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Reversible Recombination of Radicals

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The results of experimental studies on the kinetics of the reversible recombination of radicals in the liquid phase in relation to phenoxy-, C-centred, peroxy-, and nitroxy-radicals and radical-ions are surveyed. It is shown that steric hindrance has a decisive influence on the rate of recombination of many radicals. The influence of the solvent on the kinetics of the reversible recombination is considered and particular attention is given to the influence of the viscosity of the solvent on the kinetics of the recombination of radicals with a distinct anisotropy of their reactivity.
The bibliography includes 181 references.

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I. INTRODUCTION

A typical reaction characteristic of all active short-lived radicals is rapid bimolecular recombination (dimerisation, disproportionation, and electron transfer); all other reactions of short-lived radicals compete with it. If the chemical bond formed in the dimer on recombination is weakened owing to the electronic influence of substituents or if the formation of the dimer entails steric hindrance, then the recombination of radicals is reversible†:

$$R + R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D. \qquad (1)$$

Comparatively stable radicals, characterised by a high degree of delocalisation of the unpaired electron, also undergo reversible recombination. Radical–dimer systems have been investigated by spectrophotometry, the temperature jump method, flash photolysis, NMR, kinetic EPR, and EPR combined with the rotating sector method. This review considers the results of experimental studies on the kinetics and thermodynamics of reaction (1) in the liquid phase. The study of the kinetics of the reversible recombination of radicals in various media is important for the understanding of the relation between the structure and reactivity of radicals and the influence of the chemical nature of the solvent and the viscosity of the medium on radical reactions. Data for the kinetics of fast reversible recombination reactions are important for the development of a theory of diffusion-controlled processes.

II. KINETICS OF THE DESTRUCTION OF RADICALS

If the radical–dimer system is displaced from the state of equilibrium (for example, by increasing the concentration of radicals with the aid of a light flash), then k_1 and k_{-1} can be obtained from the analysis of the subsequent relaxation of the system to equilibrium[1–6]. Direct or sensitised photochemical oxidation of compounds RH by flash photolysis can lead to the formation of radicals at an initial non-equilibrium concentration $[R]_0$; subsequently the system also relaxes to equilibrium, which makes it possible to determine the corresponding kinetic parameters[1–4,7]. In the majority of studies experiments yielded the values of K and k_1, k_{-1} being determined from the relation $k_{-1} = Kk_1$. The study of temperature relations makes it possible to obtain the thermodynamic parameters of reaction (1). The following relations were used: $K = \exp(\Delta S^\circ/R)\exp(-\Delta H^\circ/RT)$ (the van't Hoff equation) and $k = (k_B T/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)$ (the Wynn-Jones and Eyring equation).

The study of the NMR spectra of diamagnetic dimers present in solution in equilibrium with the corresponding radicals permits the determination of k_{-1} and the investigation of the kinetics of all the elementary reactions occurring in the radical–dimer system[8,9].

Together with reaction (1), irreversible radical destruction or irreversible dimer decomposition reactions can occur in the solution. Possible kinetic schemes for the destruction of radicals are described below[10].

Scheme I

$$D \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} 2R \xrightarrow{k_2} \text{stable products.}$$

When $k_1 \gg k_2$, one obtains

$$-d[R]/dt = 2k_2[R]^2/(1 + 4k_1[R]/k_{-1}).$$

If $4k_1[R]/k_{-1} \gg 1$, then the radical destruction reaction will obey a first-order law with $k_{obs} = k_2 k_{-1}/2k_1$, while subject to the condition $4k_1[R]/k_{-1} \ll 1$, the radical destruction will follow a second-order law with $k_{obs} = 2k_2$. Thus at high radical concentrations the destruction is a first-order process while at low concentrations it is a second-order process.

Scheme II

$$2R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D \xrightarrow{k_2} \text{stable products.}$$

† Here and henceforth it is assumed that $-d[R]/dt = 2k_1[R]^2 - 2k_{-1}[D]$, $K = k_{-1}/k_1$, and $\Delta X^0 = \Delta X^{\neq}_{-1} - \Delta X^{\neq}_1$, where X is a thermodynamic function.

When $k_{-1} \gg k_3$, one obtains,

$$-\mathrm{d}[\mathrm{R}]/\mathrm{d}t = \frac{2k_3k_1[\mathrm{R}]^2}{k_{-1}(1+4k_1[\mathrm{R}]/k_{-1})}.$$

Similarly, when $4k_1[\mathrm{R}]/k_{-1} \gg 1$, the radical destruction obeys a first-order law with $k_{obs} = k_3/2$, and, when $4k_1[\mathrm{R}]/k_{-1} \ll 1$, it obeys a second-order law with $k_{obs} = 2k_3k_1/k_{-1}$.

On the basis of kinetic data alone, it is difficult to distinguish Schemes I and II.

Scheme III

$$2\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{D}; \quad \mathrm{R} \xrightarrow{k_4} \text{stable products.}$$

When $k_1[\mathrm{R}] \gg k_4$, one obtains

$$-\mathrm{d}[\mathrm{R}]/\mathrm{d}t = k_4[\mathrm{R}]/(1+4k_1[\mathrm{R}]/k_{-1}).$$

When $4k_1[\mathrm{R}]/k_{-1} \gg 1$, the radical destruction obeys a zero-law with $k_{obs} = k_4k_{-1}/4k_1$. When $4k_1[\mathrm{R}]/k_{-1} < 1$, a first-order radical destruction reaction with $k_{obs} = k_4$ should take place.

III. DIFFUSION-LIMITED RECOMBINATION OF RADICALS

The fundamental question which arises from the analysis of the kinetics of the fast recombination of radicals is whether the reaction is diffusion-limited. For bimolecular reactions fully limited by diffusion, the observed rate constant is directly proportional to the quantity T/η, where η is the viscosity of the solvent:

$$k \propto T/\eta. \tag{2}$$

For bimolecular reactions of radicals limited by translational diffusion, we have[15,34,52,64]

$$k = \frac{N}{1000} \cdot \sigma \cdot 4\pi\rho D \simeq \sigma \cdot \frac{8RT}{3000\eta}, \text{ litre mol}^{-1}\text{ s}^{-1},$$

where N is the Avogadro number, $\sigma = 1/4$ is a statistical factor taking into account the fact that only radical pairs which are in the singlet state during the encounter lead to the reaction products, ρ the reaction radius, and D the mutual diffusion coefficient of the radicals. For a reaction between identical radicals [reaction (1)],[15]

$$k_1 = k_{diff} \simeq \sigma \cdot \frac{4RT}{3000\eta}. \tag{3}$$

The choice of the numerical value of the coefficient $4\sigma/3000$ in Eqn.(3) is usually somewhat arbitrary: the questions of the value of σ ($1/4 < \sigma < 1$; see, for example, Nonhebel and Walton[11] and Buchachenko et al.[12]), of the replacement of the coefficient 4/3000 by 4/2000 (see, for example, Tyrrell[13]), etc. have been discussed.

For reactions controlled by translational diffusion, the following expression is valid[1,14]:

$$\Delta H^{\neq}_{diff} = B, \tag{4}$$

where B is the activation energy for the viscous flow of the solvent:

$$\eta = \eta_0 \exp(B/RT).$$

The study of the influence of the viscosity of the solvent on the observed rate of reaction makes it possible to discover, within the framework of the contact model[15], the relations between the rate constants for a diffusion-controlled reaction and the chemical reaction proper within the cage.

According to Noyes[15],

$$1/k_1 = 1/k_{diff} + 1/k_{chem.} \tag{5}$$

It is apparently always possible to select a solvent with sufficiently high viscosity in which the reaction will occur under the diffusion-dependent conditions. The relation $k_{chem} \gg k_{diff}$ and Eqn.(2) then hold. At sufficiently low viscosities deviations from Eqn.(2) may be observed and Eqn.(5) must be used.

The contact model of chemical reactions presupposes the diffusion of the reactants to the site of their contact where the distance between them is ρ and where there is a possibility of a chemical reaction with a rate constant k_{chem}. In the generalised contact model[16,52] account is taken of two important factors.

1. The last step in the process involving the mutual approach of the reactants differs from the previous step owing to the short-range interaction and is described as a jump over a finite distance at a frequency which, like the rate of irreversible process, depends on the solvation interactions of the reactants.

2. The rate of reaction between the reactants on contact is different for their different conformations or mutual orientations.

Allowance for the first condition leads to the subdivision of reactions into three stages: the mutual approach of the reactants to a distance $\rho^* > \rho$, insertion in the first coordination sphere, and the chemical reaction proper. This is reflected in the expression[16]

$$1/k = 1/k'_{diff} + 1/k_{ins} + 1/(gk_{chem}), \tag{6}$$

where $k'_{diff} = 4\sigma\pi\rho^*D$ (ρ^* is the radius of the second coordination sphere), k_{ins} is the rate constant for insertion in the first coordination sphere from the second, and the parameter g characterises the equilibrium radial distribution function. As a result of the introduction of the parameter g, Eqn.(6) takes into account the short-range order and the capacity of the reactants for the formation of complexes with the solvent ($g < 1$) or for the formation of dimers (complexes between the reactants) ($g > 1$), which increase their contact time. Evidently, like k_{diff}, the constant k_{ins} depends on the molecular mobility of the medium. However, k_{ins} can be comparatively small, whereupon the insertion in the first sphere and not translational diffusion limits the process in a viscous medium[16].

The distribution of unpaired electrons in radicals is in most cases anisotropic; the reactivity of radicals is therefore also anisotropic. The anisotropy of the reactivity is characterised by the geometrical steric factor f_g, equal to the probability of the occurrence of a mutual orientation favourable for recombination at the instant of the first contact on formation of the diffusional pair. It is usually assumed that the reactant is spherical and that the reaction region on the surface of the sphere is bounded by a circle characterised by an angle θ (the angle between the radius of the sphere bounding the reaction region and the radius directed to its centre). For bimolecular reactions between identical species, we then have $f_g = \sin^4(\theta/2)$. The anisotropy of the reactivity is partly or completely averaged out as a result of the rotational and translational movement of the reactants during their encounter (contact time)[17-21,32]. In the general case one can write for bimolecular reactions limited by molecular mobility

$$k = \sigma 4\pi\rho D f_{eff},$$

where f_{eff} is the effective steric factor and $f_g < f_{eff} \leq 1$.

The relations between f_{eff} and f_g have been considered in various theoretical studies[18–21,32].

A rigorous solution of the diffusional problem for a bimolecular reaction between anisotropic molecules (taking into account particular assumptions) usually has no simple analytical form and is carried out by numerical methods[19,20,32]. An approximate solution susceptible to an experimental test has been put forward[21]:

$$1/k = 2\,[\sigma k'_{chem}(1-\cos\theta)]^{-1} + 2\,[k_{diff}(1-\cos\theta)\theta]^{-1}, \qquad (7)$$

where k'_{chem} is the recombination rate constant for a favourable mutual orientation of the reactants in the cage.

If it is assumed that the anisotropy of the reactivity is averaged out as a result of rare rotations of the reactant by large angles, the solution of the diffusional problem leads to the expression[12,18]

$$1/k = (\sigma f_g k'_{chem})^{-1} + (1 + f_g q^{1/2})\,[(1 + q^{1/2})\,f_g k_{diff}]^{-1}, \qquad (8)$$

where q is the ratio of the contact time in the formation of the pair and the characteristic rotational diffusion time ($q = \tau_c/\tau_{rot}$). For quantitative estimates, $q = 6$ has been used[14].

Analysis of experimental data for the kinetics of the rapid recombination of many radicals (see Sections IV–X) shows that steric hindrance in recombination, characterised by the quantity f_g, has a decisive influence on k_1.

Like k_1, the constant k_{-1} depends on k_{diff} (and hence on viscosity)[22–24]:

$$1/k_{-1} = 1/k_{diss} + k_{chem}/(k_{diss}k_{diff}), \qquad (9)$$

or, in the case of anisotropic reactants[14,18],

$$1/k_{-1} = 1/k_{diss} + k_{chem}(1 + f_g q^{1/2})\,[(1 + q^{1/2})\,k_{diss}\,k_{diff}]^{-1}, \qquad (10)$$

where k_{diff} is the elementary rate constant for the association of dimers into radicals in the cage.

IV. THE INFLUENCE OF SOLVENT VISCOSITY ON THE KINETICS OF THE REVERSIBLE RECOMBINATION

The study of the influence of solvent viscosity on the kinetics of fast reversible radical recombination reactions is important for tests of theoretical ideas concerning diffusion-controlled reactions (see Section III).

The influence of the viscosity of the medium on the kinetic and thermodynamic parameters of the reversible recombination of phenoxy-radicals has been studied[1,14,16,24–27]. Binary mixtures of solvents, with widely differing viscosities but of a similar chemical type, have been used, which made it possible to vary smoothly the viscosity over a wide range; under these conditions, other parameters of the binary mixtures changed only slightly. Fig.1 presents the variation of k_1 with the viscosity of the solvent for phenoxy-radicals of different structures (see Table 1). It follows from the data in Fig.1 that the kinetics of the recombination of radicals (I)–(V) obey Eqn.(2) as well as the relations $k_1 \propto T/\eta^{0.8}$ and $k_1 \propto T/\eta^{1.2}$; the majority of the constants k_1 are smaller than the values of k_{diff} calculated by Eqn.(3) (the discrepancy between the k_1 and k_{diff} is within an order of magnitude).

