U. D. C. 541.515

Interactions between Atoms and Radicals in the Liquid Phase

E.T.Denisov

CONTENTS

I.	Introduction	31
II.	Recombination of atoms in solution	31
III.	Disproportionation and recombination of alkyl radicals	32
IV.	Reactions $HO^{\cdot}$ and $RO^{\cdot}$ radicals	34
V.	Reactions between peroxy-radicals	34
VI.	Reactions of radicals with free valences at nitrogen and tin atoms	42
VII.	Reactions between free radicals of different types	42
VIII.	Effect of the solvent. Viscosity of the solvent.	42

The review presents a compilation and an analysis of the results of quantitative kinetic studies on liquid-phase interactions between atoms and free radicals. Problems such as the diffusion mechanism for the recombination of atoms in solution, the competition between recombination and disproportionation reactions of alkyl radicals in the liquid phase, the mechanisms of the reactions of secondary and tertiary peroxy-radicals, the effect of the viscosity, internal pressure, and dielectric constant of the liquid on the rate constant for the interaction between the radicals, and also the role of radical hydrogen bonds are discussed. The rate constants for 142 interactions of atoms and radicals in different solvents are quoted. The bibliography includes 165 references.

I. INTRODUCTION

The interactions of atoms and radicals play an important role in a wide variety of free-radical reations. In chain reactions such as polymerisation, oxidation, and halogenation the elementary steps involving interactions between free radicals are responsible for chain termination (in the absence of inhibitors). For this reason, the concentration of free radicals and hence the rate of the chain process depend on the rate constants for these reactions. Atoms and radicals arise in the liquid phase under the action of light and penetrating radiation. Very frequently in such cases the reactions between free radicals determine not only the rate of formation of products but also their composition.

Reactive free radicals and atoms interact with one another very rapidly; this retarded the quantitative study of these processes for a long time. The development and extension of the kinetic methods for the investigation of fast reactions constituted an important pre-condition for the vigorous development of studies on radical reactions in the last twenty years. A large amount of data has accumulated on the kinetics of recombination and disproportionation reactions of free radicals. The interest in these reactions is not fortuitous, since they constitute an example of the interaction of chemically highly reactive species and occupy an important place in chain processes. The aim of the present review is to examine the experimental data and theoretical concepts concerning the interactions of atoms and radicals in solution.

The rate constants for the reactions of atoms and radicals are measured by the following methods: electron spin resonance (ESR), method of the non-steady-state kinetics of chain reactions (NKR), the method of intermittent illumination—the rotating sector method (RSM), flash photolysis (FP), pulse radiolysis (PR), flow methods (FM), the method of photochemical space intermittency (PSI), and the method of competing reactions (MCR). These methods have been described in monographs and individual papers [1-8].

II. RECOMBINATION OF ATOMS IN SOLUTION

In the gas phase atoms recombine in triple collisions of two atoms with a third particle (molecule or atom) which partially deactivates the excited molecule formed from the atoms. In solution a third particle (solvent molecule) is always present. Therefore the rate of recombination of atoms in solution is limited solely by their diffusion. The rate constants for the recombination of hydrogen, bromine, and iodine atoms are similar (Table 1) and lie in the range $1 \times 10^{10} - 3 \times 10^{10}$ litre mole^{-1} s^{-1}. Since in each elementary recombination step two atoms disappear and one molecule is formed, in the steady state $w_i = 2k[x]^2$, where w_i is the rate of initiation and k the recombination rate constant. Table 1 and other tables list the values of $\lg(2k)$, the dimensions of k being throughout litre mole^{-1} s^{-1}.

Table 1. Rate constants for the recombination of atoms in solution ($\theta = 4.57T/1000$).

Atom	Solvent	t, °C	$\lg(2k)$	Method	Refs.
H	H_2O, pH=3	25	10.08	PR	9
H	H_2O, pH=0,4—3	25	10.415	PR	10
H	H_2O, pH=0,1—1,0	25	10.48	PR	11
H	H_2O, pH=2	25	10.30	PR	12
	mean value		10.30±0.13		
Br	CCl_4	25	10.6	FP	13
I	CCl_4	15—35	14.40—5.6/θ	RSM	14
I	CCl_4	25	10.06	FP	15
I	CCl_4	25—50	12.49—3,2/θ	FP	16
I	CCl_4	25	10.64	FP	17
I	CCl_4	25	10.30	FP	18
	mean value for	25	10.28±0.15		
I	n-C_6H_{14}	15—35	12.20—2.4/θ	RSM	14
I	n-C_6H_{14}	25	10.30	RSM	18
I	n-C_6H_{14}	25	10.64	RSM	17
I	n-C_6H_{14}	25	10.56	RSM	16
I	$Cl_2C{=}CCl{-}CCl{=}CCl_2$	15—35	12.50—3.3/θ	RSM	14

The rate constant for diffusion is related to the diffusion coefficient by Smoluchowski's equation[19]: $k_D = 4\pi\sigma DN/1000$, where σ is the diameter of the diffusing species (cm), N the Avogadro number, and D the diffusion coefficient ($cm^2\ s^{-1}$); k_D is expressed in litre $mole^{-1}\ s^{-1}$. The diameter of the iodine atom is 4.3 Å. Table 2 lists the diffusion coefficients of iodine atoms[14] calculated from the experimental values of k, and includes for comparison the experimental diffusion coefficients of iodine molecules[20,21].

Table 2. Diffusion coefficients of atomic[14] and molecular[20,21] iodine.

Solvent	t, °C	$10^5 D_I$, $cm^2\ s^{-1}$	$10^5 D_{I_2}$, $cm^2\ s^{-1}$
$n\text{-}C_6H_{14}$	15	3.5	—
$n\text{-}C_6H_{14}$	25	4.0	4.05
CCl_4	17.5	2.1	1.30
CCl_4	25	2.5	1.50
CCl_4	38	4.1	1.84
$CCl_2{=}CCl{-}CCl{=}CCl_2$	15	1.4	—
$CCl_2{=}CCl{-}CCl{=}CCl_2$	25	1.9	—
$CCl_2{=}CCl{-}CCl{=}CCl_2$	35	2.1	—

Using the Stokes–Einstein equation $D = kT/3\pi\eta\sigma$, it is possible to calculate k_D from the viscosity η: $k_D = 8RT/3000\eta$. According to this expression, the product $k_D\eta T^{-1}$ for different solvents should be constant. However, in fact $k_D\eta/T$ for iodine atoms varies from solvent to solvent[14]: at 25 °C it is 1.29×10^5 in n-hexane, 2.22×10^5 in carbon tetrachloride, and 6.15×10^5 in hexachloroethane. Consequently the Stokes–Einstein equation does not hold rigorously for the diffusion of atoms in liquids. This can be explained by the fact that the viscosity depends on the dimensions of solvent molecules and the interaction forces between them, while the diffusion coefficient is determined by the interaction between the diffusing species and solvent molecules.

III. DISPROPORTIONATION AND RECOMBINATION OF ALKYL RADICALS

Alkyl radicals interact in two ways: they recombine with formation of a new C–C bond and disproportionate with the abstraction of a hydrogen atom by one radical from another with formation of an olefin and an alkane. The interaction between methyl and ethyl radicals may serve as an example:

$$CH_3^{\cdot} + C_2H_5^{\cdot} \rightarrow CH_3CH_2CH_3 + 80.5\ \text{kcal mole}^{-1}$$
$$CH_3^{\cdot} + C_2H_5^{\cdot} \rightarrow CH_4 + CH_2{=}CH_2 + 64\ \text{kcal mole}^{-1}$$

The heats of these reactions have been calculated from the heats of formation of the radicals quoted in Ref. 22. The ratio of the disproportionation and recombination rate constants of alkyl radicals has been measured experimentally in the following way. An azo-compound was decomposed photochemically in a solvent; this resulted in the following reactions:

$$R{-}N{=}N{-}CH_2CH_2R' \xrightarrow{h\nu} \overbrace{R^{\cdot} + R'CH_2CH_2^{\cdot}} + N_2\ ,$$
$$\overbrace{R^{\cdot} + CH_2CH_2R'^{\cdot}} \xrightarrow{k_d} RH + CH_2{=}CHR'\ ,$$
$$\overbrace{R^{\cdot} + {\cdot}CH_2CH_2R'} \xrightarrow{k_r} RCH_2CH_2R'\ .$$

The radicals disproportionated and recombined in a solvent cage. Since the olefin $CH_2{=}CHR'$ was obtained only by the disproportionation reaction and the hydrocarbon RCH_2CH_2R' by the recombination reaction, analysis of the products for the relative amounts of the olefin and the alkane yields the ratio of the rate constants: $k_d/k_r = [CH_2{=}CHR^{\cdot}]/[RCH_2CH_2R']$. Table 3 shows that this ratio depends on the structure of the reacting radicals and is in the range 0.1–1. The difference between the activation energies for recombination and disproportionation in the reactions between a methyl and an ethyl radical and between two ethyl radicals is $E_r - E_d = 0.4$ kcal $mole^{-1}$. In the solid state, in contrast to solution, $\lg(k_d/k_r)$ is independent of temperature[26].

Table 3. Relative contributions of the disproportionation and recombination of radicals with a free valence at a carbon atom ($\theta = 4.57T/1000$).

Radical	Solvent	t, °C	$\lg(k_d/k_r)$	Refs
$CH_3^{\cdot}+C_2H_5^{\cdot}$	$n\text{-}C_7H_{16}+CH_2{=}CHC_6H_5$	−75—100	$\bar{2}.416+0.40/\theta$	23
$CH_3^{\cdot}+C_2H_5^{\cdot}$	$(CH_3)_2CHCH_2C(CH_3)_3$	0	$\bar{2}.875$	24
$CH_3^{\cdot}+C_2H_5^{\cdot}$	$CH_2(OH)CH_2OH$	0	$\bar{2}.965$	24
$2C_2H_5^{\cdot}$	$(CH_3)_2CHCH_2C(CH_3)_3$	65	$\bar{1}.16$	25
$2C_2H_5^{\cdot}$	$(CH_3)_2CHCH_2C(CH_3)_3$	0	$\bar{1}.25$	26
$2C_2H_5^{\cdot}$	$C_6H_5CH_3$	0	$\bar{1}.27$	26
$2C_2H_5^{\cdot}$	$(CH_3)_2CHOH$	0	$\bar{1}.305$	26
$2C_2H_5^{\cdot}$	$CH_2(OH)CH_2OH$	0	$\bar{1}.415$	26
$2C_2H_5^{\cdot}$	$CH_2(OH)CH_2OH$	65	$\bar{1}.38$	25
$2C_2H_5^{\cdot}$	gas phase	0	$\bar{1}.115$	26
$2C_2H_5^{\cdot}$	$n\text{-}C_7H_{16}$	−75—99	$\bar{2}.94+0.37/\theta$	27
$2C_6H_5(CH_3)_2C^{\cdot}$	$C_6H_5CH(CH_3)_2$	20—60	$\bar{2}.73$	28
$2\ cyclo\text{-}C_6H_{11}^{\cdot}$	$cyclo\text{-}C_6H_{12}$	23	0.04	29
$2CH_3\dot{C}HOH$	H_2O	23	$\bar{1}.40$	30
	$cyclo\text{-}C_6H_{11}OH$	25	0.30	31
$2{\sim}CH_2\dot{C}(CH_3)COOCH_3$	$CH_2{=}C(CH_3)COOCH_3$	0—60	1.99—2.26/θ	32

The recombination of hydroxyalkyl radicals results in the formation of a diol and their disproportionation yields an alcohol and a carbonyl compound. For example:

$$2\,CH_3\dot{C}HOH \begin{cases} \xrightarrow{k_r} CH_3CH(OH)CH(OH)CH_3 \\ \xrightarrow{k_d} CH_3CHO + CH_3CH_2OH\ . \end{cases}$$

The rate constant ratios k_d/k_r have been calculated from the composition of the products formed in the radiolysis of the corresponding alcohols. The relative contributions of the disproportionation and recombination of alkyl radicals vary from solvent to solvent owing to the effect of the internal pressure of the liquid on k_d and k_r. With increase of the internal pressure in the solvent, k_d/k_r for ethyl radicals increases from 0.13 in the gas phase to 0.26 in ethylene glycol at 0 °C.[26] There is a satisfactory linear relation between $\lg(k_d/k_r)$ for ethyl radicals and $P_s^{1/2}$, where P_s is the internal pressure of the solvent[25]:

$$\lg(k_d/k_r) = -1.08 + 4.76 \times 10^{-3} P_s^{1/2}\ .$$

The explanation is that the volume of the activated complex in the disproportionation process is somewhat smaller than in recombination. For ethyl radicals, $V_r^* - V_d^* = 2.4$ cm^3 $mole^{-1}$ at 0 °C.[26]

Table 4. Overall rate constants for the interactions of radicals having a free valence at a carbon atom.

