-H)Me_2$	−19.3	26.8	8.92×10^{5}	49.6
$MeC^{\bullet}H(CH_2)_3(C-H)(O)$	−26.4	23.6	2.68×10^{6}	46.3
$MeC^{\bullet}H(CH_2)_3(C-H)HPh$	−43.3	20.1	1.78×10^{6}	43.1
$Me_2C^{\bullet}(CH_2)_3(C-H)MePh$	−45.3	19.3	1.17×10^{6}	42.3
$Me_2C^{\bullet}(CH_2)_3(C-H)HCH=CH_2$	−50.2	23.3	5.94×10^{5}	47.3
$Me_2C^{\bullet}(CH_2)_3(C-H)MeCH=CH_2$	−60.4	19.4	1.13×10^{6}	43.0

[a] Expressed in kJ mol^{-1}; [b] activation energies of mono- [E_e(m)] and bimolecular [E_e(b)] reactions expressed in kJ mol^{-1}; [c] in s^{-1}.

Reaction	E_{e0}	ΔE_{μ}
$C^{\bullet}H_2(CH_2)_3Me \rightarrow Me(CH_2)_3C^{\bullet}H_2$	52.0	0.0
$C^{\bullet}Cl_2(CH_2)_4Me \rightarrow CHCl_2(CH_2)_3C^{\bullet}HMe$	42.8	−9.2
$C^{\bullet}Cl_2(CH_2)_5Me \rightarrow CHCl_2(CH_2)_3C^{\bullet}HEt$	41.3	−10.7
$C^{\bullet}Cl_2(CH_2)_2SiEt_2CH_2Me \rightarrow CHCl_2(CH_2)_2SiEt_2C^{\bullet}HMe$	36.1	−15.9

Similar results were obtained by quantum-chemical calculations carried out by the B3LYP technique (the activation energies are expressed in kJ mol^{-1}; φ is the C···H···C angle).[19]

Reaction	E_a	$10^{10}\,r$(C···H) /m	φ /deg
$C^{\bullet}H_2(CH_2)_3Me \rightarrow Me(CH_2)_3C^{\bullet}H_2$	65.8	1.356	153.2
$C^{\bullet}Cl_2(CH_2)_3Me \rightarrow CHCl_2(CH_2)_3C^{\bullet}H_2$	50.8	1.350	101.5
$C^{\bullet}Cl_2(CH_2)_3CCl_2H \rightarrow CHCl_2(CH_2)_3C^{\bullet}Cl_2$	28.7	1.342	152.5

It can be seen that the polar effect markedly decreases the activation energy for hydrogen migration in chloroalkanes.

IV. Isomerisation of alkoxyl radicals

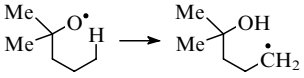
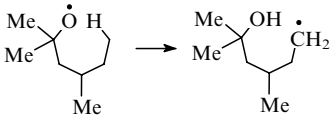
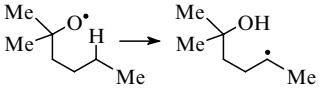
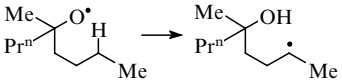
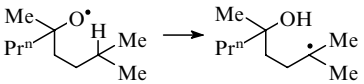
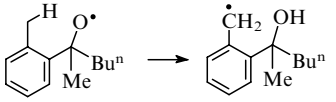
Alkoxyl radicals are highly active and rapidly enter into bimolecular hydrogen abstraction.[2,8]

$$R^1O^{\bullet} + R^2H \longrightarrow R^1OH + (R^2)^{\bullet}$$

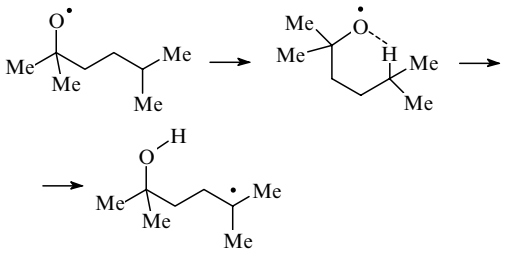
In addition, alkoxyl radicals with rather long hydrocarbon chains ($>C_4$) also undergo intraradical hydrogen migration. Table 4 presents the rate constants for these reactions calculated from the ratio of the rate constants for RO$^{\bullet}$ isomerisation and RO$^{\bullet}$ destruction.[2]

Each of the reactions implies elimination of the hydrogen atom located in the γ-position, *i.e.*, the transition state contains a six-membered ring.

Table 4. Experimental rate constants and activation energies for hydrogen migration in alkoxyl radicals.

Reaction	E_a (see [a])	log$A$ (s^{-1})	$k_{350\,K}$ (see [b])	Ref.
	30.1	9.78	1.93×10^5	2
	29.8	9.78	2.14×10^5	2
	23.4	9.60	1.29×10^5	2
	22.8	9.60	1.57×10^6	34
	25.4	9.30	3.23×10^5	34
	9.8	8.78	2.08×10^7	35

[a] Expressed in kJ mol^{-1}; [b] in s^{-1}.



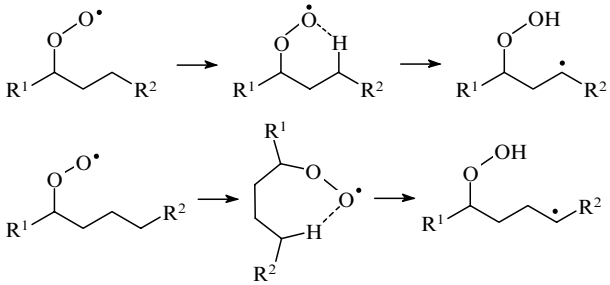
The kinetic parameters (br_e, E_{e0}, r_e and A_{C-H}) which describe this reaction in terms of the MIP are summarised in Table 5.

The hydrogen abstraction from the C−H bond located in the vicinity of the phenyl or vinyl group has a higher classical potential barrier (E_{e0}) due to stronger triplet repulsion.[20] However, the pre-exponential factor is smaller in this case due to entropy loss caused by the elimination of the free rotation of these groups in the TS. The activation energy of the thermally neutral isomerisation of alkoxyl radicals coincides with that of the bimolecular abstraction reaction:[16] E_{e0}(RO$^{\bullet}$ isomer.) = 53.4 kJ mol^{-1}, E_{e0}(RO$^{\bullet}$ + R^1H) = 53.2 kJ mol^{-1}. Thus, for the isomerisation with a non-linear TS, the relationship E(m) > E(b) expected theoretically does not hold either. The reason is apparently the same as in the case of hydrogen migration in alkyl radicals (see above).

Using MIP parameters, the activation energies and the rate constants for isomerisation of diverse alkoxyl radicals have been calculated.[16] The results of these calculations are summarised in Table 6.

V. Isomerisation of peroxyl radicals

The intraradical hydrogen migration also takes place in peroxyl radicals.[10,12,23] Hydrogen migrates from either β- or γ-position, *i.e.*, a TS with either six- or seven-membered ring is formed.



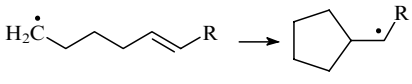
Experimental data on isomerisation of the alkyl and alkylaryl peroxyl radicals are listed in Table 7.

The MIP parameters for $RO_2^{\bullet}$ isomerisation calculated on the basis of these data are presented in Table 5. As in the case of isomerisation of alkoxyl radicals, in this case, too, the classical potential barriers (E_{e0}) are close to the E_{e0} values for the bimolecular reaction $RO_2^{\bullet}$ + RH (see Table 5). The activation energies E_{e0} of the reactions whose TS contain six- and seven-membered rings do not differ much. The activation energies and the rate constants for isomerisation of diverse peroxyl radicals calculated in terms of the MIP are summarised in Table 8.[16]

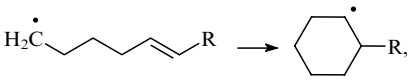
For these reactions, the E_a(m) values are close to E_a(b). The reason is apparently the same as in the case of isomerisation of the R$^{\bullet}$ and RO$^{\bullet}$ radicals.

VI. Cyclisation and ring opening in alkyl radicals

Alkyl radicals containing a multiple bond rapidly undergo intraradical cyclisation



or



resulting in the formation of cyclic five- or six-membered radicals. These reactions have been intensively studied for the last 20 years. The experimental rate constants and the activation energies for the cyclisation of alkyl radicals are summarised in Table 9.

Recently, the experimental data have been analysed by means of the MIP protocol.[18] The ΔH_e, E_e and br_e values were calculated [see Eqns (1)–(4)] using the parameters presented below [b are expressed in (kJ mol^{-1})$^{1/2}$ m^{-1}, hN_Av_i and $hN_A(v_i-v_f)$ are in kJ mol^{-1}].

Attacked bond	α	$b\times10^{-10}$	$0.5hN_Av_i$,	$0.5hN_A(v_i-v_f)$
C=C	1.202	53.89	9.9	1.7
C≡C	1.542	69.12	12.7	4.5

The br_e, E_{e0} and r_e parameters and the experimental pre-exponential factors A are listed in Table 10.

The activation energy of cyclisation is undoubtedly affected by the reaction enthalpy. This is equal to the sum of the energy of formation of the new C–C bond and the strain energy of the newly formed ring (E_{rsc}) minus the energy of rupture of the C–C π-bond. Comparison of the br_e parameters for cyclisation reac-

Table 5. Kinetic parameters of the MIP for isomerisation of alkoxyl and peroxyl radicals.[16]

Radical ($R^1O^\bullet$)	br_e /(kJ mol^{-1})$^{1/2}$	E_{e0}(m) /kJ mol^{-1}	$10^{10}\,r_e$ /m	$\log A_{C-H}$ (s^{-1})	E_{e0}(b) /kJ mol^{-1}
$R^1O^\bullet \longrightarrow (R^2)^\bullet$ (Six-membered TS)					
$Me_2C(O^\bullet)(CH_2)_2(C-H)HR$	13.13	53.4	0.351	2.0×10^9	53.2
$Me_2C(O^\bullet)(CH_2)_2(C-H)HPh$	13.53	56.8	0.361	2.0×10^8	56.5
$Me_2C(O^\bullet)(CH_2)_2(C-H)HCH=CH_2$	14.17	62.2	0.379	2.0×10^8	62.0
$R^1O_2^\bullet \longrightarrow (R^2)^\bullet$ (Six-membered TS)					
$RCH(OO^\bullet)Y(C-H)HR$	13.23	53.2	0.353	2.0×10^9	56.3
$RCH(OO^\bullet)Y(C-H)HPh$	14.38	62.8	0.384	2.0×10^8	62.3
$RCH(OO^\bullet)Y(C-H)HCH=CH_2$	14.82	66.7	0.396	2.0×10^8	70.2
$R^1O_2^\bullet \longrightarrow (R^2)^\bullet$ (Seven-membered TS)					
$RCH(OO^\bullet)YCH_2(C-H)HR$	13.43	54.8	0.359	5.6×10^8	56.3
$RCH(OO^\bullet)YCH_2(C-H)HPh$	14.58	64.6	0.390	5.6×10^7	62.3
$RCH(OO^\bullet)YCH_2(C-H)HCH=CH_2$	15.02	68.6	0.401	5.6×10^7	70.2
$(R^2)^\bullet \longrightarrow R^1O_2^\bullet$ (Six-membered TS)					
$RCH(OO-H)YC^\bullet HR$	16.25	53.2	0.353	2.0×10^8	56.3
$RCH(OO-H)YC^\bullet HPh$	17.67	62.9	0.384	2.0×10^8	62.3
$RCH(OO-H)YC^\bullet HCH=CH_2$	18.21	66.8	0.396	2.0×10^8	70.2
$(R^2)^\bullet \longrightarrow R^1O_2^\bullet$ (Seven-membered TS)					
$RCH(OO-H)YCH_2C^\bullet HR$	16.50	54.8	0.359	5.6×10^7	56.3
$RCH(OO-H)YCH_2C^\bullet HPh$	17.91	64.6	0.389	5.6×10^7	62.3
$RCH(OO-H)YCH_2C^\bullet HCH=CH_2$	18.45	68.6	0.401	5.6×10^7	70.2

Table 6. Dissociation energies, enthalpies, activation energies and rate constants for hydrogen migration in alkoxyl radicals calculated using MIP relations.[16]

