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Generation of radicals by bimolecular reactions

E T Denisov, T G Denisova

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Abstract. The published data on bimolecular processes of radical generation in chain degradation, polymerisation, oxidation and halogenation reactions of organic compounds are systematised and analysed within the framework of the parabolic model of homolytic bimolecular reactions. The specific features of these highly endothermic reactions are discussed with a special emphasis on their striking similarity to radical abstraction processes with identical reaction centres in the transition state. The feasibility of theoretical evaluation of the activation energies and the rate constants of bimolecular reactions in radical generation is demonstrated. The bibliography includes 86 references.

I. Introduction

Initiators, light and penetrating radiation are widely used to induce chain reactions. However, it is known that chain reactions can also be generated in the absence of initiating factors. Very often, the role of free radical sources in chain degradation, oxidation, halogenation and polymerisation reactions is played by various bimolecular processes. This idea was first suggested by N N Semenov.[1] Studies of autoinitiation mechanisms of liquid-phase oxidation of hydrocarbons have shown that various bimolecular reactions of hydroperoxides with the original hydrocarbon and its oxidation products, such as alcohols, ketones and acids occur in the reaction medium. The rates of such reactions are several orders of magnitude higher than the rate of the homolytic cleavage of the weak O—O bond in ROOH.[2–8] In the absence of the hydroperoxide, free radicals are formed in bi- and trimolecular reactions of oxygen with hydrocarbons involving the C—H and C=C bonds.[2, 3, 5–10]

E T Denisov, T G Denisova Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region. Fax (7-096) 524 96 76. Tel. (7-096) 252 19 14.
E-mail: edenisov@icp.ac.ru (E T Denisov), denisova@icp.ac.ru (T G Denisova)

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Generation of radicals by bimolecular reactions is largely endothermic and proceeds at a very slow rate. The methods for the study of their kinetics involve the use of free radical acceptors, inhibitors (in the case of oxidation reactions) or the rate of determination of the chain reactions triggered by bimolecular processes.[2, 7, 9] If a chain reaction does not take place in the system under study, the rate of radical generation is judged upon by the decrement of one of reaction components. Studies of such reactions present difficulties which are not always overcome. The rates of such reactions are usually low because of high activation energies. In many cases, generation of radicals occurs in parallel by several bimolecular reactions and the rate of only one of them (as a rule, the fastest reaction) can be measured. Therefore, theoretical evaluation of rate constants for such reactions is an urgent task.

As bimolecular processes of radical formation are endothermic, the determination of their activation energies E is seemingly easy. The corresponding equation may appear as:

$$E \approx \Delta H,$$

where ΔH is the enthalpy of the reaction.[1] However, this condition is not always fulfilled. Strictly speaking, for endothermic reactions:

$$E = \Delta H + \Delta E,$$

the increment ΔE can be large enough (~ 10 kJ mol^{-1}) even for highly endothermic reactions ($\Delta H \geqslant 150$ kJ mol^{-1}). The determination of the coefficient A (the pre-exponential factor) in the Arrhenius equation:

$$E = RT \ln \frac{A}{k},$$

which was found to be enthalpy-dependent, also presents a problem.[11] These difficulties were successfully overcome in the framework of the parabolic model of a bimolecular homolytic reaction. Earlier, we used this model for determining the activation energies of radical abstraction and addition reactions.[12, 13] In more recent experiments, we used the parabolic model for the description of a vast variety of bimolecular homolytic reactions.[14–28] The present review is devoted to the analysis and comparison of experimental and calculated data (*e.g.*, activation

energies and rate constants) for generation of radicals by homolytic bimolecular reactions.

II. Classification of bimolecular reactions in radical generation

A bimolecular initiation reaction can dominate over the monomolecular decomposition of the reagent molecule involving the weakest bond, if $\Delta H < D_{min}$ (where D_{min} is the bond stability).

In many bimolecular reactions, the energy of cleavage of a weak bond is compensated for by the energy of formation of a rather stable bond.

All known bimolecular homolytic reactions may be divided into three types:

1. Abstraction reactions of hydrogen or halogen (X) from the RH or the YX molecule by an acceptor molecule possessing a multiple bond (C=C, C≡N, C=O, O=O, *etc.*), *e.g.*:

$$RH + O_2 \longrightarrow R^{\bullet} + HOO^{\bullet},$$

$$RSH + CH_2{=}CHPh \longrightarrow RS^{\bullet} + MeC^{\bullet}HPh,$$

$$ArOH + OC_6H_4O \longrightarrow ArO^{\bullet} + HOC_6H_4O^{\bullet}.$$

In the first reaction, the cleavage of the C−H bond is partly compensated for by the formation of the O−H bond in the hydroperoxide radical formed. For example, for the reaction where RH is cumene for which D(C−H) = 335 kJ mol^{-1} (D is the bond strength), the enthalpy is equal to 135 kJ mol^{-1}.

$$\Delta H = D(C{-}H) - D(H{-}O_2^{\bullet}) = 355 - 220 = 135 \text{ kJ mol}^{-1}.$$

At the same time, the energy of the weakest bond C−CH$_3$ in cumene is equal to 300 kJ mol^{-1}. Hence, $\Delta H \ll D_{min}$.

The X−X (or Y−X) bonds in halogen molecules are weak, while the C−X bonds in halide molecules are strong. Thus the bond energies of F_2 , ICl and Cl_2 molecules are equal to 159, 211 and 243 kJ mol^{-1}, respectively. The enthalpy of the reaction:

$$YX + CH_2{=}CHR \longrightarrow Y^{\bullet} + XCH_2C^{\bullet}HR$$

is low and is sometimes negative. Therefore, these reactions proceed rather rapidly. The role of halogen atom acceptors in such reactions is played by alkenes, alkynes, imines, nitriles and nitro compounds.

2. Dissociative abstraction reactions in which the cleavage of two bonds is accompanied by the formation of a molecule with a strong bond, *e.g.*:

$$HR + F_2 \longrightarrow F^{\bullet} + HF + R^{\bullet}.$$

Since the F−F bond is weak (159 kJ mol^{-1}) and the H−F bond is very strong (570 kJ mol^{-1}), for many hydrocarbons with D(C−H) < 411 kJ mol^{-1} this reaction is exothermic.

A similar situation is typical of bimolecular reactions involving hydrogen peroxide and hydroperoxides:

$$RH + R'OOH \longrightarrow R^{\bullet} + H_2O + R'O^{\bullet}.$$

In these reactions, the energies of cleavage of two bonds (R−H and R′O−OH) are largely compensated for by the energy of formation of a stable O−H bond in the H_2O molecule (498 kJ mol^{-1}); in many cases, the change in the reaction enthalpy:

$$\Delta H = D(O{-}H) + D(O{-}O) - 498$$

is less pronounced than the change in the dissociation energy of the least stable O−O bond in the hydroperoxide molecule.

3. Reactions of biradical generation. The σ-C−C bond of hydrocarbons is always stronger than the π-C−C bond. For example, for the ethane molecule D(σ-C−C) = 378 kJ mol^{-1}, whereas for the ethylene molecule D(π-C−C) = 270 kJ mol^{-1}. In the presence of substituents at the double bond of a hydrocarbon molecule, a biradical is formed with relatively low energy consumption, *e.g.*:

$$PhCH{=}CH_2 + CH_2{=}CHPh \longrightarrow PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh.$$

Chain reactions are initiated in the presence of active reagents, such as oxygen or a monomer (*e.g.*, in polymerisation reactions).

Thus, the bimolecular reactions in radical generation are rather diverse: they involve C−H, N−H, O−H and S−H bonds of saturated molecules, on the one hand, and O_2, O_3, F_2, Cl_2 and other halogen-containing molecules, peroxides, disulfides and molecules containing multiple bonds, on the other hand.

III. The parabolic model of a bimolecular reaction

Generation of radicals by a bimolecular homolytic reaction, such as:

$$RH + O_2 \longrightarrow R^{\bullet} + HOO^{\bullet},$$

is interpreted within the framework of the parabolic model [12, 13] as a result of intersection of two parabolic potential curves plotted on the coordinates of the amplitude of the stretching vibration of atoms involved in bond formation *versus* potential energy. The main parameters of this reaction are as follows:

1. Reaction enthalpy ΔH_e which includes the difference between the zero-point vibrational energies of the reacting bonds:

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

where D_i and D_f are dissociation energies and ν_i and ν_f are the stretching vibration frequencies of the bond that is cleaved (i) and of the bond that is formed (f), respectively, h is Planck's constant and N_A is Avogadro's number.

2. Activation energy E_e which includes the zero-point vibrational energy of the bond being attacked:

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

where E is the experimental activation energy.

3. Distance r_e which is equal to the sum of the amplitudes of stretching vibrations of the reacting bonds in the transition state.

4. Dynamic characteristics of the bond that is cleaved (b_i) and that is formed (b_f):

$$b_i = \pi\nu_i(2\mu_i)^{1/2},$$

$$b_f = \pi\nu_f(2\mu_f)^{1/2},$$

where μ_i and μ_r are the reduced masses of the atoms forming these bonds and $2b^2$ is the force constant of the bond.

The above parameters are related to one another by the following expression:

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

where $\alpha = b_i/b_f$, $b = b_i$.

By using the parameter br_e, it is possible to calculate the activation energy of the thermally neutral reaction E_{e0}:

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

which is characteristic of the whole class of reactions with br_e = const.

As a rule, the coefficient A in the Arrhenius equation (calculated in relation to one reacting bond) for the same class of reactions is the same, which makes it possible to calculate E from the rate constant k:

$$E = RT\ln\left(n\,\frac{A}{k}\right), \quad (5)$$

where n is the number of reacting bonds.

Since in all elementary reactions $E > 0$, relation (3) is fulfilled for $\Delta H_e > \Delta H_{e\,min}$. If $\Delta H_e < \Delta H_{e\,min}$, the activation energy E is very small and is equal to 0.5 RT.[11]

In the case of highly endothermic reactions, the activation energy and the enthalpy are very close.[11] According to the parabolic model, for $\Delta H_e > \Delta H_{e\,max}$:

$$E = \Delta H + 0.5\,RT. \quad (6)$$

The threshold value of $\Delta H_{e\,max}$ is related to parameters which characterise a certain class of reactions by the following expression:[12]

$$\Delta H_{e\,max} = (br_e)^2 - 2\alpha br_e\sqrt{0.5hN_A\nu_f} + 0.5hN_A\nu_f(\alpha^2 - 1). \quad (7)$$

If reactions with high enthalpy ($\Delta H_e > \Delta H_{e\,max}$) belong to the same class, the pre-exponential factor A is not constant, but rather is a function of reaction enthalpy. Within the framework of the parabolic model, this dependence appears as:[11]

$$A = A_0\left[1 + \beta\left(\sqrt{\Delta H_e} - \sqrt{\Delta H_{e\,max}}\right)\right]^2, \quad (8)$$

where $\beta = 1.3$.

If a reaction belongs to a class described by kinetic parameters (A, r_e, b, b_i, b_f, α, $1/2hN_A\nu_i$, $1/2hN_A\nu_f$), its rate constant and activation energy can be calculated from the formula:

$$k = n\,A_0\exp\left(-\frac{E}{RT}\right), \quad (9)$$

as well as from the ratio given below.[12]

For reactions with $\Delta H_e < \Delta H_{e\,max}$:
for $\alpha = 1$:

$$\sqrt{E_e} = \frac{br_e}{2} + \frac{\Delta H_e}{2br_e}, \quad (10)$$

for $\alpha \neq 1$:

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right], \quad (11)$$

for low values of α, where $\Delta H_e(1-\alpha^2) \ll (br_e)^2$:

$$\sqrt{E_e} = \frac{br_e}{1+\alpha} + \frac{\alpha\Delta H_e}{2br_e}. \quad (12)$$

For reactions with $\Delta H_e > \Delta H_{e\,max}$, the activation energy is calculated by the formula (6) and the rate constant is calculated by the formula (13) taking into account the dependence of the pre-exponential factor on ΔH_e:

$$k = A_0 e^{-1/2}\left[1 + \beta\left(\sqrt{\Delta H_e} - \sqrt{\Delta H_{e\,max}}\right)\right]^2\exp\left(-\frac{\Delta H}{RT}\right). \quad (13)$$

The calculations of activation energies and rate constants of bimolecular homolytic reactions should take into consideration the following factors.

1. If the enthalpy of the reaction is such that $\Delta H_e < \Delta H_{e\,max}$, then $E > \Delta H$ and the activation energy should be calculated by one of the formulae (10)–(12). In its turn, the threshold value of $\Delta H_{e\,max}$ depends on parameters α, r_e, b and the zero-point vibrational energy of the bond that is cleaved. It should be borne in mind that the threshold value of $\Delta H_{e\,max}$ varies widely for different classes of reactions. The dependencies of the difference $E - \Delta H$ on ΔH for four classes of reactions are shown in Fig. 1. As can be seen, in the range where $E > \Delta H$ on going from XCl + RH to ROOH + RH reactions, the enthalpies of the reactions vary from ~20 to 250 kJ mol^{-1}, *i.e.*, by more than one order of magnitude. Consequently, before one uses a simple formula (6) for the calculation of activation energies, it is necessary to be sure that $\Delta H_e > \Delta H_{e\,max}$. However, in this case the pre-exponential factor in the Arrhenius plot depends on ΔH (*i.e.*, $A \neq$ const) due to the intersection of potential curves of the reacting bonds at a distance exceeding r_e, and the dependence is described by the formula (8), while the rate constant is described by the formula (13).

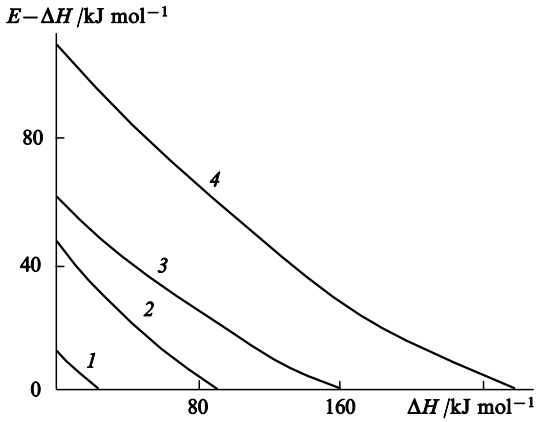


Figure 1. The dependence of the difference $E - \Delta H$ on the enthalpy ΔH for the reactions XCl + RH (*1*), XF + RH (*2*), RCH=CH$_2$ + RH (*3*), ROOH + RH (*4*).

2. Bimolecular reactions with cleavage of two bonds differ from those in which only one bond is cleaved. In the latter case, the probability of concentraton of the activation energy on one bond is expressed by the exponential function $\exp(-E/RT)$. If two bonds are cleaved, the probability of simultaneous concentration of energy on the both cleavable bonds manifests a more complex dependence on E. The rate constant for such a reaction is expressed by the formula:[29]

$$k = A_0\left(\frac{2RT}{\pi E}\right)^{1/2}\exp\left(-\frac{E}{RT}\right). \quad (14)$$

Within the framework of the parabolic model, the activation energy for the above-described case can be presented in an alternative way. For example, the activation energy of the reaction of RH with F_2 can be characterised by the coordinate of the point of intersection of the potential curves for R–H and H–F or F–F and H–F bonds. Naturally, the kinetic characteristics of the same reaction will be different. Preference in such cases will be given to the variant where both bonds (*i.e.*, that is cleaved and that is formed) involve a light atom.