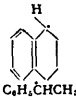
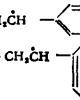
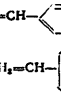
Radical	Solvent	t, °C	$\lg(2k)$	$\lg(2A)$	E, kcal mole^{-1}	Method	References
$C_2H_5^{\cdot}$	C_2H_6	—140—170	9.51 (30°)	10,11	0,83	PR	33
$CH_3(CH_2)_2CH_2^{\cdot}$	n-C_5H_{12}	25	9.30	—	—	RSM	34
$C_6H_5CH_2^{\cdot}$	$C_2H_5OH+(CH_2OH)_2CHOH$	25	7.60	—	—	PR	35
$C_6H_5CH_2^{\cdot}$	alkane	23	7.90	—	—	FP	36
$C_6H_5CH_2^{\cdot}$	$C_6H_5CH_3$	25	9.91	—	—	RSM	34
$CCl_3^{\cdot}$	$CHCl_3$	24	7.845	—	—	RSM	37
$CCl_3^{\cdot}$	$CH_2{=}CHOCOCH_3$	25	8.025	—	—	NKR	38
$CCl_3^{\cdot}$	$CH_2{=}CHOCOCH_3$	25	7.725	—	—	RSM	38
$CCl_3^{\cdot}$	$CHCl_3$	25	8.21	—	—	RSM	38
$CCl_3^{\cdot}$	$CH_2{=}CHOCOCH_3$	25	8.00	—	—	RSM	39
$CCl_3^{\cdot}$		25	8.00	—	—	NKR	40
	RH	25	6.85	—	—	RSM	41
$C_6H_5\dot{C}HCH_3$	RH	60	8.30	—	—	NKR	42
$CH_3(CH_2)_4CH{=}CH{-}\dot{C}H$ $C_2H_5OCO(CH_2)_7CH{=}\dot{C}H$	RH	25	7.18	—	—	NKR	43
$CH_2{=}C(CH_3)(CH_2)_3C(CH_3){=}CH{-}\dot{C}H{-}CH_2$ $CH_2{=}(CH_2)C(CH_2)_2CH_2C{=}\dot{C}H$	RH	25	8.415	—	—	NKR	43
$(CH_2)_2\dot{C}^{\cdot}$	cyclo-C_6H_{12}	25	9.30	—	—	RSM	44
$C_6H_4\dot{C}(CH_3)_2$	RH	60	~6.70	—	—	NKR	42
$(CH_3)_2\dot{C}CN$	C_6H_5Cl	60	~8.30	—	—	NKR	42
$(CH_3)_2\dot{C}CN$	C_6H_6	25	9.64	—	—	ESR	45
	C_6H_6	25	9.64	—	—	ESR	45
$CH_2\dot{C}HOH$	H_2O	23	9.04	—	—	PR	30
$CH_3\dot{C}HOH$	H_2O	23	9.15	—	—	PR	46
$CH_3\dot{C}HOH$	H_2O	23	9.30	—	—	PR	47
	RH	25	8.53	—	—	PR	31
	$RH+CH_2{=}C(CH_3)_2$	25	8.32	—	—	PR	31
$(C_6H_5)_2\dot{C}OH$	$(CH_3)_2CHOH$	25	7.77	—	—	FP	48
$\sim CH_2{-}\dot{C}H_2$	C_6H_6	83	9.02	—	—	RSM	49
$\sim CH_2{-}\dot{C}H_2$	$CH_2{=}CH_2$	—20	8.66	—	—	RSM	50
$C_6H_5\dot{C}HCH_2\sim$	$CH_2{=}CHC_6H_5$	0—25	6.45 (25°)	8.505	2.8	NKR	51
$C_6H_5\dot{C}HCH_2\sim$	$CH_2{=}CHC_6H_5$	28	6.78	—	—	NKR	52
$C_6H_5\dot{C}HCH_2\sim$	$CH_2{=}CHC_6H_5$	15—25	6.48 (25°)	7.875	1.9	NKR	53
$C_6H_5\dot{C}HCH_2\sim$	$CH_2{=}CHC_6H_5$	0—60	7.86 (60°)	9,27	2.4	RSM	54
		mean value		8.85	1.5		3
p-$CH_3OC_6H_4\dot{C}H_2\sim$	$CH_2{=}CHC_6H_4OCH_3$	0	6.025	—	—	NKR	55
$\sim CH_2\dot{C}HCOOCH_3$	$CH_2COOC_2H_5$	26—50	6.55	—	—	RSM	56
$\sim CH\dot{C}HCOOCH_3$	$CH_2COOC_2H_5$	30—60	6.63 (30°)	10.45	5.3	RSM	57
$\sim CH_2\dot{C}HCOOCH_3$	$CH_2COOC_2H_5$	28	8.00	—	—	NKR	52
$\sim CH_2\dot{C}HCOOC_4H_9$	$CH_2{=}CHCOOC_4H_9$	25	6.92	—	—	NKR	58
$\sim CH_2\dot{C}HCOOC_4H_9$	$CH_2{=}CHCOOC_4H_9$	25	8.52	—	—	NKR	59
$\sim CH_2\dot{C}HCOOC_4H_9$	$CH_2{=}CHCOOC_4H_9$	25	4.255	—	—	RSM	60
$\sim CH_2\dot{C}HCOOC_4H_9$	$CH_2{=}CHCOOC_4H_9$	28	7.53	—	—	NKR	52
$\sim CH_2\dot{C}(CH_3)COOCH_3$	$CH_2{=}C(CH_3)COOCH_3$	30—60	7.39 (30°)	9.41	2.8	RSM	61
$\sim CH_2\dot{C}(CH_3)COOCH_3$	$CH_2{=}C(CH_3)COOCH_3$	24—50	7.82 (24°)	8.555	1.0	RSM	62
$\sim CH_2\dot{C}(CH)_2COOCH_3$	$CH_2{=}C(CH_3)COOCH_3$	28	7.41	—	—	NKR	52
		mean value	7.69	7.69	0.4		3
$\sim CH_2\dot{C}(CH_3)COOC_2H_5$	$CH_2{=}C(CH_3)COOC_2H_5$	30	7.65	—	—	RSM	63
$\sim CH_2\dot{C}(CH_3)COOC_4H_9$	$CH_2{=}C(CH_3)COOC_4H_9$	28	8.255	—	—	NKR	52
$\sim CH_2\dot{C}(CH_3)COOC(CH_3)_3$	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CO_2C(CH_3)_3$	20—90	7.15 (30°)	7.95	1.1	RSM	64
$\sim CH_2\dot{C}(CH_3)CH_2CH(CH_3)_2$	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2CH(CH_3)_2$	30	7.08	—	—	NKR	65
$\sim CH_2\dot{C}(CH_3)CH(CH_3)_2$	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2CH(CH_3)_2$	28	8.00	—	—	NKR	52
$\sim CH_2\dot{C}HCl$		25—55	9.07 (30°)	12.115	4.2	RSM	66
$\sim CH_2\dot{C}HCN$	$HCON(CH_3)_2$	13—40	6.26	—	—	NKR	67
$\sim CH_2\dot{C}HCN$	$HCON(CH_3)_2$	0—60	7.94 (60°)	10.11	3.7	RSM	68
$\sim CH_2\dot{C}HCN$	$HCON(CH_3)_2$	60	8.89	—	—	RSM	69
$\sim CH\dot{C}HCN$	$CH_2{=}CHCN$	25	7.09	—	—	NKR	70
$\sim CH_2\dot{C}(CH_3)CN$	$CH_2{=}C(CH_3)CN$	60—80	6.23 (30°)	9.855	5.00	RSM	71
$\sim CH_2\dot{C}HCONH_2$	H_2O	25	7.16	—	—	RSM	72
$\sim CH_2\dot{C}HCONH_2$	H_2O	10—40	7.21 (30°)	10.11	4.0	RSM	73
$\sim CH_2\dot{C}H$ 	$CH_2{=}CH$ 	25	6.48	—	—	NKR	74
$\sim CH_2\dot{C}H$ 	$CH_2{=}CH$ 	25	7.52	—	—	RSM	75

Table 4 (cont'd).

Radical	Solvent	t, °C	$\lg(2k)$	$\lg(2A)$	E, kcal mole^{-1}	Method	References
~ $CH_2\dot{C}H$ — (N)	CH_2=CH— (N)	25	6.95	—	—	NKR	75
~ $CH_2\dot{C}H$ — (N, CH_3)	$CHON(CH_3)_2$	25	6.545	—	—	NKR	67
~ CF_2—$\dot{C}F_2$	H_2O	30—70	1.12 (30°)	1.26	0.2	NKR	76
~ CF_2—$\dot{C}F_2$	H_2O	40—60	1.79 (30)°	4.14	3.25	inhib. method	77

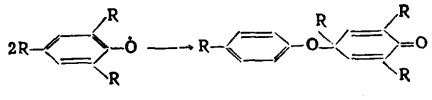
Kinetic methods make it possible to measure the overall rate constants for the interactions between alkyl radicals, which are listed in Table 4 [$k = k_d + k_r$, the values of $\lg(2k)$ are listed]. Table 4 shows that the radicals $C_2H_5^{\bullet}$,[33] $(CH_3)_3C^{\bullet}$,[44] $C_6H_5CH_2^{\bullet}$,[34] and $CH_3\dot{C}HOH$,[30,46,47] interact with very high rate constants in the range 1×10^9 – 5×10^9 litre mole^{-1} s^{-1}, which are equal [$\lg(2k)$] or close to the rate constants for the diffusion of radicals. The radicals $R_2\dot{C}CN$ recombine with formation of a C–C or C–N bond[78]:

$$2\,R_2\dot{C}CN \longrightarrow \begin{cases} \rightarrow R_2C(CN)C(CN)R \\ \rightarrow R_2C{=}C{=}N{-}C(CN)R_2 \end{cases}.$$

Tetralyl, cumenyl, and trichloromethyl radicals interact with rate constants which are significantly smaller than the diffusional rate constants. The problems associated with the interactions of macroradicals with one another in polymerisation processes have been examined in monographs[3,79] and in a review[80].

