Flash Photolysis Study of Phenyl-substituted Phenols, Quinones, and Corresponding Free Radicals. Part 2. Dimerisation of 2,6-Diphenyl-4-methoxyphenoxyl Radical in Various Solvents

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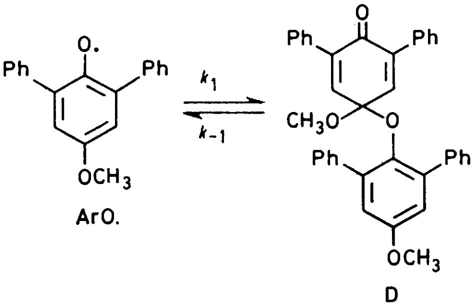
Kinetic and thermodynamic parameters of the dimerisation of 2,6-diphenyl-4-methoxyphenoxyl radical to the dimer in various solvents have been obtained. A regular decrease in the rate constant of radical dimerisation in the order hexane > carbon tetrachloride > toluene > dioxan > chloroform has been observed. In all solvents this dimerisation was found to be diffusion-controlled.

It has been shown [1,2] that the nature of the solvent has an important effect on the kinetics of radical reactions. The ability of the radical to engage in complex formation with the solvent and both specific and non-specific solvation are important factors determining the reactivity of radicals. The complex formation of stable radicals has recently been studied [3,4] in detail; however, little information is available on the effect of the medium on the kinetics of dimerisation (recombination) of short-lived radicals.



ArO.

D

(1)

A study of the effect of the medium on radical recombinations holds promise for elucidating the mechanism of this process. The dimerisation of 2,6-diphenyl-4-methoxyphenoxyl radicals (ArO•) has now been studied in various solvents. In solution ArO• is in equilibrium with its dimer, 4-(2,6-diphenyl-4-methoxyphenoxy)-4-methoxy-2,6-diphenylcyclohexa-2,5-dienone (D).[5]

RESULTS AND DISCUSSION

Flash photoexcitation of a solution of D (10^{-5}—10^{-4}M) through a light filter UFS-2 (280—380 nm) results in a concentration of ArO• different from the equilibrium concentration, Δ[ArO•] caused by photochemical decay of D.[6] The kinetic curve of Δ[ArO•] decay observed is

$$D \xrightarrow{h\nu} 2\text{ArO}\cdot \qquad (2)$$

described by equation (3), in which $\Delta[\text{ArO}\cdot]_0$ stands for the

$$\ln \frac{\Delta[\text{ArO}\cdot]_0}{\Delta[\text{ArO}\cdot]} = 4k_1\left(\overline{[\text{ArO}\cdot]} + \frac{K}{4}\right)t \qquad (3)$$

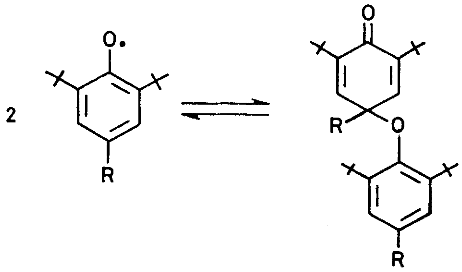
ArO• concentration change as a result of the flash ($t = 0$), and K is k_{-1}/k_1. The ArO• extinction coefficients were previously determined,[6] and the K and H_0 values were obtained by spectrophotometric measurement.[7] The kinetic and thermodynamic characteristics of reaction (1) obtained for various solvents are listed in the Table.

N.M.R. Spectroscopy.—The n.m.r. spectrum of dimer D at low temperatures (—40 to 0 °C) shows distinct absorption lines ascribed to the protons of the aromatic and cyclohexadiene part of D and also of the two methoxy-groups. When the temperature is increased the lines broaden. The single broad line corresponding to the methoxy-groups, was used to determine k_{-1} according to equation (4) [8] (for details see Experimental section). The k_{-1} and ΔH^* values obtained [9] in this

$$k_{-1} = 1/T_2 \qquad (4)$$

way show good agreement with those obtained by flash photolysis (see Table).