3. The kinetic parameters, *e.g.*, br_e, can be determined from the experimental data only for reactions where $\Delta H_e < \Delta H_{e\,max}$. Unfortunately, such reactions are very few in number. It is noteworthy that bimolecular radical and molecular reactions are similar.[25–27] If such reactions have identical reaction centres, their main characteristics (α, br_e, E_{e0} and $0.5\,hN_A\nu$) are also identical or similar. For example, the reactions:

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet},$$

$$O_3 + RH \longrightarrow HO_3^{\bullet} + R^{\bullet}$$

are characterised by the same set of parameters:[12,14] br_e = 13.61 (kJ mol^{-1})$^{1/2}$, $\alpha = 0.814$, $0.5hN_A\nu = 17.4$ kJ mol^{-1}, $0.5hN_A(\nu_i - \nu_f) = -3.8$ kJ mol^{-1} and $E_{e0} = 56.3$ kJ mol^{-1}. This makes it possible to estimate the activation energies and rate constants for homolytic reactions of the 'molecule + molecule' type by using the known parameters of reactions (with an analogous reaction centre) of the 'radical + molecule' type. Examples of generation of radicals by such bimolecular reactions and their analogues, *viz.*, radical reactions characterised by the same set of parameters, are given below.

Bimolecular homolytic reaction	Radical reaction, an analogue of the bimolecular reaction
$RCH=CH_2 + R'H \longrightarrow RC^{\bullet}HMe + R'^{\bullet}$	$R^{\bullet} + R'H \longrightarrow RH + R'^{\bullet}$
$R'R''C=O + RH \longrightarrow R'R''C^{\bullet}OH + R^{\bullet}$	$RO^{\bullet} + R'H \longrightarrow ROH + R'^{\bullet}$
$OC_6H_4O + RH \longrightarrow HOC_6H_4O^{\bullet} + R^{\bullet}$	$ArO^{\bullet} + RH \longrightarrow ArOH + R^{\bullet}$
$F_2 + RH \longrightarrow F^{\bullet} + HF + R^{\bullet}$	$F^{\bullet} + RH \longrightarrow HF + R^{\bullet}$
$F_2 + CH_2=CHR \longrightarrow F^{\bullet} + CH_2FC^{\bullet}HR$	$F^{\bullet} + CH_2=CHR \longrightarrow CH_2FC^{\bullet}HR$
$Cl_2 + RH \longrightarrow Cl^{\bullet} + HCl + R^{\bullet}$	$Cl^{\bullet} + RH \longrightarrow HCl + R^{\bullet}$
$Cl_2 + CH_2=CHR \longrightarrow Cl^{\bullet} + CH_2ClC^{\bullet}HR$	$Cl^{\bullet} + CH_2=CHR \longrightarrow CH_2ClC^{\bullet}HR$
$O_2 + RH \longrightarrow HO_2^{\bullet} + R^{\bullet}$	$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$
$O_3 + RH \longrightarrow HO_3^{\bullet} + R^{\bullet}$	$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$
$O_2 + CH_2=CHR \longrightarrow {}^{\bullet}OOCH_2C^{\bullet}HR$	$RO_2^{\bullet} + CH_2=CHR \longrightarrow ROOCH_2C^{\bullet}HR$
$ROOH + ROOH \longrightarrow RO^{\bullet} + H_2O + RO_2^{\bullet}$	$R'R''C^{\bullet}OH + ROOH \longrightarrow R'R''C=O + H_2O + RO^{\bullet}$
$RH + ROOH \longrightarrow R^{\bullet} + H_2O + RO^{\bullet}$	$RC^{\bullet}HMe + ROOH \longrightarrow RCH=CH_2 + H_2O + RO^{\bullet}$
$RCH=CH_2 + R'OOH \longrightarrow RC^{\bullet}HCH_2OH + R'O^{\bullet}$	$R^{\bullet} + ROOH \longrightarrow ROH + RO^{\bullet}$

IV. Retrodisproportionation reactions

Disproportionation of alkyl radicals proceeds at a very fast rate which is close to the rate of molecular collisions in the gas phase and the diffusion-controlled rate in the liquid phase.[30] Disproportionation is a highly exothermic reaction, *e.g.*, ΔH for the disproportionation of ethyl radicals:

$$MeC^{\bullet}H_2 + MeC^{\bullet}H_2 \longrightarrow CH_2=CH_2 + Me_2$$

is equal to -270 kJ mol^{-1}. The reverse reaction, *i.e.*, retrodisproportionation:

$$RH + CH_2=CHR' \longrightarrow R^{\bullet} + MeC^{\bullet}HR'$$

represents an endothermic process which proceeds at a very slow rate. The retrodisproportionation reactions investigated in great detail by Ruchardt *et al.*[10,31–37] play a prominent role in chain processes of hydrocarbon cracking, polymerisation and oxidation. The activation energies and enthalpies of such reactions were found to be very similar. The attack of an alkene on the weak C–H bond of the hydrocarbon playing the role of a hydrogen donor is consistent with the kinetic isotope effect.[31] The solvent polarity weakly affects the rate constant for this reaction. However, the rates of reactions in which the role of a hydrogen acceptor is played by benzoquinone strongly depend on the solvent polarity. The values of experimentally determined rate constants and activation energies for reactions of alkenes and benzoquinone with 9,10-dihydroanthracene are given in Table 1.

The structures of reaction centres of retrodisproportionation and radical abstraction reactions are similar: $C=C\cdots H\cdots R$ and $-C^{\bullet}\cdots H\cdots R$. This circumstance was taken into consideration in the calculations based on the use of the parabolic model.[15] The kinetic and thermodynamic parameters of the corresponding disproportionation reactions are given in Tables 2 and 3.†

† The alkyl, allyl and benzyl radicals in the Tables are designated as R^1, R^2 and R^3, respectively.

Table 1. The activation energies and rate constants for the retrodisproportionation reaction of 9,10-dihydroanthracene with alkenes (PhOPh is used as solvent).[31–37]

Alkene	T/K	E	log$A$	k (550 K)
Styrene	553–583	111.5	6.60	1.02×10^{-4}
2-Phenylbut-1-ene	553–583	149.1	9.48	2.09×10^{-5}
3-Methyl-2-phenylbut-1-ene	553–583	131.1	7.67	1.66×10^{-5}
3,3-Dimethyl-2-phenylbut-1-ene	553–583	148.3	8.32	1.72×10^{-6}
2,6-Dimethylstyrene	553–583	139.5	8.08	6.78×10^{-6}
1,1-Diphenylethylene	553–583	139.9	9.39	1.27×10^{-4}
1,2-Diphenylethylene	553–583	162.1	9.72	2.11×10^{-6}
Acenaphthene	553–583	114.8	7.36	2.87×10^{-4}
Indene	553–583	155.8	9.70	8.01×10^{-6}
1,2-Dihydronaphthalene	553–583	154.5	9.56	7.71×10^{-6}
2,2-Dimethyl-1-methylideneindan	553–583	132.8	8.50	7.72×10^{-5}
2,2-Diethyl-1-methylideneindan	553–583	139.1	9.13	8.31×10^{-5}
Dibenzofulvene	553–583	96.8	7.10	8.07×10^{-3}
9-Ethylidenefluorene	553–583	130.3	9.22	7.00×10^{-4}
9-Isopropylidenefluorene	553–583	141.2	9.11	5.01×10^{-5}
9-(1,1-Dicyanoethyl)-fluorene	553–583	139.9	9.17	7.65×10^{-5}
Triphenylethylene	553–583	155.0	9.02	1.99×10^{-6}
Cyclohexa-1,3-diene	553–583	129.0	8.30	1.12×10^{-4}
Cycloheptatriene	553–583	137.8	8.71	4.20×10^{-5}
2,4,4-Triacetoxybut-1-ene	553–583	137.8	8.13	1.10×10^{-5}
Azobenzene	463–523	112.0	8.43	6.21×10^{-3}
4,4′-Dimethylazobenzene	463–523	111.2	8.16	3.97×10^{-3}
4,4′-Di-*tert*-butylazobenzene	463–523	115.0	8.67	5.60×10^{-3}
4,4′-Dimethoxyazobenzene	463–523	116.6	8.51	3.11×10^{-3}
4,4′-Dichloroazobenzene	463–523	115.0	9.08	1.44×10^{-2}
4,4′-Dibromoazobenzene	463–523	119.6	9.73	2.35×10^{-2}
4,4′-Diaminoazobenzene	463–523	121.3	8.82	1.99×10^{-3}
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [a]	298–338	51.56	7.11	1.62×10^{2}
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [b]	298–338	37.4	5.11	36.2
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [c]	298–338	43.6	6.28	1.37×10^{2}

Note. Hereinafter, the dimensionalities of the activation energies, the preexponential factor A and the rate constants are kJ mol^{-1}, litre mol s^{-1} and litre mol^{-1} s^{-1}. [a] In dioxane; [b] in acetonitrile; [c] in acetic acid, respectively.

The enthalpies for the retrodisproportionation reactions involving hydrogen acceptors, such as ethylene, but-1-ene, cyclohexa-1,3-diene, *etc.*, are listed in Table 4; the calculated rate constants and activation energies of retrodisproportionation reactions involving styrene and benzoquinone as hydrogen acceptors are given in Tables 5 and 6. The results of these calculations are in good agreement with the experimental data. For example, the calculated and experimental values of k (550 K) for the retrodisproportionation of styrene with 9,10-dihydroanthracene are equal to 9.2×10^{-5} and 1.0×10^{-4} litre mol^{-1} s^{-1}, respectively.[31]

Table 2. The kinetic parameters of retrodisproportionation reactions.[15]

HY	α	$10^{-11}b$	$0.5hN_Av_i$	$0.5hN_A(v_i-v_f)$	$(r^{\neq}/r_e)_0$
$RCH=CH_2 + HY \longrightarrow RC^{\bullet}HCH_3 + Y^{\bullet}$					
HR	1.000	3.743	17.4	0.0	0.500
HNR_2	1.150	4.306	20.0	2.6	0.465
HOR	1.256	4.701	21.7	4.3	0.443
HOOR[1]	1.229	4.600	21.2	3.8	0.449
$HSiR_3$	0.767	2.871	13.1	−4.3	0.566
HSR	0.808	3.026	13.8	−3.6	0.553
$HGeR_3$	0.747	2.796	12.6	−4.8	0.572
$HSnR_3$	0.720	2.695	12.1	−5.3	0.581
$RC\equiv CH + HY \longrightarrow RC^{\bullet}=CH_2 + Y^{\bullet}$					
HR	0.945	3.743	17.4	−1.0	0.514
HNR_2	1.087	4.306	20.0	1.6	0.479
HOR	1.187	4.701	21.7	3.3	0.457
HOOR	1.161	4.600	21.2	2.8	0.463
$HSiR_3$	0.725	2.871	13.1	−5.3	0.580
HSR	0.764	3.026	13.8	−4.6	0.567
$HGeR_3$	0.706	2.796	12.6	−5.8	0.586
$HSnR_3$	0.680	2.695	12.1	−6.3	0.595
$R'R''C=O + HY \longrightarrow R'R''C^{\bullet}OH + Y^{\bullet}$					
HR	0.796	3.743	17.4	−4.3	0.557
HNR_2	0.916	4.306	20.0	−1.7	0.522
HOR	1.00	4.701	21.7	0.0	0.500
HOOR	0.978	4.600	21.2	−0.5	0.505
$HSiR_3$	0.611	2.871	13.1	−8.6	0.621
HSR	0.644	3.026	13.8	−7.9	0.608
$HGeR_3$	0.595	2.796	12.6	−9.1	0.627
$HSnR_3$	0.573	2.695	12.1	−9.6	0.636
$RCH=NR'$ (RN=NR, $RC\equiv N$) + HY $\longrightarrow$ $\longrightarrow RC^{\bullet}HNHR'$ ($RNHN^{\bullet}R$, $RC^{\bullet}=NH$) + $Y^{\bullet}$					
HR	0.869	3.743	17.4	−2.6	0.535
HNR_2	1.000	4.306	20.0	0.0	0.500
HOR	1.092	4.701	21.7	1.7	0.478
HOOR	1.068	4.600	21.2	1.2	0.484
$HSiR_3$	0.667	2.871	13.1	−6.9	0.600
HSR	0.703	3.026	13.8	−6.2	0.587
$HGeR_3$	0.649	0.279	12.6	−7.4	0.606
$HSnR_3$	0.626	2.700	12.1	−7.9	0.615

Note. Hereinafter, the dimensions of parameters b, $0.5hN_Av_i$ and $0.5hN_A(v_i-v_f)$ are (kJ mol^{-1})$^{1/2}$ m^{-1} and kJ mol^{-1}, respectively; $r^{\neq}$ is the amplitude of the oscillation of the bond that is cleaved in the transition state; the ratio $(r^{\neq}/r_e)_0$ is given for the condition $\Delta H = 0$.

Table 3. The kinetic and thermodynamic parameters of retrodisproportionation reactions.

HY	br_e	E_{e0}	$10^{-8}A_0$	$\Delta H_{e\,max}$
$RCH=CH_2 + HY \longrightarrow RC^{\bullet}HCH_3 + Y^{\bullet}$ (see Refs 26 and 27)				
R^1H	17.30	74.8	10	155.0
R^2H	18.60	86.5	1.0	190.8
R^3H	17.80	79.2	1.0	168.3
H_2NR	17.14	63.5	1.2	135.0
HNR_2	18.07	70.6	1.2	158.8
HOR	16.46	53.2	1.0	108.5
HOOR	16.73	56.3	1.0	117.2
$HSiR_3$	13.18	55.6	10	95.1
HSR	11.80	42.6	2.0	53.7
$HGeR_3$	13.82	62.6	10	112.1
$HSnR_3$	13.67	63.2	10	112.6
$RCH=CHCH=CH_2 + HY \longrightarrow RCH=CHC^{\bullet}HCH_3 + Y^{\bullet}$ (see Refs 26 and 27)				
R^1H	18.60	86.5	10	190.8
R^2H	19.25	92.6	1.0	210.0
R^3H	18.85	88.8	1.0	198.1
H_2NR	18.64	75.2	1.2	174.2
HNR_2	19.57	82.8	1.2	200.8
HOR	17.76	62.0	1.0	139.4
HOOR	18.68	70.2	1.0	166.4
$HSiR_3$	14.12	64.6	10	115.6
HSR	12.32	46.4	2.0	62.7
$HGeR_3$	14.76	71.4	10	134.0
$HSnR_3$	14.65	72.5	10	135.4
$PhCH=CH_2 + HY \longrightarrow PhC^{\bullet}HCH_3 + Y^{\bullet}$ (see Refs 26 and 27)				
R^1H	17.80	79.2	10	168.3
R^2H	18.45	85.1	1.0	186.5
R^3H	18.05	81.4	1.0	175.2
H_2NR	17.71	67.8	1.2	149.3
HNR_2	18.64	75.2	1.2	174.2
HOR	16.96	56.5	1.0	120.0
HOOR	17.60	62.3	1.0	138.1
$HSiR_3$	13.54	58.7	10	102.8
HSR	12.00	44.0	2.0	57.1
$HGeR_3$	14.18	65.9	10	120.3
$HSnR_3$	14.03	66.5	10	120.7
$RC\equiv CH + HY \longrightarrow RC^{\bullet}=CH_2 + Y^{\bullet}$ (see Refs 26 and 27)				
R^1H	16.88	75.3	10	146.1
R^2H	18.18	87.4	1.0	181.1
R^3H	17.18	78.0	1.0	153.9
H_2NR	16.72	64.2	1.2	127.0
HNR_2	17.65	71.5	1.2	150.2
HOR	15.95	53.2	1.0	99.5
HOOR	16.22	56.3	0.1	107.9
$HSiR_3$	12.00	48.4	10	74.8
HSR	11.38	41.6	0.2	47.2
$HGeR_3$	12.56	54.2	10	88.5
$HSnR_3$	12.62	56.4	10	93.1
$R'R''C=O + HY \longrightarrow R'R''C^{\bullet}OH + Y^{\bullet}$ (see Refs 26 and 27)				
R^1H	13.10	53.2	10	66.6
R^2H	14.14	62.0	1.0	87.1
R^3H	13.50	56.5	1.0	74.2
H_2NR	11.95	38.9	1.0	37.3
HNR_2	12.88	45.2	10	52.4
HOR	13.62	46.4	10	61.3
HOOR	14.13	51.0	10	70.1
$HSiR_3$	10.13	39.5	10	49.6
HSR	10.39	39.9	10	32.9

Table 3 (continued).