IV. REACTIONS OF HO• AND RO• RADICALS

The rate constant for the recombination of hydroxy-radicals is equal to the diffusion rate constant (Table 5). On the other hand, phenoxy-radicals substituted in the 2-, 4-, and 6-positions recombine very slowly. The recombination of substituted phenoxy-radicals is mainly of the "head to tail" type[81]:

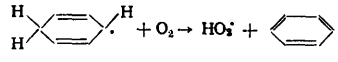


V. REACTIONS BETWEEN PEROXY-RADICALS

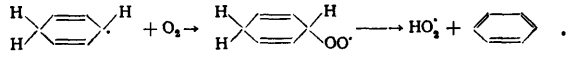
1. The Hydroperoxy-radical

The $HO_2^{\bullet}$ radical has amphoteric properties and in aqueous solution can be present in the forms $HO_2^{\bullet}$, O_2^{-}, and $H_2O_2^{\bullet+}$ depending on the pH. At pH ≥ 5 the equilibrium $HO_2^{\bullet} \rightleftharpoons H^+ + O_2^-$ is displaced to the right[92]: $pK_{HO_2^{\bullet}} = 4.4 \pm 0.4$ at 23 °C.[92] The rate constant for the reaction $O_2^- + O_2^- \rightarrow O_2 + O_2^{2-}$ is 1.5×10^7 litre mole^{-1} s^{-1} at 23 °C.[92] At pH ≤ 2 the equilibrium is displaced to the left and under these conditions the disproportionation of the HO• radicals takes place: $HO_2^{\bullet} + HO_2^{\bullet} \rightleftharpoons O_2 + H_2O_2$; $k = 2.2 \times 10^6$ litre mole^{-1} s^{-1} at 23 °C.[92] It is interesting to note that the electron transfer process between two O_2^- radical-ions which bear the same charge is much faster than the adiabatic reaction with transfer of a hydrogen atom between two neutral $HO_2^{\bullet}$ radicals. In strongly acid media at pH < 1, $HO_2^{\bullet}$ is protonated: $HO_2^{\bullet} + H^+ \rightleftharpoons H_2O_2^{\bullet+}$; at 23 °C $pK = 1.0 \pm 0.4$.[93] In this pH range the rate constant for the reaction of $HO_2^{\bullet}$ radicals depends on the ionic strength of the solution, which is characteristic of an ion–ion type of reaction. The rate constants[93] are $k = 3 \times 10^6$ litre mole^{-1} s^{-1} for the reaction between $HO_2^{\bullet}$ and $H_2O_2^{\bullet+}$ and $k = 0.5 \times 10^6$ litre mole^{-1} s^{-1} for the reaction between $2H_2O_2^{\bullet+}$ species.

In organic solvents the formation of hydroperoxy-radicals is postulated in the oxidation of cyclohexadiene, dihydronaphthalene, and 9,10-dihydrophenanthrene:



or



This is proved by the fact that in the oxidation of the above hydrocarbons hydrogen peroxide is formed and also by the similarity of the disproportionation rate constants for the peroxy-radicals derived from the hydrocarbons. For example, in chlorobenzene at 30 °C $k = 6.3 \times 10^8$ litre mole^{-1} s^{-1} in the oxidation of cyclohexadiene and $k = 3.5 \times 10^8$ litre mole^{-1} s^{-1} in the oxidation of dihydronaphthalene. The sharp difference between the rate constants for the disproportionation of hydroperoxy-radicals in organic solvents and in water can be accounted for by the fact that in water $HO_2^{\bullet}$ radicals are linked by hydrogen bonds of the type $HO_2^{\bullet}\ldots HOH$ and $^{\bullet}O_2H\ldots O\begin{matrix}H\\H\end{matrix}$, which sharply reduces the rate of their interaction. In a hydrocarbon solvent the rate constant for the interaction of $HO_2^{\bullet}$ radicals is close to the diffusional rate constant (Table 7).

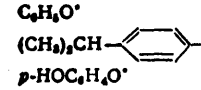
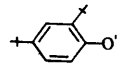
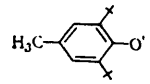
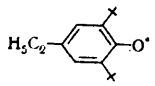
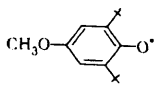
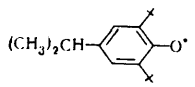
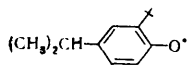
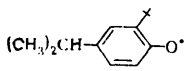
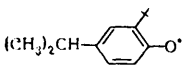
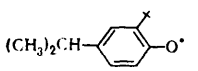
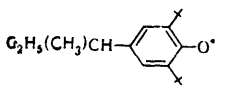
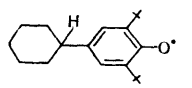
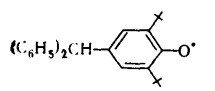
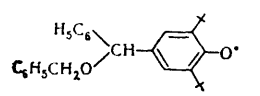
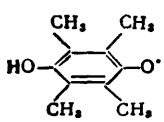
2. Tertiary Peroxy-radicals

The reaction between tertiary peroxy-radicals has been investigated in detail for cumenyl peroxy-radicals. Among the products of the initiated oxidation of cumene, Blanchard[94] detected a peroxide acetophenone and proposed the following reaction mechanism:

$$2\,RO_2^{\bullet} \rightarrow [ROOOOR] \rightarrow 2\,\overline{RO}^{\bullet} + O_2\,,$$
$$2\,\overline{RO}^{\bullet} \rightarrow ROOR\,,$$
$$RO^{\bullet} \rightarrow CH_3^{\bullet} + CH_3COC_6H_5\,.$$

The formation of oxygen in the reaction $RO_2^{\bullet} + RO^*O^{\bullet *} \rightarrow ROO^*R + OO^*$ was demonstrated by Bartlett and Traylor[95,96] in experiments with heavy oxygen (oxygen-18). Oxygen

Table 5.

Radical	Solvent	t, °C	lg ($2k$)	lg($2A$)	E, kcal mole^{-1}	Method	Refs
HO•	H_2O, pH=7	25	9.9	—	—	MCR	82
HO•	H_2O, pH=0.4÷3	25	10.08	—	—	PR	83
$(CH_3)_2CO$•	CCl_4	10—55	8.32	8.32	0	RSM	84
C_6H_5O•	H_2O	20	9.03	—	—	FP	85
	cyclo-C_6H_{12}	25	0.92	—	—	kinetic	86
p-HOC_6H_4O•	H_2O, pH=7	25	9.34	—	—	PR	87
	alkane	20	7.60	—	—	FP	85
	CCl_4	20	8.48	—	—	FP	85
	CCl_4	20	7.42	—	—	FP	85
	$CHCl_3$	—30	5.70	—	—	NMR	88
	C_6H_6	10—50	0.41 (10°)	5.24	6.23	kinetic	89
	cyclo-C_6H_{12}	10—50	0.75 (10°)	4.91	5.50	ditto	89
	p-$CH_3OC_6H_4OH$	10—50	0.55 (10°)	6.13	7.20	»	89
	C_6H_5CN	10—50	0.70 (10°)	7.02	8.16	»	89
	C_6H_5Cl	10—50	0.50 (10°)	5.88	6.94	»	89
	C_6H_6	10—50	1.78 (10°)	5.22	7.04	»	90
	C_6H_6	10—50	0.10 (10°)	6.23	7.93	»	90
	cyclo-C_6H_{22}	25	0.62	—	—	»	86
	cyclo-C_6H_{12}	25	0.145	—	—	»	86
	alkane	25	9.00	—	—	FP	91
	H_2O+C_2H_5OH	25	9.20	—	—	FP	91

was passed through cumene undergoing oxidation and containing together with $^{16}O=^{16}O$ molecules also 1–6% of $^{18}O=^{18}O$. At the outlet from the reactor the oxygen was analysed mass-spectrometrically and the presence of $^{16}O=^{18}O$ molecules was established, thus demonstrating the occurrence of the reaction $R-^{16}O-^{16}O^{\bullet} + {}^{18}O-{}^{18}O-R \rightarrow R^{16}O^{\bullet} + {}^{16}O={}^{18}O + R^{18}O^{\bullet}$. In experiments on the sensitised oxidation of cumene under conditions such that the chains

are short it was established that the amount of oxygen evolved as a result of the reaction between two peroxy-radicals exceeds by a factor of 1.7–2.6 the number of elementary steps involving the disappearance of free radicals in this reaction[96]. Consequently the interaction of two tertiary peroxy-radicals has the following mechanism:

$$2\,RO_2^{\cdot} \longrightarrow \begin{cases} \longrightarrow ROOR + O_2 \\ \longrightarrow 2\,RO^{\cdot} + O_2 \end{cases}.$$

The recombination of alkoxy-radicals and their liberation into the bulk phase has been investigated in the decomposition of di-t-butyl peroxyoxalate[97]:

$$(CH_3)_3COOCOCOOOC(CH_3)_3 \rightarrow 2\,(CH_3)_3CO^{\cdot} + 2\,CO_2\,,$$
$$\overline{2\,(CH_3)_3CO^{\cdot}} \longrightarrow (CH_3)_3COOC(CH_3)_3\,,$$
$$\overline{2\,(CH_3)_3CO^{\cdot}} \longrightarrow 2\,(CH_3)_3CO^{\cdot}\,,$$
$$(CH_3)_3CO^{\cdot} + RH \rightarrow (CH_3)_3COH + R^{\cdot}\,,$$
$$(CH_3)_3CO^{\cdot} \rightarrow CH_3COCH_3 + CH_3^{\cdot}\,,$$

The decomposition products are a peroxide and an alcohol. Table 6 shows that, with increase in the viscosity of the solvent, the yield of the peroxide increases at the expense of a reduced yield of the alcohol (temperature 45 °C).[97]

Table 6. Products of decomposition of di-t-butyl peroxalate in various solvents.

Solvent	Viscosity, cP	Yield of ROOR, %	Yield of ROH, %
n-C_5H_{12}	2.20	3.9	94.6
C_6H_6	5.6	5.5	53
$(CH_3)_3COH$	46	10	...
Nujol	1000	76.8	23.2

Evidently a similar situation arises in reactions between peroxy-radicals:

$$2\,RO_2^{\cdot} \rightarrow O_2 + 2\,\overline{RO^{\cdot}} \longrightarrow \begin{cases} \longrightarrow ROOR \\ \longrightarrow 2\,RO^{\cdot} \end{cases}.$$

This mechanism of the interaction between tertiary peroxy-radicals has been demonstrated for t-butylperoxy-radicals[98] in a study of the decomposition of t-butyl hydroperoxide initiated with azobisisobutyronitrile. It was established that the rate of decomposition of the hydroperoxide w, measured from the amount of oxygen evolved, is directly proportional to the rate of initiation w_i and the ratio w/w_i is significantly greater than unity: it is 9 at 65 °C and 4 at 36 °C. The rate constant for the reaction $2RO_2^{\cdot} \rightarrow 2RO^{\cdot} + O_2$ is 19.5×10^2 litre mole^{-1} s^{-1} at 22 °C with E = 15.5 kcal mole^{-1}, while for the reaction $2RO_2^{\cdot} \rightarrow ROOR + O_2$, $k = 3.9 \times 10^2$ mole^{-1} s^{-1} (also at 22 °C) with E = 10.2 kcal mole^{-1}.