Radical	D_i (see [a])	ΔH_e (see [a])	E_e(m) [a]	$k_{350\,K}$ /s^{-1}	E_e(b) [a]
$Me_2C(O^\bullet)(CH_2)_2(C-H)H_2$	422.0	−19.5	29.3	2.5×10^5	29.1
$Me_2C(O^\bullet)(CH_2)_2(C-H)HMe$	412.0	−29.5	25.4	6.4×10^5	25.2
$Me_2C(O^\bullet)(CH_2)_2(C-H)Me_2$	400.0	−41.5	21.1	1.4×10^6	20.8
$Me_2C(O^\bullet)CH_2NH(C-H)HMe$	378.6	−62.9	14.0	3.3×10^7	13.7
$Me_2C(O^\bullet)CH_2NMe(C-H)HMe$	367.1	−74.4	10.5	1.1×10^8	10.3
$Me_2C(O^\bullet)CH_2NH(C-H)Me_2$	357.0	−84.5	7.7	1.4×10^8	7.5
$Me_2C(O^\bullet)CH_2NMe(C-H)Me_2$	345.5	−96.0	4.7	4.0×10^8	4.5
$Me_2C(O^\bullet)(CH_2)_2(C-H)HOH$	397.4	−44.1	20.1	3.9×10^6	19.9
$Me_2C(O^\bullet)(CH_2)_2(C-H)(OH)Me$	391.5	−50.0	18.1	3.9×10^6	17.9
$Me_2C(O^\bullet)CH_2C(O)(C-H)H_2$	410.0	−31.5	24.7	1.2×10^6	24.5
$Me_2C(O^\bullet)CH_2C(O)(C-H)HMe$	397.8	−43.7	20.3	3.8×10^6	20.1
$Me_2C(O^\bullet)CH_2C(O)(C-H)Me_2$	392.7	−48.8	18.5	3.4×10^6	18.3
$Me_2C(O^\bullet)(CH_2)_2(C-H)(O)$	385.6	−55.9	16.2	7.7×10^6	15.9
$Me_2C(O^\bullet)(CH_2)_2(C-H)HPh$	368.7	−72.8	14.0	3.3×10^6	13.7
$Me_2C(O^\bullet)(CH_2)_2(C-H)MePh$	354.7	−86.8	9.9	6.6×10^6	9.7
$Me_2C(O^\bullet)(CH_2)_2(C-H)HCH=CH_2$	349.8	−91.7	13.4	4.0×10^6	13.2
$Me_2C(O^\bullet)(CH_2)_2(C-H)MeCH=CH_2$	339.6	−101.9	10.6	5.2×10^6	10.4

[a] Expressed in kJ mol^{-1}.

Table 7. Experimental enthalpies, activation energies and rate constants for hydrogen migration in alkylperoxyl radicals.

Radical	ΔH (see [a])	E_a (see [a])	$k_{350\,K}$ /s^{-1}	n [b]	Ref.
PhCH($O_2^{\bullet}$)O(C−H)HPh	1.4	44.2	1.01×10^3	6	36–38
$Me_2C(O_2^{\bullet})CH_2$(C−H)Me_2	41.4	57.4	5.43	6	39
$Me_2C(O_2^{\bullet})O$(C−H)Me_2	32.2	55.2	11.6	6	36, 40
MeCH($O_2^{\bullet}$)CH_2(C−H)HMe	47.5	68.9	0.21	6	41
MeCH($O_2^{\bullet}$)CH_2(C−H)$HC_{10}H_{21}$-n	50.2	58.8	6.71	6	42
Me(C−H)$HCH_2CH(O_2^{\bullet})C_{12}H_{25}$-n	47.5	62.2	2.09	6	43
MeCH($O_2^{\bullet}$)CH_2(C−H)(O_2H)$C_{12}H_{25}$-n	26.0	48.3	1.24×10^2	6	43
$Me_2CHCH_2C(O_2^{\bullet})MeCH_2$(C−H)$Me_2$	41.4	54.5	14.72	6	44
$Me_2C(O_2^{\bullet})C$(O)(C−H)Me_2	34.1	59.0	3.13	6	45
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)CH_2CH(O_2^{\bullet})CH_2$(C−H)HEt	47.5	56.8	13.34	6	46
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)(CH_2)_3CH(O_2^{\bullet})CH_2$(C−H)$H_2$	56.5	56.9	19.34	6	46
Ph(C−H)(O_2H)OCH($O_2^{\bullet}$)Ph	1.4	47.7	15.22	6	38, 47
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)(CH_2)_2$(C−H)$HCH_2CH(O_2^{\bullet})$Me	50.2	56.8	13.34	6	46
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)CH_2CH(O_2^{\bullet})CH_2$(C−H)($O_2$H)Et	26.0	41.9	1.12×10^3	6	46
MeCH($O_2^{\bullet}$)$(CH_2)_2$(C−H)$HC_{11}H_{23}$-n	50.2	63.1	1.53	7	43, 48
EtC(O)$OCH_2Me_2CCH(O_2^{\bullet})OC$(O)(C−H)HMe	33.3	52.5	58.47	7	49
[EtC(O)$OCH_2]_3CCH(O_2^{\bullet})OC$(O)(C−H)HMe	33.3	53.5	41.47	7	49
Me(C−H)H$(CH_2)_2CH(O_2^{\bullet})C_{11}H_{23}$-n	47.5	62.3	2.02	7	43
MeCH($O_2^{\bullet}$)$(CH_2)_2$(C−H)(O_2H)$C_{11}H_{23}$-n	26.0	52.7	27.29	7	43
[EtC(O)$OCH_2]_2(CHCH_2)CCH(O_2^{\bullet})OC$(O)(C−H)HMe	33.3	53.4	42.92	7	49
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)CH_2CH(O_2^{\bullet})(CH_2)_2$(C−H)($O_2$H)Me	26.0	46.2	2.55×10^2	7	46
[n-$C_6H_{13}C(O)OCH_2]_3CCH_2OC(O)CH_2$(C−H)($O_2$H)$(CH_2)_2CH(O_2^{\bullet})$Me	26.0	47.0	1.93×10^2	7	46

[a] Expressed in kJ mol^{-1}; [b] the number of atoms in the TS ring.

Table 8. Enthalpies, activation energies and rate constants for hydrogen migration in alkylperoxyl radicals calculated using the MIP relations.[16]

Radical	ΔH_e (see [a])	ΔE_μ (see [a, b])	E_e(m) [a]	$k_{350\,K}$ /s^{-1}	E_e(b) [a]
$CH_2(OO^{\bullet})CMe_2$(C−H)H_2	56.5	0	64.3	1.5	67.2
MeCH($OO^{\bullet}$)CH_2(C−H)HMe	46.5	0	58.7	7.0	61.6
$Me_2C(OO^{\bullet})CH_2$(C−H)Me_2	41.4	0	55.9	9.2	58.9
MeCH($OO^{\bullet}$)NH(C−H)HMe	13.1	0	41.6	2.5×10^3	44.7
MeCH($OO^{\bullet}$)NMe(C−H)HMe	1.6	0	36.3	1.5×10^4	39.4
$Me_2C(OO^{\bullet})NH$(C−H)Me_2	−1.6	0	34.9	1.2×10^4	38.0
$Me_2C(OO^{\bullet})NMe$(C−H)Me_2	−13.1	0	30.0	6.6×10^4	33.1
CH(OH)($OO^{\bullet}$)CH_2(C−H)HOH	25.8	−2.2	45.5	6.4×10^2	48.6
MeC(OH)($OO^{\bullet}$)CH_2(C−H)MeOH	19.9	−2.2	42.6	8.7×10^2	45.7
$CH_2(OO^{\bullet})C$(O)(C−H)H_2	44.5	−15.4	42.2	3.1×10^3	45.1
MeCH($OO^{\bullet}$)C(O)(C−H)HMe	32.3	−15.4	35.7	1.9×10^4	38.7
$Me_2C(OO^{\bullet})C$(O)(C−H)Me_2	34.1	−15.7	36.3	7.7×10^3	39.3
C(O)($OO^{\bullet}$)CH_2(C−H)(O)	−20.5	−8.8	18.3	3.8×10^6	21.3
PhCH($OO^{\bullet}$)CH_2(C−H)HPh	−1.4	0	44.6	8.7×10^1	44.1
PhC($OO^{\bullet}$)CH_2(C−H)MePh	−3.9	0	43.5	6.3×10^1	43.0
CH_2=CHCH($OO^{\bullet}$)CH_2(C−H)HCH=CH_2	−15.7	0	42.4	1.9×10^2	45.9
CH_2=CHC($OO^{\bullet}$)$MeCH_2$(C−H)MeCH=CH_2	−19.0	0	41.2	1.5×10^2	44.5

[a] Expressed in kJ mol^{-1}; [b] ΔE_μ is the contribution of the polar interaction to the activation energy.

tions of various alkyl radicals (see Table 10) leads to the following conclusions.

1. The br_e parameter depends on the size of the ring formed.

2. This parameter does not depend (or slightly depends) on the number and the positions of substituents in the radical which undergoes cyclisation.

3. The br_e parameters of cyclisation are equal for radicals containing rings of the same size and chains, both composed of C atoms alone and incorporating also O and Si atoms.

4. For cyclisation reactions of perfluorinated radicals, the br_e parameters are higher.

5. Cyclisation that takes place through intramolecular attack of the radical on the triple bond is described by higher br_e parameters.

Effect of the ring strain energy on the activation energy. It follows from the data listed in Table 10 that, depending on the ring size, the activation energy of the thermally neutral cyclisation passes through a maximum, E_{e0} = 85.7 kJ mol^{-1}, which is attained upon the formation of a six-membered ring. The minimum value E_{e0} = 36.4 kJ mol^{-1} is observed for the formation of a three-membered ring. For radical cyclisation reactions resulting in three- to six-carbon rings, the following linear correlation is observed:

$$E_{e0} = 85.5 - 16.4\,(6 - n), \qquad (14)$$

where E_{e0} is expressed in kJ mol^{-1}, n is the number of C atoms in the ring.

Table 9. Experimental enthalpies, activation energies and rate constants for cyclisation of alkyl radicals.

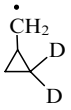
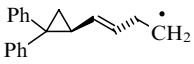
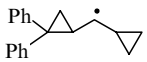
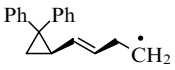
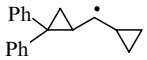
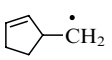
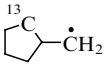
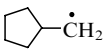
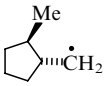
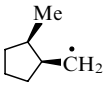
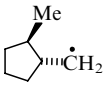
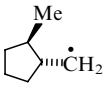
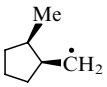
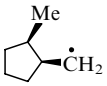
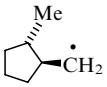
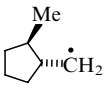
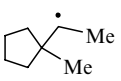
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 3$, log$A$ (s^{-1}) = 11.6						
$CH_2=CHCHMeC^{\bullet}H_2$		23.0	333 – 379	4.94×10^4	39.4	50
$CH_2=CHCH_2C^{\bullet}D_2$		23.4	252 – 276	5.37×10^3	44.9	51
$Ph_2C=CHCH_2C^{\bullet}H_2$			277 – 309	2.01×10^7	24.5	52
$PhCH=CHCH_2C^{\bullet}H_2$			280 – 321	6.53×10^6	27.3	52
			292 – 331	6.05×10^4	38.9	53
			293 – 322	8.43×10^4	38.1	53
$n = 4$, log$A$ (s^{-1}) = 11.3						
		−24.8	338	8.3×10^4	34.8	54
$n = 5$, log$A$ (s^{-1}) = 10.2						
$CH_2=\,^{13}CH(CH_2)_3C^{\bullet}H_2$		−64.4	313	1.8×10^5	29.7	55
$CH_2=CH(CH_2)_3C^{\bullet}H_2$		−64.4	188 – 373	3.75×10^4	32.1	56 – 59
$CH_2=CH(CH_2)_2CHMeC^{\bullet}H_2$		−66.7	318 – 373	4.57×10^5	25.9	60 – 62
$CH_2=CHCHMe(CH_2)_2C^{\bullet}H_2$		−66.3	298 – 373	7.74×10^4	30.3	60 – 62
$CH_2=CHCHMe(CH_2)_2C^{\bullet}H_2$		−69.8	298 – 373	3.74×10^5	26.4	60 – 62
$CH_2=CHCH_2CHMeCH_2C^{\bullet}H_2$		−66.7	318 – 373	2.40×10^5	27.5	60 – 62
$CH_2=CHCH_2CHMeCH_2C^{\bullet}H_2$		−63.2	318 – 373	2.40×10^5	27.5	60 – 62
$CH_2=CH(CH_2)_2CHMeC^{\bullet}H_2$		−63.2	318 – 373	2.40×10^5	27.5	60 – 62
$CH_2=CMe(CH_2)_3C^{\bullet}H_2$		−65.3	298 – 338	2.22×10^4	33.4	56, 62, 63
$CH_2=CH(CH_2)_3C^{\bullet}HMe$		−66.8	298 – 338	1.03×10^5	29.6	56, 62
$MeCH=CMe(CH_2)_3C^{\bullet}H_2$		−61.7	338	3.3×10^5	30.3	56

Table 9 (continued).