Table 1. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in solvents with different viscosities at 20 °C.[14,25]

Radical	Substituents in radical	Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	10^8K_1, mol^{-1} l	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
(I)	4-methoxy-2,6-diphenyl	methanol	12	840	70	1.5	11.2	9.7	11	−7	4
	"	toluene	7.5	150	20	3.0	14.0	11.0	7	0	7
	"	DBP	0.30	6.0	20	6.0	13.6	7.6	2	—	—
	"	CH–M	0.15	1.2	8.0	8.6	13.8	5.2	−5	−10	−15
(II)	4-phenyl	toluene	7.0	0.0070	0.0010	2.2	24	22	9	16	25
	"	DBP	0.6	0.00060	0.0010	5.5	30	25	3	32	35
(III)	2-phenyl	toluene	6.0	—	$\sim 5\cdot10^{-4}$	1.6	—	—	12	—	—
	"	DBP	0.23	—	$\sim 5\cdot10^{-4}$	5.8	—	—	4	—	—
(IV)	2,4-diphenyl	toluene	3.4	5.5	1.62	1.6	17.8	16.2	13	6	19
	"	DBP	0.23	0.12	0.51	5.1	24.6	19.5	6	22	28
(V)	2,6-diphenyl	toluene	2.5	0.010	0.0042	0.5	22	21	17	7	24
	"	DBP	0.17	0.00024	0.0014	5.4	28	23	6	23	29
(VI)	2-methoxy	toluene	5.7	—	—	1.9	—	—	10	—	—
	"	DBP	0.20	—	—	7.2	—	—	1	—	—
(VII)	2,6-dimethoxy	toluene	4.0	12	3.0	1.7	13.0	11.3	18	−14	4
	"	DBP	0.25	0.5	2.0	5.7	21.7	16.0	−5	15	20
(VIII)	2,6-diphenyl-4-diphenylmethyl	toluene	0.80	2.5	3.2	2.5	17.0	14.5	12	3	15
	"	DBP	0.14	0.21	1.5	4.0	20.0	16.0	11	8	19
(IX)	2,4,6-triphenyl	methanol	0.60	4200	7000	—	—	—	—	—	—
	"	E	0.15	450	3000	—	—	—	—	—	—
(X)	2,6-di-t-butyl	toluene	0.60	—	—	1.0	—	—	17	—	—
	"	DBP	0.05	—	—	5.1	—	—	9	—	—
(XI)	2,6-di-t-butyl-4-methyl	toluene	0.45	112	250	−1.0	16.5	17.5	25	9	34
	"	DBP	0.075	6.75	90	3.0	19.5	16.5	15	13	28

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively; the average errors of the determinations are 20% in the constants, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS. The viscosities are 0.58 for methanol, 0.59 for toluene, 18.4 for dibutyl phthalate (DBP), 19.9 for ethylene glycol (E), and 24.5 cP for the 5 : 1 (by volume) cyclohexanol–methanol (CH–M) mixture.

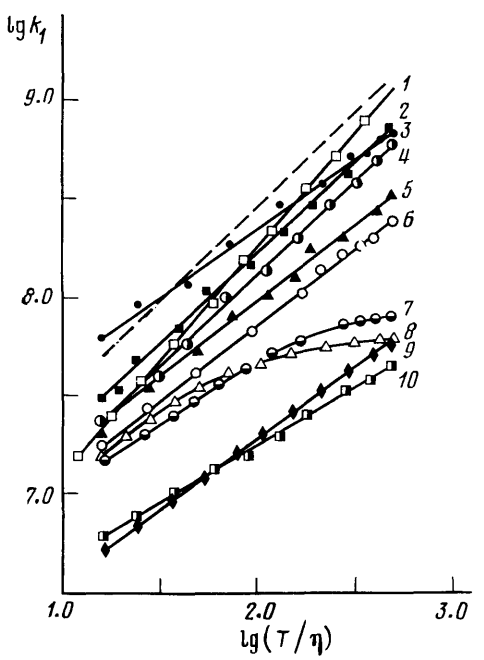


Figure 1. Relations between lg k_1 and lg (T/η) at 20 °C (η in cP) for phenoxy-radicals of different structure[1,14] [1) and 2) (I); 3) (II); 4) (III); 5) (IV); 6) (V); 7) (VIII); 8) (IX); 9) (X); 10) (XI)] in methanol–cyclohexanol (curve *1*), methanol–ethylene glycol (curve *8*), and toluene–dibutyl phthalate (curves *2–7*, *9*, and *10*) mixtures. Dashed curve—relation predicted by Eqn.(3). The names of the radicals are given in Table 1.

The discrepancy between the theoretical and experimental values of the rate constant for a diffusion-controlled reaction can apparently amount to not more than an order of magnitude due to the following causes: the lack of validity of the application of the Stokes–Einstein law; the uncertainty in the numerical value of the statistical factor σ (see Section III); the lack of validity of the assumption that the hydrodynamic radius is equal to half the reaction radius[5,16]. Thus the recombination of radicals (I)–(V) in a given range of viscosities is limited mainly by translational diffusion.

The rates of recombination of radicals (VIII) and (IX) (Fig.1) depend on the viscosity, but the reaction occurs under conditions intermediate between kinetic and diffusion-dependent. Numerical values of k_{chem} have been obtained[1,14] for these radicals using Eqn.(5) (Fig.2). For radicals characterised by linear relations between $\lg k_1$ and $\lg(T/\eta)$ (Fig.1), $k_{chem} \gg k_{diff}$ (Fig.2). The recombination of radicals (VIII) and (IX) in the cage apparently involves the overcoming of an activation barrier, since the given radicals form complexes with molecules of aromatic solvents (see Section X). The recombination probably involves desolvation, which is accompanied by the expenditure of a definite amount of energy.

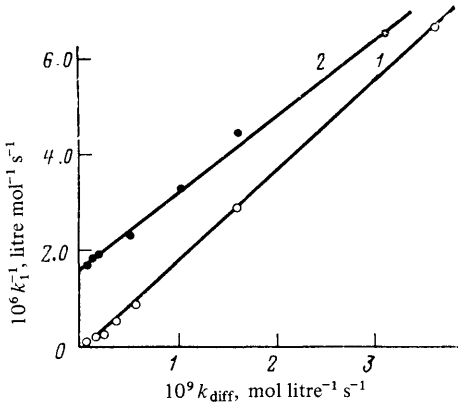


Figure 2. Relations between k_1^{-1} and k_{diff}^{-1} at 20 °C ($k_{diff} = 8RT/3000\eta$): 1) radical (I) in methanol–cyclohexanol mixture; 2) radical (IX) in methanol–ethylene glycol mixture[1].

The values of k_1 obtained for radicals (X) and (XI) are smaller by two orders of magnitude than k_{diff} (Table 1). The steric hindrance generated by the t-butyl groups leads to a low value of f_g for the recombination of radicals[7,14,25]. The value of f_g estimated by Eqn.(8) for 2,6-di-t-butylphenoxy-radicals is ~0.03.[14]

Eqn.(4) holds for radicals whose recombination is limited by translational diffusion[1,14,25]. For the recombination of radicals which occurs in only some of the encounters between the radicals in solution (for a low value of f_g), low and even negative $\Delta H_1^{\neq}$ are observed (Table 1 and Refs.7–9, 14, 25, and 28). In order to account for the low observed values of $\Delta H_1^{\neq}$, it is usually assumed that the recombination of radicals takes place not in one but in at least two stages[14,28]:

$$PhO^{\cdot} + PhO^{\cdot} \rightleftarrows (PhO^{\cdot} \ldots PhO^{\cdot}) \rightarrow \text{dimer}. \qquad (11)$$

The formation of the complex should promote the averaging of the anisotropy of the reactivity as a result of the increase of the lifetime of the radical pair[14]. The radicals in the complex are apparently linked by dipole–dipole and dispersion interactions, which are not rigorously directional and do not prevent the rotation of the radicals relative to one another. The conversion of the complex into the dimer apparently involves the rotation of the radicals relative to one another in the complex and the rate of this reaction is inversely proportional to the viscosity[14]. The observed $\Delta H_1^{\neq}$ can then be expressed as follows[14]:

$$\Delta H_1^{\neq} \simeq \Delta H_c^{\circ} + B, \qquad (12)$$

where ΔH_c° is the heat of formation of the complex and B is the activation energy for the viscous flow of the solvent. Furthermore, $\Delta H_c^{\circ} < 0$ and $\Delta H_1^{\neq} < B$.

The relations in Fig.1 have a slope less than unity for the majority of radicals. This type of relation is predicted by the theory of diffusion-controlled reactions taking into account the rotation of the reactants[19], subject to the condition that the distribution of the reaction centre over the surface of a sphere is described by a smooth and not a stepped function. This hypothesis corresponds to reality to a greater extent than the hypothesis of a centre with sharply outlined boundaries[14].

The constants k_{-1} for radicals (I)–(XI) also depends strongly on the viscosity (Table 1, Fig.3). The dependence of $\lg k_{-1}$ on $\lg(T/\eta)$ is then of the same type as the corresponding relations between $\lg k_1$ and $\lg(T/\eta)$ (cf. Figs.1 and 3). This is consistent with the theory of diffusion-controlled reactions [see Eqns.(9) and (10)].[18,22–24] The rate constants for the decomposition of the dimers of radicals (VIII) and (IX) in the cage have been obtained[24].

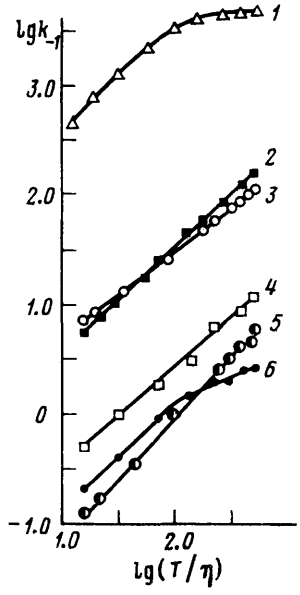
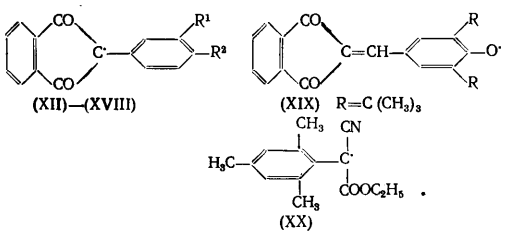


Figure 3. Relations between $\lg k_{-1}$ and $\lg(T/\eta)$ for the dissociation of the dimers of phenoxy-radicals[14,24] at 20 °C (η in cP): 1) radical (IX) in methanol–ethylene glycol mixture; 2)–6) radicals (I), (XI), (VII), (V), and (VIII) respectively in toluene–dibutyl phthalate mixture.

The relations between k_1 and η (Fig.4) have been obtained for C-centred and phenoxy-radicals having the following structures[5]:



Here R^1 = H and R^2 = $N(CH_3)_2$ (XII), R^1 = H and R^2 = $N(C_2H_5)_2$ (XIII), R^1 = H and R^2 = $N(n\text{-}C_3H_7)_2$ (XIV), R^1 = H and R^2 = $N(n\text{-}C_4H_9)_2$ (XV), R^1 = H and R^2 = $N(C_6H_5)_2$ (XVI), R^1 = R^2 = OCH_3 (XVII), and R^1 = Br and R^2 = $N(CH_3)_2$ (XVIII). Table 2 presents the kinetic and thermodynamic parameters of reaction (1) involving radicals (XII)–(XX) in chlorobenzene.

Table 2. Kinetic and thermodynamic parameters of reaction (1) involving C-centred and phenoxy-radicals (XII)–(XX) in chlorobenzene at 20 °C.[5]

Radical	$10^{-7}k_1$, l mol^{-1} s^{-1}	$10^{-6}k_{chem}$, l mol^{-1} s^{-1}	10^4k_{-1}, s^{-1}	10^6K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH°	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS°
(XII)	80	1.3	0.9	0.11	2.3	20.1	17.8	10	2	12
(XIII)	50	0.7	2.5	0.5	3.5	19.5	16.0	6	5	11
(XIV)	30	0.55	2.7	0.9	3.4	22.5	19.1	8	13	21
(XV)	35	0.65	1.75	0.5	3.6	20.3	16.7	7	4	11
(XVI)	45	100	0.016	0.0035	2.5	14.7	12.2	10	−25	−15
(XVII)	180	100	—	—	2.9	—	—	6	—	—
(XVIII)	250	100	—	—	3.0	—	—	5	—	—
(XIX)	0.055	0.00055	93	17000	3.1	18.4	15.3	22	7	29
(XX)	0.06	5	0.48	80	2.8	15.2	12.4	21	−13	8

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively; the errors of the determinations are 20% in k_1 and k_{chem}, 20% in K, 40% in k_{-1}, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS.

The relations presented in Fig.4 for radicals (XVI)–(XVIII) are represented by straight lines with a slope of unity. The values of k_1 obtained for these radicals differ by not more than a factor of 2 from k_{diff} [Eqn.(3)] and $\Delta H_1^{\neq}$ is close to B (see Table 2). The recombination of radicals (XVI)–(XVIII) is limited by translational diffusion.

The recombination of radicals (XII)–(XV) for $\eta \geqslant 5$ cP takes place under diffusion-dependent conditions and the recombination for $\eta \leqslant 2$ cP takes place under kinetic conditions (Fig.4). The values of k_{chem} have been obtained for these radicals (Table 2). The recombination of radicals (XIX) takes place under kinetic conditions over the entire range of viscosities (Fig.4 and Table 2). The values of ΔH_1 obtained for the recombination of radicals (XIX) in toluene[5] and chlorobenzene (Table 2) exceed the corresponding values of B for solvents[5].

The constant k_1 for radical (XX) in the range of viscosities 2–18.4 cP varies with the viscosity in accordance with Eqn. (2), but the values of k_1 obtained for this radical are smaller than the corresponding k_{diff} almost by three orders of magnitude (Fig.4). The structural formula of radical (XX) shows that the reaction centre is strongly shielded by substituents and the radical is characterised by a pronounced anisotropy of reactivity ($f_g < 10^{-3}$). The recombination takes place when the necessary mutual orientation of the reactants is achieved on attainment of the radius of contact, which apparently occurs only in a few encounters out of a thousand between radicals (XX) in solution. It is only possible that the recombination of radicals (XX) is limited by the rate of insertion in the first coordination sphere [see Eqn.(6)].[5,16]

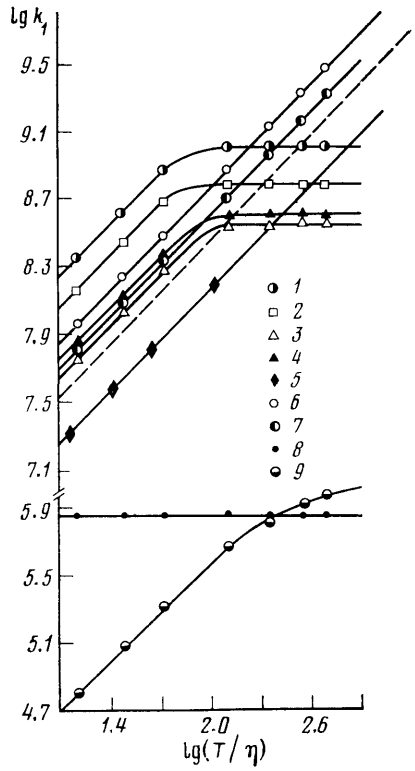
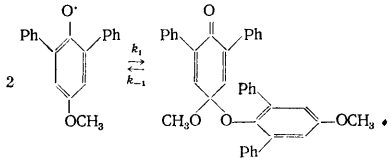


Figure 4. Relations between $\lg k_{-1}$ and $\lg(T/\eta)$ at 20 °C (η in cP) for aromatic C-centred and phenoxy-radicals in toluene–dibutyl phthalate mixture[5]: 1) (XII); 2) (XIII); 3) (XIV); 4) (XV); 5) (XVI); 6) (XVII); 7) (XVIII); 8) (XIX); 9) (XX). Dashed line—relation predicted by Eqn.(3). The formulae of the radicals are given in the text.