The data for the isotope effect in the oxidation of cumene with deuterated methyl groups are somewhat inconsistent with the above mechanism[99]. The mechanism leads to the expectation that the replacement of a CH_3 group in cumene by CD_3 should not affect the rate of reaction between two $RO_2^{\cdot}$ radicals and consequently also the rate of oxidation. However, experiments have shown that [CD_3]cumene is oxidised somewhat faster owing to a lower rate of chain termination. This contradiction can be accounted for by postulating a more complex mechanism for chain termination in cumene undergoing oxidation, in particular by the participation in these processes of the radicals $CH_3OO^{\cdot}$ (and $CD_3OO^{\cdot}$). The overall mechanism of chain termination of cumene undergoing oxidation is as follows[100]

$$2\,ROO^{\cdot} \rightarrow [ROOOOR] \begin{cases} \nearrow ROOR + O_2 \\ \searrow 2\,RO^{\cdot} + O_2 \end{cases},$$
$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}\,,$$
$$RO^{\cdot} \rightarrow CH_3^{\cdot} + CH_3COC_6H_5\,,$$
$$CH_3^{\cdot} + O_2 \rightarrow CH_3OO^{\cdot}\,,$$
$$CH_3OO^{\cdot} + ROO^{\cdot} \rightarrow ROH + O_2 + CH_2O\,,$$
$$RO^{\cdot} + ROOH \rightarrow ROH + ROO^{\cdot}\,.$$

The involvement of methylperoxy-radicals in chain termination can be avoided by introducing into cumene, cumenyl hydroperoxide at a concentration such that the following rapid transfer reaction takes place[101]:

$$CH_3OO^{\cdot} + ROOH \rightarrow CH_3OOH + RO_2^{\cdot}\,.$$

The rate constants for the reactions of tertiary peroxy-radicals are in the range 10^3–10^5 litre mole^{-1} s^{-1}.

The reaction of ozone with $KOOC(CH_3)_3$ at −78 °C yielded a solid[102] soluble in pentane which decomposes at −30 °C with formation of t-butyl peroxide and O_2. It is suggested that it is the tetroxide ROOOOR. The reaction of t-butyl hydroperoxide with lead tetra-acetate in dichloromethane at a low temperature[103] gives rise to a substance which decomposes reversibly to peroxy-radicals on raising the temperature from −110° to −85 °C. At a higher temperature (in excess of −82 °C) it decomposes with evolution of O_2 and irreversible destruction of free radicals. The results have been interpreted as follows[103]:

$$2\,RO_2^{\cdot} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ROOOOR \xrightarrow{k_2} \overline{2\,RO^{\cdot} + O_2} \begin{cases} \nearrow ROOR + O_2 \\ \searrow 2\,RO^{\cdot} + O_2 \end{cases},$$
$$K = \frac{k_{-1}}{k_1},\ \lg K = 3.55 - 6.0/\theta,\ \lg k_2 = 9.27 - 11.0/\theta\,,$$
$$\theta = 4.57\,T/1000.$$

3. Secondary Peroxy-radicals

The C–H bond is involved in the elementary reaction step between two secondary peroxy-radicals[104] as shown by the reaction products and the isotope effect. The interaction of two peroxy-radicals derived from ethylbenzene yields one molecule of acetophenone[104], while in the interaction of cyclohexylperoxy-radicals the principal products are cyclohexanol and cyclohexanone in equal amounts[31]. The isotope effect in the reaction between two $RO_2^{\cdot}$ radicals amounts to 1.9 (at 60 °C) in the case of ethylbenzene[104], while for the peroxy-radicals derived from styrene and α-deuterostyrene $k_H/k_D = 3.9$ (30 °C) with $E_D - E_H = 1.9$ kcal mole^{-1}.[105] These results agree well with the mechanism proposed by Russell[104]:

$$2R_2CHOO^{\cdot} \rightarrow R_2C{=}O + O_2 + HOCHR_2\,.$$

A reaction of this kind can take place in two ways: via a cyclic activated complex or via the intermediate formation of the tetroxide. Calculation shows[2] that the formation of a cyclic activated complex should involve a high negative entropy of activation, which leads to the calculated constant $k \simeq 1$. The pathway via the intermediate formation of the tetroxide should be faster:

$$2\,R_2CHOO^{\cdot} \rightarrow R_2CHOOOOCHR_2 \rightarrow R_2C{=}O + R_2CHOH + O_2\,.$$

This mechanism was recently confirmed by Howard and Ingold[105] in the following way. According to this mechanism and the spin conservation rule, the reactions between two peroxy-radicals should result in the formation of singlet oxygen. Singlet oxygen is known to react rapidly

with 9,10-diphenylanthracene with formation of an *endo*-peroxide. Secondary peroxy-radicals were obtained in benzene solutions by the reaction of s-butyl hydroperoxide with Ce^{4+} ions. The addition of 9,10-diphenylanthracene to this type of system leads to the formation of an *endo*-peroxide. This demonstrates the formation of singlet oxygen by the reaction

$$2\,R_2CHOO^{\cdot} \rightarrow R_2CHOOOOCHR_2 \rightarrow R_2C{=}O + R_2CHOH + {}^1O_2 .$$

If instead of a secondary hydroperoxide, a tertiary hydroperoxide is introduced, an *endo*-peroxide does not form in agreement with the mechanism

$$2\,RO_2^{\cdot} \rightarrow ROOOOR \rightarrow 2\overline{RO}^{\cdot} + {}^3O_2 .$$

The rate constants for the reactions of secondary peroxy-radicals are of the order of 10^7-10^8 litre mole^{-1} s^{-1}. This mechanism can be revised slightly on the basis of data for the decomposition of peroxy-macroradicals derived from polyethylene[106]. It has been established that bond dissociation in the sensitised oxidation of linear polyethylene takes place in the peroxy-radical stage by the following reactions

$$RO_2^{\cdot} \rightarrow \text{dissociation of C-C bond}$$
$$2\,RO_2^{\cdot} \rightarrow \text{dissociation of C-C bond,}$$

The dissociation of the C–C bond following the reaction between two $RO_2^{\cdot}$ radicals can be accounted for by postulating the formation of alkoxy-macroradicals, which subsequently break down with dissociation of the C–C bond:

$$2\,RO_2^{\cdot} \rightarrow O_2 + 2RO^{\cdot} ,$$
$$RO^{\cdot} \rightarrow \text{aldehyde} + R'^{\cdot} .$$

The linear polyethylene contained virtually no tertiary C–H bonds and therefore the alkoxy-radicals were obtained by the reaction between secondary peroxy-radicals, for which the following general mechanism may be proposed:

$$2\,ROO^{\cdot} \rightarrow ROOOOR \begin{cases} \rightarrow {}^1O_2 + \text{ketone} + \text{alcohol} \\ \rightarrow {}^3O_2 + 2\overline{RO}^{\cdot} \begin{cases} \rightarrow \text{ketone} + \text{alcohol} \\ \rightarrow ROOR \\ \rightarrow 2RO^{\cdot} \end{cases} \end{cases} ,$$
$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot} ,$$
$$RO^{\cdot} \rightarrow \text{aldehyde} + R'^{\cdot} .$$

Quantitative measurements show that in polyethylene undergoing oxidation in chlorobenzene at 115 °C there are six C–C bond dissociation steps for each 100 elementary reaction steps between two $RO_2^{\cdot}$ radicals[106]. Thus for macroradicals also the reaction $2RO_2^{\cdot} \rightarrow$ alcohol + ketone + $^1O_2$ appears to predominate.

Among the reaction products from cyclohexylperoxy-radicals obtained by pulse radiolysis in cyclohexane at 25 °C, cyclohexene and a hydroperoxide were detected, together with an alcohol and ketone, with radiation-chemical yields of 1.14 and 1.10 respectively[31]. Under these conditions (low temperature, high $RO_2^{\cdot}$ concentration), the hydroperoxide could not form in an appreciable amount by the reaction of the peroxy-radical with cyclohexane. One may postulate the formation of cyclohexene by disproportionation between two cyclohexyl radicals. Then dicyclohexyl, for which $k_d/k_r = 1$ (Table 7), should form with the same radiation-chemical yield. However, experiments have established that for dicyclohexyl $G = 0.3$, i.e. is 4 times smaller than for cyclohexene. This suggests a new disproportionation reaction of peroxy-radicals:

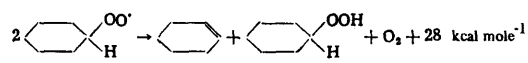


Table 7. Rate constants for the interactions of peroxy-radicals.

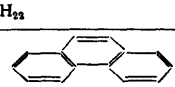
Radical	Solvent	t, °C	lg (2k)	lg(2A)	E, kcal mole^{-1}	Method	Refs.
$HO_2^{\cdot}$	H_2O, pH=0,5—1,5	1—43	6.82 (30°)	11.08	5.9	FM	107
$HO_2^{\cdot}$	H_2O, pH=2,7	25	6.40	—	—	FP	108
$HO_2^{\cdot}$	H_2O, pH=2	23	6.64	—	—	PR	90
$HO_2^{\cdot}$	H_2O, pH=2	23	6.74	—	—	PR	109
$HO_2^{\cdot}$	H_2O, pH=2	—10—50	6.40 (30°)	9.8	4.7	FM	110
$HO_2^{\cdot}$	CCl_4	30	10.05	—	—	RSM	111
$HO_2^{\cdot}$	C_6H_5Cl	30	9.10	—	—	RSM	111
$HO_2^{\cdot}$	C_6H_5Cl	30	8.85	—	—	RSM	111
$HO_2^{\cdot}$	CH_3CN	30	6.935	—	—	RSM	111
$HO_2^{\cdot}$	n-$C_{10}H_{22}$	30	9.43	—	—	RSM	111
$HO_2^{\cdot}$		30	7.78	—	—	RSM	112
$HO_2^{\cdot}$		30	7.82	—	—	RSM	111
$CH_3(CH_2)_3OO^{\cdot}$	CH_3OH	7	7.48	—	—	FM	110
$CH_3(CH_2)_3OO^{\cdot}$		30	7.60	—	—	RSM	113

Table 7 (cont'd).