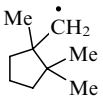
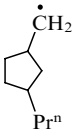
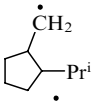
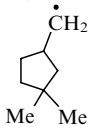
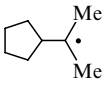
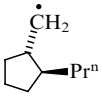
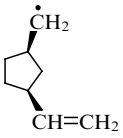
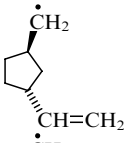
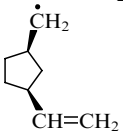
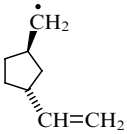
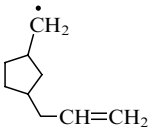
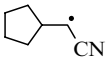
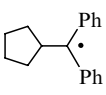
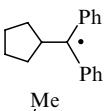
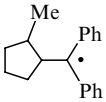
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 5$, log$A$ (s^{-1}) = 10.2						
$CH_2=CMe(CH_2)_3C^{\bullet}Me_2$		−43.8	313	6.2×10^4	32.4	63
$CH_2=CHCH_2CH(CH_2C^{\bullet}H_2)Pr^n$		−64.4	353	6.6×10^6	22.8	60, 64
$CH_2=CPr^i(CH_2)_3C^{\bullet}H_2$		−61.6	338	2.5×10^4	37.5	60
$CH_2=CH(CH_2)_2CMe_2C^{\bullet}H_2$		−64.4	298 – 353	2.81×10^6	21.4	64 – 66
$Me_2C=CH(CH_2)_3C^{\bullet}H_2$		−69.3	338	2.6×10^6	24.5	56
$CH_2=CH(CH_2)_3C^{\bullet}HPr^n$		−66.8	338	8.5×10^5	27.6	56
$CH_2=CH(CH_2)_2CH(C^{\bullet}H_2)CH=CH_2$		−60.9	353	7.8×10^5	29.1	60
$CH_2=CH(CH_2)_2CH(C^{\bullet}H_2)CH=CH_2$		−64.4	353	1.4×10^6	27.3	60
$CH_2=CHCH_2CH(CH=CH_2)CH_2C^{\bullet}H_2$		−60.9	353	2.2×10^6	26.1	60
$CH_2=CHCH_2CH(CH=CH_2)CH_2C^{\bullet}H_2$		−64.4	353	6.6×10^5	29.6	60
$C^{\bullet}H_2CH_2CH(CH_2CH=CH_2)_2$		−65.4	303 – 357	1.88×10^6	22.4	67
$N\equiv CCH=CH(CH_2)_3C^{\bullet}H_2$		−107.4	223 – 324	1.72×10^8	11.2	68
$Ph_2C=CH(CH_2)_3C^{\bullet}H_2$		−112.5	226 – 317	5.35×10^7	14.1	69
$Ph_2C=CH(CH_2)_3C^{\bullet}H_2$		−112.5	236 – 317	4.08×10^7	14.8	70
$Ph_2C=CH(CH_2)_3C^{\bullet}HMe$		–	234 – 325	2.36×10^7	16.1	70

Table 9 (continued).

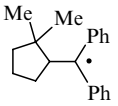
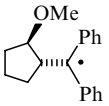
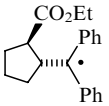
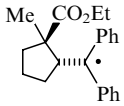
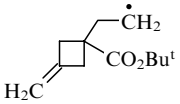
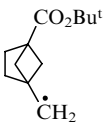
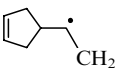
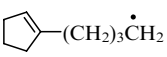
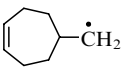
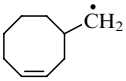
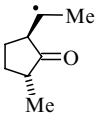
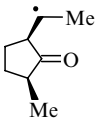
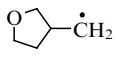
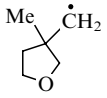
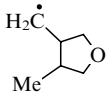
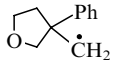
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 5, \log A\ (s^{-1}) = 10.2$						
$Ph_2C{=}CH(CH_2)_3C^{\bullet}Me_2$		–	263 – 326	1.22×10^7	17.8	70
$Ph_2C{=}CH(CH_2)_3C^{\bullet}HOMe$		−106.7	273 – 313	3.87×10^7	14.9	71
$Ph_2C{=}CH(CH_2)_3C^{\bullet}HC(O)OEt$		−98.1	273 – 313	6.55×10^7	13.6	72
$Ph_2C{=}CH(CH_2)_3C^{\bullet}MeC(O)OEt$		−87.6	273 – 333	4.39×10^5	26.0	72
		−61.6	274 – 383	2.71×10^5	27.2	73
		−51.2	366 – 403	3.91×10^3	37.7	74
		−61.9	338	1.2×10^5	33.0	56
		−53.8	280 – 470	1.67×10^5	28.4	75
		−56.4	280 – 470	6.86×10^4	30.6	75
$CH_2{=}CH(CH_2)_3C^{\bullet}(O)$		–	298	2.2×10^5		76
$MeCH{=}CH(CH_2)_2CHMeC^{\bullet}(O)$		–	298	1.8×10^5	25.1	76
$MeCH{=}CH(CH_2)_2CHMeC^{\bullet}(O)$		–	298	1.3×10^5	25.5	76
$CH_2{=}CH(CH_2)_2OC^{\bullet}H_2$		−65.7	180 – 220	3.32×10^4	32.4	65, 77
$CH_2{=}CMeCH_2OCH_2C^{\bullet}H_2$		−62.9	313	2.0×10^5	29.3	78
$CH_2{=}CHCH_2OCH_2C^{\bullet}HMe$		−96.1	338	8.8×10^6	21.1	79
$CH_2{=}CPhCH_2OCH_2C^{\bullet}H_2$		−61.6	313	1.7×10^5	29.7	78

Table 9 (continued).

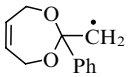
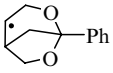
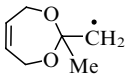
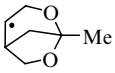
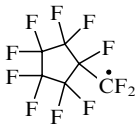
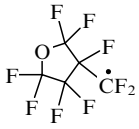
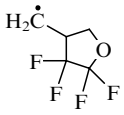
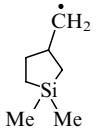
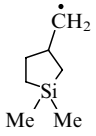
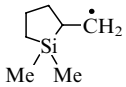
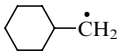
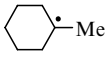
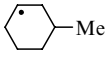
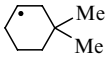
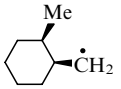
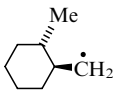
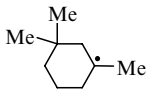
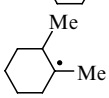
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 5, \log A\ (s^{-1}) = 10.2$						
		−92.7	298 – 423	4.96×10^5	25.7	80
		−92.7	272 – 394	8.38×10^5	24.4	80
$CF_2=CF(CF_2)_3C^{\bullet}F_2$		−136.8	231 – 353	4.22×10^5	26.1	81
$CF_2=CFO(CF_2)_2C^{\bullet}F_2$		−137.9	303	3.5×10^6	21.2	82
$CH_2=CHCH_2OCF_2C^{\bullet}F_2$		–	298	3.8×10^7	15.0	83
$CH_2=CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−64.4	298	1.0×10^3	36.6	58
$CH_2=CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−64.4	298	7.5×10^3	38.7	58
$CH_2=CHSiMe_2(CH_2)_2C^{\bullet}H_2$		−64.4	298	7.5×10^4	34.9	58, 66, 84
$HC\equiv C(CH_2)_3C^{\bullet}H_2$		−75.9	298	2.8×10^4	32.8	62
$n = 6, \log A\ (s^{-1}) = 9.7$						
$CH_2=CH(CH_2)_3C^{\bullet}H_2$		−75.3	188 – 396	1.78×10^2	42.5	56 – 58, 61, 65
$CH_2=CH(CH_2)_4C^{\bullet}H_2$		−92.5	338	2.5×10^4	34.3	85
$CH_2=CMe(CH_2)_3C^{\bullet}H_2$		−108.3	298 – 338	8.57×10^3	32.9	56, 62
$CH_2=CH(CH_2)_3C^{\bullet}HMe$		−97.6	338	9.7×10^3	36.9	56
$CH_2=CH(CH_2)_3C^{\bullet}Me_2$		−87.6	298 – 338	9.68×10^3	32.6	56, 62, 86
$CH_2=CH(CH_2)_4C^{\bullet}HMe$		−82.7	298	2.1×10^3	33.9	62
$CH_2=CH(CH_2)_4C^{\bullet}HMe$		−90.5	298	5.7×10^3	36.4	62
$CH_2=CMe(CH_2)_3C^{\bullet}Me_2$		−105.1	313	5.4×10^4	29.7	56, 73
$MeCH=CMe(CH_2)_3C^{\bullet}H_2$		−92.2	338	6.0×10^4	31.8	56

Table 9 (continued).

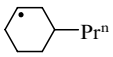
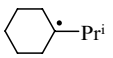
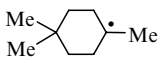
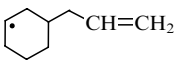
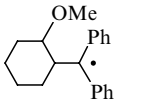
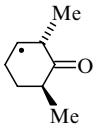
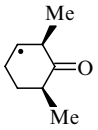
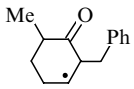
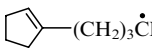
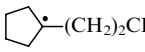
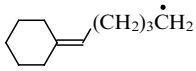
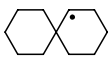
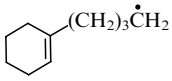
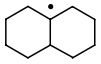
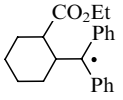
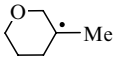
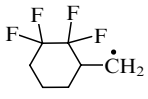
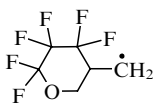
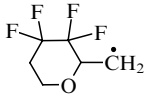
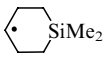
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 6$, $\log A$ (s^{-1}) = 9.7						
$CH_2=CH(CH_2)_3C^{\bullet}HPr^n$		−97.6	338	4.1×10^3	39.4	56
$CH_2=CPr^i(CH_2)_3C^{\bullet}H_2$		−103.9	338	8.0×10^4	31.0	62
$CH_2=CMe(CH_2)_2CMe_2C^{\bullet}H_2$		−105.0	318–373	2.17×10^4	30.6	64
$(CH_2=CHCH_2)_2CHCH_2C^{\bullet}H_2$		−95.3	333	2.3×10^5	27.6	71
$Ph_2C=CH(CH_2)_4C^{\bullet}HOMe$		−133.0	283–323	1.51×10^5	25.8	71
$MeCH=CH(CH_2)_2CHMeC^{\bullet}(O)$		–	298	2.0×10^4	26.8	76
$MeCH=CH(CH_2)_2CHMeC^{\bullet}(O)$		–	298	5.2×10^3	28.4	76
$PhCH_2CH=CH(CH_2)_2CHMeC^{\bullet}(O)$		−84.8	353	2.0×10^5	29.7	87
		−89.3	338	3.0×10^4	33.7	56
		−76.8	338	6.7×10^4	31.5	56
		−89.5	338	1.0×10^6	23.8	56
		−89.4	338	5.3×10^4	32.2	56
$Ph_2C=CH(CH_2)_4C^{\bullet}HC(O)OEt$		−124.5	273–313	1.99×10^7	13.7	73
$CH_2=CMeCH_2OCH_2C^{\bullet}H_2$		−80.0	313	4.6×10^3	36.2	78
$CH_2=CH(CH_2)_3CF_2C^{\bullet}F_2$		–	298	1.44×10^7	14.5	83
$CH_2=CHCH_2O(CF_2)_2C^{\bullet}F_2$		–	298	1.21×10^6	20.6	83
$CH_2=CHO(CH_2)_2CF_2C^{\bullet}F_2$		–	298	9.4×10^6	15.6	83
$CH_2=CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−95.3	298	1.6×10^4	34.0	58
$CH_2=CHSiMe_2(CH_2)_2C^{\bullet}H_2$		−95.3	298	7.5×10^4	34.7	58

Table 9 (continued).

