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Reaction between 2,2-Diphenyl-1-picrylhydrazyl and Phenols. Substituent and Solvent Effects

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A kinetic study has been made of the reaction between 2,2-diphenyl-1-picrylhydrazyl and phenols in various solvents. Polar effects in the rate-determining transition state are discussed in terms of the Hammett type relationship. Remarkable solvation effects were observed. For *p*-methoxyphenol the reaction rate is the greatest in the solvents which do not form strong H-bond with phenols, and the smallest in aprotic H-accepting solvents. For *o*-methoxyphenol the rate is the greatest in protic solvents. The results are interpreted in terms of the difference in the mode of hydrogen bondings. The rate for the reaction of the radical with α-naphthol was followed in dioxane–2,2,4-trimethylpentane mixtures. The results are explained by the theory of Kondo and Tokura, indicating that the free energy depression in the ground state takes place mainly through hydrogen bonding.

The oxidation of phenols is known to be complicated from the fact that different products are obtained from the same phenols by use of different oxidants.[1] The stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been used not only as a radical scavenger but also as a hydrogen acceptor. The strong H-accepting property of DPPH has been demonstrated by a number of reactions between the radical and compounds containing C–H, N–H, O–H, and S–H bonds.[2–7]

The hydrogen abstraction reactions of DPPH from phenols have been a subject of interest. Hogg *et al.*[6] found that the rate is first-order with respect to DPPH and phenols; about two moles of DPPH is consumed by one mol of the phenols; retardation by the major product, 2,2-diphenyl-1-picrylhydrazine ($DPPH_2$), is generally observed; the rates are roughly correlated with the Hammett σ in the range $-0.4<\sigma<0.2(\rho=-6)$, but not beyond the entire range, the *o*-substitution lowering the rate remarkably. They suggested that the H-abstraction is involved in the rate-determining step. McGowan *et al.*[4] suggested that the rate-determining step involves the removal of a hydride ion to give a cation, since the substituent effect is very similar to the solvolysis of α,α-dimethylbenzyl chlorides.

Among the factors that influence the rate, the solvent effect is considered to be one of the most important. However, information is scanty. If we select closely related phenols and carry out the reaction in a variety of selected solvents, the effect of individual factors could be observed. Bivalent phenols, *o*- and *p*-methoxyphenols, and α-naphthol were chosen and the reaction was carried out in various solvents and their binary mixtures.

Experimental

Materials. $DPPH_2$ was prepared according to the method given by Goldschmidt and Renn,[8] or Poirier *et al.*[9] Recrystallization was carried out from a chloroform–ethanol mixture. DPPH was prepared by oxidizing $DPPH_2$ in benzene with lead dioxide, and purified by repeated crystallization from a benzene–ligroin mixture, and then from carbon disulfide. Solid phenols of reagent grade were purified by means of sublimation. The reagents were stored in the dark and sublimed again just before use. *o*-Methoxyphenol was distilled twice under reduced pressure. Solvents were dried and purified in the usual way.

Procedures. DPPH exhibits a strong absorption around 520 nm. The absorbance at this wavelength was followed by means of a Hitachi 101 or 124 Spectrophotometer. The solutions of these phenols(10^{-3}—10^{-5} M) and DPPH(*ca.* 10^{-5} M) of desired concentrations were prepared separately and allowed to stand for about 30 min in a thermostat. The mixture of the two solutions was transferred quickly into a 3 cm optical cell equipped with a jacket through which thermostated water is circulated. The reaction temperature was controlled within ±0.2 °C. The absorbance at 520 nm was recorded at appropriate time intervals. In transforming the absorbance into concentration, a small correction due to the production of $DPPH_2$ was made. The rate constants were checked by duplicate runs.

Results

Effects of Oxygen, $DPPH_2$, and Picryl Chloride. It is possible that oxygen exerts some effect on the rate and nature of products. In order to examine this, the reaction was carried out in aerated and deaerated solutions. No appreciable difference in rates was observed for hydroquinone and catechol. Thus all the reactions involving them were carried out in the presence of air. No retardation was observed even when a great excess of $DPPH_2$ was added with respect to DPPH. For resorcinol, the rate was somewhat greater in aerated solutions than in deaerated ones (Table 1). Retardation occurred for phenols other than hydroquinone and

TABLE 1. RATE CONSTANTS FOR THE REACTION BETWEEN DPPH AND BIVALENT PHENOLS IN BENZENE

Temp (°C)	$k(M^{-1}\,s^{-1})$			
	Resorcinol		Hydroquinone ($\times 10^2$)	Catechol ($\times 10^2$)
	in N_2	in Air		
15	—	—	0.91	1.5_0
20	0.15_4	0.16_9	1.0_8	1.7_0
25	0.19_6	0.24_4	1.2_7	1.9_5
30	0.29_4	0.30_9	1.4_8	2.2_0
35	0.36_4	0.46_5	—	—
40	0.49_3	0.54_3	—	—
E_a(kcal/mol)	$10._5$	$10._3$	5.6_6	4.0_2
$\Delta S^{\ddagger}$(gibbs/mol)	$-28._4$	$-28._9$	$-31._9$	$-36._6$

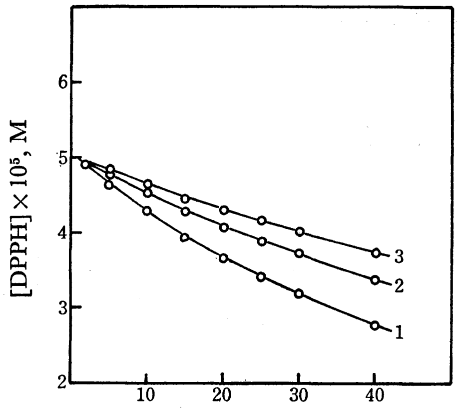


Fig. 1. Retardation effect by added $DPPH_2$ for the reaction between DPPH and resorcinol in deaerated benzene at 30 °C; $[DPPH]_0=5\times10^{-5}$ M, $[Res]_0=10^{-3}$ M, $[DPPH_2]_0$: 1, 0; 2, 2×10^{-5} M, 3, 4×10^{-5} M.

catechol in the presence of $DPPH_2$. An example is shown in Fig. 1. Picryl chloride was added to the system, since substances having a picryl group often form picrates with many compounds and this might exert a specific effect on the rate. However, no appreciable change in rate was observed.