V. PHENOXY-RADICALS

The principal channel for the destruction of phenoxy-radicals in solutions in the absence of radical acceptors involves their reaction with one another. The fastest stage in this reaction is usually recombination. The C–C or C–O bond formed as a result of recombination is fairly weak (ΔH° = 10–30 kcal mol^{-1}; see, for example, Khudyakov et al.[29]). The recombination of phenoxy-radicals is therefore reversible, for example:



In many cases a fairly high value of $K = 10^{-8}$–10^{-3} mol litre^{-1} is then observed (see, for example, Khudyakov et al.[29]).

The structures of dimerising phenoxy-radicals as well as the structures and physicochemical properties of the phenoxy-radical dimers have been considered in a number of reviews and monographs[11,30,31,33,116,169]. However, numerous studies on the kinetics and thermodynamics of the reversible recombination of the radicals have been published recently and these will be considered in the present section.

1. The Structures of Dimerising Phenoxy-Radicals

Different 2,4,6-substituted phenoxy-radicals, whose substituents do not contain reactive hydrogen atoms, can exist for a long time in solution in equilibrium with their dimers. 2,6-Di-t-butyl-4R-phenoxy-radicals[8,9,35–42,176,181], 2,6-diphenyl-4R-phenoxy-radicals[1–3,29,43–47], polyhalogenophenoxy-radicals[48,49], certain naphthoxy-radicals[50,170], radicals derived from phenanthrenols[51], and other phenoxy-radicals[181] are involved in equilibrium (1) in solution.

The equilibrium constant depends significantly on the steric hindrance due to the substituents and also on the influence of the substitutents on the electronic structures of the radical and the dimer. For example, the steric hindrance generated by the t-butyl groups in the 2,4,6-tri-t-butylphenoxy-radical precludes the formation of its dimers in solution even at −100 °C.[53,177] The 2,6-di-t-butyl-4-phenyl-radical[54] and the 2,6-di-t-butyl-4-methoxyphenoxy-radical[55] are also monomeric in solution. However, the replacement of one t-butyl group in the 2,4,6-tri-t-butylphenoxy-radical in the *ortho*-position by a benzene ring or a t-butoxy-group, which give rise to a smaller steric hindrance, makes the radical capable of the formation of dimers in the solution[56–59]. Sterically hindered phenoxy-radicals readily form dimers with sterically unhindered phenoxy-radicals[60–63,65–72].

If the substituent in the *ortho*- or *para*-position in a 2,4,6-substituted phenoxy-radical contains reactive hydrogen atoms, then the reaction between such radicals leads to the formation of stable products as a result of disproportionation. The disproportionation reaction can involve reversible dimerisation as an intermediate stage if the substituents in the phenoxy-radical do not give rise to an appreciable steric hindrance. For example, the disproportionation of the 2,6-di-t-butyl-4-methylphenoxy-radical[7,73–75], the 2,4,6-trimethylphenoxy-radical[73], the 4-methyl-2,6-diphenylphenoxy-radical[75], and the 2,6-diphenyl-4-diphenylmethylphenoxy-radical[7,75] takes place in this way.

The observed decrease of the equilibrium concentration of phenoxy-radicals as a result of the disproportionation reaction [after the establishment of equilibium (1)] obeys a first-order law when the condition $[\overline{PhO^{\cdot}}] \gg K/4$ holds (see Section II). The observed destruction of radicals was described in terms of a first-order law for the disproportionation of a series of 2,6-di-t-butyl-4R-phenoxy-radicals, where R = C_2H_5,[76] CH_2OCH_3, CH_2OCOCH_3, etc.[77,78] Consequently the fast reaction (1) takes place simultaneously with the disproportionation reaction.

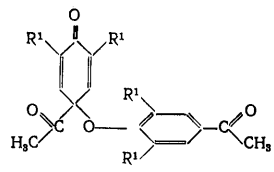
The disproportionation of the 3,6-di-t-butyl-2-hydroxyphenoxy- and 2,6-diphenyl-4-(4′-hydroxy-3′,5′-diphenylphenoxy)phenoxy-radicals has been investigated[79,80]. It was suggested on the basis of kinetic data that the disproportionation reaction is accompanied by reversible recombination.

Phenoxy-radicals without substituents in the *ortho*- or *para*-positions recombine with formation of stable dimeric products. Metastable dimers having the structure of a diketone or quinol are formed in this reaction and then enolise irreversibly with formation of the final products. The formation of metastable dimers is also reversible[25,28,29,81,82].

2. The Structures of Phenoxy-Radical Dimers

The dimerisation of phenoxy-radicals leads to the formation of C–O or C–C bonds. O–O dimers cannot be stable, since the high stabilisation energy of phenoxy-radicals (17.5 kcal mol^{-1}),[83] due to the delocalisation of the unpaired electron, leads to a low dissociation energy of the O–O bond[53].

On formation of the C–O bonds, the corresponding dimers have the structure of quinol ethers. This structure has been established reliably for dimers formed on recombination of the 2,4,6-tri-t-butylphenoxy-radical with various sterically unhindered phenoxy-radicals[60–63,65]. Dimerisation takes place via the carbon atom in the *para*-position in the 2,4,6-tri-t-butylphenoxy-radical with formation of a "heat-to-tail" structure. Quinol ethers are formed on dimerisation of the majority of 2,4,6-substituted phenoxy-radicals. The "head-to-tail" structures have been attributed to the dimers of 2,6-di-t-butylphenoxy-radicals containing the substituents CH_3,[84] OCOR,[35,37] and COR [8,9,35–37] (where R = alkyl) in the *para*-position, for example:



The dimers of the 2,4,6-triphenylphenoxy- [85,86] and 4-methoxy-2,6-diphenylphenoxy-radicals[87] have the same structure. The structure of quinol ethers has also been attributed to the dimers of radicals derived from phenanthrenol[51].

The dimerisation of 2,6-di-t-butyl-4R-phenoxy-radicals can also entail the formation of a C–O bond involving the carbon atom in the *ortho*-position. Such a structure has been postulated, for example, for the dimer of the radical with R = CO_2X (X = alkyl).[37] The third possible structure of dimers, where recombination results in the formation of a C–C bond involving the carbon atoms in the *para*-position (a "tail-to-tail" structure), is believed to be feasible for the dimers of the 2,6-di-t-butyl-4-ethoxycarbonylphenoxy-,[36] 2,6-di-t-butyl-4-diethylphosphinylphenoxy-, and 2,6-di-t-butyl-4-diethylphosphinodithionylphenoxy-radicals[88] and also in the case of the 6-t-butoxy-2,4-di-t-butylphenoxy-[59] and 2,4-di-t-butyl-6-phenylphenoxy-radicals[56]. The formation of an N–N bond on dimerisation of the 2,6-di-t-butyl-4-cyanophenoxy-radical has been postulated[30]. 2,6-Dialkyl-phenoxy-radicals containing the β-phthalylvinyl substituted in the *para*-position [e.g. radical (XIX)] dimerise with formation of a C–C bond[172].

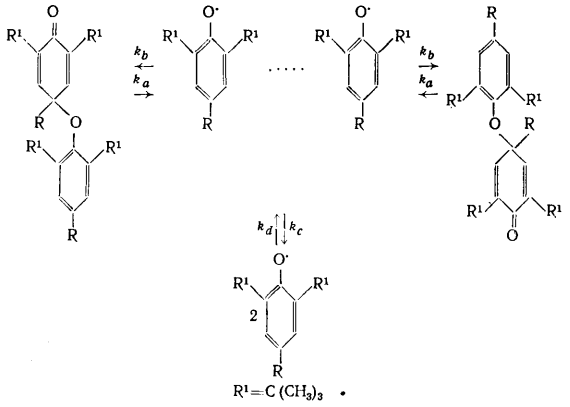
The structure of the primary dimers formed on dimerisation of phenoxy-radicals without substituents in the *ortho*- or *para*-positions can be postulated on the basis of the structure of the final stable dimerisation products. Depending on the positions and bulk of the substituents and on the nature of the solvent, the transfer or elimination of hydrogen atoms can then result in the formation of C–O or C–C bonds[11,30].

The probability of the formation of C–C bonds on dimerisation increases in dimethylformamide (DMF) and in acids compared with non-polar solvents (and also on raising the temperature)[89], which can be explained by the increase of the stability of the primary dimers with a C–C bond and by the decrease of the stability of the primary dimers with a C–O bond with increase of solvent polarity[29]. For example, 2,6-diphenylphenol is oxidised in solvents of low polarity to 2,6-diphenyl-4-(2′,6′-diphenylphenoxy)phenol[89]; consequently the primary dimer has the structure of a quinol ether of the "head-to-tail" type. However, in DMF and in acids the product is the corresponding diphenoquinone[89], which shows that the primary dimers have the "tail-to-tail" structure.

3. Kinetics of the Reversible Recombination of Phenoxy-Radicals

The rate constants for the recombination of phenoxy-radicals (k_1) and for the dissociation of the resulting dimers (k_{-1}) depend significantly on the chemical nature, bulk, and positions of the substituents in the benzene ring (Table 3).

Recombination reaction. The kinetics of the recombination of 2,6-di-t-butyl-4R-phenoxy-radicals have been investigated by NMR,[8,9] flash photolysis[14,25], and EPR [176] (Tables 1 and 3). The following mechanism of reaction (1) with participation of 2,6-di-t-butyl-4R-phenoxy-radicals has been proposed[9] on the basis of NMR data:



The dissociation of the dimer with a rate constant k_a results in the formation of an intermediate of unknown structure—a complex between the radicals. The complex can be reconverted into the initial dimer with a rate constant k_b, or into a dimer in which the radicals have changed places (also with a rate constant k_b), or it can dissociate into two free radicals with a rate constant k_c. The radicals recombine to a

Table 3. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals at 20 °C.

Radical	Substituents in radical	Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	10^8K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	$\Delta H°$	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	$\Delta S°$	References
(I)	4-methoxy-2,6-diphenyl	1-propanol	7.0	280	40	5.0	15	9.8	0	4	4	1
(II)	4-phenyl	hexane	55	—	—	0.2	—	—	12	—	—	29
(III)	2-phenyl	hexane	18	—	—	0.0	—	—	15	—	—	29
(IV)	2,4-diphenyl	hexane	18	1.3	0.074	0.5	22.5	22.0	13	20	33	29
(V)	2,6-diphenyl	hexane	8	—	—	0.5	—	—	15	—	—	29
(VI)	2-methoxy	hexane	17	—	—	0.5	—	—	13	—	—	90
(VII)	2,6-dimethoxy	hexane	4.3	11	2.6	0.2	7.2	7.0	18	—29	—11	90
(VIII)	2,6-diphenyl-4-diphenylmethyl	hexane	7.5	3.0	0.40	0.5	18.0	17.5	15	6	21	29
(X)	2,6-di-t-butyl	hexane	0.85	—	—	0.5	—	—	19	—	—	29
(XI)	2,6-di-t-butyl-4-methyl	hexane	1.1	50	45	—1.5	21.5	23.0	25	24	49	29
(XXI)	4-ethoxy-2,6-diphenyl	hexane	22	315	14	0.5	17.5	17.0	14	14	28	29
(XXI)	4-ethoxy-2,6-diphenyl	1-propanol	3.5	1000	300	4.0	14	9.6	5	4	7	1
(XXII)	2,6-diphenyl-4-stearyloxy	hexane	20	200	10	0.0	19.0	19.0	15	20	35	29
(XXII)	2,6-diphenyl-4-stearyloxy	1-propanol	1.9	1000	500	4.0	14	9.5	6	4	8	1
(XXIII)	4-acetoxy-2,6-diphenyl	hexane	22	—	—	0.5	—	—	14	—	—	29
(XXIV)	4-methyl-2,6-diphenyl	hexane	11	0.23	0.020	1.5	27.0	25.5	11	34	45	29
(XXV)	4-chloromethyl-2,6-diphenyl	hexane	13	0.027	0.0020	0.5	28.5	28.0	13	37	50	29
(XXVI)	2,6-diphenyl-4-(2′,6′-diphenylphenoxy)	hexane	0.5	30	60	1.0	16.5	15.5	20	6	26	29
(XXVII)	2,6-dicyclohexyl-4-phenyl	1-propanol	0.27	1100	4000	—	—	—	—	—	—	1
(XXVIII)	4-acetyl-2,6-di-t-butyl	deuterochloroform*	0.0077	14	3600	1.0	9.1	9.1	30	—14	16	9
(XXVIII)	4-acetyl-2,6-di-t-butyl	acetone-*d**	0.0070	3.5	1000	—4.6	7.0	11.6	48	—25	23	9
(XXVIII)	4-acetyl-2,6-di-t-butyl	carbon disulphide*	0.030	11	700	—3.5	6.8	10.3	41	—24	18	9
(XXIX)	2,6-di-t-butyl-4-(2′,2′-dimethylpropionyl)	deuterochloroform*	—	—	500000	—	—	6.9			17	9
(XXX)	methyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.050	2100	8500	—1.6	10.0	11.6	33	—5	28	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.077	190	4800	—0.4	8.5	8.8	27	—12	15.5	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	acetone-*d**	0.067	35	1000	—2.8	9.2	12.0	37	—12	25	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	carbon disulphide*	0.133	120	1900	—2.8	8.1	10.9	37	—14	22	9
(XXXII)	cyclohexyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.0007	15	43000	1.8	9.0	7.2	28	—14	13	9
(XXXIII)	2,6-di-t-butyl-4-cyano	deuterochloroform*	—	—	70000	—	—	6.1	—	—	9.3	9
(XXXIV)	4-methoxy**	chlorobenzene	0.27	0.027	0.1	0.5	20.3	19.8	28	—2	26	28
(XXXV)	4-t-butyl**	chlorobenzene	0.23	$5.2\cdot10^{-4}$	0.0023	—0.7	25.4	26.1	24	5	29	28
(XXXVI)	3-ethoxycarbonyl**	chlorobenzene	0.22	$3.4\cdot10^{-6}$	$1.54\cdot10^{-5}$	—0.2	28.8	30	26	5	31	28
(XXXVII)	3,5-dimethyl**	chlorobenzene	—	$1.4\cdot10^{-4}$	—	—	27.3	—	—	8	—	71
(XXXVIII)	4-bromo**	chlorobenzene	—	$5.5\cdot10^{-5}$	—	—	27.1	—	—	6	—	71
(XXXIX)	2,4,6-trichloro**	chlorobenzene	—	0.08	—	—	21.7	—	—	4	—	71

Note. *Dimerisation at −23 °C. **1 : 1 recombination with the 2,4,6-tri-t-butylphenoxy-radical at 60 °C. ***Complete name of the radical.

ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 20% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±2 mol^{-1} K^{-1} in ΔS.

complex with a rate constant k_d. When the above complexes are stationary and $k_b \gg k_c$ (the validity of this assumption has been confirmed by experimental data[9]), we have $k_{-1} = k_a k_c / 2k_b$ and $k_1 = k_d$. The exchange of magnetically-non-equivalent parts in a dimer is called a "flip-flop" process and is characterised by a rate constant $k_a/2$.

We may note that the quantities k_1 (and k_d) are lower by several orders of magnitude than k_{diff} (Table 3), i.e. the given complex between the radicals is by no means formed in every encounter between them in solution. It may be that the formation of the complex is a non-elementary reaction, since negative values of $\Delta H_1^{\neq}$ ($\Delta H_d^{\neq}$) are observed (Table 3). The hypothesis of the existence of complexes between sterically hindered phenoxy-radicals makes it possible to explain also the low and even negative values of $\Delta H_1^{\neq}$ (Tables 1 and 3) observed for these radicals (Section IV). It can be assumed that the recombination of phenoxy-radicals takes place in the same way as the recombination of the "related" benzyl radicals[28]. Quantum-chemical calculations have shown that, when benzyl radicals approach one another to a distance of 2.9 Å, a "sandwich" type complex between the radicals is energetically favourable, while at shorter distances the "head-to-head" structure is preferred, which is converted into the final recombination product (bibenzyl).[28]

The quantity k_1 increases significantly when the t-butyl groups in the *ortho*-positions in the phenoxy-radical are replaced by benzene rings or methoxy-groups (Table 3). The decreased shielding of the oxygen atom of the phenoxy-radical by the benzene rings compared with t-butyl groups can be understood if one takes into account the fact that the phenyl group can rotate freely and, for angles of rotation close to 90° relative to the plane of the phenoxy-ring, the steric hindrance is small.

The dimerisation reactions of mono- and di-phenylphenoxy- and 4-alkoxy-2,6-di-phenylphenoxy-radicals are limited mainly by translational diffusion (see Section IV). The data in Table 3 show that, with increase of the number of carbon atoms in the hydroxyalkyl substituent in the 4-alkoxy-2,6-diphenylphenoxy-radical, k_1 decreases, which may be caused by the fact that, with increase of the bulk of the radical, the area of the reaction region apparently remains virtually unchanged; as a result, f_g and the rate constant diminish. On replacement of the hydroxyalkyl substituent by the phenyl substituent, a further decrease of k_1 is observed, which is due to the increase of steric hindrance on dimerisation of the radicals. The constant k_1 becomes smaller still on replacement of phenyl substituents in the *ortho*-positions by the more bulky cyclohexyl groups (Table 3).

Thus the steric hindrance generated by substituents in the phenoxy-radical has a decisive influence on the kinetics of their recombination.

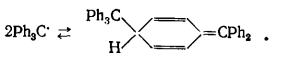
The dissociation of dimers. The rate constant for the dissociation of the dimers of 2,6-diphenyl-4R-phenoxy-radicals (k_{-1}) as well as $\Delta H_{-1}^{\neq}$ depend significantly on the nature of the substituent (Table 3). The quantity k_{-1} diminishes and $\Delta H_{-1}^{\neq}$ increases with enhancement of the electron-accepting capacity of the substituent. A similar relation has been observed for the dissociation of the 1:1 complexes formed by the 2,4,6-tri-t-butyl-phenoxy-radical with sterically unhindered phenoxy-radicals[28,71].

The constants k_{-1} for the dissociation of the complexes of the 2,4,6-tri-t-butylphenoxy-radical with *meta*- and *para*-substituted phenoxy-radicals are correlated with the parameters σ^+ of the substituents, the correlation having $\rho = -3.3$.[71] The ratio of the constant k_{-1} for the above 1:1 complexes ("dimers") to the rate constant for the abstraction of a hydrogen atom by the 2,4,6-tri-t-butylphenoxy-radical from the corresponding sterically unhindered phenol is almost independent of the substituent. Comparatively high values of k_{-1} have been observed[71] for radicals with substituents in the *ortho*-position; here $\Delta H_1^{\neq}$ were lower than the values expected on the basis of the electronic influence of the substituents. The explanation is that the *ortho*-substituents give rise to steric hindrance on dimerisation. The quinol ethers formed from the 2,4,6-tri-t-butylphenoxy-radical and *ortho*-substituted phenoxy-radicals are therefore less stable. For example, the strain energy of the C–O bond formed on dimerisation of the 2,6-dimethylphenoxy- and 2,4,6-trichlorophenoxy-radicals is 5 kcal mol^{-1}.[71]

VI. AROMATIC C-CENTRED RADICALS

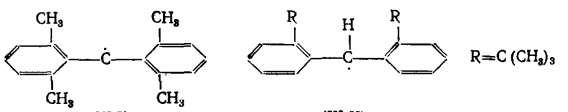
Different C-centred radicals with aryl substituents exist in solution in equilibrium with their dimers[5,6,91,92]. Phenyl substituents (±*E*-substituents) greatly facilitate the dissociation of substituted ethanes into arylmethyl radicals, stabilising the latter. The difference between the equilibrium constants for the mono-, di-, and tri-arylmethyl radicals can be explained by the method of perturbed molecular orbitals[93]. However, one should bear in mind that the steric hindrance in the recombination of radicals plays a more important role than the electronic effects; for this reason, hexa-arylethanes do not exist[93,94].

The triphenylmethyl radicals (XL) recombine reversibly with formation of 1-di-phenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene[95–97]:

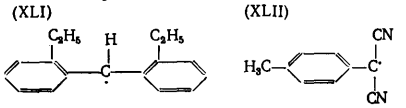


(XL)

The kinetic and thermodynamic parameters of reaction (1), which takes place with participation of the arylmethyl radicals (XX) and (XL)–(XLVII) are presented in Table 4.

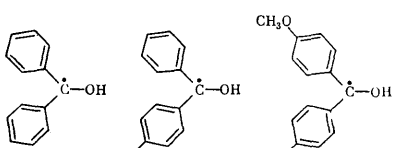


(XLI) (XLII)



(XLIII) (XLIV)

The activation energy for the dimerisation of radicals (XL) is satisfactorily consistent with the familiar general relation between the activation energy and the heat of reaction $E = 11.5 - 0.25|Q|$, kcal mol^{-1}.[96]



(XLV) (XLVI) (XLVII)

After the radical (XL) had been obtained[98], different derivatives and analogues of the triphenylmethyl radical were synthesised. The properties of these radicals have been described in numerous reviews and monographs[11,91,92,94,101,109,169]. The values of K for triphenylmethyl radicals with different substituents have been obtained[102–104]. The following conclusions can be reached on the basis of experimental data[102–104] for the stability of substituted triphenylmethyl radicals: (1) the stability of the radicals increases with increase of the bulk and number of substituents in the *ortho*-, *para*-, and *meta*-positions; (2) the stability of the radicals is very high when bulky substituents are present in all three benzene rings in the *para*-positions.

The observed regularities can be explained mainly by steric factors. Thus, despite the fact that the introduction of *ortho*-substituents increases the deviation of the benzene rings from the plane and reduces the degree of delocalisation of the unpaired electron, the constant K then increases, since the *ortho*-substituents hinder recombination[102,103].

The degree of delocalisation of the unpaired electron does not influence K. Furthermore, steric models have shown that in many arylmethyl radicals the aromatic rings have been rotated by a specific angle (and do not lie in a single plane) owing to the repulsion of the *ortho*-protons or *ortho*-substituents[92]. As a result of this, the delocalisation of the unpaired electron among the benzene rings takes place to only a small extent or not at all.

Table 4. Kinetic and thermodynamic parameters of reaction (1) involving C-centred aromatic radicals.

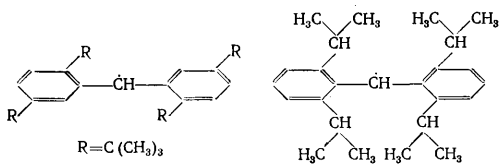
Radical	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0	Refs.
(XX)	α-chloronaphthalene	20	—	—	—	—	14.5	—	—	—13	—	107
(XL)	*m*-xylene	25	70	0.048	$6.8\cdot10^{-4}$	7.5	18.4	10.9	25	—3	22	97
(XL)	toluene	20	$3.5\cdot10^{2}$	0.25	$7.0\cdot10^{-4}$	6.4	17.8	11.2	26	—3	23	96
(XLI)	*m*-xylene	25	24	$1.1\cdot10^{-5}$	$4.6\cdot10^{-7}$	0.3	22.3	22.0	51	—6	45	97
(XLII)	*m*-xylene	25	9	$1.4\cdot10^{-5}$	$1.6\cdot10^{-6}$	5.0	24.7	19.7	36	4	40	97
(XLIII)	*m*-xylene	25	10	$1.6\cdot10^{-4}$	$1.6\cdot10^{-5}$	7.0	19.0	12.0	30	—12	18	97
(XLIV)	chlorobenzene	20	$5.0\cdot10^{7}$	0.08	$1.6\cdot10^{-9}$	6.8	15.9	9.1	—2	—8	—10	5
(XLIV)	α-chloronaphthalene	20	—	—	—	—	26	—	—	—14	—	107
(XLV)	benzene	30	$1.8\cdot10^{9}$	$5\cdot10^{-10}$	$2.8\cdot10^{-19}$	0.4	32.9	32.5	12	12	24	110
(XLV)	isopropyl alcohol	30	$1.1\cdot10^{8}$	$1.3\cdot10^{-8}$	$1.2\cdot10^{-16}$	4.3	26.7	22.4	5	—3	2	110
(XLVI)	benzene	30	$2.5\cdot10^{8}$	$8\cdot10^{-10}$	$3.2\cdot10^{-18}$	1.7	33.1	31.4	11	13	24	110
(XLVI)	isopropyl alcohol	30	$4.6\cdot10^{7}$	$1.6\cdot10^{-8}$	$3.5\cdot10^{-16}$	5.1	29.1	24.0	4	5	9	110
(XLVII)	benzene	30	$6.3\cdot10^{9}$	$1\cdot10^{-9}$	$1.6\cdot10^{-19}$	—1.1	24.7	25.8	14	12	26	110

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 20% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS.

The introduction of substituents in the *para*-position also gives rise to certain difficulties in dimerisation via the *para*-carbon atoms (the second reaction centre)[102]. The *meta*-substituents are in the *ortho*-positions relative to the second reaction centre and act analogously to substituents in the *ortho*-position relative to the central carbon atom[102,104].

The influence of substituents on K is determined solely by their bulk and number. Regardless of whether they are donors or acceptors, substituents exert the same influence on the equilibrium[102,103]. Triphenylmethyl radicals containing both methoxy-groups and chlorine atoms in all the *ortho*-positions relative to the central carbon atom have been isolated in a pure state[101].

Analogous conclusions are applicable to diarylmethyl radicals. Equilibrium shifts towards the radicals when they contain sterically bulky substituents; for example, the dimer of the bis-2,5-di-t-butylphenylmethyl radical is fully dissociated in solution[105]. Bis-2,6-di-isopropylphenylmethyl radicals do not dimerise either[106].

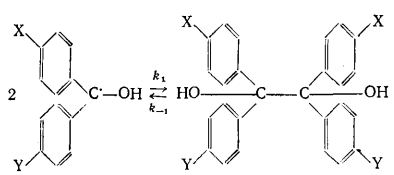


The reversible recombination of triphenylmethyl and diarylmethyl radicals (XL)–(XLIII) has been studied by EPR and that of the monoarylmethyl radicals (XX) and (XLIV) has been investigated by flash photolysis and NMR (Table 4). The values of k_1 for radicals (XL)–(XLIV) are lower than $k_{diff} \approx 5 \times 10^9$ litre mol^{-1} s^{-1} and $\Delta H_1^{\neq}$ differs significantly from the activation energy for the viscous flow of *m*-xylene and chlorobenzene ($B \approx 2.0$ kcal mol^{-1}) (Table 4). The recombination of radicals (XL)–(XLIV) takes place in the kinetic region.

The very low rate constants for the recombination of radicals (XL)–(XLIII) are caused by steric hindrance, as shown by the large negative values of $\Delta S^{\neq}$ (Table 4). Owing to the steric hindrance due to the *ortho*-substituents, the recombination of the diarylmethyl radicals (XLI)–(XLIII) also leads to the formation of a dimer having the ethane and not the cyclohexadiene structure[97]. In the recombination of the radical (XX) via the α-carbon atom the steric hindrance is so great (see Section III) that an asymmetric dimer linked by a C–N bond is formed[107].