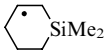
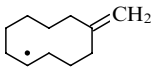
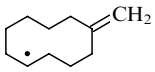
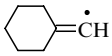
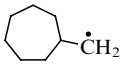
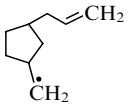
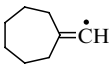
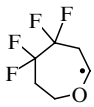
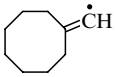
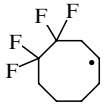
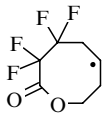
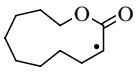
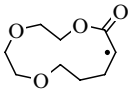
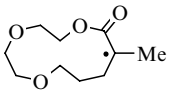
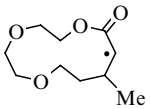
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 6$, log$A$ (s^{-1}) = 9.7						
$CH_2=CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−95.3	298	1.4×10^4	34.9	66
		−136.2	313–396	9.97×10^8	4.0	88
		−149.6	313–396	3.21×10^9	1.1	88
$HC\equiv C(CH_2)_4C^{\bullet}H_2$		−58.9	333	4.6×10^4	32.1	59
$n = 7$, log$A$ (s^{-1}) = 9.1						
$CH_2=CH(CH_2)_4C^{\bullet}H_2$		−53.5	338	4.8×10^3	35.0	85
$CH_2=CH(CH_2)_5C^{\bullet}H_2$		−64.6	338	8.3×10^2	39.9	85
		−73.4	338	3.0×10^3	37.7	67
$HC\equiv C(CH_2)_5C^{\bullet}H_2$		−85.3	333	2.5×10^3	36.3	59
$CH_2=CHO(CH_2)_2CF_2C^{\bullet}F_2$		–	298	3.4×10^6	14.2	83
$n = 8$, log$A$ (s^{-1}) = 8.8						
$HC\equiv C(CH_2)_6C^{\bullet}H_2$		−58.5	333	1.2×10^2	42.8	59
$CH_2=CH(CH_2)_4CF_2C^{\bullet}F_2$		–	298	2.0×10^4	25.7	83
$CH_2=CH(CH_2)_2OC(O)CF_2C^{\bullet}F_2$		–	298	3.6×10^4	24.2	83
$n = 11$, log$A$ (s^{-1}) = 7.1						
$CH_2=CHC(O)O(CH_2)_6C^{\bullet}H_2$		–	353	2.8×10^3	20.5	89
$n = 12$, log$A$ (s^{-1}) = 6.5						
$CH_2=CHC(O)O(CH_2CH_2O)_2CH_2C^{\bullet}H_2$		–	353	1.5×10^5	7.4	89
$CH_2=CMeC(O)O(CH_2CH_2O)_2CH_2C^{\bullet}H_2$		–	353	7.0×10^4	9.3	89
E-$MeCH=CHC(O)O(CH_2CH_2O)_2CH_2C^{\bullet}H_2$		–	353	6.6×10^3	15.0	89

Table 9 (continued).

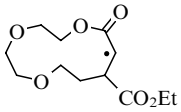
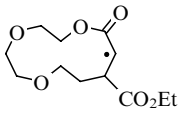
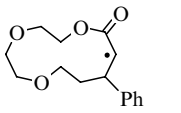
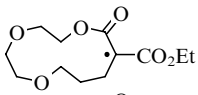
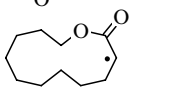
Reactant	Product	ΔH /kJ mol^{-1}	T /K	$k_{298\,K}$ /s^{-1}	E_a /kJ mol^{-1}	Ref.
$n = 12$, log$A$ (s^{-1}) = 6.5						
Z-(EtOC(O))CH=CHC(O)O(CH$_2$CH$_2$O)$_2$CH$_2$C$^{\bullet}$H$_2$		–	353	6.0×10^3	15.3	89
E-(EtOC(O))CH=CHC(O)O(CH$_2$CH$_2$O)$_2$CH$_2$C$^{\bullet}$H$_2$		–	353	9.4×10^4	8.6	89
E-PhCH=CHC(O)O(CH$_2$CH$_2$O)$_2$CH$_2$C$^{\bullet}$H$_2$		–	353	2.9×10^3	17.0	89
CH$_2$=C(C(O)OEt)CH$_2$O(CH$_2$CH$_2$O)$_2$CH$_2$C$^{\bullet}$H$_2$		–	353	1.4×10^5	7.6	89
CH$_2$=CHC(O)O(CH$_2$)$_7$C$^{\bullet}$H$_2$		–	353	4.8×10^3	15.8	89

Table 10. MIP parameters for cyclisation of alkyl radicals and ring strain energies.[18,33]

n (see [a])	br_e (see [b])	E_{e0} (see [c])	E_{rsc} (see [c])	$10^{10}\,r_e$ /m	log$A$ (s^{-1})
3	13.28 ± 0.59	36.4	115.1	0.246	11.60
4	15.13	47.2	110.9	0.281	11.30
5	18.39 ± 0.60	69.7	26.7	0.341	10.20
6	20.39 ± 0.64	85.7	0.7	0.378	9.90
7	19.45 ± 0.66	78.0	26.8	0.361	9.10
5 (see [d])	21.38	94.3	26.7	0.397	10.20
5 (see [e])	22.98	81.7	26.7	0.332	10.20

[a] The number of atoms in the ring; [b] in (kJ mol^{-1})$^{1/2}$; [c] in kJ mol^{-1}; [d] for C_nF_{2n}; [e] for RC≡CR.

When a linear hydrocarbon is transformed into a cyclic one, a ring strain energy appears. This is due to the fact that the C–C–C angle best suited for sp^3-hybridisation (109°) decreases upon cyclisation, for example, to 60° in the case of cyclopropane, and this enhances the energy of the cyclic molecule. This strain in the formed ring may affect the E_{e0} value. The published [33] strain energies (E_{rsc}) for some rings are presented in Table 10; Fig. 2 juxtaposes the E_{e0} and E_{rsc} values.

The E_{e0} and E_{rsc} values (expressed in kJ mol^{-1}) obey the following linear correlation:

$$E_{e0} = (85.5 \pm 2.8) - (0.43 \pm 0.05)E_{rsc}\,. \qquad (15)$$

Thus, the higher the strain energy in the ring, the lower the classical potential barrier to the thermally neutral reaction. In addition, the higher the E_{rsc}, the higher the reaction enthalpy and, hence, the higher the activation energy of cyclisation, which depends on ΔH. Substitution of expression (14) into Eqn (4) followed by transformations gives an expression for calculating the activation energy E_e:

$$\sqrt{E_e} = 3.28\sqrt{194.4 - E_{rsc}}\left(1.202\sqrt{1 + \frac{0.208\Delta H_e}{194.4 - E_{rsc}}} - 1\right), \qquad (16)$$

which allows one to calculate the Arrhenius activation energy (E_a) of cyclisation from the reaction enthalpy ΔH ($\Delta H_e = \Delta H + 1.7$) and the strain E_{rsc} of the ring formed. Presented below are the results of calculation of the E_a values for the reactions

$$CH_2{=}CH(CH_2)_{n-2}C^{\bullet}HR \longrightarrow \text{cyclo-}[CHR(CH_2)_{n-2}CH(C^{\bullet}H_2)],$$

where $n = 3-10$ is the number of C atoms in the ring; the enthalpies and the activation energies are expressed in kJ mol^{-1}, $T = 350$ K.

n	ΔH_e	E_{rsc}	E_{e0}	E_a(calc)	E_a(exp)
3	21.7	115.1	36.4	38.9	44.9
4	16.7	110.1	54.1	38.1	34.8
5	–62.7	26.7	69.7	34.5	32.1
6	–90.8	0.7	85.7	33.5	34.3
7	–36.9	26.3	78.0	46.4	–
8	–19.8	40.6	–	48.7	–
10	–8.4	52.0	–	49.6	–

It can be seen that the lowest calculated E_a(calc) value corresponds to the formation of a six-membered ring, and starting from $n = 7$, the activation energy depends only slightly on the ring size. The influence of ΔH_e and E_{rsc} on the activation energy is largely compensated.

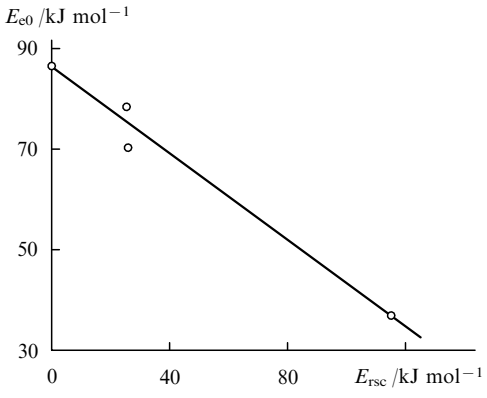


Figure 2. Activation energy of thermally neutral reaction (E_{e0}) *vs.* ring strain energy (E_{rsc}) for cyclisation of alkyl radicals.

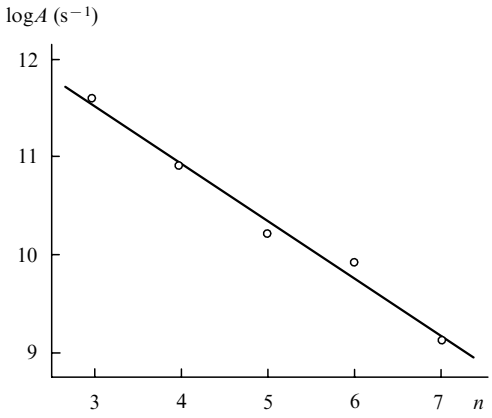


Figure 3. Dependence of log$A$ on the number (n) of carbon atoms in the ring for cyclisation of alkyl radicals.

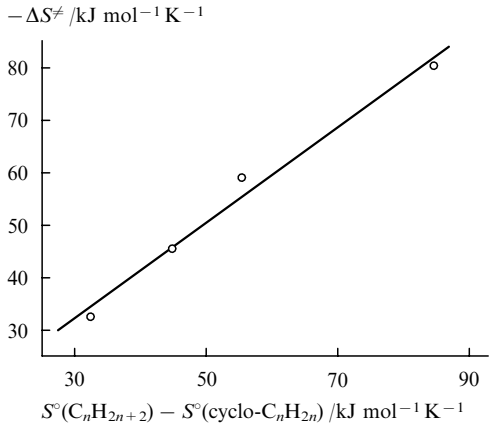


Figure 4. Correlation between the activation entropy ($\Delta S^{\neq}$) for cyclisation of alkyl radicals and the difference between the formation entropies (S°) of the corresponding linear and cycic hydrocarbons.

Effect of the ring size on the pre-exponential factor for cyclisation. As noted above (see Table 10), the pre-exponential factor for the radical cyclisation reaction depends on the size of the ring formed. Figure 3 shows the dependence of log$A$ on the number of atoms (n) in the ring of the resulting molecule.

For $n \geqslant 3$, this linear dependence is described by the relation

$$\log A\ (s^{-1}) = (13.34 \pm 0.21) - (0.60 \pm 0.04)\, n. \qquad (17)$$

This type of dependence of the pre-exponential factor on the ring size is due to the decrease in the activation entropy caused by the formation of a ring. The formation of a cyclic TS from a linear radical, for example, $CH_2{=}CH(CH_2)_{n-2}C^{\bullet}H_2$, eliminates free rotation of radical fragments around the corresponding C–C bonds. This results in a lower TS entropy compared to the starting radicals. The magnitide of this entropy change can be evaluated by comparing the S° values of the linear and the corresponding cyclic hydrocarbon molecules. The termination of rotation of one CH_2 group around a C–C bond decreases the entropy of a species by about 40 J mol^{-1} K^{-1}; therefore, the variation of log$A$ *vs.* n is linear. The entropies (S°) of the linear (C_nH_{2n+2}) and cyclic (cyclo-C_nH_{2n}) molecules, the difference between them (ΔS°) and the activation entropy ($\Delta S^{\neq}$) (J mol^{-1} K^{-1}) are presented below.

n	log$A$ (s^{-1})	$-\Delta S^{\neq}$	S°(cyclo-C_nH_{2n})	$S^{\circ}(C_nH_{2n+2})$	ΔS°
3	11.60	32.5	237.4	270.0	32.6
4	10.90	48.4	265.2	310.0	44.8
5	10.20	59.3	293.1	348.9	55.8
6	9.90	65.2	298.6	388.1	89.5
7	9.10	80.5	342.6	427.9	85.3

It can be seen that the difference $\Delta S^{\circ} = S^{\circ}$(cyclo-$C_nH_{2n}$) $- S^{\circ}(C_nH_{2n+2})$ increases with an increase in the ring size (for $n = 3-7$). This trend is caused by the following: the greater the number of C–C bonds in the ring around which the rotation takes place, the more pronounced the entropy loss that accompanies the cyclisation of a molecule or a radical. The cyclohexane ring provides an exception [$\Delta S^{\circ}(n = 6) > \Delta S^{\circ}(n = 7)$], probably, due to the presence of two conformations (a chair and a boat) where transition from one conformation to the other increases the entropy of the six-membered ring. It can be seen from Fig. 4 that the activation entropy ($-\Delta S^{\neq}$) depends linearly on the ΔS° value for $n = 3, 4, 5$ and 7; the reaction giving a cyclohexane ring ($n = 6$) is an exception. The variation of $\Delta S^{\neq}$ *vs.* ΔS° (both are in J mol^{-1} K^{-1}) is linear having a slope ratio close to unity (see Fig. 4):

$$-\Delta S^{\neq} = (5.36 \pm 0.08) + \\ + (0.90 \pm 0.08)\,[S^{\circ}(C_nH_{2n+2}) - S^{\circ}(\text{cyclo-}C_nH_{2n})]. \qquad (18)$$

This attests to a purely entropy influence of the ring size on the pre-exponential factor.