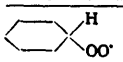
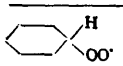
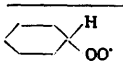
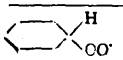
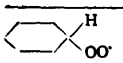
Radical	Solvent	t, °C	lg (2k)	lg(2A)	E, kcal mole^{-1}	Method	Refs.
$(CH_3)_2C{=}CCH_2OO^{\cdot}$ (CH$_3$ above CH$_2$)	RH	30	5.805	—	—	RSM	113
$C_6H_5CH_2OO^{\cdot}$	RH	30	8.48	—	—	RSM	112
m-$CH_3C_6H_4CH_2OO^{\cdot}$	RH	30	8.48	—	—	RSM	112
o-$CH_3C_6H_4CH_2OO^{\cdot}$	RH	30	8.18	—	—	RSM	112
p-$CH_3C_6H_4CH_2OO^{\cdot}$	RH	30	8.48	—	—	RSM	112
$CH_3CH(OO^{\cdot})CH_2CH_3$		30	6.18	—	—	RSM	113
$(CH_3)_2C(OO^{\cdot})CH(CH_3)CH(CH_3)_2$	RH	42—78	5.545	—	—	RSM	114
	RH	23	6.505	—	—	PR	115
		30	6.30	—	—	RSM	113
		40—70	6.68 (30°)	7.84	1.6	NKR	116
	$CH_3COOC_2H_5$	40—70	5.37 (30°)	9.64	5.9	NKR	116
	CH_3COOH	40—70	5.31 (30°)	9.72	6.1	NKR	116
$(CH_3)_2C{=}CHCH(OO^{\cdot})C_2H_5$	RH	40—60	6.48 (30°)	7.415	1.2	NKR	117
$CH_2{=}CHCH(OO^{\cdot})(CH_2)_6CH_3$	RH	25	7.08	—	—	PR	31
$CH_2{=}CHCH(OO^{\cdot})(CH_2)_4CH_3$	RH	30	8.41	—	—	RSM	113
$CH_2{=}CHCH(OO^{\cdot})(CH_2)_6CH_3$	RH	25—40	5.3	—	—	NKR	118
$CH_2{=}CHCH(OO^{\cdot})CH{=}CH_2$	RH	30	9.03	—	—	RSM	119
$C_2H_5CH{=}CHCH(OO^{\cdot})C_2H_5$	RH	30	6.84	—	—	RSM	119
$CH_3(CH_2)_2CH{=}CH(OO^{\cdot})CH$	RH	11	5.70	—	—	RSM	118
$C_2H_5OOC(CH_2)_7CH{=}CH$	RH	25	5.48	—	—	NKR	118
$CH_3(CH_2)_7CH(OO^{\cdot})CH{=}CH(CH_2)_7CO_2CH_3$	RH	30	6.02	—	—	RSM	119
$(CH_3)_2C{=}CHCH(OO^{\cdot})CH_2C(CH_3){=}CHCH_3$	RH	0	5.59	—	—	NKR	118
$(CH_3)_2C{=}CHCH(OO^{\cdot})CH_2C(CH_3){=}CHCH_3$	RH	15	5.72	—	—	RSM	118
$(CH_3)_2C{=}CHCH(OO^{\cdot})CH_2C(CH_3){=}CHCH_3$	RH	25	5.72	—	—	NKR	118
$CH_3(CH_2)_4CH{=}CHCH(OO^{\cdot})CH$ / $CH_3OOC(CH_2)_7CH{=}CH$	RH	30	6.945	—	—	RSM	119
$CH_3CH_2CH{=}CHCH(OO^{\cdot})CH{=}CHCH_2$ / $CH_3OOC(CH_2)_7CH{=}CH$	RH	30	7.555	—	—	RSM	119
$CH_2{=}C(CH_3)(CH_2)_2C(CH_3){=}CH{-}CH(OO^{\cdot}){-}CH_2{=}(CH_3)C(CH_2)_2CH{=}CH{-}CH_3$	RH	25	5.45	—	—	NKR	118
		40	5.00			NKR	118
$CH_3(CH_2)_2C{\equiv}CCH(OO^{\cdot})(CH_2)_2CH_3$	RH	30	7.145	—	—	RSM	118

Table 7 (cont'd).

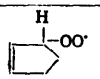
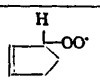
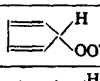
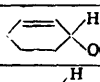
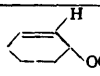
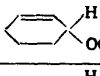
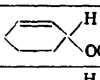
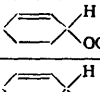
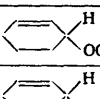
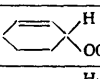
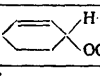
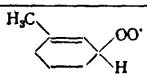
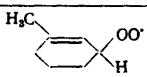
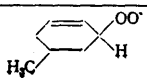
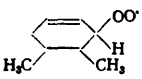
Radical	Solvent	t, °C	lg (2k)	lg (2A)	E, kcal mole^{-1}	Method	Refs.
	CH_3OH	30	7.175	—	—	FM	100
	RH	30	6.79	—	—	RSM	119
	RH	30	9.03	—	—	RSM	119
	RH	15	5.98	—	—	RSM	118
	RH	20—50	6.20	—	—	NKR	121
	RH	56	6.30	—	—	RSM	122
	RH	15	5.855	—	—	RSM	123
		30	6.75	—	—	RSM	120
	RH	30	6.42	—	—	NKR	124
	RH	mean value	6.25	—	—		
	CH_3OH	30	6.45	10.8	6.0	FM	110
	RH	15	5.70	—	—	RSM	118
	RH	40	5.935	—	—	NKR	121
	RH	40	6.52	—	—	NKR	125
	RH	40	6.43	—	—	NKR	125
$C_6H_5CH(CH_3)OO^{\cdot}$	RH	50—90	7.28	—	—	RSM	126
$C_6H_5CH(CH_3)OO^{\cdot}$	RH	30	7.60	—	—	RSM	120
$C_6H_5CH(CH_3)OO^{\cdot}$	RH	30	7.60	—	—	NKR	127
$C_6H_5\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	13—50	7.71 (30°)	9.01	1.8	RSM	128
$C_6H_5\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}DCH_2\sim$	C_6H_5Cl	13—50	7.12 (30°)	9.80	3.7	RSM	105
$p\text{-}CH_3OC_6H_4\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	7.64	—	—	RSM	105
$p\text{-}CH_3C_6H_4\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	7.75	—	—	RSM	105
$C_6H_5\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	7.86	—	—	RSM	105
$p\text{-}ClC_6H_4\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	7.99	—	—	RSM	105
$m\text{-}ClC_6H_4\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	8.03	—	—	RSM	105
$p\text{-}CNC_6H_4\underset{\displaystyle OO^{\cdot}}{\underset{\vert}{C}}HCH_2\sim$	C_6H_5Cl	40	9.45	—	—	RSM	105

Table 7 (cont'd).

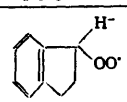
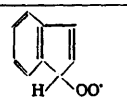
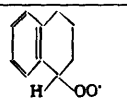
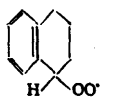
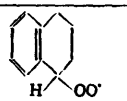
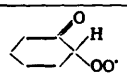
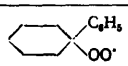
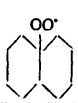
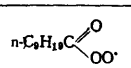
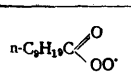
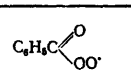
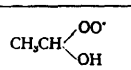
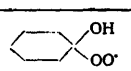
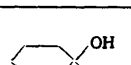
Radical	Solvent	t, °C	lg ($2k_2$)	lg ($2k_4$)	E, kcal mole^{-1}	Method	Refs.
$C_6H_5\dot{C}HCH(CH_3)\sim$	C_6H_5Cl	30	7.505	—	—	RSM	129
$C_6H_5\dot{C}HCH{=}CH_2$	C_6H_5Cl	30	8.645	—	—	RSM	120
$C_6H_5\dot{C}HCH{=}CHCH_3$	RH	30	6.58	—	—	RSM	119
$(C_6H_5)_2CHOO^{\cdot}$	RH	30	8.20	—	—	RSM	120
$(C_6H_5)_2CDOO^{\cdot}$	RH	30	8.06	—	—	RSM	120
$C_6H_5\dot{C}HCH_2C_6H_5$	RH	30	7.30	—	—	RSM	112
	RH	30	6.91	—	—	RSM	112
	C_6H_5Cl	30	7.70	—	—	RSM	129
	RH	25	7.33	—	—	RSM	130
	RH	40	6.98	—	—	NKR	124
	RH	13—50	6.82 (30°)	9.93	4.3	RSM	120
	CH_3OH	—10—50	6.67 (30°)	10.0	4.6	FM	110
$C_6H_5(n\text{-}C_3H_7)CHOO^{\cdot}$	RH	30	7.70	—	—	RSM	112
$(CH_3)_2\dot{C}CHC(CH_3)_3$	CH_3OH	—10—50	3.92 (30°)	11.0	9.8	FM	110
$(CH_3)_2\dot{C}CHC(CH_3)_3$	C_6H_6	—10—50	4.18 (30°)	9.2	7.0	FM	110
$CH_3\dot{C}OCHCH_3$	RH	35—75	6.35 (30°)	7.48	1.7	NKR	116
$CH_3\dot{C}OCHC_2H_5$	RH	35—75	6.32 (30°)	7.48	1.6	NKR	116
	RH	75	6.43	—	—	NKR	131
$(CH_3)_3COO^{\cdot}$	CH_3OH	—10—50	3.54 (30°)	10.4	9.2	FM	110
$(CH_3)_3COO^{\cdot}$	CH_3OH	36—65	2.59 (22°)	10.56	10.2	FM	96
$(CH_3)_3COO^{\cdot}$	C_6H_6	—10—50	3.11 (30°)	6.4	4.5	FM	110
$(CH_3)_3COO^{\cdot}$	$C_6H_5CH(CH_3)_2$	25—65	3.15 (35°)	9.8	7.0	NKR	132
$(CH_3)_3COO^{\cdot}$	$n\text{-}C_6H_{14}$	—41	4.115	9.145	7.2	ESR	133
$(CH_3)_3COO^{\cdot}$		+48— —24	4.06 (41°)	9.99	8.5	ESR	133
$(CH_3)_3COO^{\cdot}$		+48— —24	4.19 (41°)	10.12	8.5	ESR	133
$(CH_3)_3COO^{\cdot}$	$C_2H_5CH(CH_3)C_2H_5$	+48— —24	4.26 (41°)	10.12	8.4	ESR	133
$(CH_3)_3COO^{\cdot}$	$(CH_3)_3COOH$	—38—0	4.00 (41°)	9.79	8.3	ESR	101
$(CH_3)_3COO^{\cdot}$	$C_6H_5CH(CH_3)_2$	30	3.11	—	—	FM	101
$(CH_3)_3CCH_2\dot{C}(CH_3)_2OO^{\cdot}$	$C_6H_5CH(CH_3)_2$	30	4.01	—	—	FM	101

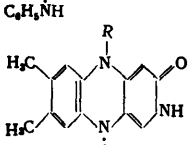
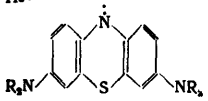
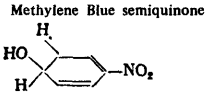
Table 7 (cont'd).