For the decomposition of the molecules into complex fragments, the average value of the pre-exponential factor A is 10^6 s^{-1} ($\Delta S_{-1}^{\neq} \approx 11$–$12$ kcal mol^{-1} K^{-1}).[108] Smaller values of $\Delta S_{-1}^{\neq}$ have been obtained for the decomposition of the dimers of radicals (XX) and (XL)–(XLIV) (Table 4). The steric hindrance in the transition state of the decomposition of the dimers apparently hinders the rocking and torsional vibrations relative to the bond undergoing dissociation, which leads to a decrease of $\Delta S_{-1}^{\neq}$ compared with the average value of this quantity[5,6,53].

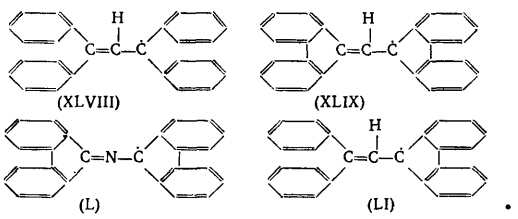
The ketyl radicals formed in the decomposition of benzopinacols can be regarded as substituted diphenylmethyl radicals. Benzopinacol, 4,4″-dibromobenzopinacol, and 4,4′,4″,4‴-tetramethoxybenzopinacol exist in benzene and isopropyl alcohol in equilibrium with the corresponding ketyl radicals at 80–141 °C:[110]



X, Y = H or substituent.

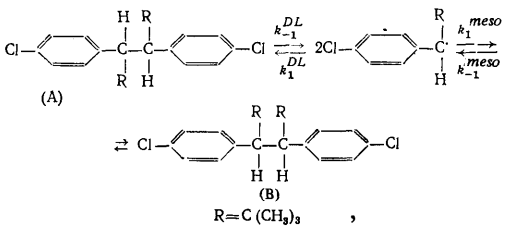
The kinetic and thermodynamic parameters obtained for reaction (1) involving ketyl radicals are listed in Table 4. Values of $\Delta H_1^{\neq}$ smaller than the corresponding values of B for the solvents were observed (2.9 and 6.4 kcal mol^{-1} for benzene and isopropyl alcohol respectively). It is extremely likely that the recombination of unsubstituted ketyl radicals (XLV) is limited by diffusion[110].

The recombination of tetraphenylallyl and related radicals has been studied by EPR and spectrophotometric methods[111]:



It was established that, in contrast to radicals (XLIX)–(LI), radical (XLVIII) does not form dimers in solution [benzene and ether, from −60° to 50 °C (20 °C)]. $\Delta H° = 12.2 \pm 0.4$, 8.9 ± 0.3, and 14.7 kcal mol^{-1} were obtained for radicals (XLIX), (L), and (LI) respectively. The bond in the dimer is formed between the α-carbon atoms or between the α- and γ-carbon atoms of the allyl groups. The inability of radical (XLVIII) to form a dimer can be explained by steric hindrance[111]. The extents of steric hindrance for radicals (XLIX) and (L) are the same and the differences between the $\Delta H°$ are then caused by the differences between the degrees of delocalisation of the unpaired electron.

Sterically hindered radicals can recombine diastereoselectively and exist in solution in equilibrium with two stereoisomeric dimers, for example[112]:



where (A) = DL-3,4-di-(*p*-chlorophenyl)-2,2,5,5-tetramethylhexane and (B) = *meso*-3,4-di-(*p*-chlorophenyl)-2,2,5,5-tetramethylhexane. The 1-(*p*-chlorophenyl)2,2-dimethylpropyl radicals, obtained on thermal decomposition of the corresponding azo-compound in 1-methylnaphthalene with 10 vol.% of thiophenol, are in equilibrium at ~300 °C with the *meso*- and DL-dimers; at 135 °C the ratio DL-dimer/*meso*-dimer equals 1.7.[112]

Like many C-centred radicals with phenyl substituents, 2-arylindan-1,3-dionyl radicals exist in solution in equilibrium with their dimers[5,6]. The interest in 2-arylindan-1,3-dionyl radicals increased recently, because they are effective inhibitors of liquid-phase oxidation processes[113]. The kinetic and thermodynamic parameters of reaction (1) involving the 2-arylindan-1,3-dionyl radicals (XII)–(XVIII) are listed in Table 2. Evidently the equilibrium constant depends significantly on the nature of the substituent in the phenyl fragment of radicals (XII)–(XVIII) (Table 2). In the recombination of radicals (XII)–(XVIII) (or the dissociation of the corresponding dimers), containing the phthaloyl fragment, the steric hindrance can be regarded as virtually identical and the difference between the values of K is therefore caused by electronic effects. In the dissociation of a dimer of similar structure, the C–C dimer of radical (XIX), equilibrium (1) is strongly displaced towards the formation of radicals compared with radicals (XII)–(XVIII) (Table 2). This is related to the fact that dissociation of the dimer (XIX) leads to the formation of relatively stable radicals, in which the unpaired electron is delocalised over the system of π-bonds, including the *p* orbital of the oxygen atom. The introduction of a bromine atom in the *ortho*-position relative to the dimethylamino-group in 1,2-bis-(4′-dimethylaminophenyl)diphthaloylethane fully displaces the equilibrium in this instance [radical (XVIII)] towards the formation of the dimer. The bromine atom displaces the dimethylamino-group from the plane of the ring, which leads to the breakdown of conjugation between the unshared electron pair of the nitrogen atom and the phenylindandionyl fragment[114] and hence reduces the degree of delocalisation of the unpaired electron.

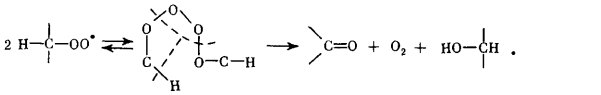
Comparison of the kinetic and thermodynamic parameters of reaction (1) for the dimers of radicals (XII)–(XVIII) (Table 2), triphenylmethyl radicals (Table 4), and phenoxy-radicals (Tables 1 and 3) shows that the dimers of radicals (XII) to (XVIII) dissociate much less and are characterised by higher bond dissociation energies.

VII. PEROXY- AND NITROXY-RADICALS

Tertiary peroxy-radicals are in equilibrium with the corresponding tetroxides at low temperatures[99,100,115–119]:

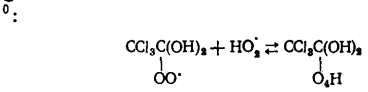
$$RO_2^{\cdot} + RO_2^{\cdot} \rightleftarrows ROOOOR \rightarrow \underset{\text{(cage)}}{[RO^{\cdot}\ldots O_2\ldots{}^{\cdot}OR]} .$$

The reactions were investigated by EPR. The values of K and $\Delta H°$ obtained for the peroxy-radicals are listed in Table 5. The data in this table show that the values of K, $\Delta H°$, and $\Delta S°$ depend little on the nature of the alkyl groups[100]. Consequently, the difference between the rates of chain termination on recombination of tertiary peroxy-radicals is caused mainly by the difference between the rates of the irreversible decomposition of the tetroxide[118]. The irreversible destruction of the tertiary alkylperoxy-radicals is negligible at $t < -115$ °C. There is evidence for the reversible formation of tetroxides from secondary peroxy-radicals[117–119]:



However, the thermodynamic parameters of the reversible formation of these tetroxides could not be obtained in view of the low concentration of the radicals and their rapid irreversible destruction even at $t < -115$ °C.[117,118] This mechanism of the destruction of secondary peroxy-radicals has been criticised by Benson[100].

The occurrence of reversible cross-recombination of the following radicals has been demonstrated by kinetic measurements[120]:

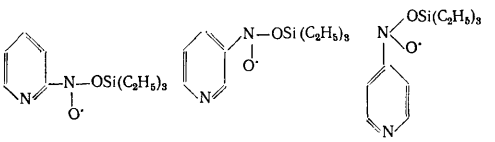


The equilibrium is displaced towards the formation of radicals (water, $t \cong 20$ °C). The tetroxide decomposes with liberation of oxygen.

The destruction of the phosphoranylperoxy-radical $C(CH_3)_3O(RO)_3POO^{\cdot}$, where R = CH_3, C_2H_5, or iso-C_3H_7, in cyclopropane takes place in the same way as the destruction of alkylperoxy-radicals[121]. In the range from −70° to −45 °C the destruction of these radicals obeys a first-order law and at $t < -90$ °C a second-order law. $k_1 \cong 10^4$ litre mol^{-1} has been obtained for three phosphoranylperoxy-radicals in

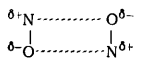
cyclohexane at −90 °C and $\Delta H_1^{\neq} = 4$ kcal mol^{-1} and $k_1 = 3 \times 10^4$ litre mol^{-1} s^{-1} (−90 °C) have been found for $C(CH_3)_3O(CH_3O)_3$. .POO· in the temperature range between −116° and −89 °C.[121]

Nitroxy-radicals of different structure also dimerise reversibly in solution[122–127,167]. Table 5 presents the kinetic and thermodynamic parameters of the dimerisation of nitroxy-radicals of different structure, obtained by EPR. It has been shown[127] that the destruction of nitroxy-radicals having the structure



in triethylsilane at temperatures in the range from −33° to 25 °C obeys a first-order law. It has been observed that the radicals are in equilibrium with diamagnetic dimers and that their destruction proceeds in accordance with Scheme II (see Section II).[127]

The thermodynamic parameters of the dimerisation of nitroxy-radicals in isopentane are close to the corresponding parameters of the reversible recombination of t-alkylperoxy-radicals in alkanes[116], for example of t-butylperoxy-radicals in isopentane (Table 5). However, the recombination of nitroxy-radicals leads to the formation of dimers via a 4-centre bond[122]



and not via the O—O linkage.

VIII. RADICAL-IONS

Despite electrostatic repulsion, radical-ions dimerise reversibly in solution[128–134]. The dimerisation of radical-ions was first described in detail by Michaelis and Schubert[135], who analysed titration curves. The dimerisation reaction is usually accompanied by the electron transfer reaction between radical-ions, but, having selected the appropriate conditions, it is possible to suppress fully one of these reactions[135].

The following relation is valid for the reversible dimerisation of many aromatic radical-anions[136]:

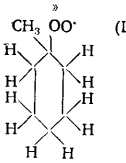
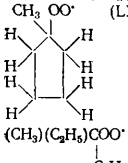
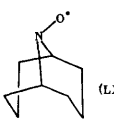
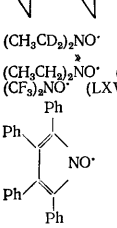
$$\Delta G^0 = \Delta\xi_\pi + \text{const},$$

where $\Delta\xi_\pi$ is the change in the energy of π-electrons.

The dimerisation of ion pairs is a well known phenomenon, which is induced by Coulombic attraction[137]. Electrostatic forces promote the formation of π−π′ bonds between suitable reactants, which results in the formation of ion pair dimers having fundamentally new properties compared with electrostatically linked ion pairs[137].

The zinc-octaethylporphyrin radical-cations (LXX) form diamagnetic dimers in a 10:1 (by volume) methanol–chloroform mixture in the temperature range between −20° and 50 °C.[138] The reaction was investigated by optical spectroscopy, EPR, NMR, and the temperature jump method (Table 6). The porphyrin rings in the dimer are located in parallel planes and are linked by a π−π′ bond[138] formed as a result of the overlap of half-filled orbitals. This bond [bond dissociation energy 17 kcal mol^{-1} (Table 6)] is stronger than the usual covalent bond in "hexaphenylethane" [11 kcal mol^{-1} (Table 4)].

Table 5. Thermodynamic parameters of the reversible dimerisation of peroxy- and nitroxy-radicals.

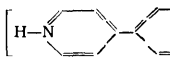
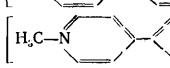
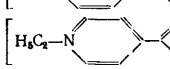
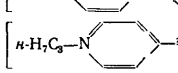
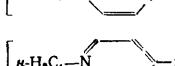
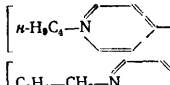
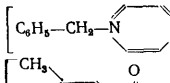
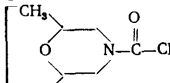
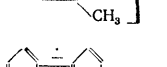
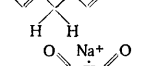
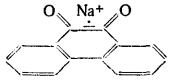
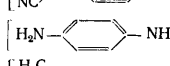
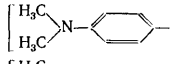
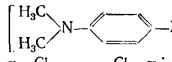
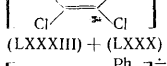
Radical	Solvent	K, mol l^{-1}	ΔH^0	ΔS^0	Refs.
$(CH_3)_3COO\cdot$ (LII)	CH_2Cl_2 *	$4.9\cdot10^{-5}$	6	—	115
»	CF_2Cl_2	—	8.8	34	116, 117
»	CF_2Cl_2	—	8.0	31	116, 117
»	isopentane	—	8.4	30	116, 117
$(CH_3)_2C(C_2H_5)OO\cdot$ (LIII)	2-methylbutane	$1.5\cdot10^{-5}$	8.9	36	118
»	CF_2Cl_2	—	7.5	29	116, 117
$(CH_3)_2C(CH(CH_3)C_2H_5)OO\cdot$ (LIV)	2-methylpentane	$6.7\cdot10^{-5}$	8.9	39	118
$(CH_3)_2C(C(CH_3)_2H)OO\cdot$ (LV)	isopentane	—	8.6	33	116, 117
$CH_3C(OO\cdot)(C_2H_5)_2$ (LVI)	3-methylpentane	$5.5\cdot10^{-5}$	9.7	44	118
$CH_3C(OO\cdot)CH(CH_3)_2$ (LVII)	2,3-dimethylbutane	$5.3\cdot10^{-5}$	8.2	34	118
$(CH_3)_2C(C(CH_3)_3)OO\cdot$ (LVIII)	2,2,3-trimethylbutane	$7.7\cdot10^{-5}$	8.7	38	118
$(CH_3)_2C(C_6H_5)OO\cdot$ (LIX)	cumene	$3.1\cdot10^{-6}$	11.2	48	118
»	CF_2Cl_2	—	9.2	32	116, 117
»	CF_2Cl_2	—	10.6	—	116, 117
 (LX)	CF_2Cl_2	—	7.0	35	116, 117
$(CH_3)_2C(CH_2C(CH_3)_3)OO\cdot$ (LXI)	CF_2Cl_2	—	7.8	31	116, 117
 (LXII)	CF_2Cl_2	—	8.0	30	116, 117
$(CH_3)(C_2H_5)C(C_6H_5)OO\cdot$ (LXIII)	CF_2Cl_2	—	11.0	—	116, 117
 (LXIV)	isopentane**	0.2	8.2	25	122
ditto	$CFCl_3$ + 10% isopentane**	0.5	5.6	17.5	122
»	CCl_4 **	0.9	—	—	122
 (LXV)	isopentane**	1.0	8.5	28.6	122
$(CH_3CD_2)_2NO\cdot$ (LXVI)	isopentane**	0.63	7.6	24.8	123
»	CF_2Cl_2 **	0.018	2.6	0.1	123
$(CH_3CH_2)_2NO\cdot$ (LXVII)	CF_2Cl_2 **	0.34	6	18	123, 126
$(CF_3)_2NO\cdot$ (LXVIII)	CF_2Cl_2 **	0.45	2.4	6.5	124
 (LXIX)	CH_2Cl_2 **	0.001	13	30	125

Note. *−95 °C; **25 °C—in the remaining cases −120 °C. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1}. The average errors of the determination are 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±5 cal mol^{-1} K^{-1} in ΔS.