Role of the force constant in cyclisation reactions. The activation energy of the bimolecular elimination–addition reaction depends on the force constants on the reacting bonds.[20] The classical potential barrier to the thermally neutral reaction (E_{e0}) is determined, according to the MIP, by three parameters, namely, the total elongation of the reacting bonds (r_e) and the force constants of the bond being cleaved (b) and the bond being formed (b_f) [see Eqns (4), (5)]. The force constant of the triple C≡C bond is greater than that of the double C=C bond; therefore, it should be expected that the classical potential barrier (E_{e0}) to cyclisation involving a triple bond should be higher than that for cyclisation at a double bond. The data on cyclisation of the $CH_2{=}CH(CH_2)_3C^{\bullet}H_2$ and $HC{\equiv}CH(CH_2)_3C^{\bullet}H_2$ radicals confirm this assumption (see Table 10). This can also be seen from comparison of the MIP parameters [br_e in (kJ mol^{-1})$^{1/2}$, E_{e0} in kJ mol^{-1}, b in (kJ mol^{-1})$^{1/2}$ m^{-1}, r_e in m] for the cyclisation of radicals yielding a five-membered ring.

Bond	br_e	E_{e0}	$10^{-10}\,b$	$10^{10}\,r_e$
C=C	18.39	69.7	53.89	0.341
C≡C	22.98	81.7	69.12	0.332

Notably, the r_e parameters for reactions of these two classes are similar. Therefore, the difference between the activation energies of these reactions is due only to different force constants of the double and triple bonds.

Polar interaction. Cyclisation of perfluorinated radicals has a higher classical potential barrier than the cyclisation of hydrocarbon radicals (see Table 10): for $n = 5$, the E_{e0} values are 94.3 and 69.7 kJ mol^{-1}, respectively. The difference between the activation energies, $\Delta E_{e0} = 24.6$ kJ mol^{-1}, is rather high and characterises the contribution of the polar interaction of the C–F bonds to the TS energy.

Comparison of cyclisation with other reactions. Previously, bimolecular radical addition reactions have been analysed in terms of the MIP.[90] It appears pertinent to compare the kinetic parameters of these, rather similar reactions. Since the transition state of the bimolecular reaction is acyclic, these reactions should be compared most legitimately with the cyclisation resulting in a six-membered ring, devoid of bond strain, as the cyclic transition state. The parameters for these two types of reaction are listed below.

Parameter	Cyclisation ($n = 6$)	Bimolecular reaction
br_e /(kJ mol^{-1})$^{1/2}$	20.39 ± 0.64	20.01 ± 0.41
E_{e0} /kJ mol^{-1}	85.6 ± 2.7	82.6 ± 1.7
$10^{10}\, r_e$ /m	0.378 ± 0.012	0.371 ± 0.008
A	8.0×10^9 s^{-1}	5.0×10^8 litre mol^{-1} s^{-1}

It can be seen that the MIP parameters virtually coincide to within the error of determination. Thus, the activation energies of the bimolecular addition and the cyclisation giving rise to a six-membered ring do not differ much for the same enthalpy of the addition. Their rates are expected to be similar when the monomer concentration (c_m) is 16 mol litre^{-1}, where

$$A(\text{cycl}) = A(\text{b})\, c_m.$$

Section III outlines an analysis of intraradical hydrogen abstraction reactions

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

It is of interest to compare isomerisations of radicals with hydrogen migration and with addition of the free valence to a double bond. The kinetic parameters [br_e in (kJ mol^{-1})$^{1/2}$, E_{e0} in kJ mol^{-1}, r_e in m], which describe the reactions of these two types giving rise to five-, six- and seven-membered rings in the TS are presented below.[90]

Type of reaction	n	br_e	E_{e0}	$10^{10}\, r_e$
Addition	5	18.39	69.7	0.341
Abstraction of H	5	17.03	72.5	0.455
Addition	6	20.39	85.7	0.378
Abstraction of H	6	14.42	52.0	0.385
Addition	7	19.45	78.0	0.361
Abstraction of H	7	14.40	51.8	0.385

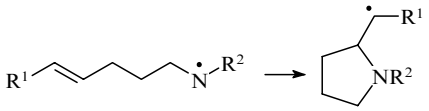
From comparison of the activation energies of thermally neutral reactions, it can be seen that hydrogen abstraction is characterised by lower E_{e0} values than addition for rings with $n \geqslant 6$, while in the case of the five-membered ring, the E_{e0} values are similar (69.7 and 72.5 kJ mol^{-1}, respectively). The dependences of E_{e0} on the ring size are antiparallel: for addition reactions, the $E_{e0}(n = 6)$ value is the highest, whereas for abstraction, $E_{e0}(n = 6)$ is the lowest. Hence, ring strain has different effects on the height of the classical potential barrier E_{e0} of the intramolecular addition and hydrogen abstraction in alkyl radicals. The difference between the E_{e0} values is probably due to the following circumstance. In the addition reaction, the cyclic TS structure coincides with the cyclic structure of the product and differs from the initial linear structure of the reactant. In the intramolecular abstraction, only the TS has a cyclic structure, while both the reactant and the product are linear.

Thus, the activation energies and the rate constants for cyclisation of alkyl radicals are determined by the following three factors: the reaction enthalpy, the size of the ring formed and the force constants of the reacting bonds. The ring size influences both the reaction enthalpy and the classical potential barrier to the thermally neutral reaction. The activation entropy also depends on the number of atoms in the ring, being directly proportional to the loss of entropy upon transition from linear to ring hydrocarbon structure [see Eqn (18)].

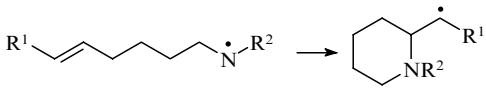
Ring opening in the cyclic alkyl radicals is the reverse reaction with respect to cyclisation. Experimental data on these reactions are summarised in Table 11.

VII. Cyclisation and ring opening in aminyl radicals

Aminyl radicals containing a double bond in the alkyl substituent undergo cyclisation, like alkyl radicals, giving rise to heterocyclic alkyl radicals. This may give either five- or six-membered rings.

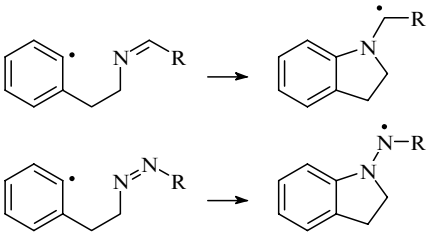


(A)



(B)

The aryl radicals with an imino group and a diazo group in the side chain also undergo cyclisation.



The experimental data on this type of isomerisation are summarised in Table 12. Cyclisation processes involving aminyl,

Table 11. Experimental activation energies, rate constants and pre-exponential factors for ring opening in alkyl radicals.

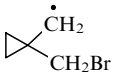
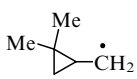
Reactant	Product	T /K	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$k_{298\,K}$ /s^{-1}	Ref.
	$CH_2=CHCH_2C^{\bullet}H_2$	128 – 362	28.4	13.00	1.05×10^8	91 – 96
	$CH_2=CMeCH_2C^{\bullet}H_2$	310 – 58	31.0	13.15	5.20×10^7	96
	$CH_2=CHCH_2C^{\bullet}HMe$	310 – 378	25.5	13.00	3.39×10^8	50, 96
	$CH_2=CHCH_2C^{\bullet}HMe$	333 – 379	31.4	13.50	9.91×10^7	50, 96
	$BrCH_2C(=CH_2)CH_2C^{\bullet}H_2$	318	–	–	2.6×10^8	97
	$CH_2=CHCH_2C^{\bullet}Me_2$	195 – 379	30.1	13.2	8.39×10^7	96, 98

Table 11 (continued).

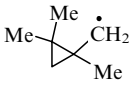
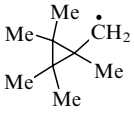
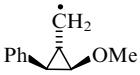
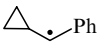
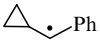
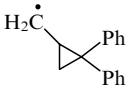
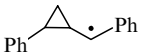
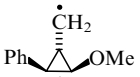
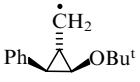
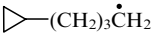
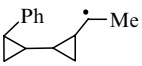
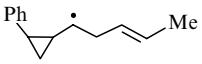
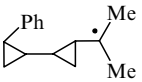
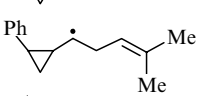
Reactant	Product	T /K	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$k_{298\,K}$ /s^{-1}	Ref.
	$CH_2=CMeCH_2C^{\bullet}Me_2$	310 – 358	26.8	12.85	1.42×10^{8}	96
	$CH_2=CMeCMe_2C^{\bullet}Me_2$	310 – 358	20.5	13.15	3.60×10^{9}	96
	$MeCH=CHCH_2C^{\bullet}H_2$	310 – 353	32.2	13.2	3.60×10^{7}	96, 99
	$Me_2C=CHCH_2C^{\bullet}H_2$	298 – 358	32.8	13.4	4.47×10^{7}	96,99,100
	$Me(Et)C=CHCH_2C^{\bullet}H_2$	233 – 382	42.1	14.5	1.31×10^{7}	101
	$MeCH=CEtCH_2C^{\bullet}H_2$	310	32.1	13.15	5.4×10^{7}	96
	$MeCH=CH(C^{\bullet}H_2)Pr^{n}$	310	28.0	12.85	1.4×10^{8}	96
	$MeCH=CHCH_2C^{\bullet}HEt$	310	23.4	12.85	8.6×10^{8}	96
	$Bu^{t}CH=CHC^{\bullet}H_2$	243	–	–	1.0×10^{3}	102
	$CH_2=CHCH(OMe)C^{\bullet}HPh$	225 – 298	14.0	13.94	3.06×10^{11}	103, 104
	$CH_2=CHCH_2C^{\bullet}HPh$	225 – 298	13.0	13.90	4.18×10^{11}	103
	$PhCH=CHCH_2C^{\bullet}H_2$	315 – 353	52.7	14.0	5.79×10^{4}	99, 105
	$PhCH=CHCH_2C^{\bullet}H_2$	280 – 321	47.7	13.3	8.69×10^{4}	52
	$CH_2=CHCH_2C^{\bullet}Ph_2$	225 – 298	8.4	13.10	4.24×10^{11}	104
	$Ph_2C^{\bullet}CH=CH_2$	351	–	–	4.0×10^{6}	106
	$C^{\bullet}H_2CH_2CH=CPh_2$	277 – 309	51.9	12.3	1.60×10^{3}	52
	$PhC^{\bullet}HCH_2CH=CHPh$	313	–	–	3.8×10^{8}	107
	$PhC^{\bullet}HCH(OMe)CH=CH_2$	252 – 311	15.2	14.55	7.70×10^{11}	108
	$PhC^{\bullet}HCH(OBu^{t})CH=CH_2$	257 – 311	16.4	14.54	4.63×10^{11}	108
		333 – 353	36.0	13.6	1.95×10^{7}	99
		284	–	–	5.6×10^{7}	109
		283	–	–	3.0×10^{7}	109
		200 – 303	22.2	13.1	2.10×10^{9}	96, 110

Table 11 (continued).

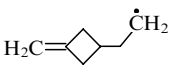
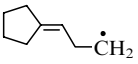
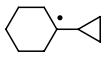
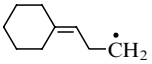
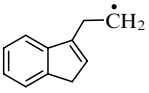
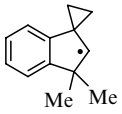
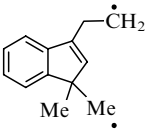
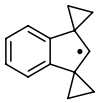
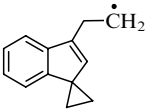
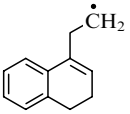
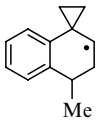
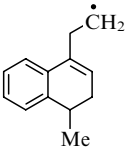
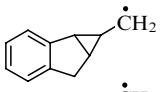
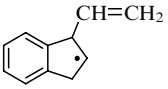
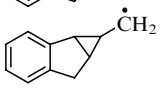
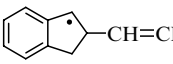
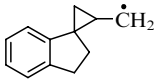
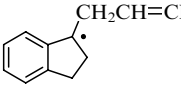
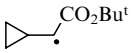
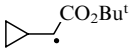
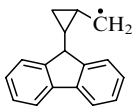
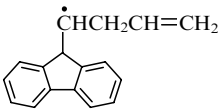
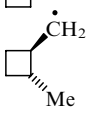
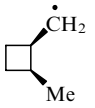
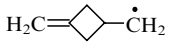
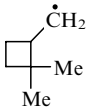
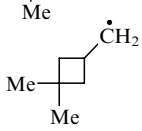
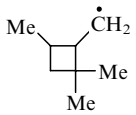
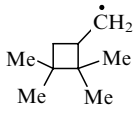
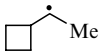
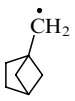
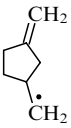
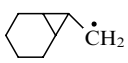
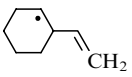
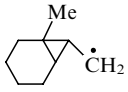
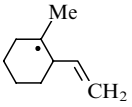
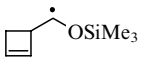
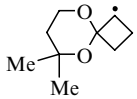
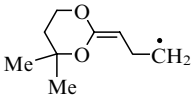
Reactant	Product	T /K	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$k_{298\,K}$ /s^{-1}	Ref.
		161 – 333	29.7	12.3	1.24×10^7	111, 112
		298 – 331	29.3	12.3	1.46×10^7	113
		298	–	–	1.1×10^7	113
	$PhCH_2C^{\bullet}H_2$	108 – 198	11.7	9.2	1.41×10^7	114
		348	–	–	2.1×10^9	115
		348	–	–	8.6×10^9	115
		348	–	–	5.3×10^8	115
		348	–	–	3.0×10^9	115
		348	–	–	3.6×10^9	115
		228 – 326	13.4	13.6	1.78×10^{11}	116
		195 – 327	14.2	13.9	2.58×10^{11}	116
		195 – 298	7.1	13.0	5.70×10^{11}	116
	(*Z*)-Bu^{t}OC(O)CH = CHCH$_2$C$^{\bullet}$H$_2$	284 – 332	51.9	14.0	8.00×10^4	99
	(*E*)-Bu^{t}OC(O)CH = CHCH$_2$C$^{\bullet}$H$_2$	284 – 332	44.8	13.7	7.04×10^5	99
		193 – 296	8.8	14.3	5.72×10^{12}	116
	$CH_2 = CH(CH_2)_2C^{\bullet}H_2$	148 – 363	48.3	13.43	9.20×10^4	117 – 119
	$CH_2 = CHC^{\bullet}HCH = CH_2$	214 – 298	42.2	12.23	6.81×10^4	111, 112
	$Me_2C = CH(CH_2)_2C^{\bullet}H_2$	273 – 333	58.1	13.63	2.79×10^3	117, 119

Table 11 (continued).