HY	br_e	E_{e0}	$10^{-8}A_0$	$\Delta H_{e\,max}$
$R'R''C=O + HY \longrightarrow R'R''C^{\bullet}OH + Y^{\bullet}$ (see Refs 26 and 27)				
$HGeR_3$	10.56	43.8	10	58.8
$HSnR_3$	11.00	48.9	10	69.0
$RCH=NH + HY \longrightarrow RC^{\bullet}HNH_2 + Y^{\bullet}$ (see Ref. 28)				
R^1H	14.90	63.6	1.5	101.3
R^2H	16.21	75.2	0.15	131.9
R^3H	15.40	67.9	0.15	112.5
H_2NR	21.00	110.2	4.0	253.2
HNR_2	21.90	119.9	2.0	283.7
HOR	13.05	38.9	0.2	46.7
HOOR	11.54	31.1	0.2	25.7
$RCH=NH + HY \longrightarrow RC^{\bullet}HNH_2 + Y^{\bullet}$ (see Ref. 28)				
$HSiR_3$	11.44	47.1	1.5	68.4
HSR	9.75	32.8	0.2	23.6
$HGeR_3$	12.26	55.3	1.5	67.7
$HSnR_3$	11.05	46.2	1.5	57.8
$R'CH=NR'' + HY \longrightarrow R'C^{\bullet}HNHR'' + Y^{\bullet}$ (see Ref. 28)				
R^1H	15.80	71.5	1.5	121.9
R^2H	17.10	83.7	0.15	154.6
R^3H	16.30	76.1	0.15	134.1
H_2NR	21.90	119.9	4.0	283.7
HNR_2	22.80	130.0	2.0	315.9
HOR	13.94	44.4	0.2	122.8
HOOR	12.44	36.2	0.2	38.7
$HSiR_3$	12.34	54.8	1.5	67.6
HSR	10.65	39.1	0.2	36.3
$HGeR_3$	13.16	63.7	1.5	85.2
$HSnR_3$	11.95	54.0	1.5	63.7
$RCH=NPh + HY \longrightarrow RC^{\bullet}HNHPh + Y^{\bullet}$ (see Ref. 28)				
R^1H	13.00	48.4	1.5	63.1
R^2H	14.30	58.5	0.15	88.4
R^3H	13.50	52.2	0.15	72.4
$RCH=NPh + HY \longrightarrow RC^{\bullet}HNHPh + Y^{\bullet}$ (see Ref. 28)				
H_2NR	19.10	91.2	4.0	194.0
HNR_2	20.00	100.0	2.0	221.1
HOR	13.45	41.3	0.2	87.5
HOOR	11.94	33.3	0.2	31.3
$HSiR_3$	9.54	32.8	1.5	23.0
HSR	7.85	21.2	0.2	2.1
$HGeR_3$	10.36	39.5	1.5	35.6
$HSnR_3$	9.15	31.7	1.5	20.3
$RC\equiv N + HY \longrightarrow RC^{\bullet}=NH + Y^{\bullet}$ (see Ref. 28)				
R^1H	15.33	67.3	3.0	111.0
R^2H	16.64	79.3	0.3	142.7
R^3H	15.83	71.7	0.3	122.6
H_2NR	21.43	114.8	8.0	267.6
HNR_2	22.33	124.7	4.0	298.9
HOR	14.00	44.8	0.4	127.7
HOOR	12.50	36.5	0.4	39.6
$HSiR_3$	11.90	51.0	3.0	59.6
HSR	10.18	35.7	0.4	29.5
$HGeR_3$	12.70	59.3	3.0	76.0
$HSnR_3$	11.50	50.0	3.0	55.7
$RN=NR + HY \longrightarrow RN^{\bullet}NHR + Y^{\bullet}$ (see Ref. 28)				
R^1H	13.80	54.5	3.0	78.3
R^2H	15.10	65.3	3.0	105.7
R^3H	14.30	58.5	3.0	88.4
H_2NR	19.90	99.0	4.0	218.0
HNR_2	20.80	108.2	4.0	246.6
HOR	12.44	35.4	4.0	32.9
HOOR	10.94	28.0	0.4	18.0
$HSiR_3$	10.37	38.7	3.0	241.5
HSR	8.65	25.7	4.0	10.3
$HGeR_3$	11.17	45.9	3.0	48.3
$HSnR_3$	10.03	38.0	3.0	32.3

Note. Hereinafter, the dimensions of parameter br_e and the enthalpies of the reaction are $(kJ\ mol^{-1})^{1/2}$ and $kJ\ mol^{-1}$, respectively.

Table 4. The enthalpies of the retrodisproportionation reactions RH + X = Y.[15]

RH	$CH_2=CH_2$	$CH_2=CHEt$	1,3-cyclo-C_6H_8	$PhN=CH_2$	PhC(O)H	$OC=CH_2$	$MeN=CH_2$	PhN=O	MeN=NMe
$EtMeHC-H$	262.6	273.0	207.6	239.2	263.0	246.6	262.9	190.0	248.7
Me_3C-H	249.6	260.0	194.6	226.2	250.0	233.6	249.9	177.0	235.7
	268.1	278.5	213.1	244.7	268.5	252.1	268.4	195.5	254.2
	258.0	268.4	203.0	234.6	258.4	242.0	258.3	185.4	244.1
	253.5	263.9	198.5	230.1	253.9	237.5	253.8	180.9	239.6
	245.1	255.5	190.1	221.7	245.5	229.1	245.4	172.5	231.2
cis-Decalin	237.2	247.6	182.2	213.8	237.6	221.2	237.5	164.6	223.3
$H_2(CH_2=CH)C-H$	217.6	228.0	162.6	194.2	218.0	201.6	217.9	145.0	203.7
$H(CH_2=CH)C(Me)-H$	199.4	209.8	144.4	176.0	199.8	183.4	199.7	126.8	185.5
$Me_2(CH_2=CH)C-H$	189.2	199.6	134.2	165.8	189.6	173.2	189.5	116.6	175.3
cis-$MeCH=CHC(H)(Me)-H$	193.6	204.0	138.6	170.2	194.0	177.6	193.9	121.0	179.7
$H(Me_2C=CH)C(Me)-H$	181.6	192.0	126.6	158.2	182.0	165.6	181.9	109.0	167.7

Table 4 (continued).

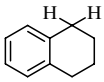
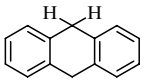
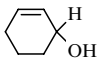
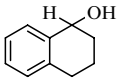
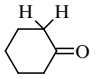
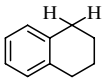
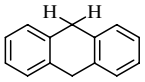
RH	$CH_2=CH_2$	$CH_2=CHEt$	1,3-cyclo-C_6H_8	$PhN=CH_2$	PhC(O)H	$OC=CH_2$	$MeN=CH_2$	PhN=O	MeN=NMe
$Me_2(Me_2C=CMe)C-H$	172.4	182.8	117.4	149.0	172.8	156.4	172.7	998.0	158.5
$Me(CH_2=CH)_2C-H$	156.8	167.2	101.8	133.4	157.2	140.8	157.1	842.0	142.9
	191.1	201.5	136.1	167.7	191.5	175.1	191.4	118.5	177.2
	180.5	190.9	125.5	157.1	180.9	164.5	180.8	107.9	166.6
	162.2	172.6	107.2	138.8	162.6	146.2	162.5	896.0	148.3
	150.6	161.0	956.0	127.2	151.0	134.6	150.9	780.0	136.7
$Me_2(MeC\equiv C)C-H$	179.0	189.4	124.0	155.6	179.4	163.0	179.3	106.4	165.1
$MePhHC-H$	213.7	224.1	158.7	190.3	214.1	197.7	214.0	141.1	199.8
Me_2PhC-H	204.3	214.7	149.3	180.9	204.7	188.3	204.6	131.7	190.4
	195.2	205.6	140.2	171.8	195.6	179.2	195.5	122.6	181.3
	171.6	182.0	116.6	148.2	172.0	155.6	171.9	990.0	157.7
$Me_2(NH_2)C-H$	229.1	239.5	174.1	205.7	229.5	213.1	229.4	156.5	215.2
$(CH_2=CHC(H)-H)_3N$	195.2	205.6	140.2	171.8	195.6	179.2	195.5	122.6	181.3
$Me_2C(OH)-H$	240.1	250.5	185.1	216.7	240.5	224.1	240.4	167.5	226.2
	179.3	189.7	124.3	155.9	179.7	163.3	179.6	106.7	165.4
$HO(MeCH=CMe)C(Me)-H$	174.8	185.2	119.8	151.4	175.2	158.8	175.1	102.2	160.9
	187.1	197.5	132.1	163.7	187.5	171.1	187.4	114.5	173.2
$PhC(O)-H$	197.6	208.0	142.6	174.2	198.0	181.6	197.9	125.0	183.7
	243.7	254.1	188.7	220.3	244.1	227.7	244.0	171.1	229.8
$Me_2(Pr^iO)C-H$	240.4	250.8	185.4	217.0	240.8	224.4	240.7	167.8	226.5
$(CH_2=CHC(H)-H)_2O$	209.6	220.0	154.6	186.2	210.0	193.6	209.9	137.0	195.7
$Ph_2C(OMe)-H$	203.8	214.2	148.8	180.4	204.2	187.8	204.1	131.2	189.9
$Ph(COOH)C(H)-H$	216.6	227.0	161.6	193.2	217.0	200.6	216.9	144.0	202.7
Bu^tOO-H	208.2	218.6	153.2	184.8	208.6	192.2	208.5	135.6	194.3
Bu^t_3Si-H	200.6	211.0	145.6	177.2	201.0	184.6	200.9	128.0	186.7
Ph_3Ge-H	172.1	182.5	117.1	148.7	172.5	156.1	172.4	99.5	158.2
Ph_3Sn-H	146.5	156.9	915.0	123.1	146.9	130.5	146.8	73.9	132.6

Table 5. The rate constants and activation energies for the reactions $PhCH=CH_2 + RH \longrightarrow PhC^{\bullet}HCH_3 + R^{\bullet}$ calculated within the framework of the parabolic model.[15]

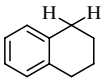
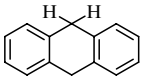
RH	D [a]	n	E	log$A$	k (550 K)	RH	D [a]	n	E	log$A$	k (550 K)
$EtMeHC-H$	413.0	4	225.0	10.70	2.15×10^{-11}	$Me_2(CH_2=CH)C-H$	339.6	1	161.0	8.00	5.12×10^{-8}
Me_3C-H	400.0	1	212.0	9.94	6.40×10^{-11}	*cis*-$MeCH=CHC(H)(Me)-H$	344.0	2	164.2	8.30	5.08×10^{-8}
	418.5	8	230.5	11.06	1.48×10^{-11}	$H(Me_2C=CH)C(Me)-H$	332.0	2	155.6	8.30	3.34×10^{-7}
						$Me_2(Me_2C=CMe)C-H$	322.8	1	149.1	8.00	6.91×10^{-7}
						$Me(CH_2=CH)_2C-H$	307.2	1	138.5	8.00	7.02×10^{-6}
	408.4	10	220.4	11.05	1.31×10^{-10}		341.5	4	162.4	9.60	1.50×10^{-6}
	395.5	1	207.5	9.88	1.49×10^{-10}		330.9	4	154.9	9.60	7.74×10^{-6}
cis-Decalin	387.6	2	199.6	10.06	1.27×10^{-9}						
$H_2(CH_2=CH)C-H$	368.0	3	182.0	8.48	1.57×10^{-9}		312.6	4	142.1	9.60	1.27×10^{-4}
$H(CH_2=CH)C(Me)-H$	349.8	2	168.4	8.30	2.03×10^{-8}						

Table 5 (continued).

RH	D [a]	n	E	log$A$	k (550 K)	RH	D [a]	n	E	log$A$	k (550 K)
	301.0	2	134.1	9.30	3.67×10^{-4}	$(CH_2=CHC(H)-H)_3N$	345.6	6	169.5	8.78	4.81×10^{-8}
						$Me_2C(OH)-H$	390.5	1	202.5	9.81	3.79×10^{-10}
$Me_2(MeC\equiv C)C-H$	329.4	1	153.8	8.00	2.47×10^{-7}		329.7	1	158.9	9.00	8.11×10^{-7}
$MePhHC-H$	364.1	2	176.1	8.30	3.76×10^{-9}						
Me_2PhC-H	354.7	1	169.7	8.00	7.65×10^{-9}	$HO(MeCH=CMe)C(Me)-H$	325.2	1	155.8	8.00	1.60×10^{-7}
	345.6	4	162.5	9.60	1.47×10^{-6}	$PhC(O)-H$	348.0	1	164.3	8.00	2.49×10^{-8}
							394.1	4	206.1	10.46	7.70×10^{-10}
	322.0	4	131.7	9.60	9.20×10^{-5}	$Ph_2C(OMe)-H$	354.2	1	168.9	8.00	9.11×10^{-9}
						$Ph(COOH)C(H)-H$	367.0	2	179.0	8.30	2.00×10^{-9}
						Bu^tOO-H	358.6	1	170.0	9.83	4.84×10^{-7}
$Me_2(NH_2)C-H$	379.5	1	191.5	9.61	2.65×10^{-9}	Bu^t_3Si-H	351.0	1	163.0	10.27	6.16×10^{-6}

[a] Hereinafter, the strength of the bond (D) has dimensions kJ mol^{-1}.