The reversible dimerisation of the radical-cations of substituted viologens (1,1'-di-R,4,4'-bipyridylium monocations) (LXXI)–(LXXVII) in methanol at temperatures between −90° and 40 °C was investigated by EPR.[129,139,140] Table 6 presents the thermodynamic parameters obtained for these radicals. With increase of the size of the radical-cation, the reaction becomes more endothermic and its entropy increases. At room temperature the entropy of reaction has the dominant influence and, with increase in the size of the radical, the equilibrium shifts towards the formation of radicals. A linear relation has been observed between $\Delta H°$ and $\Delta S°$.[139]

It was to be expected that $\Delta S° > 0$ for the decomposition of dimers; however, the data in Table 6 show that the majority of radical-cations $\Delta S° < 0$, which means that the opposite

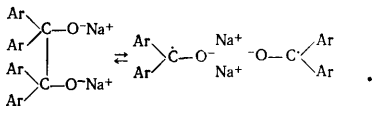
Table 6. Kinetic and thermodynamic parameters of reaction (1) involving radical-ions and ion pairs.

Radical ion or ion pair	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H°$	$\Delta S°$	Refs.
Radical-cation of zinc-octaethylporphyrin (LXX)	10:1 (by volume) methanol–chloroform	20	$1.3\cdot10^8$	$5.0\cdot10^3$	$4\cdot10^{-5}$	17.5	38	138
 (LXXI)	methanol	−13.5	—	—	$4.3\cdot10^{-3}$	1.0	−8.3	139
 (LXXII)	methanol	25	—	—	$1.5\cdot10^{-3}$	1.6	−7.7	139
 (LXXIII)	methanol	−11	—	—	$8.7\cdot10^{-4}$	2.0	−6.3	139, 140
 (LXXIV)	methanol	−10	—	—	$1.0\cdot10^{-3}$	2.5	−3.8	139
 (LXXV)	methanol	−12.5	—	—	$7.2\cdot10^{-4}$	3.0	−2.5	139
 (LXXVI)	methanol	−20	—	—	$7.2\cdot10^{-4}$	5.5	7.5	139
  (LXXVII)	methanol	−11	—	—	$6.3\cdot10^{-4}$	10.8	27.5	129
 (LXXVIII)	dimethoxyethane	23	—	—	$2\cdot10^{-3}$	−2.5	−29	144
 (LXXIX)	tetrahydrofuran	20.9	$1.0\cdot10^{4}$*	—	$1.96\cdot10^{-2}$	6	13	137
 (LXXX)	water + 0.2 M LiCl	15	$3.5\cdot10^8$	$9.0\cdot10^4$	$2.5\cdot10^{-4}$	10.4	18	130, 145
 (LXXXI)	1:2 ether–alcohol	~−100	—	—	—	8	—	131
 (LXXXII)	1:2 ether–alcohol	~−100	—	—	—	10	—	131
 (LXXXIII)	1:2 ether–alcohol	~−150	—	—	—	5	—	131
 (LXXXIV)	ethanol	−139	—	—	$5.0\cdot10^{-4}$	4.5	18.7	132
(LXXXIII) + (LXXX) **	acetonitrile	23	$6\cdot10^9$	$4\cdot10^8$	$7\cdot10^{-2}$	−4	−17	147
 (LXXXV) ***	acetonitrile	20	$5\cdot10^9$	$5.5\cdot10^8$	$1.1\cdot10^{-8}$	2.4	−20	148
(LXXXV) + (LXXXIII)								

Note. *In tetrahydropyran at 25 °C. ** Here k_{-1} is expressed in litre mol^{-1} s^{-1} and K is a dimensionless quantity [see Eqn.(13)]. *** See Eqn.(14).
$\Delta H°$ and $\Delta S°$ are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, k_{-1}, and K, ±0.5 kcal mol^{-1} in $\Delta H°$, and ±2 cal mol^{-1} K^{-1} in $\Delta S°$.

effect, causing an increase of entropy on dimerisation of two monomeric species, operates; this involves the removal of solvent molecules from the solvation shell of the radical-cation on dimerisation. With increase of the size of the radical-cation, the forces maintaining solvent molecules near it are weakened and ΔS° diminishes on desolvation during the dimerisation process. On this basis, one can assume that the radicals dimerise via a "plane-to-plane" mechanism, this type of dimerisation ensuring effective desolvation. By analogy with earlier studies[138,141], Evans et al.[139,140] suggested that the radicals in the diamagnetic dimer are linked by a $\pi-\pi'$ bond. Kosower and Cotter[142] postulated that the dimer (LXXII) is a biradical. The strongest bond between the viologen radical-cations is formed on dimerisation of (LXXVII) (Table 6). This behaviour can be due to the greater degree of delocalisation of the unpaired electron in (LXXVII), which ensures a more effective overlap between the π-type molecular orbitals of the radical-cations[140]. The reversible dimerisation of (LXXII) has also been observed by Blandmer et al.[143]

Apparently all alkali metal derivatives of aromatic ketyls are involved in equilibrium (1) in etheral solutions[144], which has been investigated by EPR and spectrophotometric methods. The ketyl dimer can have different structures and, depending on the solvent, can be paramagnetic or diamagnetic[144]. In non-polar solvents mainly the reversible conversion of the diamagnetic dimer into the paramagnetic dimer is observed:



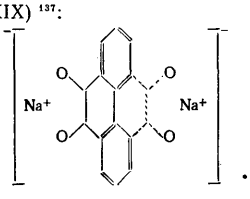
In ethers the paramagnetic dimer is formed preferentially. The data for equilibrium (1) involving sodium fluorenyl (LXXVIII) are presented in Table 6.

The sodium salts of radical-anions (ion pairs) of 9,10-phenanthrenequinone (LXXIX) and acetonaphthoquinone form diamagnetic dimers linked by a $\pi-\pi'$ bond[137]:

$$2(PhQ^{\cdot-}, Na^+) \rightleftarrows (D^{2-}, 2Na^+) .$$

The reactions were investigated by stopped flow and spectrophotometric methods (Table 6). The following structure has been postulated for the dimer (LXXIX):[137]

(LXXIX)[137]:



The tetracyanoquinodimethane radical-anions (LXXX) dimerise reversibly in aqueous and aqueous alcoholic solutions at room temperature[130,145]. The value of k_1 obtained by the temperature jump method (Table 6) is smaller by a factor of 5 than that calculated by the Debye formula taking into account the electrostatic repulsion. It may be that reaction (1) is diffusion-limited[145].

p-Phenylenediamine bromide (LXXXI), *N*,*N*-dimethyl-*p*-phenylenediamine perchlorate (Wurster's red) (LXXXII), and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine perchlorate (Wurster's blue) (LXXXIII) dimerise reversibly in solution (Table 6), being apparently linked to a single counterion[131]:

$$2R^{\dot{+}} + X^- \rightleftarrows (R_2X)^+.$$

The weak binding of radical (LXXXIII) is caused by the steric repulsion of the methyl groups: this radical is present in solution at room temperature as the monomer[131].

The radical-anions of quinones are involved in reversible dimerisation reactions at reduced temperatures, apart from the disproportionation reaction via one-electron transfer[132]. Table 6 presents data for the chloranil radical-anion (LXXXIV).

Radical-anions and radical-cations undergo rapid reversible electron transfer reactions with one another:

$$R^{\dot{+}} + Q^{\dot{-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R + Q. \qquad (13)$$

For example, Table 6 presents data for reaction (13) involving radicals (LXXXIII) and (LXXX) obtained by the temperature jump method. This reaction can include a stage in which a charge-transfer complex (CTC) is formed:

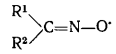
$$R^{\dot{+}} + Q^{\dot{-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CTC \rightleftarrows R + Q. \qquad (14)$$

For example, the formation of both the corresponding radical-anions and CTC has been observed in polar solvents[148]. The kinetic and thermodynamic parameters of reaction (14) with participation of (LXXXIII) and the 2,6-diphenyl-1,4-benzoquinone radical-anion (LXXXV) have been obtained by flash photolysis and spectrophotometry (Table 6). The constant k_1 agrees satisfactorily with the rate constant for a reaction between charged radicals limited by translational diffusion[148].

IX. OTHER RADICALS

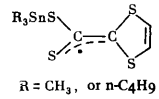
1-Alkyl-4-methoxycarbonylpyridyl radicals (LXXXVI)–(LXXXVIII) (Table 7) dimerise reversibly in isopentane at temperatures between −207° and −63 °C.[141,174] The reaction has been investigated spectrophotometrically. It has been suggested that the radical dimers are charge-transfer complexes[141] and it has been shown[149] that the irreversible destruction of 4-carbamoyl-1-methylpyridyl radicals in acid aqueous solution is preceded by reversible dimerisation[149]. Certain pyridyl radicals disproportionate reversibly via the transfer of a single electron[173].

Diaryliminoxy-, alkylaryliminoxy-, and dialkyliminoxy-radicals having the structure



dimerise reversibly in benzene with formation of N–N, N–O, and C–O bonds[10]. Sterically unhindered dialkyliminoxy-radicals are involved in an equilibrium which is displaced towards the dimers. For the majority of the diaryliminoxy-, alkylaryliminoxy-, and sterically hindered dialkylimonoxy-radicals, the equilibrium is displaced towards the radicals. For these radicals, ΔH° = 15–20 kcal mol^{-1} in toluene[10]. Irreversible reactions also take place in the system[10].

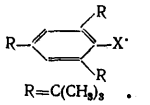
The 1-thioallyl radicals, having the structure



R = CH_3, or n-C_4H_9

and obtained from tetrathiofulvalene, have been investigated by EPR.[150] It was established that these sterically hindered radicals are in equilibrium with diamagnetic dimers in toluene at 25 °C and below. The dimer is probably formed via the S–S coupling reaction[150].

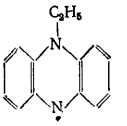
The recombination of 2,4,6-tri-t-butyl-substituted benzyl (LXXXIX), phenylaminyl (LXL), phenylthiayl (LXLI), and phenoxy-radicals in hydrocarbons as well as di-t-butyl peroxide has been investigated by EPR:[53]



The radicals are isoelectronic and are characterised by the same extent of steric hindrance around the reaction centre. It has been established that the benzyl radicals recombine irreversibly to form bibenzyl (Table 7). The phenylaminyl radical is in equilibrium with the corresponding dimer (hydrazine) at room temperature (Table 7). The data in Table 7 show that the recombination of sterically hindered phenylaminyl radicals is slower by four orders of magnitude than that of benzyl radicals. The phenylthiyl radicals in solution are in equilibrium with the corresponding disulphide (Table 7).

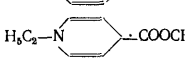
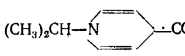
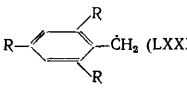
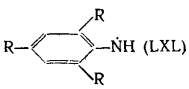
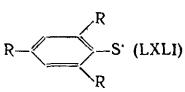
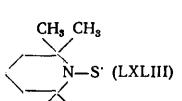
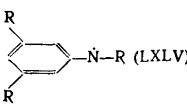
The difference between the reactivities of radicals (LXXXIX)–(LXLI) is due to the difference between the dissociation energies of the bonds formed on "head-to-head" recombination. The dissociation energy of the bonds in the dimers varies in the sequence C–C > S–S > N–N > O–O; the O–O bond dissociation energy is apparently close to zero[53]. With increase of the strength of the bond formed, the rate of recombination of radicals also increases, which can be accounted for on the basis of Hammond's postulate. Indeed the more exothermic the reaction, the greater the similarity between the transition state and the reactants. For sufficiently exothermic reactions, the bond can then be formed over a comparatively large distance between the reactants, where the influence of t-butyl groups is small[53]. The values of $\Delta S_{-1}^{\neq}$ are much smaller than the "normal" value (see Section VI) for radicals (LXL) (Table 7) and (LXXXIX).[53]

The study of the absorption spectra and magnetic susceptibility of *N*-ethylphenazyl



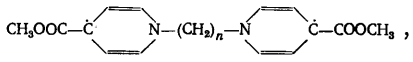
(solvent 2 : 1 alcohol–ether) showed that the radicals dimerise reversibly at low temperatures (~–180 °C); the radicals in the dimer are located in parallel planes[146].

Table 7. Kinetic and thermodynamic parameters of reaction (1) involving radicals of different structure.