Reactant	Product	T /K	E_a /kJ mol^{-1}	log$A$ (s^{-1})	$k_{298\,K}$ /s^{-1}	Ref.
	$CH_2=CMe(CH_2)_2C^{\bullet}H_2$	333	54.4	14.90	2.30×10^6	117
	$CH_2=CH(CH_2)_2C^{\bullet}HMe$	333 – 363	48.5	15.06	3.62×10^6	117
	$CH_2=CH(CH_2)_2C^{\bullet}HMe$	333 – 363	44.8	15.26	2.55×10^7	117
	$CH_2=CHCH_2C(C^{\bullet}H_2)=CH_2$	211 – 400	48.1	12.9	2.94×10^4	119, 120
	$Me_2C^{\bullet}(CH_2)_2CH=CH_2$	333 – 363	39.3	15.27	2.41×10^8	117
	$CH_2=CHCH_2CMe_2C^{\bullet}H_2$	333 – 363	56.9	14.88	8.06×10^4	117
	$CH_2=CHCHMeCH_2C^{\bullet}Me_2$	333 – 363	38.9	15.32	3.17×10^8	117
	$CH_2=CHCH_2CMe_2C^{\bullet}Me_2$	333 – 363	42.2	15.37	9.40×10^7	117
	(*E*)-MeCH = $CH(CH_2)_2C^{\bullet}H_2$	333 – 363	54.4	14.54	1.01×10^5	117
		195 – 228	38.9	12.0	1.52×10^5	110
		298	–	–	3.0×10^8	92
		273	–	–	5.0×10^7	92
		413 – 493	56.5	13.6	4.97×10^3	121
	$CH_2=CHC^{\bullet}HCH=CHOSiMe_3$	214 – 247	45.1	12.23	2.11×10^4	118
		199 – 224	43.9	12.5	6.38×10^4	122

iminoalkyl and diazoalkyl radicals and resulting in five-membered rings are described, in terms of the MIP, by the parameters presented below [r_e in m, hN_Av and $hN_A(v_i - v_f)$ in kJ mol^{-1}].

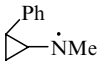
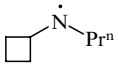
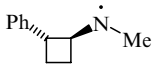
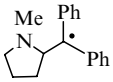
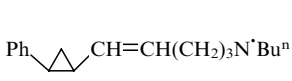
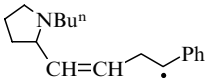
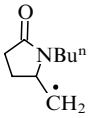
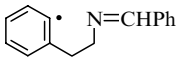
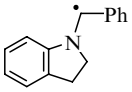
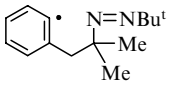
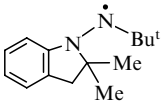
Radical (n = 3, 4)	α	$10^{10}\,r_e$	$0.5\,hN_Av$	$0.5\,hN_A(v_i - v_f)$
$R^1CH=CH_2(CH_2)_nN^{\bullet}R^2$	1.410	0.539	9.9	3.1
$R^1N=CH_2(CH_2)_nC^{\bullet}HR^2$	1.478	0.565	10.0	3.2
$R^1N=N(CH_2)_nC^{\bullet}HR^2$	1.593	0.609	10.8	4.0

The br_e, E_{e0}, and r_e parameters calculated from the data of Table 12 are presented in Table 13.

Unlike alkyl radicals, cyclisation of aminyl radicals to give a six-membered ring is characterised by lower activation energies E_{e0} than the cyclisation to give a five-membered ring. Obviously, this is due to the strain energy in the ring being formed, as follows from comparison of the E_{e0} and E_{rsc} values (in kJ mol^{-1}).

Table 12. Experimental enthalpies, activation energies and rate constants for cyclisation of aminyl radicals.

A. Experimental enthalpies and activation energies

Reactant	Product	ΔH /kJ mol^{-1}	E_a /kJ mol^{-1}	Ref.
Opening of a three-membered ring				
	$PhC^{\bullet}HCH_2CH=NMe$	15.0	14.5	122
Opening of a four-membered ring				
	$C^{\bullet}H_2(CH_2)_2CH=NPr^n$	–	43.9	123
	$PhC^{\bullet}H(CH_2)_2CH=NMe$	24.7	13.2	121
Formation of a five-membered ring				
$CH_2=CH(CH_2)_3N^{\bullet}Bu^n$		−49.0	34.0	124
$PhCH=CH(CH_2)_3N^{\bullet}Me$		−70.3	27.6	125
$Ph_2C=CH(CH_2)_3N^{\bullet}Me$		−90.9	26.3	125
		−73.0	38.3	109
$CH_2=CH(CH_2)_2C(O)N^{\bullet}Bu^n$		−49.0	38.3	126
Formation of a five-membered ring				
		−114.1	17.7	127
		−131.2	6.9	128, 129

B. Experimental rate constants

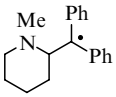
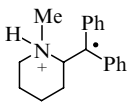
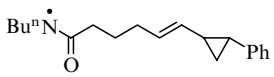
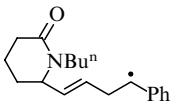
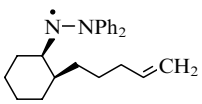
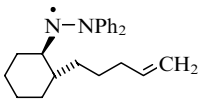
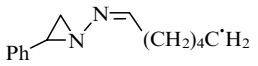
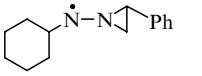
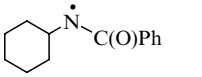
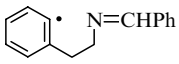
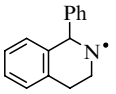
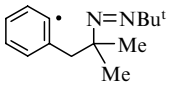
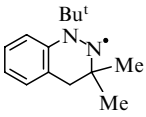
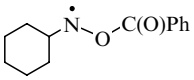
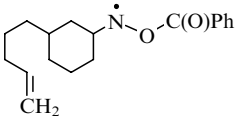
Reactant	Product	T /K	k /s^{-1}	Ref.
Formation of a six-membered ring				
$Ph_2C=CH(CH_2)_4N^{\bullet}Me$		293	7.0×10^3	125
$Ph_2C=CH(CH_2)_4\overset{+}{N}{}^{\bullet}HMe$		293	9.0×10^7	130
		298	1.2×10^7	109
$Ph_2NN=CH(CH_2)_4C^{\bullet}H(CH_2)_3CH=CH_2$		353	9.4×10^5	81

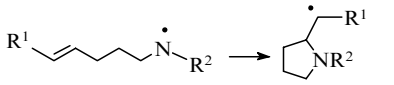
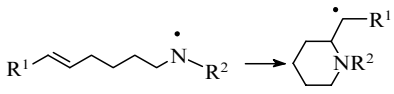
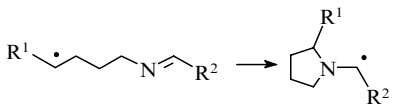
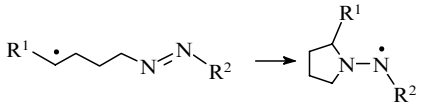
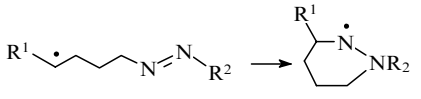
Table 12 (continued).

Reactant	Product	T /K	k /s^{-1}	Ref.
Formation of a six-membered ring				
$Ph_2NN=CH(CH_2)_4C^{\bullet}H(CH_2)_3CH=CH_2$		353	9.4×10^5	81
		353	4.7×10^6	131
$PhC(O)N=CH(CH_2)_4C^{\bullet}H_2$		353	6.7×10^5	132
		355	1.6×10^8	127
		355	2.3×10^9	128, 129
$PhC(O)ON=CH(CH_2)_4C^{\bullet}H_2$		353	2.4×10^6	133
$PhC(O)ON=CH(CH_2)_3CH(C^{\bullet}H_2)(CH_2)_3CH=CH_2$		353	4.1×10^6	133

Reaction	E_{e0}	E_{rsc}	E_{e0}(b)
(A)	75.2	26.7	61.0
(B)	61.5	3.1	61.0

The same trend is observed for cyclisations occurring through addition to an N=N bond [$E_{e0}(n=5)$ = 66.7 kJ mol^{-1}, $E_{e0}(n=6)$ = 62.4 kJ mol^{-1}]. It is noteworthy that classical potential barriers to intraradical and bimolecular addition of alkyl radicals to a C=C bond are equal, $E_{e0}(m) = E_{e0}(b)$ (see above).

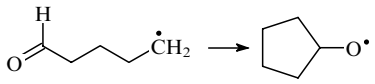
Table 13. MIP-derived kinetic parameters for cyclisation of radicals containing nitrogen atoms.

Reaction	br_e (see [a])	E_{e0} (see [b])	$10^{10}\,r_e$ (see [c])
	20.90	75.2	0.388
	19.44	61.5	0.344
	22.00	78.8	0.389
	21.18	66.7	0.348
	20.49	62.4	0.336

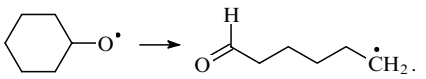
[a] Expressed in (kJ mol^{-1})$^{1/2}$; [b] in kJ mol^{-1}; [c] in m.

VIII. Cyclisation and ring opening in oxygen-containing radicals

As examples, one can consider the cyclisation of oxoalkyl radicals



and the reverse ring opening reaction in cycloalkoxyl radicals



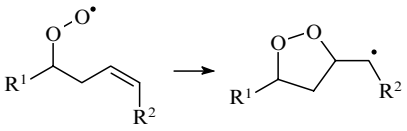
The MIP parameters for cyclisation and ring opening in oxygen-containing radicals are summarised in Table 14. Experimental data for these reactions are given in Table 15. The kinetic parameters found using the MIP relations for various classes of cyclisation and ring opening reactions for these radicals are presented in Table 16.

It can be seen that the E_{e0} values for the forward and reverse reactions coincide to within the error of measurements (±2 kJ mol^{-1}). For a five-membered ring, the activation energy (E_{e0} = 38 kJ mol^{-1}) is higher than that for a six-membered ring (E_{e0} = 32 kJ mol^{-1}). The bimolecular reaction

$$(R^1)^{\bullet} + O=CR^2R^3 \longrightarrow R^1R^2R^3CO^{\bullet}$$

has a higher activation energy (73 kJ mol^{-1}).

Peroxyl radicals undergo cyclisation to give a five-membered ring.[139]

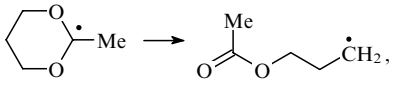


The thermally neutral cyclisation of peroxyl radicals has the activation energy $E_{e0} = 67.4$ kJ mol^{-1} (see Table 16), which is much higher than the E_{e0} value for cyclisation of the oxoalkyl radicals considered above. The bimolecular analogue of these reactions, namely, the addition of $R^1O_2^{\bullet}$ to the double bond of olefins

$$R^1O_2^{\bullet} + CH_2{=}CHR^2 \longrightarrow R^1OOCH_2C^{\bullet}HR^2,$$

is characterised by a much higher potential barrier, $E_{e0} = 90.5$ kJ mol^{-1}.