A similar equilibrium system (5) has been studied by n.m.r.[8] The k_{-1} and ΔH_{-1}^* values obtained by us are of the same order of magnitude as those obtained in the t-butyl case.[8]



(5)

Solvent Polarity.—As seen from the Table, the solvent has a great effect on the K value, which indicates a different extent of solvation of the radicals on the one, and the dimer on the other hand. With increasing solvent polarity, the k_{-1} value increases by more than an order of magnitude (Figure 1, Table). A similar effect of the solvent on K was observed for the 2,4,6-triphenylphenoxyl radical.[10]

Viscosity.—The dimerisation of ArO• seems to be diffusion-controlled. The activation enthalpy ($\Delta H_1^\ddagger$)

observed may be compared with the diffusion-controlled value [equation (6), where B is the activation energy of

$$\Delta H_1^{\ddagger} = -R\,[\delta \ln(k_{\text{diff.}}/T\ \delta T]_p = B \qquad (6)$$

viscous flow, $\eta = \eta_0 \exp(B/RT)$]. The $\Delta H^{\ddagger}$ values (Table, Figure 2) for all solvents studied do not differ by more than 1 kcal mol^{-1} from the activation energy of viscous flow, and the k_1 values are 5—10 times lower than the diffusion rate constants calculated by the Debye expression.

As a rule, however, the Debye expression yields overestimated values ($k_{\text{diff.}} = 8RT/3\,000\eta$) of the radical recombination constants.[11] The dependence of k_1 values on the nature of the solvent is complicated. For individual solvents a correlation between k_2 and η is not observed. However, it is necessary to mention that the viscosities of the solvents used vary within a narrow range (*ca.* 2 cP). In that case other properties of the solvent used, *e.g.* the ability to form complexes, may produce a greater effect on the rate constant. The use of binary mixtures of solvents of the same nature, *e.g.* alcohols having different viscosities, enables one to alter the viscosity over a wide range, keeping the other parameters of the solvent system relatively constant.

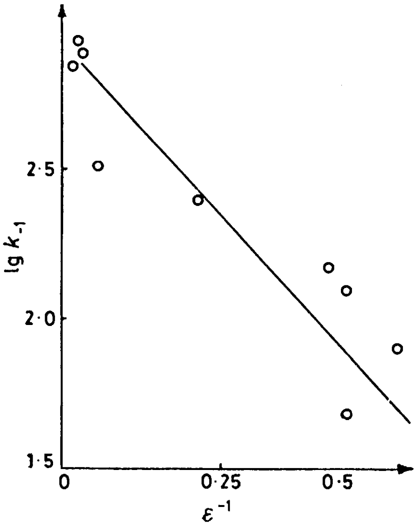


FIGURE 1 k_{-1}, as a function of the dielectric constant of the solvent

Kinetic and thermodynamic parameters of reaction (1) in various solvents (20 °C) *

Solvent	$10^7\ K$/ mol l^{-1}	$10^{-8}\ k_1$/ l mol^{-1} s^{-1}	k_{diff}/ $2k_1$	$10^{-2}k_{-1}$/s^{-1}	ΔH°	$\Delta H_1\ddagger$	$\Delta H_{-1}\ddagger$	ΔS°	$\Delta S_1\ddagger$	$\Delta S_{-1}{}^\circ$	ΔG°	$\Delta G_1\ddagger$	$\Delta G_{-1}\ddagger$
Hexane	0.25	32	3.1	0.8	12.3	0.5	12.8	7	−12	−5	10.3	4.1	14.4
Carbon tetrachloride	0.55	8.5	4.0	0.5	12.3	2.5	1.48	8	−8	0	9.9	4.9	1.48
Methanol–cyclohexanol (1 : 4 v/v)	0.80	0.15	8.3	0.012	5.2	8.6	13.8	−15	5	−10	9.6	7.1	16.7
Toluene	2	7.5	7.5	1.5	11.0	3.0	14.0	7	−7	0	9.0	5.0	14.0
Dioxan	4	3	8.5	1.2	11.4	3.0	14.4	10	−9	1	8.6	5.5	14.1
Propanol	4	7	2.2	2.8	9.8	5.0	14.8	4	0	4	8.6	5.0	13.6
Methanol	7	12	4.6	8.4	9.7	1.5	11.2	4	−11	−7	8.4	4.7	13.1
Acetonitrile	12	6	15	7.2	8.5	2.0	10.5	2	−11	−9	8.0	5.1	13.1
Chloroform	13	2	29	2.5	8.0	2.0	10.0	0	−13	−13	8.0	5.7	13.7
Dimethylformamide	16	5	8	8.0							7.8	5.2	13.0