Table 6. The rate constants and activation energies for the reactions p-OC_6H_4O + RH ⟶ p-$HOC_6H_4O^{\bullet}$ + $R^{\bullet}$ calculated within the framework of the parabolic model.[15]

RH	D	n	ΔH	log$A$	k (550 K)	RH	D	n	ΔH	log$A$	k (550 K)
$EtMeHC-H$	413.0	4	186.7	11.70	5.64×10^{-7}	$Me_2(MeC\equiv C)C-H$	329.4	1	103.1	9.81	0.62
Me_3C-H	400.0	1	173.7	11.03	2.05×10^{-6}	$MePhHC-H$	364.1	2	137.8	10.97	4.57×10^{-3}
						Me_2PhC-H	354.7	1	128.4	10.56	1.41×10^{-2}
	418.5	8	192.2	12.03	3.61×10^{-7}		345.6	4	119.3	11.05	0.31
	408.4	10	182.1	12.08	3.64×10^{-6}						
	395.5	1	169.2	11.00	5.14×10^{-6}		322.0	4	95.70	10.60	19.5
cis-Decalin	387.6	2	161.3	11.25	5.14×10^{-5}	$Me_2(NH_2)C-H$	379.5	1	153.2	10.89	1.33×10^{-4}
$H_2(CH_2=CH)C-H$	368.0	3	141.7	11.00	2.12×10^{-3}	$(CH_2=CHC(H)-H)_3N$	345.6	6	119.3	10.98	0.27
$H(CH_2=CH)C(Me)-H$	349.8	2	123.5	10.57	4.20×10^{-2}	$Me_2C(OH)-H$	390.5	1	164.2	10.97	1.43×10^{-5}
$Me_2(CH_2=CH)C-H$	339.6	1	113.3	10.08	0.12						
cis-$MeCH=CHC(H)(Me)-H$	344.0	2	117.7	10.47	0.12		329.7	1	103.4	9.82	0.59
$H(Me_2C=CH)C(Me)-H$	332.0	2	105.7	10.19	0.84						
$Me_2(Me_2C=CMe)C-H$	322.8	1	96.50	8.43	0.18	$HO(MeCH=CMe)C(Me)-H$	325.2	1	98.90	9.66	1.11
$Me(CH_2=CH)_2C-H$	307.2	1	80.90	8.00	0.53	$PhC(O)-H$	348.0	1	121.7	10.48	5.02×10^{-2}
	341.5	4	115.2	10.72	0.36		394.1	4	167.8	11.59	2.74×10^{-5}
	330.9	4	104.6	10.45	1.99	$Me_2(Pr^iO)C-H$	390.8	2	164.5	11.27	2.68×10^{-5}
						$Ph_2C(OMe)-H$	354.2	1	127.9	10.56	1.55×10^{-2}
	312.6	4	86.30	9.52	12.5	$Ph(COOH)C(H)-H$	367.0	2	140.7	11.00	2.59×10^{-3}
						Bu^tOO-H	358.6	1	132.3	10.71	8.31×10^{-3}
						Bu^t_3Si-H	351.0	1	124.7	10.84	5.90×10^{-2}
	301.0	2	74.70	8.30	2.42						

V. Thermal generation of radicals in monomers

Radical polymerisation reactions are triggered by various processes. However, in some cases spontaneous polymerisation of monomers occurs without initiation.[38,39] Using spontaneous polymerisation of styrene as an example, Mayo[40] has shown that the rate of thermal generation of radicals is directly proportional to the third power of the styrene concentration. More recent findings suggest that thermal polymerisation is initiated by monorather than by biradicals. Two mechanisms of thermal initiation of radical polymerisation are described below.[39]

1. The interaction of two monomeric molecules yields a biradical, *e.g.*:

$$PhMeC=CH_2 + CH_2=CMePh \rightleftharpoons PhMeC^{\bullet}CH_2CH_2C^{\bullet}MePh,$$

which further enters into a radical abstraction reaction with the monomeric molecule:

$$PhMeC^{\bullet}(CH_2)_2C^{\bullet}MePh + CH_2=CMePh \longrightarrow$$
$$\longrightarrow PhMeCH(CH_2)_2C^{\bullet}MePh + CH_2=C(Ph)C^{\bullet}H_2.$$

Each of the radicals formed initiates the growth of the macromolecule.

2. The biradical formed in the course of a reversible bimolecular reaction enters into a reaction of hydrogen transfer from the radical to the monomer:

$$PhCH=CH_2 + CH_2=CHPh \rightleftharpoons PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh,$$

$$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh + CH_2=CHPh \longrightarrow$$
$$\longrightarrow PhCH=CHCH_2C^{\bullet}HPh + CH_3C^{\bullet}HPh.$$

The rate of radical generation for both reaction mechanisms is determined from the following ratio:

$$v_i = kK[CH_2=CHR]^3, \quad (15)$$

where k is the rate constant for the reaction of the biradical with the monomer and K is the equilibrium constant of the reversible reaction of biradical formation.

The values of the constant K (ΔH and ΔS values are taken from the database[41]) and the dissociation energies of the C—H bonds (see Ref. 42) calculated by the equation:

$$-RT\ln K = \Delta H - T\Delta S \quad (16)$$

are given in Table 7; the values of E and k for bimolecular radical reactions established with the use of the parabolic model and the parameters listed in Table 2 are given in Tables 8 and 9.

Table 7. The enthalpy, entropy, Gibbs potential (ΔG /kJ mol^{-1}) and equilibrium constant of the reaction $2RCH=CH_2 \longrightarrow RC^{\bullet}HCH_2CH_2C^{\bullet}HR$.[41,42]

Monomer	ΔH	ΔS	ΔG (298 K)	K (450 K)
$CH_2=CH_2$	177.0	−111.0	210.1	4.54×10^{-24}
$CH_2=CHMe$	182.9	−128.1	221.1	1.20×10^{-28}
$CH_2=CHEt$	185.4	−126.6	223.1	7.36×10^{-29}
$CH_2=CHCH=CH_2$	86.5	−103.4	117.3	4.60×10^{-16}
$CH_2=CHPh$	98.7	−127.8	136.8	7.38×10^{-19}
$CH_2=CMePh$	99.0	−148.8	143.3	5.45×10^{-20}
$CH_2=CHCOOMe$	170.4	−125.2	207.7	4.80×10^{-27}
$CH_2=CMeCOOMe$	166.2	−140.8	208.2	2.26×10^{-27}
$CH_2=CHCOOEt$	169.4	−125.2	206.7	6.27×10^{-27}
$CH_2=CHCl$	167.0	−117.0	201.9	3.19×10^{-26}

Table 8. The activation energies and rate constants for the reaction $RCH=CH_2 + RC^{\bullet}HCH_2CH_2C^{\bullet}HR \longrightarrow RC^{\bullet}HCH_3 + RCH=CHCH_2C^{\bullet}HR$ calculated within the framework of the parabolic model.[15]

$RCH=CH_2$	$RC^{\bullet}HCH_2CH_2C^{\bullet}HR$	E	log$A$	k (450 K)	Kk (450 K) (see [a])
$CH_2=CH_2$	$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	53.6	9.60	2.41×10^{3}	1.09×10^{-20}
$CH_2=CHCH=CH_2$	$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	44.0	9.60	3.12×10^{4}	1.42×10^{-19}
$CH_2=CHPh$	$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	40.0	9.30	4.55×10^{4}	2.07×10^{-19}
$CH_2=CH_2$	$(CH_2=CHC^{\bullet}HCH_2)_2$	77.4	9.60	4.15	1.91×10^{-15}
$CH_2=CHCH=CH_2$	$(CH_2=CHC^{\bullet}HCH_2)_2$	70.3	9.60	2.77×10	1.27×10^{-14}
$CH_2=CHPh$	$(CH_2=CHC^{\bullet}HCH_2)_2$	66.8	9.30	3.52×10	1.62×10^{-14}
$CH_2=CH_2$	$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	78.4	9.60	3.17	2.34×10^{-18}
$CH_2=CHCH=CH_2$	$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	60.2	9.60	4.11×10^{2}	3.03×10^{-16}
$CH_2=CHPh$	$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	60.1	9.30	2.11×10^{2}	1.56×10^{-16}
$CH_2=CH_2$	$(CH_2C^{\bullet}MeCOOMe)_2$	56.5	9.60	1.11×10^{3}	2.51×10^{-24}
$CH_2=CHCH=CH_2$	$(CH_2C^{\bullet}MeCOOMe)_2$	46.6	9.60	1.56×10^{4}	3.52×10^{-23}
$CH_2=CHPh$	$(CH_2C^{\bullet}MeCOOMe)_2$	42.6	9.30	2.27×10^{4}	5.13×10^{-23}
$CH_2=CMeC(O)_2Me$	$(CH_2C^{\bullet}MeCOOMe)_2$	55.0	9.30	8.26×10^{2}	1.87×10^{-24}
$CH_2=CH_2$	$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	60.4	9.60	3.90×10^{2}	1.24×10^{-23}
$CH_2=CHCH=CH_2$	$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	49.9	9.60	6.45×10^{3}	2.06×10^{-22}
$CH_2=CHPh$	$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	46.0	9.30	9.15×10^{3}	2.92×10^{-22}
$CH_2=CHCl$	$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	57.8	9.30	3.91×10^{2}	1.25×10^{-23}

[a] Hereinafter, the parameter Kk has the dimension litre^2 mol^{-2} s^{-1}.

Table 9. The activation energies and rate constants for the reaction $(RC^{\bullet}HCH_2)_2 + CH_2=CRCH_3 \longrightarrow RC^{\bullet}HCH_2CH_2CH_2R + CH_2=CRC^{\bullet}H_2$ calculated within the framework of the parabolic model.[15]

$(RC^{\bullet}HCH_2)_2$	$CH_2=CRCH_3$	E	log$A$	k (450 K)	Kk (450 K)
$(MeC^{\bullet}HCH_2)_2$	$CH_2=CHMe$	50.4	9.78	8.51×10^{3}	1.02×10^{-24}
$(MeC^{\bullet}HCH_2)_2$	$CH_2=CHEt$	42.7	9.60	4.42×10^{4}	5.30×10^{-24}
$(MeC^{\bullet}HCH_2)_2$	$CH_2=CMePh$	45.7	8.78	2.97×10^{3}	3.56×10^{-25}
$(MeC^{\bullet}HCH_2)_2$	$CH_2=CMeCO_2Me$	46.9	8.78	2.16×10^{3}	2.59×10^{-26}
$(EtC^{\bullet}HCH_2)_2$	$CH_2=CHMe$	49.3	9.78	1.14×10^{3}	8.39×10^{-25}
$(EtC^{\bullet}HCH_2)_2$	$CH_2=CHEt$	41.7	9.60	5.78×10^{4}	4.25×10^{-24}
$(EtC^{\bullet}HCH_2)_2$	$CH_2=CMePh$	44.7	8.78	3.89×10^{3}	2.86×10^{-25}
$(EtC^{\bullet}HCH_2)_2$	$CH_2=CMeCO_2Me$	45.9	8.78	2.82×10^{3}	2.07×10^{-25}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2=CHMe$	80.0	9.78	3.10	1.69×10^{-15}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2=CHEt$	70.8	9.60	24.2	1.32×10^{-18}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2=CMePh$	74.4	8.78	1.39	7.57×10^{-20}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2=CMeCO_2Me$	75.9	8.78	0.93	5.07×10^{-20}
$[MeOC(O)C^{\bullet}HCH_2]_2$	$CH_2=CHMe$	56.3	9.78	1.75×10^{3}	8.40×10^{-24}
$[MeOC(O)C^{\bullet}HCH_2]_2$	$CH_2=CHEt$	48.2	9.60	1.02×10^{4}	4.90×10^{-27}
$[MeOC(O)C^{\bullet}HCH_2]_2$	$CH_2=CMePh$	51.4	8.78	6.48×10^{2}	3.11×10^{-26}
$[MeOC(O)C^{\bullet}HCH_2]_2$	$CH_2=CMeCO_2Me$	52.7	8.78	4.58×10^{2}	2.20×10^{-24}

VI. Reactions involving halogen molecules

Molecular fluorine reacts with organic molecules at very fast rates even at low (200 K and lower) temperatures.[1, 39, 43] High reactivity of the fluorine molecule is due to the low degree of binding between the atoms [D(F–F) = 159 kJ mol^{-1}], whereas the C–F and F–H bonds in the fluorination products are strong [D(F–H) = 570 kJ mol^{-1} and D(H_3C–F) = 464 kJ mol^{-1}].[44] Therefore, radical generation reactions involving molecular fluorine are exothermic and proceed at fast rates. Two radical generation reactions involving fluorine were predicted by N N Semenov[1] and are widely known.

One of them includes abstraction of the hydrogen atom from the C–H bond by the fluorine molecule resulting in the formation of the HF molecule and the fluorine atom:[45]

$$RH + F_2 \longrightarrow R^{\bullet} + HF + F^{\bullet}.$$

This reaction is exothermic even for isobutane [D(R–H) = 400 kJ mol^{-1}]; its enthalpy is ΔH = 400 + 159 – 570 = –11 kJ mol^{-1}.

Other fluorine-containing molecules react analogously:

$$RH + FY \longrightarrow R^{\bullet} + HF + Y^{\bullet}$$

The values of enthalpies for such reactions are given in Table 10.

The reaction centres of the transition state (F···H···R) of the reaction indicated above and those involving F$^{\bullet}$:

$$RH + F^{\bullet} \longrightarrow R^{\bullet} + HF$$

are similar.

The kinetic parameters which characterise, in the framework of the parabolic model, the reactions involving fluorine- and chlorine-containing molecules are given in Tables 11 and 12; the results of the calculation of the activation energies and rate

Table 10. The enthalpies of reactions of hydrogen abstraction by fluorine-containing molecules RH + FY ⟶ R$^{\bullet}$ + HF + Y$^{\bullet}$.

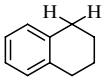
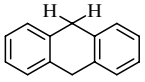
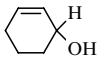
RH	D	ΔH					
		F_2	FCl	FBr	FI	FOH	CFOF
EtMeHC–H	413.0	1.4	98.9	92.9	114.3	57.2	24.7
Me_3C–H	400.0	–11.6	85.9	79.9	101.3	44.2	11.7
	418.5	6.9	104.4	98.4	119.8	62.7	30.2
	408.4	–3.2	94.3	88.3	109.7	52.6	20.1
	395.5	–16.1	81.4	75.4	96.8	39.7	7.2
cis-Decalin	387.6	–24.0	73.5	67.5	88.9	31.8	–70.0
$H_2(CH_2=CH)C-H$	368.0	–43.6	53.9	47.9	69.3	12.2	–20.3
$H(CH_2=CH)C(Me)-H$	349.8	–61.8	35.7	29.7	51.1	–6.0	–38.5
$Me_2(CH_2=CH)C-H$	339.6	–72.0	25.5	19.5	40.9	–16.2	–48.7
cis-MeCH=CHC(H)(Me)–H	344.0	–67.6	29.9	23.9	45.3	–11.8	–44.3
$H(Me_2C=CH)C(Me)-H$	332	–79.6	17.9	11.9	33.3	–23.8	–56.3
$Me_2(Me_2C=CMe)C-H$	322.8	–88.8	8.7	2.7	24.1	–33.0	–65.5
$H(CH_2=CMe)(CH_2=CH)C-H$	307.2	–104.4	–6.9	–12.9	8.5	–48.6	–81.1
	341.5	–70.1	27.4	21.4	42.8	–14.3	–46.8
	330.9	–80.7	16.8	10.8	32.2	–24.9	–57.4
	312.6	–99.0	–1.50	–7.5	13.9	–43.2	–75.7
	301.0	–110.6	–13.1	–19.1	2.3	–54.8	–87.3
$Me_2(MeC\equiv C)C-H$	329.4	–82.2	15.3	9.3	30.7	–26.4	–58.9
PhMeHC–H	364.1	–47.5	50.0	44.0	65.4	8.3	–24.2
$PhMe_2C-H$	354.7	–56.9	40.6	34.6	56.0	–1.1	–33.6
	345.6	–66.0	31.5	25.5	46.9	–10.2	–42.7
	322.0	–89.6	7.9	1.9	23.3	–33.8	–66.3
$Me_2(NH_2)C-H$	379.5	–32.1	65.4	59.4	80.8	23.7	–88.0
$[CH_2=CHC(H)-H]_3N$	345.6	–66.0	31.5	25.5	46.9	–10.2	–42.7
$Me_2C(OH)-H$	390.5	–21.1	76.4	70.4	91.8	34.7	2.2
	329.7	–81.9	15.6	9.6	31.0	–26.1	–58.6

Table 10 (continued).