Radical	Solvent	t, °C	lg (2k)	lg(2A)	E, kcal mole^{-1}	Method	Refs.
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	56	5.155	—	—	NKR	122
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	50	4.45	—	—	RSM	134
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	65	4.52	—	—	RSM	134
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	23	4.64	—	—	ESR	135
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	40	4.38	—	—	NKR	124
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	60	4.68	—	—	NKR	127
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	80	4.175	—	—	RSM	112
$C_6H_5(CH_3)_2COO^{\cdot}$	CH_3OH	—10—50	5.09 (30°)	10.7	7.8	FM	110
$C_6H_5(CH_3)_2COO^{\cdot}$	C_6H_6	—10—50	4.57 (30°)	8.8	5.8	FM	110
$C_6H_5(CH_3)_2COO^{\cdot}$	RH	25—65	4.27 (30°)	8.58	5.96	RSM	133
$C_6H_5C(CD_3)_2$ (OO·)	RH	30	4.08			RSM	136
p-$CH_3OC_6H_4C(CH_3)_2OO^{\cdot}$	RH	30	4.60	—	—	RSM	136
m-$CH_3OC_6H_4C(CH_3)_2OO^{\cdot}$	RH	30	4.90	—	—	RSM	136
o-$CH_3OC_6H_4C(CH_3)_2OO^{\cdot}$	RH	30	4.48	—	—	RSM	136
$(C_6H_5)_2(CH_3)COO^{\cdot}$	RH	30	4.97	—	—	RSM	112
$(C_6H_5)_2(CH_3)COO^{\cdot}$	RH	30	4.81	—	—	RSM	101
$(C_6H_5)_2(CH_3)COO^{\cdot}$	RH	50—88	5.98 (30°)	11.04	7.0	ESR	137
$(C_6H_5)_2(CH_3)COO^{\cdot}$	C_6H_6	—10—50	6.34 (30°)	8.1	2.5	FM	110
$C_6H_5(CH_3)(C_2H_5)COO^{\cdot}$	CH_3OH	—10—50	5.46 (30°)	9.4	5.5	FM	110
$C_6H_5(CH_3)(C_2H_5)COO^{\cdot}$	RH	30—56	4.43 (30°)	8.48	5.6	RSM	101
$C_6H_5(CH_3)(n\text{-}C_3H_7)COO^{\cdot}$	RH	30	5.64	—	—	RSM	112
	RH	30	5.20	—	—	RSM	112
$C_6H_5C(CH_3)CH_2\sim$ (OO·)	C_6H_5Cl	13—50	5.82 (30°)	8.50	3.7	RSM	129
	RH	60	5.18	—	—	NKR	127
$(CH_3)_2CCN$ (OO·)	C_6H_5Cl	80	7.20	—	—	NKR	138
$CH_3COC(CH_3)_2OO^{\cdot}$	RH	35—75	6.32 (30°)	7.48	1.6	NKR	116
	$n\text{-}C_{10}H_{22}$	5	7.53	—	—	RSM	139
	RH	5	6.875	—	—	RSM	139
	RH	5	8.32	—	—	RSM	140
	RH	23	8.08	—	—	PR	141
	RH	23	7.255	—	—	PR	31
	RH	75—90	5.37 (30°)	7.10	2.4	NKR	142

VI. REACTIONS OF MOLECULES WITH FREE VALENCES AT NITROGEN AND TIN ATOMS

Aromatic radicals with a free valence at a nitrogen atom interact very rapidly (Table 8). Very high rate constants have been obtained for the radicals R_3Sn.[44]

Table 8. Rate constants for the interactions of radicals having free valences at nitrogen and tin atoms.

Radical	Solvent	t, °C	lg (2k)	Method	References
$C_6H_5\dot{N}H$	H_2O	25	9.18	FP	143
	H_2O	25	8.48	FP	144
 Methylene Blue semiquinone	H_2O	25	9.38	FP	145
	H_2O	25	9.18	FP	146
	H_2O	25	8.78	PR	147
$(C_6H_5)_3Sn^{\cdot}$	cyclo-C_6H_{12}	25	9.48	RSM	44
$n\text{-}C_4H_9)_3Sn^{\cdot}$	cyclo-C_6H_{12}	25	9.18	RSM	44

VII. REACTIONS BETWEEN FREE RADICALS OF DIFFERENT TYPES

The reactions between H· and OH·, between H· and $HO_2^{\cdot}$, and between HO· and $HO_2^{\cdot}$ radicals are very rapid and their rates are limited by diffusion (Table 8). The rate of recombination of alkyl radicals with peroxy-radicals is not limited by diffusion but the reaction takes place as a rule with higher rate constants than the reaction between two peroxy-radicals (Table 9). In particular this is the reason for the inhibiting effect of triphenylmethane when the latter is introduced, for example, into cumene undergoing oxidation. The $C-O_2^{\cdot}$ bond in the radical $(C_6H_5)_3COO^{\cdot}$ is weak, its energy amounting to only 9 kcal mole^{-1},[148] and under oxidation conditions the following equilibrium obtains:

$$(C_6H_5)_3COO^{\cdot} \rightleftarrows (C_6H_5)_3C^{\cdot} + O_2 .$$

Therefore in a hydrocarbon undergoing oxidation there is always a fairly high concentration of triphenylmethyl radicals (the higher the temperature the higher the concentration) and there is rapid chain termination by the reaction

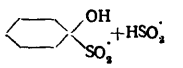
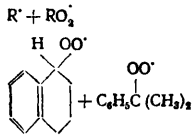
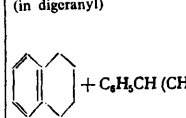
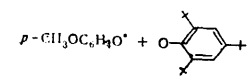
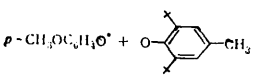
$$RO_2^{\cdot} + (C_6H_5)_3C^{\cdot} \rightarrow ROOC(C_6H_5)_3 .$$

VIII. EFFECT OF THE SOLVENT. VISCOSITY OF THE SOLVENT

If atoms or free radicals interact very rapidly so that $k > k_D$, diffusion limits the rate of the process and the diffusional rate constant k_D is measured experimentally. Then the viscosity of the solvent affects k_D: the higher the viscosity, the lower is the value of k_D. For low-molecular-weight radicals, $k_D \simeq 10^9-10^{10}$ litre mole^{-1} s^{-1}. Macroradicals diffuse much more slowly, so that even in not very viscous media diffusion may be rate-limiting for the reaction between two macroradicals. Since the viscosity of the solution increases as polymerisation proceeds, this entails a decrease of the rate constant for chain termination[79]. Data for the photopolymerisation of methyl methacrylate at 32 °C may be quoted as an example[59]:

% polymer.	0	15	25	35
$10^{-4}k$, litre mole^{-1} s^{-1}	570	140	35	8.8

Table 9. Rate constants for the interactions of radicals of different types.

Reaction	Solvent	t, °C	lgk	Method	Refs;
H·+·OH	H_2O	25	10.08	PR	9
H·+·OH	H_2O, pH = 0,4 ÷ 3	25	10.505	PR	10
H·+·OH	H_2O, 0,8 N H_2SO_4	25	9.85	PR	149
H·+·OH	H_2O, 0,4 N H_2SO_4	25	10.65	PR	15
$H^{\cdot}+HO_2^{\cdot}$	H_2O, acid medium	25	10.30	PR	151
$HO^{\cdot}+HO_2^{\cdot}$	H_2O, pH = 0,4 ÷ 3	25	10.175	PR	10
$HO^{\cdot}+HO_2^{\cdot}$	H_2O	25	10.04	PR	151
$HO^{\cdot}+HO_2^{\cdot}$	H_2O, pH = 0,5 ÷ 6,7	25	9.85	PR	152
$C_6H_5CH_2^{\cdot}+CH_3^{\cdot}CHOH$	$C_2H_5OH+HOCH_2CH(OH)CH_2OH$	25	8.30	PR	35
	cyclo-$C_6H_{11}OH$	25	8.45	PR	31
$(CH_3)_3C^{\cdot} + (n\text{-}C_4H_9)_3Sn^{\cdot}$	cyclo-C_6H_{12}	25	9.30	RSM	44
$(C_6H_5)_3C^{\cdot} + (C_6H_5)_3COO^{\cdot}$	$(C_6H_5)CH(CH_2)_2$	30	8.175	RSM	101
$R^{\cdot} + RO_2^{\cdot}$	(in ethyl linoleate)	25	7.70	NKR	118
$R^{\cdot} + RO_2^{\cdot}$	(in digeranyl)	25	7.00	NKR	118
		90	6.78	MCR	153
$C_6H_5COOO^{\cdot} + n\text{-}C_9H_{19}COOO^{\cdot}$	$C_6H_5CHO + n\text{-}C_9H_{19}CHO$	5	7.93	MCR	154
$C_6H_5C(CH_3)_2(OO^{\cdot}) + C_6H_5CHCH_3(OO^{\cdot})$	$C_6H_5CH(CH_3)_2 + C_6H_5C_2H_5$	60	5.87	MCR	155
$C_6H_5C(CH_3)_2(OO^{\cdot}) + C_6H_5CHCH_3(OO^{\cdot})$	$C_6H_5CH(CH_3)_2 + C_6H_5C_2H_5$	80	5.945	MCR	155
	C_6H_5Cl	24	7.725	SFT*	156
	C_6H_5Cl	24	8.00	SFT*	156

*The significance of the Russian abbreviation (TsINR, not explained in the text) is obscure, but the authors quoted used a stop-flow technique (SFT) (Ed. of Translation).

1. Internal Pressure of the Liquid

Since recombination of two radicals to give one molecule is accompanied by a decrease of free volume, an increase of the rate constant for the reaction between two free radicals with increasing internal pressure of the liquid is to be expected. Unfortunately there have been no systematic studies on this problem. A distinct effect of the internal pressure of the liquid on the reaction between

two radicals has been established for the process involving the competition between the disproportionation and recombination reactions of ethyl radicals[25], where a linear relation between $\lg(k_d/k_r)$ and $\Delta P_S^{1/2}$ has been demonstrated, P_S being the internal pressure of the solvent.

2. Non-specific Solvation

A free radical with a dipole moment is solvated in a polar solvent, i.e. it is surrounded by a "coating" of polar solvent molecules. If the solvent molecules do not form hydrogen bonds or π-complexes (specific solvation) with the free radical, then the solvation of a polar radical is due to electrostatic forces between its dipole and the polar medium. The rate constant for the reaction between polar species depends on the dielectric constant of the medium. If the dipole moment of the activated complex is higher than for the initial species, the reaction is faster in more polar media. The quantitative relation between the reaction rate constant and the dipole moments of the initial species and the activated complex on the one hand and the dielectric constant of the medium on the other is expressed by the following formula due to Kirkwood[157]:

$$\ln k = \ln k_0 - \frac{1}{kT}\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu_A^2}{r_A^3}+\frac{\mu_B^2}{r_B^3}-\frac{\mu_{\neq}^2}{r_{\neq}^3}\right),$$

where k is the Boltzmann constant, ϵ the dielectric constant of the medium, r_A, r_B, and $r_{\neq}$ are the radii of the initial species and of the activated complex, and μ_A, μ_B, and $\mu_{\neq}$ are their dipole moments. This formula was derived on the assumption that the medium surrounding the species is isotropic and the macroscopic dielectric constant ϵ holds also for the interaction between the species and the solvent molecules. Since strictly speaking this is not true, the above formula is approximate. The effect of non-specific solvation on the interaction between free radicals was investigated in detail by Zaikov, Maizus, and Emanuel' in the case of peroxy-radicals[116,158-160].

It was established that, when ethyl methyl ketone is diluted with various solvents (benzene, carbon tetrachloride, acetic acid, decane, and *p*-dichlorobenzene), the rate constant for the reaction between the peroxy-radicals derived from ethyl methyl ketone increases with ϵ and Kirkwood's formula holds satisfactorily:

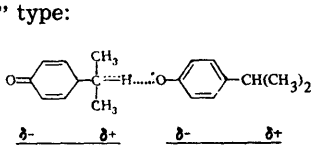
$$\lg k = A + B\frac{\varepsilon-1}{2\varepsilon+1}.$$

At 60°C $A = 3.36$ and $B = 6.0$. By extrapolation to $\epsilon = 0$ and $1/\epsilon \to 0$, the activation energies $E_{\epsilon\to 0} = 6.5$ kcal mole^{-1} and $E_{\epsilon\to\infty} = 1.2$ kcal mole^{-1} were obtained.