Radical	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0	Refs.
 (LXXXVI)	isopentane	—196	—	—	$1.4\cdot10^{-4}$	—	—	—	—	—	—	141
 (LXXXVII)	isopentane	—196	—	—	$2.9\cdot10^{-5}$	—	—	—	—	—	—	141
 (LXXXVIII)	isopentane	—196	—	—	$1.2\cdot10^{-4}$	—	—	—	—	—	—	141
 (LXXXIX)	di-t-butyl peroxide	24	$5\cdot10^{8}$	—	—	—	—	—	—	—	—	53
 (LXL)	di-t-butyl peroxide	20	$3\cdot10^{4}$	7.5	$2.5\cdot10^{-4}$	2.0	15.0	13.1	—32	—5	27	53
 (LXLI)	iso-octane	18	—	—	$1.7\cdot10^{-12}$	—	—	23.3	—	—	27	53
$(CH_3)_3\dot{C}Se\dot{C}[C(CH_3)_3]_2$ (LXLII)	pentane	—15÷—50	—	—	—	—	—	18.2	—	—	37.5	152
 (LXLIII)	t-butylbenzene	25	$8.3\cdot10^{8}$	$3\cdot10^{-3}$ **	$1.5\cdot10^{-12}$	3.4	13	28	—7	20	27	153
$[(CH_3)_2CH]_2N\dot{S}$ (LXLIV)	t-butylbenzene	11	$6.0\cdot10^{8}$	$5\cdot10^{-7}$ **	$1\cdot10^{-15}$	3.4	27	24	—7	9	16	153
 (LXLV)	methylcyclohexane	—13.8	1,6	—	$6.0\cdot10^{-6}$ ***	—2.2	29	31.2	—65	8	73	154

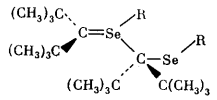
Note. *At 71 °C. **Calculated from the formula $k_{-1} = Kk_1$. ***At 47.7 °C.
ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The errors of the determinations of the various quantities differ markedly and are given in the original papers.

Biradicals can form diamagnetic dimers. Pyridyl biradicals having the structure



where $n = 3$ or 4, exhibit a significantly smaller paramagnetism than expected[151,174]. The ends of the pyridyl radicals are involved in intermolecular association and form a singlet (diamagnetic) species. There is virtually no association of radicals with $n = 2$, 5, and 10.[151,174]

The bimolecular reactions of the radicals $RSeC[C(CH_3)_3]_2$, where R = CH_3, $(CH_3)_3C$ (LXLII), CF_3, C_6H_5, $(n\text{-}C_4H_9)_3Si$, $(CH_3)_3Sn$, $(CH_3)_3Ge$, $(CH_3)_3CO$, or $(CH_3)_3CS$, have been investigated by EPR.[152] The majority of these radicals (possibly all of them) are in equilibrium with diamagnetic dimers at low temperatures. The dimers apparently have a "head-to-tail" structure:



The data for radicals (LXLII) are presented in Table 7. Together with reversible recombination, the irreversible destruction of the radicals takes place. The destruction follows a first-order law in conformity with Scheme II (Section II).

The 2,2,6,6-tetramethylpiperidinylthiyl radical (LXLIII) and the diisopropylaminothiyl radical (LXLIV) have been obtained[153] by the photolysis of the corresponding disulphides in the resonator of the EPR spectrometer. The equilibrium

$$2R_2NS^{\cdot} \rightleftarrows R_2NSSNR_2$$

is established at 40–130 °C. The destruction of radicals (LXLIII) and (LXLIV) at room and lower temperatures obeys a second-order law in t-butylbenzene (Table 7); the rate of reaction is apparently limited by diffusion.

The recombination of the radicals $R_2NS^{\cdot}$ differs from the recombination of the related dialkylnitroxy-radicals $R_2NO^{\cdot}$ by the fact that it takes place via a "head-to-head" mechanism with formation of a stronger bond (Table 7). The nitroxy-radical dimers have a bond dissociation energy not exceeding 13 kcal mol^{-1} (Table 5).

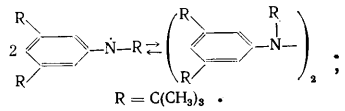
Like arylethanes and the dimer (XL) (Section VI), arylhydrazines dissociate reversibly into diarylaminyl radicals on heating or irradiation:

$$2Ar_2N^{\cdot} \rightleftarrows Ar_2N{-}NAr_2 .$$

This reaction has been described in monographs[11,101,168,169] and reviews[178,180]. The EPR spectra of diarylaminyl radicals containing the electron-donating substitutents $N(CH_3)_2$, CH_3O, and CH_3 in the aromatic ring have been recorded[179].

On thermal dissociation of arylhydrazines, not all substituents capable of delocalising the unpaired electron increase the degee of dissociation. The following sequence based on the influence of the substitutents is observed: $N(CH_3)_2 > OCH_3 > CH_3 > H > COOC_2H_5 > CN > NO_2$.[178] This sequence of substituents shows that the dissociation of substituted hydrazines is determined mainly by the interaction within the hydrazine molecule (the interaction of the unshared electron pair with the substituents in the *para*-position) and much less so by the delocalisation of the unpaired electron in the radical[178].

The *N*-3,5-tri-t-butylphenylaminyl radical (LXLV) recombines reversibly to a dimer at temperatures between −13° and −103 °C in methylcyclohexane (Table 7):[154]



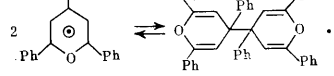
The reaction was investigated by EPR. At low temperatures ($t < -13$ °C) the equilibrium is fully displaced towards the formation of the dimer; the radical can be regenerated by photolysis and the kinetics of its destruction can be studied.

The value of $\Delta H°$ obtained (Table 7) is close to the dissociation energy of the N–N bond in hydrazobenzene (37.7 kcal mol^{-1}) [154] and the introduction of t-butyl groups into hydrazobenzene should reduce this quantity. The value of $\Delta S°$ obtained for this radical is extremely high compared with $\Delta S°$ for phenoxy- (Tables 1 and 3), nitroxy- (Table 5), triphenylmethyl (Table 4), and arylindan-1,3-dionyl (Table 2) radicals as well as radical-ions (Table 6). The given dimer is sterically hindered to an extremely large extent as a result of the coupling reaction and its decompositon leads to the possibility of the free rotation of the t-butyl groups.

The negative values of $\Delta H_1^{\neq}$ obtained for the recombination of radicals (LXLV) were observed also for other radicals—phenoxy (Tables 1 and 3) and nitroxy-radicals[123], and were interpreted on the assumption of an equilibrium preceding the slowest stage of the reaction. The high negative value of $\Delta S_1^{\neq}$ (Table 7) indicates a very rigid transition state in the recombination reaction. In fact the rate of recombination is controlled by the activation entropy.

The appreciable shielding of the N atom in aminyl radicals leads to the formation of dimers linked by C–N and even C–C bonds[155,178].

The 2,4,6-triphenylpyranyl radicals recombine reversibly to a dimer in acetonitrile at temperatures between −40° and 30 °C:[156]



The reaction was investigated by EPR and ultraviolet spectroscopy. $\Delta H_1^{\neq} = 6.4$ kcal mol^{-1} was obtained.

X. THE INFLUENCE OF THE SOLVENT ON THE KINETICS OF REVERSIBLE RECOMBINATION

The solvent is known to have a significant influence on the rates of radical reactions in the liquid phase[157]. The solvent viscosity, the formation of complexes by radicals with the solvent, and specific and non-specific solvation influence the reactivity of radicals. The difference between the degrees of solvation of the radicals and the dimer influences the constant of equilibrium (1). The rate of reaction (−1) in polar solvents depends on the ratio of the dipole moments of the transition states in this reaction. The influence of the solvent on reaction (1) for radicals of different classes is examined below.

1. Phenoxy-Radicals

The influence of specific solvation on the kinetics of the reversible recombination of phenyl-, methoxy-, and t-butylphenoxy-radicals has been studied in detail[1,7,25–27,29,75,90,158].

Tables 8 and 9 present the kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in various solvents.

Table 8. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in different solvents at 20 °C.

Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	10^8K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
				(I) [1]					
Hexane	32	80	2.5	0.5	12.8	12.3	12	—5	7
Carbon tetrachloride	8.5	50	5.5	2.5	14.8	12.3	3	0	8
Toluene	7.5	150	20	3.0	14.0	11.0	7	0	7
Dioxan	3	120	40	3.0	14.4	11.4	9	1	10
Methanol	12	840	70	1.5	11.2	9.7	11	—7	4
Acetonitrile	6	720	120	2.0	10.5	8.5	11	—9	2
Chloroform	2	250	130	2.0	10.0	8.0	13	—13	0
DMF	5	800	160	—	—	—	—	—	—
				(II) [25]					
Carbon tetrachloride	14	—	—	0.3	—	—	14	—	—
Toluene	7.0	0.0070	0.001	2.2	24	22	9	16	25
Benzene	6.5	—	—	2.3	—	—	9	—	—
THF	6.0	—	—	1.9	—	—	10	—	—
Chlorobenzene	3.2	0.096	0.03	3.2	19	17	11	8	19
Chloroform	2.0	—	—	2.0	—	—	9	—	
Dichloromethane	3.8	—	—	1.1	—	—	14	—	
Acetone	8.0	—	—	0.7	—	—	14	—	
Acetonitrile	10	0.06	0.006	0.5	22	21	14	11	25
Acetic acid	3.6	—	—	2.3	—	—	13	—	
Formic acid	4.5	—	—	1.3	—	—	13	—	
				(IV) [25]					
Carbon tetrachloride	3.1	0.71	0.23	1.6	22.3	20.7	13	18	31
Toluene	3.4	5.5	1.62	1.6	17.8	16.8	13	6	19
Benzene	3.0	2.4	0.81	1.5	20.7	19.2	13	15	28
THF	2.2	3.0	1.38	1.8	19.0	17.2	13	9	22
Chlorobenzene	2.2	2.3	1.03	1.9	20.9	19.0	12	16	28
Chloroform	1.4	6.6	4.71	2.6	17.2	14.6	11	5	16
Dichloromethane	2.2	8.0	3.62	1.2	18.7	17.5	15	11	26
Acetone	2.4	6.5	2.71	1.3	17.8	16.5	14	7	21
Acetonitrile	5.5	9.7	1.77	0.9	16.0	15.1	14	2	16
Acetic acid	2.0	17	8.7	2.2	18.7	16.5	12	12	24
Formic acid	3.0	—	—	1.7	—	—	12		
				(V) [25]					
Carbon tetrachloride	2.3	—	—	0.2	—	—	18	—	—
Toluene	2.5	0.010	0.0042	0.5	22	21	17	7	24
Benzene	2.0	—	—	1.7	—	—	13	—	—
THF	3.0	—	—	0.9	—	—	15	—	—
Chlorobenzene	1.3	0.014	0.011	1.1	20	19	16	1	17
Chloroform	0.36	—	—	1.1	—	—	19	—	—
Dichloromethane	1.1	—	—	0.1	—	—	20	—	—
Acetone	3.8	—	—	0.6	—	—	16	—	—
Acetonitrile	7.0	0.049	0.0070	0.4	15	15	15	—11	4
Acetic acid	2.2	—	—	1.7	—	—	13	—	—
Formic acid	3.0	—	—	2.0	—	—	11	—	—
				(VII) [90]					
Carbon tetrachloride	11	22	2.0	1.5	8.6	7.1	10	—22	—12
Toluene	4.0	12	3.0	1.7	13.0	11.3	19	—14	4
Benzene	7.2	17	2.3	1.0	12.0	11.0	13	—11	2
THF	2.6	2.5	0.96	0.8	15.8	15.0	17	—2	15
Chlorobenzene	6.7	10	1.5	0.8	12.6	11.8	13	—9	4
Chloroform	2.5	27	11	2.0	14.9	14.7	19	0	19
Dichloromethane	5.6	26	4.7	1.2	16.7	15.5	14	6	20
Acetone	0.97	0.87	1.0	3.2	21.0	17.8	11	14	25
Acetonitrile	6.1	4.6	0.75	0.2	20.1	19.9	17	14	31
Acetic acid	1.5	3.5	2.3	1.6	15.6	14.0	11	2	13
Formic acid	0.60	—	—	3.0	—	—	21	—	—
				(VIII) [7, 75]					
Toluene	0.80	2.5	3.2	2.5	17.0	14.5	12	3	15
Benzene	0.50	3.5	7.1	2.5	17.5	15.0	13	5	18
Chloroform	0.20	1.2	6.0	4.5	17.5	13.0	8	3	11
Acetonitrile	1.7	4.0	2.4	1.0	15.0	14.0	16	—3	13
				(XI) [7, 75]					
Toluene	0.45	112	250	—1.0	16.5	17.5	25	9	34
Benzene	0.7	110	160	—0.5	17.0	17.5	23	10	33
				(XXIV) [7,75]					
Benzene	3.1	0.85	0.28	1.5	22.0	20.5	14	19	33
Chloroform	0.9	2.8	3.1	2.5	17.5	15.0	13	5	18
Acetonitrile	4.7	6.1	1.3	0.5	17.5	17.0	17	6	23
Formic acid	2.7	3.0	1.1	2.0	20.0	18.0	12	9	23

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 30% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±1 cal mol^{-1} K^{-1} in ΔS. See also Table 13.

Table 9. The rate and equilibrium constants for reaction (1) involving radical (IX) in various solvents at 20 °C.[1,27]

Solvent	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	Solvent	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}
Hexane	5.4	1600	300	t-Butyl alcohol	0.175	525	3 000
Carbon tetrachloride	1.75	1750	1 000	Acetonitrile	0.26	2900	11 000
Toluene	0.7	2100	3 000	Isopropyl alcohol	0.55	1650	3 000
Benzene	0.65	2600	4 000	1-Butanol	0.62	2500	4 000
Dioxan	0.19	3000	16 000	1-Propanol	0.81	3200	4 000
Chlorobenzene	0.11	2000	18 000	Ethanol	0.86	2600	3 000
Chloroform	0.050	1100	22 000	DMF	0.095	1400	15 000
Pyridine	0.022	550	25 000				

Note. The average errors of the determinations are 10% in k_1, 20% in K, and 30% in k_{-1}. See also Table 1.

The recombination reaction. V-shaped relations between k_1 and the empirical parameter E_T, characterising the solvent polarity, have been observed for phenylphenoxy-radicals (Tables 8 and 9).[1] The above relations are more pronounced for radicals whose recombination takes place under kinetic conditions [radicals (VIII) and (IX)] than for phenylphenoxy-radicals whose recombination is limited by diffusion[1,90]. This fact is consistent with the general observation that the solvent has a more significant influence on slow reactions than on fast reactions.