RH	D	ΔH					
		F_2	FCl	FBr	FI	FOH	CFOF
HO(MeCH=CMe)C(Me)−H	325.2	−86.4	11.1	5.1	26.5	−30.6	−63.1
PhC(O)−H	348.0	−63.6	33.9	27.9	49.3	−7.8	−40.3
	394.1	−17.5	80.0	74.0	95.4	38.3	5.8
$Ph_2C(OMe)-H$	354.2	−57.4	40.1	34.1	55.5	−1.6	−34.1
Ph(COOH)C(H)−H	367.0	−44.6	52.9	46.9	68.3	11.2	−21.3
Bu^tOO-H	358.6	−53.0	44.5	38.5	59.9	2.8	−29.7
Bu^t_3Si-H	351.0	−60.6	36.9	30.9	52.3	−4.8	−37.3

Table 11. The kinetic parameters of reactions involving fluorine- and chlorine-containing molecules.[22]

Reaction	α	$10^{-11}\,b$	$0.5\,hN_A\nu_i$	$0.5\,hN_A$ $(\nu_i-\nu_f)$	$(r^{\neq}/r_e)_0$
$RCH=CH_2+YF$	1.422	5.389	9.9	3.6	0.413
$RCH=CHCH=CH_2+$ $+YF$	1.678	5.389	11.7	5.4	0.373
$RC\equiv CH+YF$	1.824	6.912	12.7	6.4	0.354
$RCH=CH_2+YCl$	1.639	5.389	9.9	5.0	0.379
$RCH=CHCH=CH_2+$ $+YCl$	1.934	5.389	11.7	6.8	0.341
$RC\equiv CH+YCl$	2.102	6.912	12.7	7.8	0.322
$HR+XF$	0.694	3.743	17.4	−7.4	0.590
HNR_2+XF	0.798	4.306	20.0	−4.8	0.556
$HOR+XF$	0.871	4.701	21.7	−3.1	0.534
$HOOR+XF$	0.853	4.600	21.2	−3.6	0.540
$HSiR_3+XF$	0.511	2.756	12.6	−12.2	0.662
$HSR+XF$	0.561	3.026	13.8	−11.0	0.641
$RH+XCl$	0.951	3.743	17.4	−0.5	0.513
$H_2NR+XCl$	1.094	4.306	20.1	2.1	0.478
$HOR+XCl$	1.194	4.701	21.7	3.8	0.456
$HOOR+XCl$	1.169	4.600	21.2	3.3	0.461
$HSiR_3+XCl$	0.700	2.756	12.6	−5.3	0.588
$HSR+XCl$	0.769	3.026	13.8	−4.1	0.565

Table 12. The kinetic and thermodynamic parameters of reactions involving fluorine- and chlorine-containing molecules.[22]

HY	br_e	E_{e0}	$10^{-10}\,A_0$	$\Delta H_{e\,max}$
$XF + HY \longrightarrow X^{\bullet} + HF + Y^{\bullet}$ (gas phase)[32]				
R^1H	12.85	57.5	2.2	63.4
R^2H	13.73	65.7	0.25	80.7
R^3H	13.20	60.7	0.25	70.1
NH_3	14.40	64.1	7.5	83.9
H_2NR	14.67	66.6	75	89.6
HNR_2	14.86	68.3	75	93.7
HOR	13.53	52.3	1.2	59.7
HOOR	14.00	57.1	1.2	70.3
$HSiR_3$	11.00	53.0	2.2	47.4
HSR	12.18	60.9	7.5	63.3
$XCl + HY \longrightarrow X^{\bullet} + HCl + Y^{\bullet}$ (gas phase)[32]				
R^1H	9.90	25.7	1.0	16.6
R^2H	11.10	32.4	1.0	32.2
R^3H	10.25	27.6	1.0	20.9
NH_3	10.52	25.2	1.6	16.8
H_2NR	11.05	27.8	0.16	23.3
HNR_2	10.38	24.6	0.16	15.2
HOR	15.28	48.5	4.2	86.7
HOOR	14.90	47.2	1.6	81.3
$HSiR_3$	9.25	29.6	2.5	21.6
HSR	9.85	31.0	1.0	25.6
$XF + CH_2=CHR \longrightarrow X^{\bullet} + FCH_2C^{\bullet}HR$ (see Ref. 33)				
$CH_2=CHR$	19.30	63.5	2.5	240.0
$CH_2=CHCH=CHR$	21.20	76.6	2.5	303.3
$CH_2=CHPh$	20.55	72.0	2.5	280.8
$XCl + CH_2=CHR \longrightarrow X^{\bullet} + ClCH_2C^{\bullet}HR$ (see Ref. 33)				
$CH_2=CHR$	18.47	49.0	0.9	215.4
$CH_2=CHCH=CHR$	20.35	59.5	0.9	274.7
$CH_2=CHPh$	19.73	55.9	0.9	254.5

constants are given in Table 13. The calculated and experimental values are very similar. For example, the experimental rate constant for the reaction:

$$CH_4 + F_2 \longrightarrow C^{\bullet}H_3 + HF + F^{\bullet}$$

is equal to $2.0\times10^9\exp(-47.0/RT) = 1.5\times10^3$ litre mol^{-1} s^{-1} (400 K),[45] whereas the calculated rate constant is equal to $1.8\times10^{10}\exp(-51.0/RT) = 3.9\times10^3$ litre mol^{-1} s^{-1}.

Generation of radicals in yet another fluorine-induced reaction, which was also predicted by N N Semenov,[1] is the addition of fluorine to the double bond:

$$F_2 + CH_2=CHR \longrightarrow FCH_2C^{\bullet}HR + F^{\bullet}.$$

The activation energies and rate constants for this type of reaction were calculated within the framework of the parabolic model and using kinetic parameters of the given reaction (see Tables 11 and 12) (Table 14). The calculated rate constant for the reaction of F_2 with ethylene is equal to 1.69×10^4 litre mol^{-1} s^{-1} (300 K), *i.e.*, is similar to the experimental values of k, *viz.*, $k = 2.04\times10^4$ (for 298 K),[46] 1.81×10^4 (for 298 K)[47] and 4.16×10^4 litre mol^{-1} s^{-1} (for 315 K).[48]

It may be assumed that analogous reactions occur with molecular chlorine:

$$Cl_2 + RH \longrightarrow Cl^{\bullet} + HCl + R^{\bullet},$$

$$Cl_2 + CH_2=CHR \longrightarrow Cl^{\bullet} + ClCH_2C^{\bullet}HR.$$

The enthalpies of these reactions are much lower than the dissociation energy of the Cl−Cl bond, but it is these reactions that seem to be the main radical sources in chain chlorination reactions in the absence of external initiators. Among chlorine-containing molecules, nitrosyl chloride ClNO has proved to be the most active hydrogen acceptor. The abstraction of the hydrogen atom by YCl molecules occurs with an activation energy similar to the reaction enthalpy [see formula (6)]. The rate constants for some of these reactions (Tables 11 and 12) calculated within the framework of the parabolic model are given in Table 15.

Table 13. The enthalpies, activation energies and rate constants for the reactions $F_2 + RH \longrightarrow F^{\bullet} + HF + R^{\bullet}$ calculated within the framework of the parabolic model.[22]

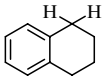
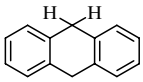
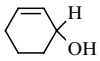
RH	D	n	ΔH_e	E	log$A$	k (300 K)
H_3C-H	440.0	4	21.0	51.0	10.26	24.0
$EtMeHC-H$	413.0	4	−6	36.5	10.94	8.02×10^3
Me_3C-H	400.0	1	−19	31.5	10.34	1.60×10^4
	418.5	8	−0.5	38.7	11.25	6.60×10^3
	408.4	10	−10.6	33.0	11.34	8.60×10^4
	395.5	1	−23.5	28.2	10.34	6.38×10^4
cis-Decalin	387.6	2	−31.4	25.4	10.64	4.12×10^5
$H_2(CH_2=CH)C-H$	368.0	3	−51	26.7	10.82	3.62×10^5
$H(CH_2=CH)C(Me)-H$	349.8	2	−69.2	21.1	10.64	2.53×10^6
$Me_2(CH_2=CH)C-H$	339.6	1	−79.4	18.1	10.34	4.57×10^6
cis-$MeCH=CHC(H)(Me)-H$	344.0	2	−75	23.5	10.64	9.19×10^5
$H(Me_2C=CH)C(Me)-H$	332.0	2	−87	20.1	10.64	3.88×10^6
$Me_2(Me_2C=CMe)C-H$	322.8	1	−96.2	17.6	10.34	5.66×10^6
$Me(CH_2=CH)_2C-H$	307.2	1	−111.8	13.7	10.34	3.06×10^7
	341.5	4	−77.5	22.8	10.94	2.46×10^6
	330.9	4	−88.1	19.8	10.94	8.80×10^6
	312.6	4	−106.4	15.0	10.94	6.92×10^7
	301.0	2	−118	12.2	10.64	1.18×10^8
$Me_2(MeC\equiv C)C-H$	329.4	1	−89.6	19.4	10.34	2.62×10^5
$MePhHC-H$	364.1	2	−54.9	24.8	10.64	5.31×10^5
Me_2PhC-H	354.7	1	−64.3	21.9	10.34	9.05×10^5
	345.6	4	−73.4	19.3	10.94	1.09×10^7
	322.0	4	−97	13.0	10.94	1.66×10^8
$Me_2(NH_2)C-H$	379.5	1	−39.5	26.7	10.34	1.20×10^5
$[CH_2=CHC(H)-H]_3N$	345.6	6	−73.4	23.9	11.12	2.35×10^6
$Me_2C(OH)-H$	390.5	1	−28.5	30.5	10.34	2.44×10^4
	329.7	1	−89.3	19.5	10.34	2.51×10^6
$PhC(O)-H$	348.0	1	−71	20.0	10.34	2.03×10^6
	394.1	4	−24.9	31.8	10.94	5.64×10^4
$Me_2CHOC(Me_2)-H$	390.8	2	−28.2	30.6	10.64	4.68×10^4
$Ph_2C(OMe)-H$	354.2	1	−64.8	21.8	10.34	9.45×10^5
$Ph(COOH)C(H)-H$	367.0	2	−52	25.7	10.64	3.64×10^5
Bu^tOO-H	358.6	1	−56	18.4	10.34	4.02×10^6
Bu^t_3Si-H	351.0	1	−72.8	16.8	10.34	7.98×10^6

Table 14. The enthalpies, activation energies and rate constants for the reactions of YF with alkenes calculated within the framework of the parabolic model.[28]

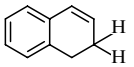
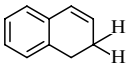
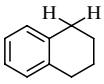
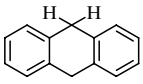
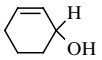
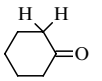
Alkene	ΔH_e	E	log$A$	k (300 K)	Alkene	ΔH_e	E	log$A$	k (300 K)
Fluorinating reagent F_2					Fluorinating reagent CF_3OF				
$CH_2=CH_2$	−29.1	38.6	11.00	1.69×10^{4}	$CH_2=CH_2$	−5.8	51.4	10.70	5.63×10
$Me_2C=CH_2$	−32.3	36.9	10.70	1.88×10^{4}	$Me_2C=CH_2$	−9.0	49.6	10.40	5.81×10
$EtHC=CH_2$	−27.7	39.3	10.70	7.20×10^{3}	$EtCH=CH_2$	−4.4	52.2	10.40	2.05×10
	−33.7	36.2	11.00	4.98×10^{4}		−10.4	48.8	10.70	1.60×10^{2}
$CH_2=CHCH=CH_2$	−74.5	13.4	11.00	4.64×10^{7}	$CH_2=CHCH=CH_2$	−51.6	24.6	10.70	2.61×10^{6}
$CH_2=CHCH=CMe_2$	−80.1	11.0	10.70	6.09×10^{8}	$CH_2=CHCH=CMe_2$	−56.8	21.8	10.40	4.02×10^{6}
$Me_2C=C(Me)C(Me)=CMe_2$	−109.5	0.03	11.00	9.88×10^{10}	$Me_2C=C(Me)C(Me)=CMe_2$	−86.2	8.4	10.70	1.73×10^{9}
	−91.3	6.4	11.00	7.68×10^{9}		−68.0	16.4	10.70	6.99×10^{7}
$PhCH=CH_2$	−70.0	26.7	10.70	1.12×10^{6}	$PhCH=CH_2$	−46.7	37.8	10.40	6.58×10^{3}
$PhCH=CHMe$	−66.2	28.4	10.70	5.69×10^{5}	$PhCH=CHMe$	−42.9	39.7	10.40	3.07×10^{3}
$Ph_2C=CH_2$	−137.2	1.9	10.70	2.34×10^{10}	$Ph_2C=CH_2$	−114.1	9.1	10.40	6.54×10^{8}
	−66.2	28.4	10.70	5.69×10^{5}		−42.9	39.7	10.40	3.07×10^{3}

Table 15. The enthalpies, activation energies and rate constants for the reactions $RH + Cl_2 \rightarrow R^{\bullet} + HCl + Cl^{\bullet}$ calculated within the framework of the pababolic model.

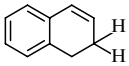
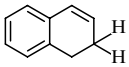
RH	D	n	ΔH	log$A$	k (400 K)	RH	D	n	ΔH	log$A$	k (400 K)
$EtMeHC-H$	413.0	4	224.0	11.95	2.94×10^{-19}	$Me_2(MeC\equiv C)C-H$	329.4	1	140.4	11.00	3.39×10^{-9}
Me_3C-H	400.0	1	211.0	11.33	3.62×10^{-19}	$MePhHC-H$	364.1	2	175.1	11.52	2.95×10^{-13}
	418.5	8	229.5	12.26	1.12×10^{-19}	Me_2PhC-H	354.7	1	165.7	11.19	2.40×10^{-12}
	408.4	10	219.4	12.34	2.87×10^{-18}		345.6	4	156.6	11.77	1.45×10^{-10}
	395.5	1	206.5	11.32	1.37×10^{-17}		322.0	4	133.0	11.7	1.61×10^{-7}
cis-Decalin	387.6	2	198.6	11.61	4.88×10^{-16}	$Me_2(NH_2)C-H$	379.5	1	190.5	11.29	1.40×10^{-15}
$H_2(CH_2=CH)C-H$	368.0	3	179.0	11.59	9.85×10^{-13}	$[CH_2=CHC(H)-H]_3N$	345.6	6	156.6	11.83	1.67×10^{-10}
$H(CH_2=CH)C(Me)-H$	349.8	2	160.8	11.37	1.61×10^{-11}	$Me_2C(OH)-H$	390.5	1	201.5	11.31	6.08×10^{-17}
$Me_2(CH_2=CH)C-H$	339.6	1	150.6	11.03	1.64×10^{-10}		329.7	1	140.7	11.00	3.10×10^{-9}
cis-$MeCH=CHC(H)(Me)$-H	344.0	2	155.0	11.35	8.95×10^{-11}	$HO(MeCH=CMe)C(Me)$-H	325.2	1	136.2	10.98	1.16×10^{-8}
$H(Me_2C=CH)C(Me)-H$	332.0	2	143.0	11.31	3.14×10^{-9}	$PhC(O)-H$	348.0	1	159.0	11.18	1.80×10^{-11}
$Me_2(Me_2C=CMe)C-H$	322.8	1	133.8	10.97	2.36×10^{-8}		394.1	4	205.1	11.92	8.31×10^{-17}
$Me(CH_2=CH)_2C-H$	307.2	1	118.2	10.90	2.33×10^{-6}	$Me_2(Pr^iO)C-H$	390.8	2	201.8	11.61	1.11×10^{-16}
	341.5	4	152.5	11.60	3.40×10^{-10}	$Ph_2C(OMe)-H$	354.2	1	165.2	11.19	2.08×10^{-12}
	330.9	4	141.9	11.60	8.53×10^{-9}	$Ph(COOH)C(H)-H$	367.0	2	178.0	11.52	1.22×10^{-13}
	312.6	4	123.6	11.53	1.91×10^{-6}	Bu^tOO-H	358.6	1	169.6	10.63	2.02×10^{-13}
	301.0	2	112.0	11.17	2.86×10^{-5}	Bu^t_3Si-H	351.0	1	162.0	10.92	3.98×10^{-12}

The addition of chlorine to the double bond:

$$Cl_2 + CH_2=CHR \longrightarrow Cl^{\bullet} + ClCH_2C^{\bullet}HR$$

is a slow endothermic process. The rate constants for some reactions of this type are given in Table 16.