Ring opening in 1,3-dioxa-2-cycloalkyl radicals, for example,



proceeds rather fast and is accompanied by heat evolution (see Table 15). It can be seen from Table 16 that for these reactions, too, $E_{e0}(n = 6) < E_{e0}(n = 5)$; the difference between these values is 47 kJ mol^{-1}. Thus, for all cyclisation and ring opening reactions in oxygen-containing radicals studied, the inequality $E_{e0}(n = 6) < E_{e0}(n = 5)$ also holds.

Table 14. MIP parameters for cyclisation and ring opening of some oxygen-containing radicals.[20]

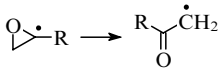
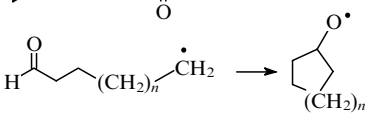
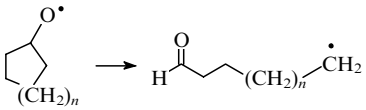
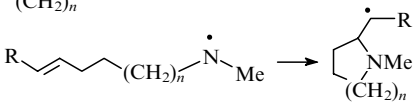
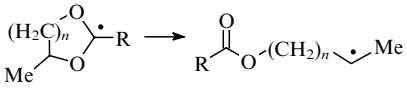
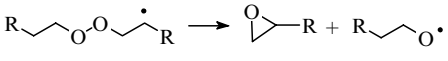
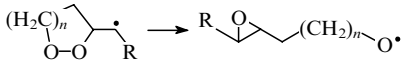
Reaction	α	$10^{-11}\,b$ /(kJ mol^{-1})$^{1/2}$ m^{-1}	$0.5\,hN_Av$ /kJ mol^{-1}	$0.5\,hN_A(v_i - v_f)$ /kJ mol^{-1}
	0.637	3.816	6.6	−3.7
	1.336	5.991	10.3	2.1
	0.748	4.483	8.2	−2.1
	1.410	5.389	9.9	3.1
	0.655	3.922	6.7	−3.6
	0.826	3.238	5.1	−1.6
	0.826	3.238	5.1	−1.6

Table 15. Experimental kinetic parameters for cyclisation and ring opening of oxygen-containing radicals.

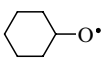
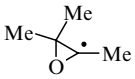
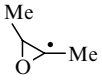
Reactant	Product	$-\Delta H$ /kJ mol^{-1}	E_a /kJ mol^{-1}	br_e (kJ mol^{-1})$^{1/2}$	Ref.
Cyclisation					
$HC(O)(CH_2)_3C^{\bullet}H_2$		−2.3	28.8	14.51	134
$HC(O)(CH_2)_4C^{\bullet}H_2$		33.2	8.3	13.83	134
Opening of a three-membered ring					
	$Me_2C^{\bullet}HCH(O)$	−113.9	40.1	14.69	102
	$MeC(O)C^{\bullet}H_2$	−118.0	56.7	16.34	102
	$Me_2C^{\bullet}C(O)Me$	−113.1	47.3	15.37	102
	$MeC^{\bullet}HC(O)Me$	−121.0	49.4	15.77	102

Table 15 (continued).

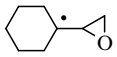
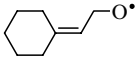
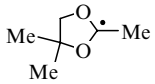
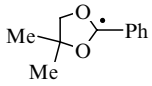
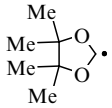
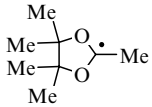
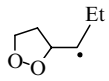
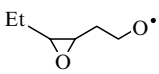
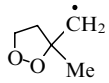
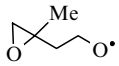
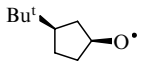
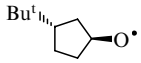
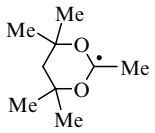
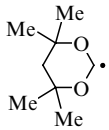
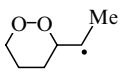
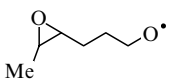
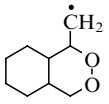
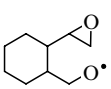
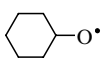
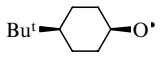
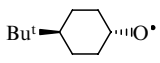
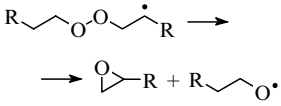
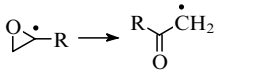
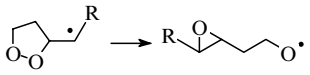
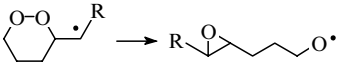
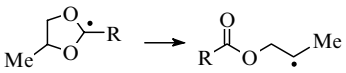
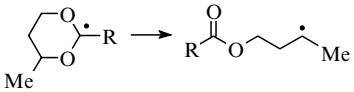
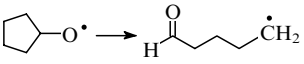
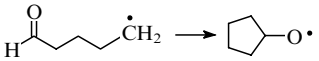
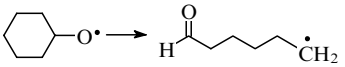
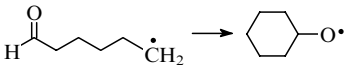
Reactant	Product	$-\Delta H$ /kJ mol^{-1}	E_a /kJ mol^{-1}	br_e (kJ mol^{-1})$^{1/2}$	Ref.
Opening of a three-membered ring					
		–	19.0	–	135
Opening of a five-membered ring					
	$MeC(O)OCH_2C^{\bullet}Me_2$	127.9	60.2	17.04	122, 136
	$PhC(O)OCH_2C^{\bullet}Me_2$	49.6	77.4	16.53	122
	$Me_2C^{\bullet}CMe_2OCH(O)$	93.0	58.7	16.08	136
	$Me_2C^{\bullet}CMe_2OCMe(O)$	127.9	52.1	16.34	136
		127.6	43.3	17.84	137
		136.5	48.7	18.66	137
	$CH(O)(CH_2)_3C^{\bullet}H_2$	−2.3	27.9	10.30	138
	$CH(O)(CH_2)_2CH(Bu^t)C^{\bullet}H_2$	−2.3	33.5	11.11	28
	$CH(O)(CH_2)_2CH(Bu^t)C^{\bullet}H_2$	−2.3	32.2	10.93	28
Opening of a six-membered ring					
	$MeC(O)OCMe_2CH_2C^{\bullet}Me_2$	35.3	35.1	12.04	136
	$CH(O)OCMe_2CH_2C^{\bullet}Me_2$	57.0	29.1	12.09	136
		102.3	15.3	13.54	137
		90.6	26.4	14.64	137
	$CH(O)(CH_2)_4C^{\bullet}H_2$	−33.2	38.5	9.58	138
	$CH(O)(CH_2)_2CH(Bu^t)CH_2C^{\bullet}H_2$	−33.2	39.4	9.74	28
	$CH(O)(CH_2)_2CH(Bu^t)CH_2C^{\bullet}H_2$	−33.2	42.2	10.20	28

Table 16. MIP-derived kinetic parameters α, br_e and E_{e0} for various types of cyclisation and ring opening reactions of O-containing radicals.

Reaction	α	br_e (see [a])	E_{e0} (see [b])
	0.826	15.13 ± ± 0.44	68.7 ± 2.0
	0.637	15.28 ± ± 0.45	87.1 ± 2.2
	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	99.4 ± 2.1
	0.655	12.06 ± ± 0.55	53.1 ± 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

[a] In (kJ mol^{-1})$^{1/2}$; [b] in kJ mol^{-1}.

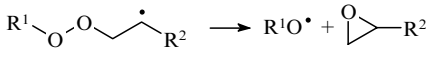
IX. Decomposition and ring opening in peroxoalkyl radicals to give epoxides

The oxidation of monomers follows a chain mechanism and includes the following chain propagation steps:[11, 12, 23]

$$R^1O_2^{\bullet} + CH_2{=}CHR^2 \longrightarrow R^1OOCH_2C^{\bullet}HR^2,$$

$$R^1OOCH_2C^{\bullet}HR^2 + O_2 \longrightarrow R^1OOCH_2CH(OO^{\bullet})R^2.$$

The last reaction is accompanied by parallel cyclisation of the peroxoalkyl radical, resulting in the epoxide.



The kinetic data for decomposition of peroxoalkyl radicals with different structures are presented in Table 17.

Decomposition of cyclic peroxoalkyl radicals results in the formation of one (rather than two) alkoxyl radical with an epoxide ring.

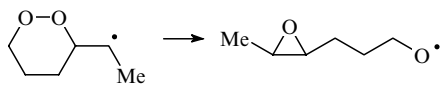
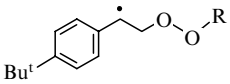
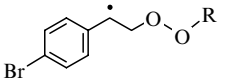
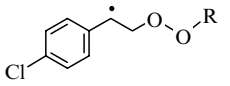
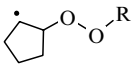
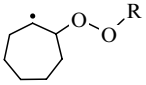
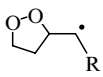
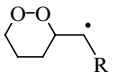


Table 17. Kinetic parameters for decomposition of alkylperoxyl radicals to give epoxides.[10, 31]

Radical	$-\Delta H$ (see [a])	T/K	k/s^{-1}	E_a (see [a])	br_e (see [b])
$ROOMeCHC^{\bullet}HMe$	76.6	363	9.1×10^6	38.3	15.55
$ROOCH_2C^{\bullet}MePr$	70.3	343	9.1×10^6	36.2	15.06
$ROOMe_2CC^{\bullet}HMe$	62.5	333	6.7×10^6	36.0	14.73
$ROOCH_2C^{\bullet}HPh$	31.8	323	7.6×10^3	53.0	15.38
$ROOCH_2C^{\bullet}MePh$	28.1	323	6.8×10^4	47.2	14.57
	35.0	368	6.6×10^4	53.8	15.60
	30.4	368	4.7×10^4	54.9	15.53
	35.5	368	7.6×10^4	53.4	15.58
	68.5	323	4.5×10^6	36.0	14.97
	64.5	333	2.9×10^7	32.0	14.32

[a] Expressed in (kJ mol^{-1})$^{1/2}$; [b] in kJ mol^{-1}.

During this reaction, the weak O–O bond is cleaved (D_{O-O} = 162 kJ mol^{-1}) to give a stronger C–O bond. Therefore, such reactions are exothermic. Their enthalpies vary in the range from −28 to −102 kJ mol^{-1} (see Table 17). The br_e parameters calculated for these reactions are very similar (see Table 16). For decomposition of cyclic peroxoalkyl radicals, the br_e and E_{e0} values depend on the ring size, as follows from the data given below.

Radical	$R^1OOCH_2C^{\bullet}HR^2$		
br_e/(kJ mol^{-1})$^{1/2}$	15.13	18.25	14.09
E_{e0}/kJ mol^{-1}	68.7	99.9	59.5
E_{rsc}/kJ mol^{-1}	0	29	10

It can be seen that for this reaction $E_{e0}(n = 5) > E_{e0}(n = 6)$ again. This is consistent with the E_{rsc} value: the higher the ring strain, the higher the activation energy of the thermally neutral reaction.

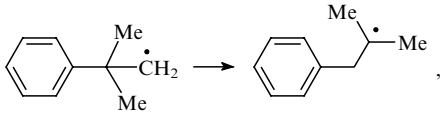
The bimolecular reaction of the alkyl radical with the peroxide

$$(R^1)^{\bullet} + R^2OOR^2 \longrightarrow R^1OR^2 + R^2O^{\bullet}$$

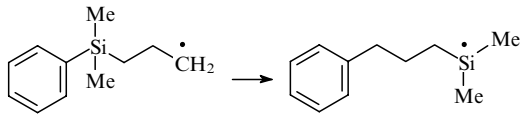
is characterised by a much higher E_{e0} value (122.7 kJ mol^{-1}).[140] For these reactions, the intraradical attack by the alkyl radical on the peroxy bridge proceeds more easily (with less potential energy required).