A linear relation between E and $(\epsilon-1)/\epsilon$ holds for the disproportionation reaction of 2,6-di-t-butyl-4-isopropylphenoxy-radicals[89]:

$$E = E_0 + A\frac{\varepsilon-1}{\varepsilon}.$$

This relation is consistent with theoretical calculations. The reaction of two phenoxy-radicals constitutes, from the electrostatic standpoint, the interaction of two dipoles of the "head to tail" type:



When the dielectric constant changes from ϵ_1 to ϵ_2, the energy of this interaction is altered by an amount:

$$\Delta E = -\frac{28.9\,\mu_A\mu_B\Delta\varepsilon}{\varepsilon_1\varepsilon_2 r^3},$$

or on transition from $\epsilon = 1$ to $\epsilon = \epsilon$ with $\mu_A = \mu_B$, we obtain

$$\Delta E = \frac{28.9\,\mu^2(\varepsilon-1)}{\varepsilon r^3},$$

which agrees with the experimental relation.

3. Specific Solvation

Radicals with a free valence at nitrogen and oxygen atoms can form a hydrogen bond of the type Y...H–X, which should be reflected in their reactivity. A hydrogen bond of the type ROO...H–X has been suggested[161] and its formation has been proved by Zaikov, Maisuz, and Emanuel'.[116,162-164]

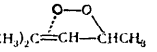
According to Zaikov et al.[162], the equilibrium constant for the reaction

$$CH_3COCHOO^{\cdot} + H_2O \rightleftarrows CH_3COCH_2OO^{\cdot}\ldots HOH$$

corresponds to $\lg K = 4.88 + 4.8/\theta$, where $\theta = 4.57T/1000$ (K is expressed in litre mole^{-1}).

The radical hydrogen bond appreciably retards the reaction between two peroxy-radicals[162,163]. However, for the peroxy-radical derived from ethyl methyl ketone[163], $2k(RO_2^{\cdot} + RO_2^{\cdot}) = 18\times10^5$ litre mole^{-1} s^{-1} and $2k(RO_2^{\cdot}\ldots HOH + RO_2^{\cdot}\ldots HOH) = 0.70\times10^5$ litre mole^{-1} s^{-1} at 60°C, $E_{RO_2^{\cdot}} = 1.6$ kcal mole^{-1}, $E_{RO_2^{\cdot}\ldots HOH} = 4.6$ kcal mole^{-1}, $\lg 2A_{RO_2^{\cdot}} = 7.30$, and $\lg 2A_{RO_2^{\cdot}\ldots HOH} = 7.86$. The existence of the hydrogen bond has been demonstrated kinetically for the cyclohexylperoxy-radical and t-butyl alcohol[116], the equilibrium constant corresponding to $\lg K = 3.69 + 3.5/\theta$ with $\theta = 4.57T/100$ (K expressed in litre mole^{-1}).

The rate constants for the interaction of cyclohexylperoxy-radicals do not differ greatly for solvated and unsolvated radicals[116]: $2k_{RO_2^{\cdot}} = 5.0\times10^6$ and $2k_{RO_2^{\cdot}\ldots MOR'} = 1.6\times10^6$. Thus a hydrogen bond to a free radical lowers the rate of its destruction by reaction with other radicals and consequently increases the steady-state concentration of radicals in the system. However, the overall rate of the chain reaction usually falls in the presence of a solvent forming hydrogen bonds, since the hydrogen bond also retards the chain propagation reaction. Thus, as a result of the formation of hydrogen bonds in the system, free radicals become less active but their steady-state concentration increases. An interesting exception are the peroxy-radicals of 2-methylpent-2-ene[165], the rate constants for the interaction of which with one another and with the hydrocarbon increase as alcohol is added to the hydrocarbon. This has been explained by the formation of an intramolecular π-bond:



which in the presence of an alcohol dissociates as a result of the formation of the hydrogen bond; the hydrogen-bonded peroxy-radicals are apparently less active than the radicals with the intramolecular π-bond.

REFERENCES

1. E. F. Caldin, "Fast Reactions in Solution" (Translated into Russian), Izd. Mir, Moscow, 1966.
2. N. M. Emanuel', E. T. Denisov, and Z. K. Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidfoi Faze" (Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase), Izd. Nauka, Moscow, 1965.
3. Kh. S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966.
4. D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance" (Translated into Russian), Inostr. Lit., Moscow, 1961.
5. L. A. Blyumenfel'd, V. V. Voevodskii, and A. G. Semenov, "Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii" (Applications of Electron Spin Resonance in Chemistry), Izd. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1962.
6. V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, N. V. Zakharov, A. A. Vichutinskii, and V. F. Tsepalov, "Khemilyuminestsentnye Metody Issledovaniya Medlennykh Khimicheskikh Protsessov" (Chemiluminescence Methods for the Investigation of Slow Chemical Processes), Izd. Nauka, Moscow, 1966.
7. A. K. Pikaev, "Impul'snyi Radioliz Vody i Vodnykh Rastvorov" (Pulse Radiolysis of Water and Aqueous Solutions), Izd. Nauka, Moscow, 1965.
8. R. M. Noyes, J. Amer. Chem. Soc., 81, 565 (1959).
9. J. K. Thomas, J. Phys. Chem., 67, 2593 (1963).
10. H. Friche and J. K. Thomas, Rad. Res. Suppl., 4, 35 (1964).
11. H. A. Schwarz, J. Phys. Chem., 67, 2827 (1963).
12. J. P. Sweet and J. K. Thomas, J. Phys. Chem., 68, 1363 (1964).
13. R. L. Strong, J. Amer. Chem. Soc., 87, 3563 (1965).
14. H. Rosman and R. M. Noyes, J. Amer. Chem. Soc., 80, 1410 (1958).
15. R. L. Strong and J. E. Willard, J. Amer. Chem. Soc., 79, 2098 (1957).
16. S. Aditya and J. E. Willard, J. Amer. Chem. Soc., 79, 2680 (1957).
17. R. Marshall and N. Davidson, J. Chem. Phys., 21, 1086 (1953).
18. J. Zimmerman and R. M. Noyes, J. Chem. Phys., 18, 658 (1950).
19. M. Smoluchowski, Z. Phys. Chem., 92, 129 (1917).
20. R. H. Stokes, P. J. Dunlop, and J. R. Hall, Trans. Faraday Soc., 49, 886 (1953).
21. E. W. Haycock, B. J. Alder, and J. H. Hildebrand, J. Chem. Phys., 21, 1601 (1953).
22. Handbook, "Energii Razryva Khimicheskikh Svyazei, Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Akad. Nauk SSSR, Moscow, 1962.
23. S. Fuhita, S. Kodama, and O. Toyama, Bull. Chem. Soc. Japan, 39, 1323 (1966).
24. P. S. Dixon, A. P. Stefani, and M. Szwarc, J. Amer. Chem. Soc., 85, 3344 (1963).
25. A. P. Stefani, J. Amer. Chem. Soc., 90, 1694 (1968).
26. P. S. Dixon, A. P. Stefani, and M. Szwarc, J. Amer. Chem. Soc., 85, 2551 (1963).
27. S. Kodama, S. Fujita, J. Takeiski, and O. Toyama, Bull. Chem. Soc. Japan, 39, 1009 (1966).
28. S. F. Nelsen and P. D. Bartlett, J. Amer. Chem. Soc., 88, 137 (1966).
29. W. A. Cramer, J. Phys. Chem., 71, 1171 (1967).
30. I. A. Taub and L. M. Dorfman, J. Amer. Chem. Soc., 84, 4053 (1962).
31. R. L. McCarthy and A. MacLachlan, Trans. Faraday Soc., 57, 1107 (1961).
32. J. C. Bevington, H. W. Melville, and R. P. Taylor, J. Polymer Sci., 12, 449 (1954); 14, 463 (1954).
33. R. F. Fessenden, J. Phys. Chem., 68, 1508 (1964).
34. R. D. Burkhart, J. Amer. Chem. Soc., 90, 273 (1968).
35. R. L. McCarthy and A. MacLachlan, Trans. Faraday Soc., 56, 1187 (1960).
36. G. Porter and M. W. Windsor, Nature, 180, 187 (1957).
37. D. J. Carlsson, J. A. Howard, and K. U. Ingold, J. Amer. Chem. Soc., 88, 4726 (1966).
38. W. I. Bengough and R. A. M. Thomson, Trans. Faraday Soc., 57, 1928 (1961).
39. H. W. Melville, J. C. Robb, and R. C. Tutton, Discuss. Faraday Soc., 14, 150 (1953).
40. Kh. S. Bagdasar'yan and A. F. Revzin, Kinetika i Kataliz, 4, 844 (1963).
41. C. H. Bamford and M. J. S. Dewar, Proc. Roy. Soc. A, 198, 252 (1949).
42. A. A. Vichutinskii, "Khemilyuminestsentnye Metody Kolichestvennogo Issledovaniya Zhidkofaznogo Okisleniya Uglevodorodov" (Chemiluminescence Methods for the Quantitative Study of the Liquid-Phase Oxidation of Hydrocarbons), Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1965.
43. L. Bateman, J. L. Bolland, and G. Gee, Trans. Faraday Soc., 47, 274 (1951).
44. D. J. Carlson and K. U. Ingold, J. Amer. Chem. Soc., 90, 1055 (1968).
45. S. Weiner and G. S. Hammond, J. Amer. Chem. Soc., 90, 1659 (1968).
46. L. M. Dorfman and I. A. Taub, J. Amer. Chem. Soc., 85, 2370 (1963).
47. W. A. Seddon and A. O. Allen, J. Phys. Chem., 71, 1914 (1967).
48. A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).
49. Z. Laita, J. Polymer Sci., 38, 247 (1959); Z. Laita and Z. Machacek, J. Polymer Sci., 38, 459 (1959).
50. W. Rabel and K. Uberreiter, Ber. Buns. Phys. Chem., 67, 514, 710 (1963).
51. C. H. Bamford and M. J. S. Dewar, Proc. Roy. Soc. A, 192, 308 (1948).
52. K. I. Gibov and G. P. Gladyshev, Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., 53 (1967).
53. G. M. Barnett, Trans. Faraday Soc., 46, 772 (1950).
54. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Amer. Chem. Soc., 73, 1700 (1951).
55. R. Axford, Proc. Roy. Soc. A, 197, 374 (1949).
56. Z. A. Sinitsyna and Kh. S. Bagdasar'yan, Zhur. Fiz. Khim., 32, 1319 (1958).
57. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Amer. Chem. Soc., 73, 5395 (1951).
58. W. Bengough and H. Melville, Proc. Roy. Soc. A, 225, 330 (1954).
59. W. I. Bengough and H. W. Melville, Proc. Roy. Soc. A, 249, 445 (1959).
60. H. W. Melville and A. F. Bickel, Trans. Faraday Soc., 45, 1049 (1949).
61. M. S. Matheson, E. B. Bevilacqua, E. E. Auer, and E. J. Hart, J. Amer. Chem. Soc., 71, 497 (1949).
62. M. H. Mackay and H. W. Melville, Trans. Faraday Soc., 45, 323 (1949).