Table 16. The enthalpies, activation energies and rate constants of the reactions $YCl + CH_2=CHR \longrightarrow Y^{\bullet} + ClCH_2C^{\bullet}HR$ calculated within the framework of the parabolic model.

$RCH=CH_2$	ΔH_e	E	$\log A$	k (300 K)
Chlorinating reagent Cl_2				
$CH_2=CH_2$	168.2	169.3	10.56	2.96×10^{-13}
$Me_2C=CH_2$	165.0	166.5	10.26	3.46×10^{-13}
$EtCH=CH_2$	169.6	170.5	10.26	1.02×10^{-13}
	155.6	158.3	10.56	8.23×10^{-12}
$HC\equiv CH$	183.7	205.5	10.86	7.91×10^{-18}
$MeC\equiv CMe$	199.4	218.8	10.86	1.38×10^{-19}
$CH_2=CHCH=CH_2$	122.8	131.3	10.56	3.90×10^{-15}
$CH_2=CHCH=CMe_2$	118.2	127.5	10.26	4.38×10^{-9}
$Me_2C=C(Me)C(Me)=CMe_2$	88.8	103.4	10.56	9.29×10^{-6}
	98.0	110.8	10.56	1.09×10^{-6}
$PhCH=CH_2$	128.3	140.8	10.26	9.07×10^{-10}
$PhCH=CHMe$	123.1	136.6	10.26	3.27×10^{-9}
$Ph_2C=CH_2$	67.9	93.8	10.26	1.52×10^{-3}
	124.6	137.8	10.26	2.26×10^{-9}
Chlorinating reagent $ClNO_2^-$				
$CH_2=CH_2$	67.4	86.8	10.26	1.21×10^{-2}
$Me_2C=CH_2$	64.2	84.4	9.95	1.26×10^{-2}
$EtHC=CH_2$	68.8	87.9	9.95	4.37×10^{-3}
	54.8	77.5	10.26	2.12×10^{-1}
$HC\equiv CH$	82.9	123.8	10.56	2.54×10^{-7}
$MeC\equiv CMe$	98.6	136.0	10.56	6.08×10^{-9}
$CH_2=CHCH=CH_2$	22.0	52.6	10.26	10.3
$CH_2=CHCH=CMe_2$	17.4	49.4	9.95	13.1
$Me_2C=C(Me)C(Me)=CMe_2$	−12.4	29.6	10.26	8.50×10^{3}
	−2.8	35.8	10.26	1.39×10^{3}
$PhCH=CH_2$	26.1	61.3	9.95	6.59
$PhCH=CHMe$	20.9	57.8	9.95	19.2
$Ph_2C=CH_2$	−34.3	24.4	9.95	6.54×10^{5}
	22.4	58.8	9.95	1.53×10^{2}

VII. Generation of radicals by ozone-induced bimolecular reactions

Ozone reacts very rapidly with alkenes and organoelement compounds without the formation of free radicals.[49–53] However, it reacts with the C–H bonds of hydrocarbons and other organic compounds to generate free radicals.[3] Evidence for this assumption can be derived from the following facts. Ozone initiates the chain oxidation of hydrocarbons in both gas and liquid phases.[54–57] The peroxy radicals produced in the oxidation of hydrocarbons and polymers by an O_3-O_2 mixture were identified by EPR.[58, 59] The formation of peroxy radicals is confirmed by chemiluminescence induced by oxidation of hydrocarbons with the above mixture due to disproportionation of the peroxy radicals.[55, 60] Deuterated hydrocarbons are oxidised by ozone more slowly, which suggests that the ozone attack at the C–H and C–D bonds is a limiting step of the oxidation.[53, 61–65] The oxidation of hydrocarbons by ozone in carbon tetrachloride yields alkyl chlorides:[60, 66, 67]

$$R^{\bullet} + CCl_4 \longrightarrow RCl + C^{\bullet}Cl_3,$$

whereas the oxidation of alcohols yields hydrogen chloride:[68]

$$RC^{\bullet}HOH + CCl_4 \longrightarrow RC(O)H + HCl + C^{\bullet}Cl_3.$$

Ozone is decomposed in the gas phase at elevated temperatures to generate molecular and atomic oxygen; the latter initiates the formation of radicals:

$$O + RH \longrightarrow {}^{\bullet}OH + R^{\bullet}.$$

Hydrogen abstraction concomitant with cage radical processes is the most feasible reaction in the liquid phase:

$$RH + O_3 \longrightarrow [R^{\bullet} + HO_3^{\bullet}],$$

$$[R^{\bullet} + HO_3^{\bullet}] \longrightarrow ROOOH,$$

$$[R^{\bullet} + HO_3^{\bullet}] \longrightarrow R^{\bullet} + HO_3^{\bullet}.$$

The labile compounds ROOOH and $HO_3^{\bullet}$ are rapidly decomposed to generate the radicals:

$$ROOOH \longrightarrow RO_2^{\bullet} + HO^{\bullet},$$

$$HO_3^{\bullet} \longrightarrow O_2 + HO^{\bullet}.$$

The reactive hydroxyl radical reacts rapidly with RH:

$$HO^{\bullet} + RH \longrightarrow H_2O^{\bullet} + R^{\bullet}.$$

This mechanism is consistent with the high probability (p) of the exit of radicals to the bulk:

$$p = \frac{k_i}{2k_d},$$

where k_i and k_d are the rate constants determined experimentally for radical generation and ozone consumption, respectively (Table 17).[69–72]

Table 17. The values of k_i, k_d (litre mol^{-1} s^{-1}) and e for the oxidation reactions by ozone.

RH	k_i	k_d	p	Ref.
cyclo-C_6H_{12}	1.1×10^{-3}	1.8×10^{-3}	0.30	69
Me_2PhCH	1.6×10^{-2}	0.32	2.5×10^{-2}	70
$Me_2PhCOOH$	1.5×10^{-1}	0.1	0.68	71
PhCHO	2.0	2.0	0.50	72
MeCHO	1.6	2.7	0.30	72

Table 18. The kinetic parameters of the reactions involving ozone and oxygen.

Oxygen acceptor	α	$10^{-11}b$	$0.5hN_Av_i$	$0.5hN_A(v_i-v_f)$	$(r^{\neq}/r_e)_0$
$O_2(O_3) + HY \longrightarrow HO_2^{\bullet}(HO_3^{\bullet}) + Y^{\bullet}$					
RH	0.814	3.743	17.4	−3.8	0.551
HNR_2	0.936	4.306	20.0	−1.2	0.516
ROH	1.022	4.701	21.7	0.5	0.495
ROOH	1.000	4.600	21.2	0.0	0.500
$HSiR_3$	0.624	2.871	13.1	−8.1	0.616
RSH	0.658	3.026	13.8	−7.4	0.603
$HGeR_3$	0.608	2.796	12.6	−8.6	0.622
$HSnR_3$	0.586	2.695	12.1	−9.1	0.630
$O_2 + CH_2=CHR \longrightarrow {}^{\bullet}OOCH_2C^{\bullet}HR$					
$CH_2=CHR$	1.737	5.389	9.9	4.6	0.366

Table 19. The kinetic and thermodynamic parameters of the reactions involving ozone and oxygen.[14–21]

Oxygen acceptor	br_e	E_{e0}	$10^{-9}A_0$	$\Delta H_{e\,max}$
$O_2 + HY \longrightarrow HO_2^{\bullet} + Y^{\bullet}$ (see Refs 16 and 18)				
R^1H	13.61	56.3	5.0	76.1
R^2H	15.20	70.2	5.0	110.1
R^3H	14.32	62.3	5.0	90.6
NH_3	9.36	23.4	4.0	4.3
H_2NR	10.80	31.1	4.0	20.9
HNR_2	11.73	36.7	4.0	33.9
ROH	14.45	51.1	5.0	73.7
ROOH	13.13	43.1	5.0	51.5
$HSiR_3$	12.41	58.4	5.0	69.7
RSH	10.39	39.3	5.0	33.0
$HGeR_3$	12.74	62.8	5.0	77.6
$HSnR_3$	12.35	60.6	5.0	72.0
$O_2 + CH_2{=}CHR \longrightarrow {}^{\bullet}OOCH_2C^{\bullet}HR$ (see Ref. 19)				
$CH_2{=}CHR$	26.04	90.5	2.0	408.5
$CH_2{=}CHPh$	27.23	99.0	0.2	540.3
$O_3 + HY \longrightarrow HO_3^{\bullet} + Y^{\bullet}$ (see Refs 20 and 21)				
R^1H	13.61	56.3	0.2	76.1
R^2H	15.20	70.2	0.02	110.1
R^3H	14.32	62.3	0.02	90.6
NH_3	9.36	23.4	0.2	4.3
H_2NR	10.80	31.1	0.2	20.9
HNR_2	11.73	36.7	0.2	33.9
ROH	14.45	51.1	0.2	73.7
ROOH	13.13	43.1	0.2	51.5
$HSiR_3$	12.41	58.4	0.2	69.7
RSH	10.39	39.3	0.06	33.0
$HGeR_3$	12.74	62.8	0.1	77.6
$HSnR_3$	12.35	60.6	0.1	72.0

The low value of p for cumene is due to the fact that ozone reacts simultaneously with the C–H bond and with the π-bonds of the benzene ring without the formation of free radicals.[70] A similar situation takes place in the reaction of ozone with carbonyl compounds. Ozone reacts with both the C–H bond with the formation of radicals and the carbonyl group to yield a labile tetraoxide. The latter is rapidly decomposed to yield singlet oxygen.[66]

$$RC(O)H + O_3 \longrightarrow RCHO_4,$$

$$RCHO_4 \longrightarrow RC(O)OOOH,$$

$$RC(O)OOOH \longrightarrow RC(O)OH + {}^1O_2.$$

Since the reaction centres of the reactions $RH + O_3$ and $RO_2^{\bullet} + RH$ are similar, this has been used to calculate the kinetic and thermodynamic parameters of ozone-mediated reactions (Tables 18–20).[14,20]

The experimental data for the reaction $RH + O_3$ can be found elsewhere.[3,8,51,52]

VIII. Chain generation in reactions with molecular oxygen

Chains are generated in the early steps of the oxidation of hydrocarbons in the absence of a hydroperoxide:[3]

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet},$$

which was proposed by Bolland and Gee.[73] The fact that this reaction occurs for oxidisable aldehydes was proved by Cooper and Melville.[74] The main experimental evidence in favour of this mechanism can be summarised as follows.[7,9]

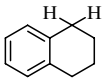
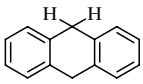
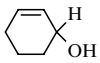
1. The rate of the radical formation in an $RH + O_2$ system measured by the free radical acceptor method for different compounds is directly proportional to the product of the concentrations $[RH] \times [O_2]$.

2. The rate constant for the reaction $RH + O_2$ increases with the decrease in stability of the weakest C–H bond in the molecule

Table 20. The enthalpies, activation energies and rate constants for the reactions $2RH + O_3 \longrightarrow R^{\bullet} + HO_3^{\bullet}HR$ calculated within the framework of the parabolic model.[14]

RH	D	n	ΔH_e	E	$\log A$	k (300 K)
EtMeHC–H	413.0	4	66.2	74.9	9.60	3.62×10^{-4}
Me_3C–H	400.0	1	53.2	67.2	9.00	1.99×10^{-3}
	418.5	8	71.7	78.3	9.90	1.85×10^{-4}
	408.4	10	61.6	72.1	10.00	2.80×10^{-3}
	395.5	1	48.7	64.7	9.00	5.43×10^{-3}
cis-Decalin	387.6	2	40.8	60.3	9.30	6.32×10^{-2}
$H_2(CH_2{=}CH)C$–H	368.0	3	21.2	63.9	8.48	2.26×10^{-3}
$H(CH_2{=}CH)C(Me)$–H	349.8	2	3.0	55.4	8.30	4.51×10^{-2}
$Me_2(CH_2{=}CH)C$–H	339.6	1	−7.2	50.8	8.00	0.14
cis-$MeCH{=}CHC(H)(Me)$–H	344.0	2	−2.8	52.8	9.30	1.28
$H(Me_2C{=}CH)C(Me)$–H	332.0	2	−14.8	47.6	8.30	1.03
$Me_2(Me_2C{=}CMe)C$–H	322.8	1	−24.0	43.7	8.00	2.46
$H(CH_2{=}CMe)(CH_2{=}CH)C$–H	307.2	1	−39.6	37.6	8.00	28.4
	341.5	4	−5.3	51.7	9.60	3.97
	330.9	4	−15.9	47.1	9.60	25.1
	312.6	4	−34.2	39.6	9.60	5.07×10^2

Table 20 (continued).

RH	D	n	ΔH_e	E	log$A$	k (300 K)
	301.0	2	−45.8	35.2	9.30	1.47×10^3
$Me_2(MeC{\equiv}C)C-H$	329.4	1	−17.4	46.5	8.00	0.80
$MePhHC-H$	364.1	2	17.3	54.2	8.30	7.31×10^{-2}
Me_2PhC-H	354.7	1	7.9	49.7	8.00	0.22
	345.6	4	−1.2	45.6	9.60	45.7
	322.0	4	−24.8	35.6	9.60	2.52×10^3
$Me_2(NCH_2)-H$	379.5	1	32.7	56.0	9.00	0.18
$[CH_2{=}CHC(H)-H]_3N$	345.6	6	−1.2	53.5	8.78	0.29
$Me_2C(OH)-H$	390.5	1	4.4	61.9	9.00	1.67×10^{-2}
	329.7	1	−17.1	32.7	9.00	2.02×10^3
$HO(MeCH{=}CMe)C(Me)-H$	325.2	1	−21.6	44.7	8.00	1.65
$PhC(O)-H$	348.0	1	1.2	54.5	9.00	0.32
	394.1	4	47.3	63.9	9.60	2.98×10^{-2}
$Me_2(Pr^iO)C-H$	390.8	2	44.0	62.0	9.30	3.21×10^{-2}
$Ph_2C(OMe)-H$	354.2	1	7.4	49.5	8.00	0.24
$Ph(COOH)C(H)-H$	367.0	2	20.2	55.6	8.30	4.17×10^{-2}
Bu^tCOO-H	358.6	1	15.6	31.2	9.00	3.69×10^3
Bu^t_3Si-H	351.0	1	−1.0	46.5	9.00	8.01

to be oxidised. Substitution of deuterium for the hydrogen atom in the RH molecule lowers the reaction rate, *e.g.*, the k_H/k_D ratio for diethyl sebaceate is equal to 5.2 (413 K).[75]

3. In polar solvents, the reaction RH + O_2 proceeds more rapidly, which is consistent with the polar nature of the transition state $R(\delta^+)\cdots H\cdots(\delta^-)O_2$.[75]

4. The polarity causes a multidipole effect, *viz.*, the rate constant for a reaction increases with an increase in the number of polar groups in the molecule to be oxidised.[76]

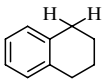
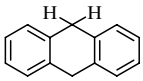
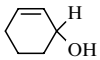
The values of rate constants for the reaction RH + O_2 can be found in numerous reviews and reference books (see, *e.g.*, Refs. 3, 7–9).