Phenylphenoxy-radicals form charge-transfer complexes with solvent molecules. The charge-transfer bands in the spectra of solutions of radical (IX) in different solvents have been observed.[159] The solvation of the radicals leads as a rule to a decrease of their diffusion coefficient and possibly to shielding of the reaction centre, which entails a decrease of k_1. Furthermore, the recombination of radicals is accompanied by the dissociation of complexes, which increase $\Delta H_1^{\neq}$. As a consequence, k_1 diminishes with increase of E_T from 31 (hexane) to 40 (chloroform). In chloroform k_1 has the lowest value; chloroform molecules form complexes with phenoxy-radicals as a result of interaction with the oxygen atom or the π-electrons of the benzene rings[158].

The causes of the increase of k_1 in solvents with $E_T > 40$ are less clear. DMF, acetonitrile, and alcohols have high dielectric constants and an unshared electron pair; alcohols are capable of forming hydrogen bonds with phenoxy-radicals. The redistribution of charges on the atoms of phenoxy-radicals due to their specific solvation by these solvents apparently promotes a rapid attainment of the required orientation for the recombination of the radicals in the cage[1,158]. As a result of this, the constant k_1 should increase. The V-shaped relation between k_1 and E_T for the recombination of radicals (VIII) and (IX) under kinetic conditions can be explained as follows[1,27,90]. The recombination of the radicals is accompanied by the dissociation of the complexes, which increases $\Delta H_1^{\neq}$. At the same time the decomposition of the complexes increases the degree of disorder and hence the activation entropy $\Delta S_1^{\neq}$. Since $\Delta H_1^{\neq}$ and $T\Delta S_1^{\neq}$ have opposite signs as components of $\Delta G_1^{\neq}$, the observed relation can occur when, on changing the solvent, k_1 is initially influenced predominantly by the change in $\Delta H_1^{\neq}$ and then by the change in $\Delta S_1^{\neq}$.

Polar solvents can also solvate the molecules of the dimers as a result of which the recombination of the radicals is not accompanied by the dissociation of the complexes[90]. Indeed, the recombination of radicals (VIII) is accompanied by an increase of $\Delta H_1^{\neq}$ in the sequence hexane < toluene (benzene) < chloroform (Tables 3 and 8), owing to the increase of the stability of the radical–solvent complex. At the same time an increase of $\Delta S_1^{\neq}$ is observed (compensation effect). However,

in a polar solvent (acetonitrile) low values of $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ are observed. In this case the dimer molecules as well as the radical are solvated and the solvation energies of the radical and the dimer are similar[90].

The influence of the composition of the binary mixture on k_1 for phenylphenoxy-radicals has been studied[1,26,27] using binary mixtures of solvents corresponding to different branches of the V-shaped relation between k_1 and E_T as well as binary mixtures one of the components of which was chloroform. The low value of k_1 in chloroform is caused by the specific solvation of the radical by the solvent and not by the properties of the medium as a "continuum"[1]. It was suggested that in binary hexane–chloroform and carbon tetrachloride–chloroform mixtures hexane and carbon tetrachloride do not form complexes with phenoxy-radicals (PhO$^{\cdot}$), while chloroform (S) forms 1 : 1 solvate complexes (PhO$^{\cdot}_S$):

$$PhO^{\cdot} + S \underset{}{\overset{K_{RS}}{\rightleftharpoons}} PhO^{\cdot}_S,$$

$$PhO^{\cdot} + PhO^{\cdot} \xrightarrow{k_1} \text{dimer},$$

$$PhO^{\cdot} + PhO^{\cdot} \xrightarrow{k_{RS}} \text{dimer},$$

$$PhO^{\cdot}_S + PhO^{\cdot}_S \xrightarrow{k_{SS}} \text{dimer}.$$

The kinetic parameters for which the given scheme describes the observed dependence of k_1 on the chloroform concentration in the binary mixture were estimated[1]:

$K_{RS}=0.9\pm0.2$ litre mol^{-1}, $k_{RS}=(1.2\pm0.5)\cdot10^7$ litre mol^{-1} s^{-1}

[radical (IX) in a chloroform–hexane mixture];

$K_{RS}=0.45\pm0.10$ litre mol^{-1}, $k_{RS}=(9.0\pm2.0)\cdot10^6$ litre mol^{-1} s^{-1}

[radical (IX) in a chloroform–carbon tetrachloride mixture];

$K_{RS}=0.18\pm0.05$ litre mol^{-1}, $k_{RS}=(2.0\pm1.0)\cdot10^8$ litre mol^{-1} s^{-1}

[radical (I) in a chloroform–carbon tetrachloride mixture]. In all cases $k_{SS} \ll k_{RS}^1$.

The above ideas proved to be inapplicable to binary mixtures containing an alcohol. The relations between $k_1\eta$ and the compositions of such binary mixtures showed maxima and minima[1,90], which is due to the fact that the mixtures have a complex structure which varies with the component ratio. The solutions differ significantly from regular solutions and there is a possibility of microlayer formation in the mixture. When methanol is diluted with carbon tetrachloride or chloroform, the fraction of alcohol dimers and trimers, which form more stable complexes with the radicals, increases[1].

The rate of the diffusion-controlled recombination of radicals reflects the changes in the structure of the solution as a function of its composition. In these mixtures the microviscosity differs significantly from the macroviscosity and the changes in k_1 are determined by the behaviour of excess thermodynamic functions. Thus the study of the rate of diffusion-controlled recombination reactions constitutes together with spin exchange in binary mixtures, a method for the quantitative study of phenomena of this kind[1].

The constants k_1 for t-butyl- and methoxy-phenoxy-radicals depend only slightly on the chemical nature of the solvent (Table 8). The data of Kuz'min et al.[160] permit the conclusion that the k_1 for the *o*-methylphenoxy-radical also depends on the nature of the solvent only slightly. Thus specific solvation has a significant influence on the recombination of only those phenoyx-radicals which contain aryl substituents.

It has been observed that k_1 for the *o*-methylphenoxy-radical diminishes with increase of the ionic strength of the aqueous solution[161], but this is apparently caused by the increased viscosity of the medium.

Dissociation reaction of the dimers. The solvent also has a significant influence on k_{-1}. For example, k_{-1} for radical (I) increases by more than an order of magnitude with increase of solvent polarity (Table 8). An analogous solvent effect was observed for radical (XXIV) (Table 8). For dimers with a "head-to-tail" structure, $\Delta H_{-1}^{\neq}$ decreases with increased solvent polarity [radicals (I), (VIII), (IX), and (XXIV); Tables 8 and 9]. Under these conditions, k_{-1} either increases [radicals (I) and (XXIV)] or depends only slightly on the solvent [radicals (VIII) and (IX)] due to the compensation effect.

The influence of the solvent on $\Delta H_{-1}^{\neq}$ has been examined[29] as a function of the ratio of the dipole moments of the transition state ($\mu^{\neq}$) and the initial dimer (μ_d). 2,6-Diphenyl-4R-phenoxy-radicals form dimers having the structure of quinol ethers ("head-to-tail"). An increase of the solvating capacity of the solvent lowers $\Delta H_{-1}^{\neq}$ for such dimers, since in this case $\mu^{\neq} > \mu_d$. The dimerisation of radicals (VII) results in the formation of C–C dimers ("tail-to-tail"). In this case $\mu^{\neq} < \mu_d$ and the increase of the solvating capacity of the solvent leads to an increase of $\Delta H_{-1}^{\neq}$ (Table 8).

2. Aromatic C-Centred Radicals

The values of K for the triphenylmethyl radical (XL) and its substituted derivatives in various solvents have been determined calorimetrically[162–164,175] and the constants k_{-1} have been obtained in experiments involving the addition of oxygen or nitric oxide to the dimer (Table 10). The values of k_{-1} obtained[162,175] for radical (XL) in 28 solvents at 0 °C varied from 1.1×10^{-3} to 4.2×10^{-3} s^{-1}.

Table 10. The equilibrium constants and enthalpies of reaction (1) involving radical (XL) in various solvents at 20 °C.[163]*

Solvent	$10^4\cdot K$, mol l^{-1}	$\Delta H°$, kcal mol^{-1}	Solvent	$10^4\cdot K$, mol l^{-1}	$\Delta H°$, kcal mol^{-1}
Propionitrile	1.20	11.1	Ethylene dibromide	3.90	11.4
Ethyl benzoate	1.67	12.0	Benzene	4.10	11.3
Acetophenone	1.70	11.5	Chloroform**	6.90	10.5
Dioxan	2.50	11.6	Carbon disulphide***	19.2	11.0
Bromobenzene	3.70	11.5			

Note. *See also Table 4; **$k_{-1} = 0.219$ s;[164] $k_1 = 3.2\times10^2$ litre mol^{-1} s^{-1}; ***$k_{-1} = 0.252$ s^{-1};[164] $k_1 = 1.3\times10^2$ litre mol^{-1} s^{-1}.
The errors of the determinations are ~5% in K and k_{-1}, ~10% in k_1, and ±0.3 kcal mol^{-1} in $\Delta H°$.

A relation of the Brønsted type, $\ln k = \alpha \ln K$ + const., is known to hold for a number of reactions[165]. It has been shown[165] that the relation holds satisfactorily for the dissociation of the dimer of (XL) in various solvents and $\alpha = 0.2$. According to the author, the transition state in the decomposition reaction resembles the dimer more than the radicals. The initial dimer and the transition state cannot interact with the solvent for steric reasons[165]. The influence of the solvent on the kinetics of

reaction (1) with participation of 2-aryl-indan-1,3-dionyl radicals having structures (XII) and (XVI) has been studied[166]. The values of k_1 for radical (XII) differ insignificantly in all the solvents investigated (Table 11).

Table 11. Kinetic and thermodynamic parameters of reaction (1) involving radicals (XII) in various solvents at 20 °C.[166]

Solvent	$10^7\ k_1$, l mol^{-1} s^{-1}	$10^2\ k_{-1}$, s^{-1}	$10^6\ K$, mol l^{-1}	$\Delta H_1^{\neq}$	ΔH_{-1}	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
Toluene	10.5	2	$1.9\cdot10^{-1}$	3.5	24.2	20.7	3.9	16.2	20.1
Chloroform	8	7	$9.1\cdot10^{-1}$	2.6	21.9	19.3	7.5	10.9	18.4
Acetic acid	3.75	11.5	3.1	2.3	21.0	18.7	9.7	9.0	19.1
Tetrachloroethane	3.6	16	4.5	2.0	19.9	17.9	10.2	6.7	17.1
DMF	7.5	45	6.0	1.0	18.0	17.0	12.6	2.0	14.7

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1}. The errors of the determinations are 10% in k_1, 20% in K, 30% in k_{-1}, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS; see also Table 2.

The linear relation observed[166] between $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ is apparently a consequence of purely random experimental errors. Generally speaking, the range of variation of $\Delta H_1^{\neq}$ for reaction (1) is very insignificant compared with the errors in the determination of this quantity; as a result, it is difficult to demonstrate the existence of an isokinetic relation for reaction (1). A V-shaped relation between k_1 and the parameter E_T has been observed[166] for radical (XVI) containing phenyl substituents, as for phenylphenoxy-radicals[1,25].

The constant K for radical (XLV) increases by a factor of 430 at 30 °C on transfer from benzene to isopropyl alcohol (Table 4).[110] This is caused by the specific solvation of the radical in isopropyl alcohol with formation of hydrogen bonds. The heats of formation of the benzopinacol dimer in benzene and isopropyl alcohol are approximately the same. According to estimates, the solvation of the above radical in isopropyl alcohol is more exothermic by 3–7 kcal mol^{-1} than in benzene[110]. The quantity $\Delta(\Delta S)$ for solvation is 10.8 cal mol^{-1} K^{-1} on transfer from benzene to toluene. Such values are usually observed on formation of a hydrogen bond with oxygen-containing acceptors[110].

3. Other Radicals

The thermodynamic parameters $\Delta H°$ and $\Delta S°$ for the dimerisation of the nitroxy-radicals (LXIV) and (LXVI) (Table 5) depend on the solvent. In isopentane, which is a poor solvent for nitroxy-radicals and their dimers, the thermodynamic parameters for the above two radicals are similar (Table 5). The radicals are more polar than the dimers and, on transfer from isopentane to polar solvents such as $CFCl_3$ and CF_2Cl_2, $\Delta H°$ and $\Delta S°$ diminish[122,123] (Table 5).

The solvent can solvate the radicals and dimers to different extents as a consequence of the difference in the steric hindrance around the active centre in the radical and the dimer. In the paramagnetic dimers of aromatic sodium ketyls two sodium ions are surrounded by two large ketyl anions and the solvation is therefore hindered[144]. In the monomer more space is available for solvent molecules and the radical pair is solvated to a greater extent than the dimer. The difference between the degrees of order in the solvent for the monomer and dimer is reflected in the negative values of $\Delta S°$ (−29 – −37 cal mol^{-1} K^{-1}).[144]

The thermodynamic parameters of equilibrium (1) involving the tetracyanoquinodimethane radical-anion (LXXX) in aqueous ethanol have been determined[128] and it has been established that $\Delta G°$ decreases with increase of the ethanol content, while $\Delta H°$ and $\Delta S°$ pass through a maximum. These relations have been explained on the basis of the proposed model of solvation: water molecules are more strongly attracted to the radical-anion dimer than ethanol molecules. The Li^+, Na^+, and K^+ counterions do not have an appreciable influence on the dimer–monomer equilibrium and are apparently not present in the vicinity of the anions.

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Thus the reversible recombination of radicals in solution with formation of dimers is a fairly general phenomenon, characteristic of organic radicals of different classes, such as the arylmethyl, phenoxy-, alkylperoxy-, iminoxy-, nitroxy-, diarylaminyl, and many others. Numerous radicals present in solution at an appreciable concentration are not stable monomers and are involved in a dynamic equilibrium with the corresponding diamagnetic dimers. The solutions of these radicals are usually coloured and give rise to an EPR signal. The solutions do not obey the Beer–Lambert–Bouguer law. Heating or irradiation of the solutions increase the concentration of radicals.

In the study of the magnetic susceptibilities of solutions of organic free radicals, a deviation from the Curie law, caused by the equilibrium between the paramagnetic monomers and the diamagnetic dimers, is frequently observed.

Together with the reversible recombination reaction, irreversible radical disproportionation or dimer decomposition reactions can take place in solution. The decrease of the steady-state concentration of radicals frequently obeys a kinetic first-order law under these conditions. The dimers undergoing reversible decomposition have found a practical application as photochromic and thermochromic compounds[171] and also as effective inhibitors[113].

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