* ΔH and ΔG in kcal mol^{-}, ΔS in cal mol^{-1} K^{-1}; error in ΔH determination is ± 0.5 kcal mol^{-1}; error in ΔG is ± 0.2 kcal mol^{-1}, error in ΔS is ± 2 kcal mol^{-1} K^{-1}; error in k_1 determination is 10%, error in K is 20%, error in k_{-1} is 30%.

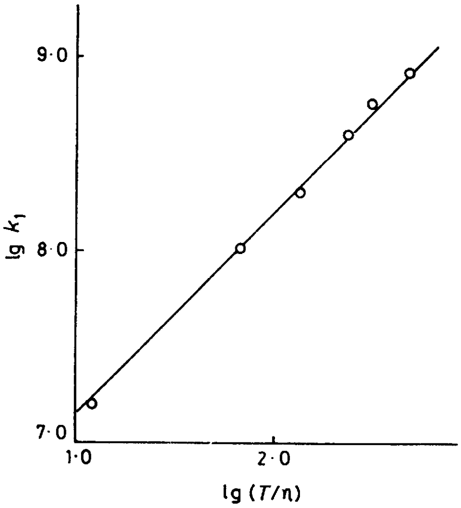


FIGURE 2 Plot of lg k_{-1} *versus* lg (T/η) for a cyclohexanol–methanol mixture

The plot of lg k_1 *versus* lg (T/η) is shown in Figure 2 for cyclohexanol (η 50 cP)–methanol (η 2 cP) mixtures. According to the Debye expression the plot should have a slope of unity and the agreement is seen to be good.

Solvation.—We also studied the influence of the composition of hexane–propanol mixtures with different solvating abilities. A continuous growth of k_1 with increasing hexane is observed (Figure 3). From Figures 2 and 3 it can be concluded that the rate constant k_1 is not only affected by macroscopic solvent parameters but also by specific solvation.

EXPERIMENTAL

The spectra and decay kinetics of intermediates were studied by flash photolysis. The apparatus is described elsewhere.[12]

N.m.r. spectra were recorded with a JEOL JNH-4H 100-MHz spectrometer, tetramethylsilane being used as an internal standard. Dimer D in CDCl$_3$ at −40 °C shows lines at τ 6.05 and 7.05 ascribed to the methoxy-groups of the aromatic and cyclohexadienone parts of D, respectively, at τ 3.03 and 3.55, corresponding to the *meta*-proton of the aromatic and cyclohexadienone parts of D respectively, and also a broad line at τ 2.20—2.90 ascribed to the protons of the pendant phenyl rings.[5] A single broad line corresponding to the methoxy-groups (τ 6—7) observed at 0 °C, was used to determine k_{-1}.

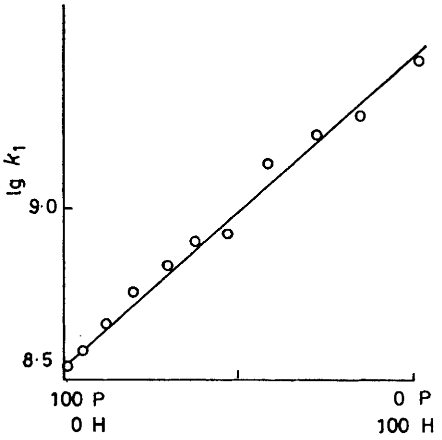


FIGURE 3 lg *k*, as a function of the composition of hexane(H)–propanol(P) mixture

Absorption spectra in the u.v.–visible region were obtained on a Specord spectrophotometer.

The dimer 4-(2,6-diphenyl-4-methoxyphenoxy)-4-methoxy-2,6-diphenylcyclohexa-2,5-dienone was synthesized as described before.[5]

All solvents were purified by distillation.

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