The structures of the transition states of the reactions RH + O_2 and $RO_2^{\bullet}$ + RH are similar. The kinetic and thermodynamic parameters of the reaction RH + O_2, which characterise this reaction within the framework of the parabolic model, coincide with the corresponding parameters of the reaction RH + O_3 (see Tables 18 and 19). As the H–O bond in the radical $H-O_2^{\bullet}$ formed is weak (220 kJ mol^{-1}), the activation energy of this reaction is close to its enthalpy; the pre-exponential factor A_0 depends on enthalpy.[7, 11] The values of the activation energy and the rate constant for this reaction calculated within the framework of the parabolic model are given in Table 21.

Table 21. The enthalpies, activation energies and rate constants for the reactions RH + $O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}$ calculated within the framework of the parabolic model.[16]

RH	D	n(C–H)	ΔH	ΔH_{max}	log$A$	k (450 K)
Bu^tH_2C-H	422.0	12	202.0	76.1	12.508	8.17×10^{-12}
$EtMeHC-H$	413.0	4	193.0	76.1	12.06	2.68×10^{-11}
Me_3C-H	400.0	1	180.0	76.1	11.38	1.86×10^{-10}
	418.5	8	198.5	76.1	12.39	1.32×10^{-11}
	408.4	10	188.4	76.1	12.43	2.16×10^{-10}
	395.5	1	175.5	76.1	11.35	5.68×10^{-10}
cis-Decalin	387.6	2	167.6	76.1	11.60	8.31×10^{-9}
$H_2(CH_2{=}CH)C-H$	368.0	3	148.0	110.1	11.12	5.25×10^{-7}
$H(CH_2{=}CH)C(Me)-H$	349.8	2	129.8	110.1	10.58	1.96×10^{-5}

Table 21 (continued).

RH	D	n(C–H)	ΔH	ΔH_{max}	log$A$	k (450 K)
$Me_2(CH_2=CH)C-H$	339.6	1	119.6	110.1	9.96	4.47×10^{-4}
cis-MeCH=CHC(H)(Me)–H	344.0	2	124.0	110.1	10.41	6.27×10^{-5}
$H(Me_2C=CH)C(Me)-H$	332.0	2	112.0	110.1	9.89	4.70×10^{-4}
$Me_2(Me_2C=CMe)C-H$	322.8	1	102.8	110.1	8.63	3.02×10^{-4}
$H(CH_2=CMe)(CH_2=CH)C-H$	307.2	1	87.2	110.1	9.47	1.34×10^{-1}
	341.5	4	121.5	110.1	10.63	2.02×10^{-4}
	330.9	4	110.9	110.1	10.12	1.06×10^{-3}
	312.6	4	92.6	110.1	9.48	3.27×10^{-2}
	301.0	2	81.0	110.1	10.17	3.55
$Me_2(MeC\equiv C)C-H$	329.4	1	109.4	110.1	9.41	3.09×10^{-4}
PhH_2C-H	375.0	3	155.0	90.6	11.02	6.47×10^{-8}
PhMeHC–H	364.1	2	144.1	90.6	11.21	1.81×10^{-6}
$PhMe_2C-H$	354.7	1	134.7	90.6	10.79	8.59×10^{-6}
	345.6	4	125.6	90.6	11.25	2.82×10^{-4}
	322.0	4	102.0	90.6	10.66	3.94×10^{-2}
$H_2(Me_2N)C-H$	379.5	1	159.5	76.1	11.24	3.16×10^{-8}
$[CH_2=CHC(H)-H]_3N$	345.6	6	125.6	110.1	10.94	1.38×10^{-4}
$Me_2C(OH)-H$	390.5	1	170.5	76.1	11.32	2.00×10^{-9}
	329.7	1	109.7	76.1	10.66	5.08×10^{-3}
HO(MeCH=CMe)C(Me)–H	325.2	1	105.2	110.1	9.00	3.72×10^{-4}
PhC(O)–H	348.0	1	128.0	90.6	9.69	4.02×10^{-6}
	394.1	4	174.1	76.1	11.94	3.24×10^{-9}
$Ph_2C(OMe)-H$	354.2	1	134.2	90.6	10.78	9.60×10^{-6}
Bu^tOO-H	358.6	1	138.6	51.5	11.39	1.21×10^{-5}
Bu^t_3Si-H	351.0	1	131.0	69.7	11.02	3.92×10^{-5}

For compounds with weak C–H bonds [D(C–H) < < 330 kJ mol^{-1}], the chain generation follows a trimolecular mechanism:[7,9]

$$RH + O_2 + HR \longrightarrow R^{\bullet} + H_2O_2 + R^{\bullet}.$$

In the oxidation of unsaturated compounds, the chains appear in the reaction of O_2 addition to the double bond:[5,7,9]

$$RCH=CH_2 + O_2 \longrightarrow RC^{\bullet}HCH_2OO^{\bullet},$$

$$RC^{\bullet}HCH_2OO^{\bullet} + O_2 \longrightarrow RCH(OO^{\bullet})CH_2OO^{\bullet}.$$

This process was suggested by Farmer[77] and experimentally proved for styrene by Miller and Mayo.[78] The reaction is endothermic, but its activation energy significantly exceeds ΔH.[5]

Monomer	ΔH /kJ mol^{-1}	E /kJ mol^{-1}
$CH_2=CH_2$	80.8	–
$CH_2=CHEt$	80.4	–
$CH_2=CHPh$	20.4	118
$CH_2=CHC(O)OMe$	84.8	117
$CH_2=C(Me)C(O)OMe$	86.9	115

With an increase in the solvent polarity, the rate of this reaction increases. For example, the reaction of O_2 addition to butyl methacrylate at 363 K is described by the rate constants equal to 8.1×10^{-7} litre mol^{-1} s^{-1} in *N*,*N*-dimethylformamide and 3.4×10^{-7} litre mol^{-1} s^{-1} in chlorobenzene.[5] This may be preceded by the formation of a charge transfer complex:

$$RCH=CH_2 + O_2 \longrightarrow RCH=CH_2(\delta^+)\cdot O_2(\delta^-),$$

$$RCH=CH_2(\delta^+)\cdot O_2(\delta^-) \longrightarrow RC^{\bullet}HCH_2OO^{\bullet}.$$

For some unsaturated compounds, chain generation follows a trimolecular mechanism, most probably, with the simultaneous formation of a biradical containing a peroxide bridge.[5]

$$RCH=CH_2 + O_2 + CH_2=CHR \longrightarrow RC^{\bullet}HCH_2OOCH_2C^{\bullet}HR.$$

IX. Bimolecular reactions of hydroperoxides

The O–O bond of hydroperoxides is weak; the cleavage of this bond occurs with the formation of radicals:[2,7]

$$ROOH \longrightarrow RO^{\bullet} + HO^{\bullet}.$$

This reaction is responsible for the autoacceleration of the gas phase oxidation of hydrocarbons. In the case of liquid-phase oxidation of organic compounds, the autoacceleration of the chain reaction is due to diverse bimolecular reactions involving ROOH which proceed much faster than the monomolecular decomposition of the hydroperoxide.

The bimolecular reaction of hydroperoxide decomposition:

$$ROOH + ROOH \longrightarrow RO_2^{\bullet} + H_2O + RO^{\bullet}$$

was discovered by Bateman *et al.*[79,80] in the study of kinetics of autoxidation of unsaturated acid esters. It was found that the rate of radical generation in the developed oxidation reaction is proportional to the square of the ROOH concentration. Later, this reaction was studied by the free radical acceptor method over a broad range of ROOH concentrations. The following kinetic scheme for radical generation was proposed:[81]

$$ROOH \xrightarrow{k_{i1}} RO^{\bullet} + HO^{\bullet},$$

$$2\,ROOH \overset{K}{\rightleftharpoons} ROO(H)\cdots HOOR,$$

$$ROO(H)\cdots HOOR \xrightarrow{k_{i2}} RO^{\bullet} + H_2O + RO_2^{\bullet}.$$

According to this scheme, the rate of radical generation is equal to:

$$v_i = k_{i1}[ROOH] + k_{i2}K[ROOH]^2(1 + K[ROOH])^{-1}$$

For Me_3COOH (see Ref. 81) and $PhMe_2COOH$ (see Ref. 82), the following parameters were determined (363 K):

Hydroperoxide	K /litre mol^{-1}	$10^7 k_{i2}$ /litre mol^{-1} s^{-1}	$10^6 k_{i2}K$ /litre mol^{-1} s^{-1}
Me_3COOH	1.9	8.61 (Ref. 81)	1.64
$PhMe_2COOH$	1.3	1.23 (Ref. 82)	0.16

The experimental data on bimolecular decomposition of hydroperoxides can be found in the reference books.[3,8]

Table 22. The kinetic parameters of the reactions involving peroxides.[25–27]

Second reactant	α	$10^{-11}\,b$	$0.5\,hN_A\nu_i$	$0.5\,hN_A(\nu_i-\nu_f)$	$(r^{\neq}/r_e)_0$
$ROOH + HY \longrightarrow RO^{\bullet} + HOH + Y^{\bullet}$					
HR	0.788	3.743	17.4	−4.8	0.559
HNR_2	0.907	4.306	20.0	−2.2	0.524
HOR	0.990	4.701	21.7	−0.5	0.502
HOOR	0.969	4.600	21.2	−1.0	0.508
$HSiR_3$	0.604	2.871	13.1	−9.1	0.623
HSR	0.637	3.026	13.8	−8.4	0.611
$HGeR_3$	0.589	2.796	12.6	−9.6	0.629
$HSnR_3$	0.567	2.695	12.1	−10.1	0.638
$ROOR + HY \longrightarrow RO^{\bullet} + ROH + Y^{\bullet}$					
HR	0.796	3.743	17.4	−4.3	0.557
HNR_2	0.916	4.306	20.0	−1.7	0.522
HOR	1.000	4.701	21.7	0.0	0.500
HOOR	0.978	4.600	21.2	−0.5	0.505
$HSiR_3$	0.611	2.871	13.1	−8.6	0.621
HSR	0.644	3.026	13.8	−7.9	0.608
$HGeR_3$	0.595	2.796	12.6	−9.1	0.627
$HSnR_3$	0.573	2.695	12.1	−9.6	0.636
$ROOH + CH_2{=}CHR \longrightarrow RO^{\bullet} + HOCH_2C^{\bullet}HR$					
$CH_2{=}CHR$	0.889	3.238	5.1	−1.1	0.529
$ROOR + CH_2{=}CHR \longrightarrow RO^{\bullet} + ROCH_2C^{\bullet}HR$					
$CH_2{=}CHR$	0.849	3.238	5.1	−1.5	0.541

In the bimolecular ROOH decomposition reaction, the hydroxy group of one molecule attacks the O—O bond of another molecule and results in its cleavage. The reaction centres of this reaction and of the reaction of hydrogen peroxide reduction by the ketyl radical:

$$R_2C^{\bullet}OH + HOOH \longrightarrow R_2C{=}O + H_2O + HO^{\bullet}$$

are similar.

The bimolecular decomposition of hydroperoxides is described well in terms of the kinetic parameters of the reaction of the ketyl radical with hydrogen peroxide,[25,27] these parameters are given in Tables 22 and 23, and the activation energies and rate constants for these reactions calculated within the framework of the parabolic model are given in Table 24.

The formation of radicals in a bimolecular reaction of a hydroperoxide with an alkene was proved experimentally using the reaction of styrene with cumyl hydroperoxide as an example:[83]

$$ROOH + CH_2{=}CHPh \longrightarrow RO^{\bullet} + HOCH_2C^{\bullet}HPh.$$

The rate of radical generation in this reaction is calculated by the formula:[84]

$$v_i = k_i[ROOH][CH_2{=}CHPh],$$

where:

$$k_i = 1.2 \times 10^4 \exp\left(-\frac{72.0}{RT}\right) \text{ litre mol}^{-1}\text{ s}^{-1}.$$

Table 23. The kinetic and thermodynamic parameters for the reactions involving peroxides.[25–27]

Second reagent	br_e	E_{e0}	$10^{-9}\,A_0$	$\Delta H_{e\,max}$
$ROOH + HY \longrightarrow RO^{\bullet} + H_2O + Y^{\bullet}$				
R^1H	19.85	123.2	1.0	239.7
R^2H	21.15	139.9	0.1	283.5
R^3H	20.35	129.5	0.1	256.2
H_2NR	17.33	82.6	10	149.7
HNR_2	18.48	93.9	10	181.2
HOR	19.94	101.4	10	213.0
HOOR	20.45	107.9	10	228.6
$HSiR_3$	15.80	97.0	1.0	145.6
HSR	18.40	126.3	1.0	214.9
$HGeR_3$	16.71	110.6	1.0	172.0
$HSnR_3$	17.15	119.8	1.0	187.4
$ROOR + HY \longrightarrow RO^{\bullet} + ROH + Y^{\bullet}$				
R^1H	21.34	141.2	2.0	289.2
R^2H	22.64	158.9	0.2	336.7
R^3H	21.84	147.9	0.2	307.1
H_2NR	18.82	96.5	20	190.2
HNR_2	19.97	108.6	20	225.0
HOR	21.43	114.8	20	259.6
HOOR	21.94	123.0	20	280.5
$HSiR_3$	18.37	130.0	2.0	219.3
HSR	18.63	128.4	2.0	222.6
$HGeR_3$	18.80	138.9	2.0	235.2
$HSnR_3$	19.24	149.6	2.0	252.9
$HOOR' + RCH{=}CH_2 \longrightarrow R'O^{\bullet} + RC^{\bullet}HCH_2OH$				
$CH_2{=}CHR$	18.93	100.4	1.0	273.2
$CH_2{=}CHCH{=}CHR$	19.92	111.2	1.0	307.3
$CH_2{=}CHPh$	19.32	104.6	1.0	286.4
$R'OOR' + RCH{=}CH_2 \longrightarrow R'O^{\bullet} + RC^{\bullet}HCH_2OR'$				
$CH_2{=}CHR$	19.82	114.9	2.0	304.5
$CH_2{=}CHCH{=}CHR$	20.82	126.8	2.0	340.8
$CH_2{=}CHPh$	19.21	107.9	2.0	283.4

Table 24. The enthalpies, activation energies and rate constants for the reactions $2ROOH \longrightarrow RO_2^{\bullet} + H_2O + RO^{\bullet}$ calculated within the framework of the parabolic model.[25–27]

ROOH	n	ΔH_e	E	log$A$	k (350 K)
HOOH	2	50.0	114.1	8.93	7.97×10^{-9}
Pr^iCHOOH	1	46.5	112.2	8.63	7.68×10^{-9}
	1	46.5	112.2	8.63	7.68×10^{-9}
Bu^tOOH	1	39.6	108.4	8.64	2.90×10^{-8}
$PhMe_2COOH$	1	39.6	108.4	8.64	2.90×10^{-8}
$Me_2C(OH)OOH$	1	52.6	115.5	8.63	2.47×10^{-9}
Cl_3COOH	1	88.2	135.8	8.60	2.15×10^{-12}
Br_3COOH	1	88.0	135.7	8.60	2.23×10^{-12}
CCl_3CCl_2OOH	1	88.2	135.8	8.60	2.15×10^{-12}

This reaction is similar to the thermally neutral reaction, since $\Delta H = 9.7$ kJ mol^{-1}.