X. Migrations of aryl and vinyl groups in alkyl radicals

Alkylaromatic radicals undergo isomerisation accompanied by 1,2-transfer of the aromatic ring,[2] for example,

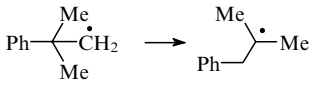
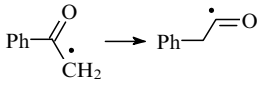
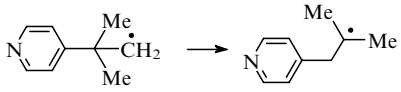
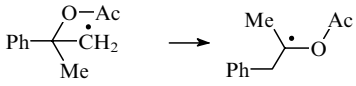
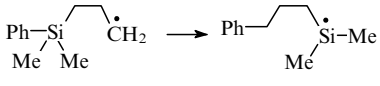
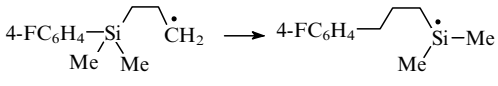
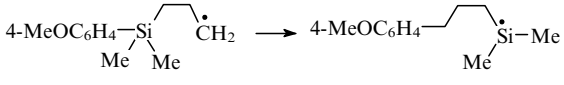
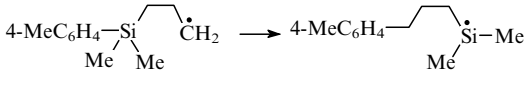
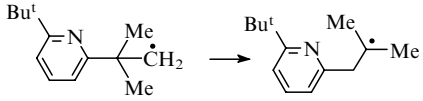
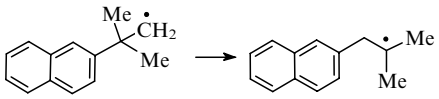
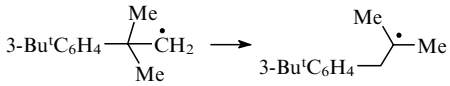
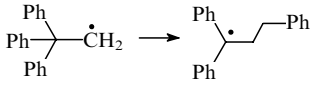
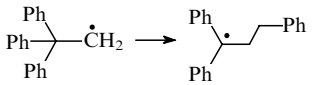
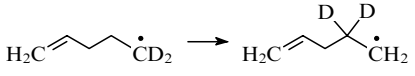
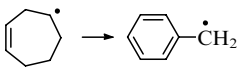
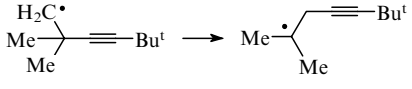


or by 1,4-transfer of the aromatic ring,[2] for example,

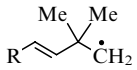
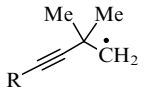
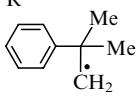
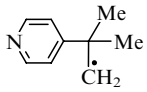
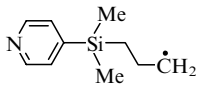


Reactions of this type have also been reported for alkyl radicals with naphthyl, pyridine, vinyl and acetylene fragments in the β-position relative to the carbon atom bearing a free valence. The enthalpies and the rate constants for these reactions are summarised in Table 18.

Table 18. Enthalpies and rate constants for the migration of aryl, vinyl and methylidine groups in alkyl radicals.

Reaction	$-\Delta H$ /kJ mol^{-1}	T /K	k /s^{-1}	Ref.
Migration of the aryl group				
	22.0	283–307	$50\times10^{11}\exp(-56/RT)$	141
	30.8	298–375	$6.3\times10^{11}\exp(-61.5/RT)$	142
	22.0	235–291	$6.3\times10^{11}\exp(-48/RT)$	141
	29.7	343	5×10^{3}	143
	44.0	413	7.3×10^{3}	144
	44.0	413	6.1×10^{3}	144
	44.0	413	1.9×10^{4}	144
	44.0	413	8.3×10^{3}	144
	22.0	235–291	$5.0\times10^{11}\exp(-50.1/RT)$	141
	22.0	237–256	$5.6\times10^{11}\exp(-46.0/RT)$	141
	22.0	283–307	$5.0\times10^{11}\exp(-56.4/RT)$	141
	73.2	298–318	$6.3\times10^{11}\exp(-35.6/RT)$	117
	73.2	373	5.0×10^{7}	145
Migration of the vinyl group				
	0	298	$1.1\times10^{11}\exp(-38.0/RT)$	51
	38.0	338	2.5×10^{4}	117
Migration of the methylidine group				
	22.0	318–361	$2.5\times10^{12}\exp(-61.1/RT)$	146

The isomerisation reactions presented in Table 18 are exothermic, some of them proceeding very rapidly, for example the fairly exothermic isomerisation of the 2,2,2-triphenylethyl radical. The average pre-exponential factor A for the 1,2-migration is 5.6×10^{11} s^{-1} ($\log A = 11.75 \pm 0.05$). The Ar–C bonds cleaved and formed during this migration are of the same type; therefore $\alpha = 1$ (MIP, see above). Analysis of the experimental data given in Table 18 within the framework of the MIP provided the following parameters for isomerisation reactions accompanied by transfer of a group bearing an unpaired π-electron.

Radical	br_e /(kJ mol^{-1})$^{1/2}$	E_{e0} /kJ mol^{-1}	$10^{10}\, r_e$ /m
	17.00	72.2	0.379
	17.21	74.0	0.384
	17.04 ± 0.33	72.6 ± 1.4	0.380
	16.36 ± 0.13	66.9 ± 0.5	0.365
	17.46 ± 0.17	76.2 ± 0.7	0.389

It can be seen that the 1,2-migrations of the vinyl, acetylene and phenyl groups are characterised by the same E_{e0} value (72.9 ± 0.8 kJ mol^{-1}). The activation energy for the 1,4-migration of the phenyl group is not much different (E_{e0} = 76.2 kJ mol^{-1}). The potential barrier to the 1,2-migration of pyridine is somewhat lower (66.9 kJ mol^{-1}). Upon comparison of the 1,2-migration of the vinyl group with the cyclisation of radicals containing a vinyl group (see above), one can note that the E_{e0} values for 1,2-migration (72.2 kJ mol^{-1}) and for cyclisation giving a five-membered ring (69.7 kJ mol^{-1}) are similar. Meanwhile the 1,2-migration of groups with π-bonds proceeds much more readily than the addition of the R$^{\bullet}$ radical to a double bond (E_{e0} = 82.6 kJ mol^{-1}).[122]

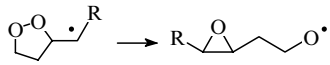
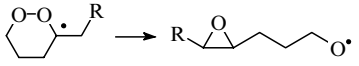
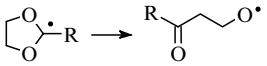
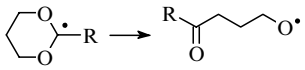
XI. Conclusion

The material considered in this review provides conclusions concerning the influence of various factors on the kinetic parameters of radical reactions of diverse classes.

The size of the ring formed. This factor is very important for both hydrogen migration and cyclisation or ring opening. First, this affects the reaction enthalpy, as the strain energy of the resulting ring (E_{rsc}) is included with a plus sign in the cyclisation enthalpy and, correspondingly, with a minus sign in the ring opening enthalpy. For three- and four-membered rings, the E_{rsc} value exceeds 100 kJ mol^{-1} (see Section III). Second, as follows from comparison of the activation energies of thermally neutral cyclisation and ring opening reactions, the ring strain influences also the classical potential barrier to the thermally neutral reaction (E_{e0}). For the cyclisation of alkyl radicals, this dependence obeys Eqn (15) (see Section VI): the higher E_{rsc}, the lower E_{e0}. The type of influence involved in the cyclisation of aminyl, iminoalkyl and ω-formyl radicals is different. This can be seen from comparison of the $E_{e0}(n = 6)$ and $E_{e0}(n = 5)$ values presented below (in kJ mol^{-1}) for the above-mentioned radicals.

Radical	$E_{e0}(n = 6)$	$E_{e0}(n = 5)$	$E_{rsc}(n = 5) - E_{rsc}(n = 6)$
$CH_2{=}CH(CH_2)_n\dot{N}R$	68.4	75.1	24
$\dot{C}H_2(CH_2)_nCH{=}CHR$	77.8	66.7	24
$\dot{C}H_2(CH_2)_nCHO$	31.7	38.0	26

A similar regularity is also found for the activation energy (in kJ mol^{-1}) of ring opening in the radicals formed from 1,2- and 1,3-dioxacyclanes (see Section V):

Reaction	$E_{e0}(n = 6)$	$E_{e0}(n = 5)$
	–	99.9
	59.5	–
	–	54.3
	101.6	–

Thus, a different pattern of dependence can be followed for cyclisation of N- and O-containing radicals, namely, the higher the ring strain, the higher the classical potential barrier to the thermally neutral reaction. This also holds for hydrogen migration.

Third, the size of the resulting ring influences the activation entropy and, hence, the pre-exponential factor [see Eqn (17)].

Electronegativity of atoms involved in the ring formation. In radical abstraction reactions

$$X^{\bullet} + HY \longrightarrow XH + Y^{\bullet}$$

the electronegativity (EA) of the atoms X and Y plays an important role by affecting the activation energy E_{e0}.[18] The greater the electronegativity difference (ΔEA) between the atoms X and Y, the lower the E_{e0} value. Does this factor influence also the activation energy of cyclisation? In the cyclisation reactions considered in this review, we were dealing with the the C···C···Y type reaction centres in the TS, where Y = C, N, O. To find out whether or not the electronegativity difference between the C and Y atoms (ΔEA) influences the E_{e0} value for cyclisation, let us juxtapose the kinetic parameters with the ΔEA values for the C···C…C, C…C···N and C···C…O reaction centres. Since the E_{e0} value for addition reactions depends also on the force constants of the reacting bonds,[20] which are different for the C=C, C=N, C=O, C–C, C–O and C–N bonds, we will juxtapose the electronegativity difference ΔEA with the r_e parameter, which does not depend on the force constants of the reacting bonds (underlined) but determines the E_{e0} value [see Eqn (5)].

Radical	Reaction centre	$10^{10}\, r_e$ /m	ΔEA /kJ mol^{-1}
$R^{\bullet}CH(CH_2)_3CH{=}CH_2$	C···C…C	0.378	0
$RCH{=}CH(CH_2)_4\dot{N}R$	C…C···N	0.333	29.5
$CH(O)(CH_2)_4\dot{C}H_2$	C···C…O	0.225	78.5

It can be seen that the r_e value decreases with an increase in the electronegativity difference for the C and Y atoms (Y = N, O). For the three classes of reactions considered, the r_e (in m) and ΔEA (in kJ mol^{-1}) values are correlated satisfactorily through the following relation (Fig. 5):

$$r_e \times 10^{11} = 3.81 \pm 0.06 - (1.91 \pm 0.23) \times 10^{-2}\, \Delta EA. \qquad (19)$$

Thus, the electronegativity of atoms in the reaction centre does really influence the activation energy of cyclisation. The

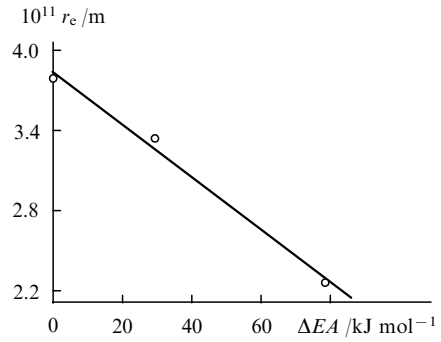


Figure 5. Parameter r_e describing the elongation of the reacting bonds upon cyclisation *vs.* electronegativity of atoms in the reaction centre (ΔEA).

higher the electronegativity difference between the C and Y atoms, the smaller the r_e parameter, and, correspondingly, E_{e0} [see Eqn (5)].

Role of the bending vibrations in the attaining of the activation barrier. According to the transition state theory, bimolecular radical abstraction reactions usually involve a linear configuration of atoms in the reaction centre, *i.e.*, the X···H···Y atoms occur in one straight line. This is confirmed by *ab initio* quantum-chemical calculations.[17] As a rule, the C···H···Y angle in these reactions equals 180° or is close to this value. In the intramolecular migration of the hydrogen atom in the alkyl radical, the corresponding angle in the TS inevitably differs from 180°. Therefore, as noted above, one should expect that $E_{e0}(b) \geqslant E_{e0}(m, n = 6)$ for abstraction reactions. However, it was shown in Section III that this is not really the case.

Reaction	$(R^1)^{\bullet} + R^2H$	$R^1O^{\bullet} + R^2H$	$R^1O_2^{\bullet} + R^2H$
$E_{e0}(m, n = 6)$ /kJ mol^{-1}	46.6	53.4	53.2
$E_{e0}(b)$ /kJ mol^{-1}	74.8	53.2	56.3

It can be seen that for the six-membered ring in the TS, $E_{e0}(m) \leqslant E_{e0}(b)$. This is due to an additional involvement of 'soft' bending vibrations in the radical activation towards isomerisation. A similar situation is observed for the cyclisation reactions resulting in a six-membered ring, namely, $E_{e0}(b) \geqslant E_{e0}(m)$ to within the error of measurements (± 2 kJ mol^{-1}).

Reaction	$E_{e0}(m)$ /kJ mol^{-1}	$E_{e0}(b)$ /kJ mol^{-1}
$R^{\bullet} + C{=}C$	85.7	82.6
$(R^1)^{\bullet} + O{=}CR_2^2$	32	72.9
$RO_2^{\bullet} + C{=}C$	67.4	90.5
$(R^1)^{\bullet} + R^2OOR^2$	59.5	122.7

Obviously, the 'soft' bending vibrations of the C–C bonds in the resulting ring play an important role in the formation of the transition state for cyclisation and for the reverse ring opening reaction and this is responsible for the lower activation energy compared to that for the bimolecular reaction.

Thus, the activation energy of radical isomerisation is determined by, at least, the following four factors: first, the enthalpy; second, the strain energy in the ring in the transition state; third, the electronegativity difference between the atoms forming the reaction centre; and fourth, the involvement of the bending vibrations of bonds in the radical activation.

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