63. G. Burnett, P. Evans, and H. Melville, Trans. Faraday Soc., 49, 1096, 1105 (1953).
64. D. H. Grant and N. Grassie, Trans. Faraday Soc., 55, 1042 (1959).
65. A. M. North and G. A. Reed, J. Polymer Sci., A1, 1311 (1963).
66. G. Burnett and W. Wright, Proc. Roy. Soc. A, 221, 28, 37, 41 (1954).
67. A. F. Revzin and Kh. S. Bagdasar'yan, Zhur. Fiz. Khim., 38, 1020 (1964) [Russ. J. Phys. Chem., No. 4 (1964)].
68. N. Colebourne, E. Collinson, D. J. Currie, and F. S. Dainton, Trans. Faraday Soc., 59, 1357 (1963).
69. C. Bamford, A. Jenkins, and R. Johnston, Proc. Roy. Soc. A, 241, 364 (1957).
70. W. Bengough, J. Polymer Sci., 28, 475 (1958).
71. N. Grassi and E. Vance, Trans. Faraday Soc., 52, 727 (1957).
72. E. Collinson, F. Dainton, and G. McNaughton, Trans. Faraday Soc., 53, 476, 499 (1957).
73. F. S. Dainton and W. D. Siley, Trans. Faraday Soc., 59, 1369 (1963).
74. P. Onyon, Trans. Faraday,Soc., 51, 400 (1955).
75. W. I. Bengough and W. Henderson, Trans. Faraday Soc., 61, 141 (1965).
76. E. F. Nosov, Kinetika i Kataliz, 8, 680 (1967).
77. A. N. Plyusnin and N. M. Chirkov, Teor. Eksper. Khim., 2, 777 (1966).
78. Chin-Hua S. Wu, G. S. Hammond, and J. M. Wright, J. Amer. Chem. Soc., 82, 5386 (1960).
79. G. P. Gladyshev and K. M. Gibov, "Polimerizatsiya pri Glubokikh Stepenyakh Prevrashcheniya i Metody Ee Issledovaniya" (Polymerisation at High Conversions and the Method for Its Investigation), Izd. Nauka, Alma-Ata, Kazakh. SSR, 1968.
80. A. F. Revzin, Uspekhi Khim., 35, 173 (1966) [Russ. Chem. Rev., No. 1 (1966)].
81. L. M. Strigun, L. S. Vartanyan, and N. M. Emanuel', Uspekhi Khim., 37, 969 (1968) [Russ. Chem. Rev., No. 6 (1968)].
82. H. A. Schwarz, J. Phys. Chem., 66, 255 (1962).
83. J. K. Thomas, J. Phys. Chem., 67, 2593 (1963).
84. D. J. Carlsson and K. U. Ingold, J. Amer. Chem. Soc., 89, 4891 (1967).
85. E. J. Land and G. Porter, Trans. Faraday Soc., 59, 2016 (1963).
86. A. Hubele, H. Suhr, and U. Heilmann, Ber., 95, 639 (1962).
87. G. E. Adams and B. D. Michael, Trans. Faraday Soc., 63, 1171 (1967).
88. D. J. Williams and R. Kreilick, J. Amer. Chem. Soc., 89, 3408 (1967).
89. C. D. Cook and B. E. Norcross, J. Amer. Chem. Soc., 81, 1176 (1959).
90. C. D. Cook and N. D. Gilmour, J. Org. Chem., 25, 1428 (1960).
91. N. K. Bridge and G. Porter, Proc. Roy. Soc. A, 244, 276 (1958).
92. G. Czapski and B. H. J. Bielski, J. Phys. Chem., 67, 2180 (1963).
93. B. H. J. Bielski and A. O. Allen, "Proceedings of the Second Tihany Symposium on Radiation Chemistry", Budapest, 1967, p. 81.
94. H. S. Blanchard, J. Amer. Chem. Soc., 81, 4548 (1959).
95. T. G. Taylor and P. D. Bartlett, Tetrahedron Letters, 30 (1960).
96. P. D. Bartlett and T. G. Traylor, J. Amer. Chem. Soc., 85, 2407 (1963).
97. R. Hiaft and T. G. Traylor, J. Amer. Chem. Soc., 87, 3766 (1965).
98. J. R. Thomas, J. Amer. Chem. Soc., 87, 3935 (1965).
99. C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wightman, J. Amer. Chem. Soc., 78, 1506 (1956).
100. T. G. Traylor and C. A. Russell, J. Amer. Chem. Soc., 87, 3698 (1965).
101. J. A. Howard and K. U. Ingold, Canad. J. Chem., 46, 2655 (1968).
102. N. A. Milas and S. M. Djokic, Chem. Ind., 405 (1962).
103. P. D. Bartlett and G. Guaraldi, J. Amer. Chem. Soc., 89, 4799 (1967).
104. G. A. Russell, J. Amer. Chem. Soc., 79, 3871 (1957).
105. J. A. Howard and K. U. Ingold, Canad. J. Chem., 43, 2737 (1965); J. Amer. Chem. Soc., 90, 1056 (1968).
106. P. A. Ivanchenko, V. V. Kharitonov, and E. T. Denisov, Vysokomol. Soed., A11, 1622 (1969).
107. B. H. J. Bielski and E. Saito, J. Phys. Chem., 66, 2266 (1962).
108. J. H. Baxendale, Rad. Res., 17, 312 (1962).
109. G. Czapski and L. M. Dorfman, J. Phys. Chem., 68, 1169 (1964).
110. J. R. Thomas and K. U. Ingold, Adv. Chem. Series, 75, 258 (1968).
111. J. A. Howard and K. U. Ingold, Canad. J. Chem., 45, 785 (1967).
112. J. A. Howard and K. U. Ingold, Canad. J. Chem., 45, 793 (1967).
113. J. A. Howard and K. U. Ingold, J. Amer. Chem. Soc., 90, 1058 (1968).
114. A. L. Buchachenko, K. Ya. Kaganskaya, and M. B. Neiman, Kinetika i Kataliz, 2, 44 (1961).
115. R. L. McCarthy and A. MacLachlan, J. Chem. Phys., 35, 1625 (1961).
116. G. E. Zaikov, "Rol' Sredy v Radikal'no-Tsepnykh Reaktsiyakh Okisleniya Organicheskikh Veshchestv" (The Role of the Medium in Radical-Chain Oxidation Reactions of Organic Substances), Doctoral Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Moscow, 1968.
117. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel', Izv. Akad. Nauk SSSR, Ser. Khim., 2265 (1968).
118. L. Bateman and G. Gee, Trans. Faraday Soc., 47, 155 (1951).
119. J. R. Thomas and K. U. Ingold, "Symposium on Oxidation, San Francisco, 1967", p. 1.
120. J. A. Howard and K. U. Ingold, Canad. J. Chem., 44, 1119 (1966).
121. J. C. Robb and M. Shahin, J. Inst. Petrol., 44, 283 (1958).
122. J. H. Howard and J. C. Robb, Trans. Faraday Soc., 59, 1590 (1963).
123. L. Bateman and G. Gee, Proc. Roy. Soc. A, 195, 391 (1948).
124. H. Berger, A. M. W. Blaaum, M. M. Al, and P. Smael, Adv. Chem. Series, 75, 346 (1968).
125. J. C. Robb and M. Shahin, Trans. Faraday Soc., 55, 1753 (1959).
126. V. F. Tsepalov and V. Ya. Shlyapintokh, Kinetika i Kataliz, 3, 870 (1962).
127. A. A. Vichutinskii, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1965.
128. J. A. Howard and K. U. Ingold, Canad. J. Chem., 43, 2729 (1965).
129. J. A. Howard and K. U. Ingold, Canad. J. Chem., 44, 1113 (1966).
130. C. H. Bamford and M. J. S. Dewar, Proc. Roy. Soc. A, 198, 252 (1949).

131. A. L. Aleksandrov and E. T. Denisov, Kinetika i Kataliz, 10, 912 (1969).
132. D. J. Hendry, J. Amer. Chem. Soc., 89, 5433 (1967).
133. W. J. Maguire and P. C. Pink, Trans. Faraday Soc., 63, 1097 (1967).
134. H. W. Melville and S. Richards, J. Chem. Sci., 944 (1954).
135. J. J. Zwolenik, J. Phys. Chem., 71, 2464 (1967).
136. J. A. Howard, K. U. Ingold, and M. Symonds, Canad. J. Chem., 46, 1017 (1968).
137. A. F. Guk, V. F. Tsepalov, V. F. Shuvalov, and V. Ya. Shlyapintokh, Izv. Akad. Nauk SSSR, Ser. Khim., 2250 (1968).
138. V. M. Gol'dberg and L. K. Obukhova, Dokl. Akad. Nauk SSSR, 164, 860 (1965).
139. H. R. Cooper and H. W. Melville, J. Chem. Soc., 1984 (1951).
140. T. A. Ingles and H. W. Melville, Proc. Roy. Soc. A, 218, 175 (1953).
141. A. MacLachlan, J. Amer. Chem. Soc., 87, 960 (1965).
142. A. L. Aleksandrov and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1737 (1966).
143. E. J. Land and G. Porter, Trans. Faraday Soc., 59, 2027 (1963).
144. B. Hölmström, Bull. Soc. Chim. belges, 71, 869 (1962).
145. C. G. Hatchard and C. A. Parker, Trans. Faraday Soc., 57, 1093 (1961).
146. C. A. Parker, J. Phys. Chem., 63, 26 (1959).
147. K. D. Adams, B. Cercek, M. Ebert, H. Henglein, and A. Wigger, Trans. Faraday Soc., 63, 2435 (1967).
148. E. G. Janzen, E. J. Johnston, and C. L. Ayers, J. Amer. Chem. Soc., 89, 1176 (1967).
149. J. K. Thomas, Trans. Faraday Soc., 61, 702 (1965).
150. A. K. Pikaev, P. Ya. Glazunov, and V. I. Spitsyn, Dokl. Akad. Nauk SSSR, 150, 1077 (1963).
151. H. W. Schwarz, Rad. Res. Suppl., 4, 89 (1964).
152. K. Sehested and O. L. Rasmussen, J. Phys. Chem., 72, 626 (1968).
153. G. A. Russell, J. Amer. Chem. Soc., 77, 4583 (1955).
154. T. A. Ingles and H. W. Melville, Proc. Roy. Soc. A, 218, 163 (1953).
155. V. F. Tsepalov, V. Ya. Shlyapintokh, and Chou P'ei Huang, Zhur. Fiz. Khim., 38, 52 (1964) [Russ. J. Phys. Chem., No. 1 (1964)].
156. L. R. Mahoney and M. A. DaRooge, J. Amer. Chem. Soc., 89, 5619 (1967).
157. S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes" (Translated into Russian), GNIL, Moscow, 1948.
158. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel', Kinetika i Kataliz, 7, 401 (1966).
159. G. E. Zaikov, A. A. Vichutinskii, Z. N. Maizus, and N. M. Emanuel', Dokl. Akad. Nauk SSSR, 168, 1096 (1966).
160. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel', Teor. Eksper. Khim., 3, 612 (1967).
161. E. T. Denisov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 53 (1960).
162. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel', Dokl. Akad. Nauk SSSR, 173, 859 (1967).
163. G. E. Zaikov, L. M. Andronov, Z. K. Maizus, and N. M. Emanuel', Dokl. Akad. Nauk SSSR, 174, 127 (1967).
164. L. M. Andronov, G. E. Zaikov, and Z. K. Maizus, Zhur. Fiz. Khim., 41, 1122 (1967) [Russ. J. Phys. Chem., No. 5 (1967)].
165. G. E. Zaikov and Z. K. Maizus, Izv. Akad. Nauk SSSR, Ser. Khim., 2265 (1968).

Institute of Chemical Physics
of the USSR Academy of
Sciences,
Chernogolovka Branch