Later, such reactions were studied for some other monomers.[5] Thus studies of reactions with esters of polyatomic alcohols revealed the effect of the multidipole interaction.[84, 85] Presumably, this reaction is preceded by the formation of a charge transfer complex.

$$ROOH + CH_2{=}CHR^1 \rightleftharpoons ROOH(\delta^-)\cdot CH_2{=}CHR'(\delta^+),$$

$$ROOH(\delta^-)\cdot CH_2{=}CHR^1(\delta^+) \longrightarrow [RO^{\bullet} + HOCH_2C^{\bullet}HR'],$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR'] \longrightarrow ROH + HOCH{=}CHR',$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR'] \longrightarrow HOCH_2C(OR)HR',$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR'] \longrightarrow RO^{\bullet} + HOCH_2C^{\bullet}HR'.$$

The reaction centres of this reaction and the substitution reaction involving alkyl radicals:[86]

$$R^{\bullet} + R'OOH \longrightarrow ROH + R'O^{\bullet}$$

are similar. This circumstance can be used to calculate activation energies and rate constants of peroxides reactions. The kinetic and thermodynamic parameters are given in Tables 22, 23 and 25.

The condition $\Delta H < D(O-O)$ [$D(O-O) = 175$ kJ mol^{-1}] must be met to ensure successful competition of bimolecular reactions of the type:

$$ROOH + HY \longrightarrow RO^{\bullet} + H_2O + Y^{\bullet}$$

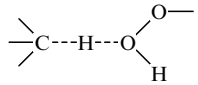
with monomolecular decomposition of the hydroperoxide. This condition is fulfilled for the majority of reactions of organic compounds, since $D(Y-H) < D(HO-H)$ [$D(HO-H) = 498$ kJ mol^{-1}]. For example, the enthalpy of the reaction of a hydroperoxide with cumene is equal to 41 kJ mol^{-1}. However,

Table 25. The enthalpies, activation energies (kJ mol^{-1}) and rate constants (litre mol^{-1} s^{-1}) for the reactions $Me_3COOH + CH_2{=}CHR \longrightarrow Me_3CO^{\bullet} + HOCH_2C^{\bullet}HR$ calculated within the framework of the parabolic model.[25]

$CH_2{=}CHR$	n_C (see [a])	ΔH_e	E	log$A$	k (350 K)
$CH_2{=}CH_2$	2	53.5	124.0	9.00	6.23×10^{-10}
$CH_2{=}CHMe$	1	55.2	124.9	9.00	2.29×10^{-10}
$CH_2{=}CMe_2$	1	50.3	122.3	9.00	5.60×10^{-10}
$CH_2{=}CHEt$	1	54.9	124.8	9.00	2.37×10^{-10}
	2	55.2	124.9	9.00	2.29×10^{-10}
	2	52.2	123.3	9.00	3.97×10^{-10}
$HC{\equiv}CH$	2	33.2	113.3	9.30	4.91×10^{-8}
$HC{\equiv}CMe$	1	36.9	115.2	9.30	1.28×10^{-8}
$MeC{\equiv}CMe$	2	48.9	121.5	9.30	2.93×10^{-9}
$CH_2{=}CHCH{=}CH_2$	2	63.0	110.8	9.00	5.81×10^{-8}
$CH_2{=}CHCMe{=}CH_2$	1	54.0	110.4	9.00	3.34×10^{-8}
$CH_2{=}CHCH{=}CMe_2$	1	−0.3	107.7	9.00	8.45×10^{-8}
	2	−13.4	101.1	9.00	8.16×10^{-7}
$CH_2{=}CHPh$	1	13.6	107.7	9.00	8.45×10^{-8}
$CH_2{=}CMePh$	1	13.1	107.5	9.00	9.05×10^{-8}
$MeCH{=}CMePh$	1	3.0	102.6	9.00	4.87×10^{-7}
$Me_2C{=}CMePh$	1	3.0	102.6	9.00	4.87×10^{-7}
$CH_2{=}CPh_2$	1	−45.7	80.5	9.00	9.69×10^{-4}
	1	12.9	107.4	9.00	9.37×10^{-8}

[a] The number of carbon atoms subject to the attack.

within the framework of the parabolic model[25–27] the activation energy of this reaction is rather high (the calculated value for the reaction of *tert*-butyl hydroperoxide with cumene is 135.6 kJ mol^{-1}), which may be attributed to high repulsion energy in a non-linear transition state complex.



The kinetic parameters for the reactions involving C–H, N–H and O–H bonds (hydrocarbons, amines, alcohols, acids) are given in Tables 22 and 23; the results of calculations within the framework of the parabolic model are given in Table 26.

Table 26. The enthalpies, activation energies and rate constants for the reactions $ROOH + HR \longrightarrow RO^{\bullet} + H_2O + R^{\bullet}$ calculated within the framework of the parabolic model.[25]

RH	D	n(R–H)	ΔH_l	E	log$A$	k (400 K)
EtMeHC–H	413.0	4	90.2	151.3	9.60	8.38×10^{-12}
Me_3C–H	400.0	1	77.2	140.6	9.00	5.41×10^{-11}
	418.5	8	95.7	150.4	9.90	2.16×10^{-11}
	408.4	10	85.6	145.0	10.00	1.41×10^{-10}
	403.9	14	81.1	142.6	10.15	4.06×10^{-10}
	395.5	1	72.7	138.2	9.00	1.10×10^{-10}

Table 26 (continued).

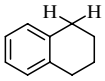
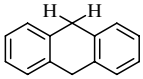
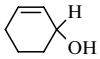
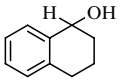
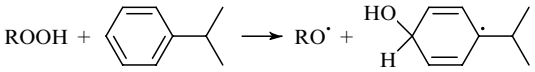
RH	D	n(R – H)	ΔH_1	E	log$A$	k (400 K)
cis-Decalin	387.6	2	64.8	134.2	9.30	7.57×10^{-10}
$H_2(CH_2=CH)C-H$	368.0	3	45.2	141.0	9.48	1.44×10^{-10}
$H(CH_2=CH)C(Me)-H$	349.8	2	27.0	132.3	9.30	1.32×10^{-9}
$Me_2(CH_2=CH)C-H$	339.6	1	16.8	139.0	9.00	8.84×10^{-11}
cis-$MeCH=CHC(H)(Me)-H$	344.0	2	21.2	141.0	9.30	9.59×10^{-11}
$H(Me_2C=CH)C(Me)-H$	332.0	2	9.2	135.5	9.30	5.04×10^{-10}
$Me_2(Me_2C=CMe)C-H$	322.8	1	0.0	131.4	9.00	8.75×10^{-10}
$H(CH_2=CMe)(CH_2=CH)C-H$	307.2	1	−15.6	124.7	9.00	6.88×10^{-9}
	341.5	4	18.7	139.8	9.60	2.72×10^{-10}
	330.9	4	8.1	135.0	9.60	1.17×10^{-9}
	312.6	4	−10.2	127.0	9.60	1.36×10^{-8}
	301.0	2	−21.8	122.0	9.30	3.07×10^{-8}
$Me_2(MeC\equiv C)C-H$	329.4	1	6.6	134.3	9.00	3.59×10^{-10}
$MePhHC-H$	364.1	2	41.3	150.4	9.30	5.46×10^{-12}
Me_2PhC-H	354.7	1	31.9	135.6	9.00	2.46×10^{-10}
	345.6	4	22.8	131.3	9.60	3.59×10^{-9}
	322.0	4	−0.8	120.7	9.60	9.22×10^{-8}
$Me_2(NH_2)C-H$	379.5	1	56.7	141.4	9.00	4.21×10^{-11}
$[CH_2=CHC(H)-H]_3N$	345.6	6	22.8	131.3	9.78	5.39×10^{-9}
$Me_2C(OH)-H$	390.5	1	67.7	147.0	9.00	7.75×10^{-12}
	329.7	1	6.9	134.5	9.00	3.44×10^{-10}
$HO(MeCH=CMe)C(Me)-H$	325.2	1	2.4	124.8	9.00	6.61×10^{-9}
	337.5	1	14.7	119.9	9.00	2.91×10^{-8}
$PhC(O)-H$	348.0	1	25.2	124.7	9.00	6.68×10^{-9}
	394.1	4	71.3	141.1	9.60	1.83×10^{-10}
$(Me_2C-H)_2O$	390.8	2	68.0	139.4	9.30	1.53×10^{-10}
$[CH_2=CHC(H)-H]_2O$	360.0	4	37.2	140.7	9.60	2.05×10^{-10}
$Ph_2C(OMe)-H$	354.2	1	31.4	127.7	9.00	2.75×10^{-9}
$Ph(COOH)C(H)-H$	367.0	2	44.2	133.8	9.30	8.57×10^{-10}
Bu^t_3Si-H	351.0	1	23.9	95.2	9.00	5.54×10^{-5}
Ph_3Ge-H	322.5	1	−5.1	97.0	9.00	3.17×10^{-5}
Ph_3Sn-H	296.9	1	−31.2	98.2	9.00	2.17×10^{-5}
$H_2NN(H)-H$	366.1	4	45.9	139.3	9.60	3.16×10^{-10}
$HEtN-H$	418.4	2	98.2	173.8	9.30	4.02×10^{-14}
Et_2N-H	382.8	1	62.6	160.9	9.00	1.12×10^{-13}
$EtO-H$	440.0	1	121.5	205.7	9.00	1.39×10^{-19}
Pr^iO-H	443.0	1	124.5	207.8	9.00	7.40×10^{-20}
Bu^tO-H	446.0	1	127.5	209.9	9.00	3.93×10^{-20}
	437.1	1	118.6	203.6	9.00	2.65×10^{-19}
$ONO-H$	327.6	1	9.1	134.2	9.00	3.77×10^{-10}
$MeC(O)O-H$	442.7	1	124.2	207.6	9.00	7.86×10^{-20}
$PhCH_2C(O)O-H$	443.5	1	125.0	208.1	9.00	6.76×10^{-20}

Table 27. The experimental and calculated rate constants of the reactions $RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}$ and $RH + ROOH \longrightarrow R^{\bullet} + H_2O + RO^{\bullet}$.

Reaction	T /K	k		Ref.
		experimental	calculated	
$Me_2Pr^iC-H + O_2$	800	1.0×10^{-1}	5.14×10^{-2}	24
 $+ O_2$	400	3.47×10^{-7}	3.48×10^{-6}	11
 $+ O_2$	600	7.2×10^{-1}	3.5×10^{-1}	27
$PhMe_2C-H + O_2$	400	1.95×10^{-7}	9.41×10^{-8}	12
HOOH + HOOH	350	4.76×10^{-9}	5.81×10^{-9}	5
$Bu^tOOH + Bu^tOOH$	350	4.99×10^{-7}	2.04×10^{-8}	3
$Me_2EtCOOH$ + $Me_2EtCOOH$	350	7.52×10^{-8}	2.04×10^{-8}	6
$Me_2PhCOOH$ + $Me_2PhCOOH$	350	2.71×10^{-9}	2.04×10^{-8}	9
$Me_2PhCOOH$ + $Me_2PhCOOH$	350	6.55×10^{-8}	2.04×10^{-8}	82
$CH_2=CHPh + Bu^tOOH$	350	2.21×10^{-7}	8.45×10^{-8}	12
$PhMe_2CH + Me_2PhCOOH$	400	2.92×10^{-7}	2.03×10^{-10}	9
$EtMe_2COH + EtMe_2COOH$	400	2.27×10^{-4}	3.02×10^{-19}	6

A comparison of the experimental and calculated values of the rate constants revealed that the former exceed the latter by several orders of magnitude (Table 27). Presumably, under the given experimental conditions the investigators deal with other, more efficient mechanisms of radical generation from the same reactants.

A comparison of rate constants and activation energies for the reactions ROOH + RH and ROOH + C=C revealed that the latter reaction proceeds faster and with lower activation energies (see Table 27). Probably, reactions of hydroperoxides with alkylaromatic hydrocarbons, *e.g.*, cumenes, of the type:



proceed faster.

The generation of radicals in the reaction of a hydroperoxide with a carboxylic acid follows, most probably, the mechanism of an acid-catalysed reaction as this takes place in an ROOH + mineral acid system where the formation of radicals is preceded by the protonation of the hydroperoxide.[7]

$$ROOH + HOC(O)R' \rightleftharpoons ROOH_2^+ + R'CO_2^-,$$

$$ROOH_2^+ + ROOH \longrightarrow RO^{\bullet} + RO_2^{\bullet} + H_3O^+,$$

$$ROOH_2^+ + R'C(O)OH \longrightarrow RO^{\bullet} + H_3O^+ + R'CO_2^{\bullet},$$

$$ROOH + HOR' \rightleftharpoons ROOH_2^+ + R'O^-,$$

$$ROOH_2^+ + R'OH \longrightarrow RO^{\bullet} + H_3O^+ + R'O^{\bullet}.$$

In the reaction of alcohols with hydroperoxides

$$ROOH + HOR' \longrightarrow RO^{\bullet} + H_2O + R'O^{\bullet}$$

the radicals are also formed much faster (by 4–5 orders of magnitude) than in the bimolecular reaction of hydroperoxide decomposition (see Table 27).

Apparently, in these systems, too, a more rapid acid-catalysed hydroperoxide cleavage takes place.

X. Conclusion

Bimolecular reactions leading to radical generation are extremely diverse. Very often, they proceed much faster than monomolecular dissociation of molecules involving the weakest bond. Presumably, the fulfilment of the condition E(a bimolecular reaction) < D(a weak bond) depends on the enthalpy ratio of these reactions, *viz.*, E(a bimolecular reaction) < D(a weak bond), if ΔH(a bimolecular reaction) < D(a weak bond). However, judging from the activation energies of individual reactions, this condition is insufficient.

First, for the dissociation reaction:

$$E_d = D + RT \approx D,$$

whereas for the bimolecular endothermic reaction:

$$E = \Delta H + \Delta E,$$

ΔE being dependent on the type of the reaction and ΔH (see Fig. 1). Therefore, a concrete analysis of the reactions that are compared is necessary.

Second, the pre-exponential factor A in the Arrhenius equation for the monomolecular decomposition reaction is $\sim 10^{13}-10^{16}$ s^{-1}, while that for the bimolecular reaction (due to a negative activation enthropy) is equal to $\sim 10^8-10^{10}$ litre mol^{-1} s^{-1}. Moreover, proper allowance must be made for the fact that in the case of endothermic processes with $\Delta H_e > \Delta H_{e\,max}$ the pre-exponential factor increases with the enthalpy of the reaction. The parabolic model takes proper account of all these factors and allows the estimation of activation energies and rate constants for any bimolecular homolytic reaction for which an analogous bimolecular radical reaction exists.

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