Stoichiometry and Reaction Products. Aliquots of the DPPH and phenol solutions were mixed and allowed to stand. After the reaction had ceased, the concentrations of the remaining DPPH were determined and plotted against $[DPPH]_0/[Phenol]_0$. We see that the molar ratios of DPPH to both hydroquinone and catechol reacted are 2: 1 (Fig. 2). The same holds for α-naphthol. For resorcinol the reaction was too slow to determine the ratio exactly, more than two moles of DPPH being consumed per mole of resorcinol after a long time. More than 75% of consumed DPPH was converted into $DPPH_2$, the isolation of which from a reaction mixture being made by alumina column chromatography. The quantities of the produced quinones were estimated by iodometry recommended by Mahoney and DaRooge.[10] It was found that 90 and 93% of hydroquinone and catechol were converted into the corresponding quinones, respectively. Isolation and identification of the products from other phenols were unsuccessful.

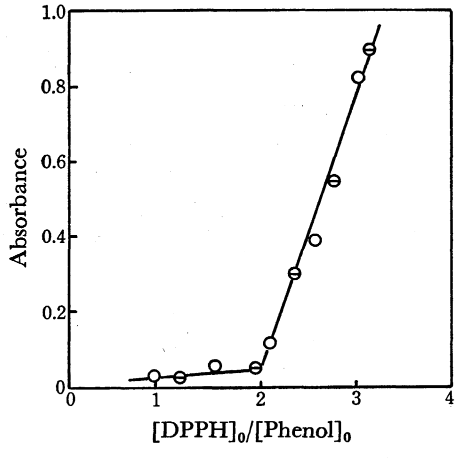


Fig. 2. Stoichiometry for the reaction between DPPH and bivalent phenols. ○: Catechol, ⊖: hydroquinone.

Order of Reaction. The reaction between DPPH and hydroquinone (and catechol) was found to follow strictly the second-order kinetics over almost the entire course of reaction. The apparent rate constants were estimated on the basis of the integrated second-order rate equation in which the above stoichiometry was taken into account. For other phenols, the conventional initial-rate method was applied to determine the order. The reaction was found to be first-order with respect to both DPPH and the phenols.

Reaction Rates. The values of the rate constants in benzene at various temperatures are given in Table 1 together with the Arrhenius parameters. The rate constants in various solvents are given in Tables 2 and 3. The activation parameters in benzene are $E_a=9.4$ kcal/mol. $\Delta S^{\neq}(300\ K)=-25$ gibbs/mol for *o*-methoxyphenol, and $E_a=4.7$ kcal/mol, $\Delta S^{\neq}(300\ K)=-22$ gibbs/mol for *p*-methoxyphenol. The values for the latter are in good agreement with those reported.[6] The difference in the activation energies (4.7 kcal/mol) in benzene can be ascribed to the energy of intramolecular H-bonding for the *o*-isomer. The rate constants for α-naphthol in the binary dioxane-2,2,4-trimethylpentane(isooctane) mixtures are given in Table 4 together with the activation parameters.

TABLE 2. RATE CONSTANTS FOR THE REACTION OF DPPH WITH HYDROQUINONE AND CATECHOL IN VARIOUS SOLVENTS

Solvent	Temp (°C)	$k(M^{-1}\ s^{-1})$	
		Hydroquinone	Catechol
Benzene	30	$1.4_8\times10^2$	$2.2_0\times10^2$
Carbon tetrachloride	28.8	—[a]	$1.8_1\times10^2$
Dioxane	25	6.3_0	2.1_2
Acetone	30	5.4_5	1.8_7
Diethyl ether	28.8	2.3_0	1.5_5
Ethanol[b]	28.8	≈5	≈20
Methanol[b]	28.8	≈20	—

a) Insoluble. b) Reproducibility poor. Contamination by a trace of water possibly responsible.[11]

TABLE 3. RATE CONSTANTS FOR THE REACTION OF DPPH WITH METHOXYPHENOLS AT 20 °C

Solvent	$k(M^{-1}\ s^{-1})$	
	p-Isomer	*o*-Isomer
Carbon tetrachloride	120	0.67
Benzene	40	0.47
Methanol[a]	≈16	≈5
2-Propanol[a]	≈9	≈3
Diethyl ether	1.23	0.087
Dioxane	0.60	0.039

a) Reproducibility poor as compared with that in the other solvents.

TABLE 4. RATE CONSTANTS FOR THE REACTION OF DPPH WITH α-NAPHTHOL IN ISOOCTANE–DIOXANE MIXTURES

Mole fraction of isooctane	k_{mix}, ($\mathrm{M^{-1}\,s^{-1}}$) 15 °C	20 °C	25 °C	E_a kcal/mol	log A $\mathrm{s^{-1}}$
0.000	0.42 (14.5 °)	0.61	0.75	9.9	7.1
0.049	0.53	0.65	0.88	8.5	6.2
0.121	0.60	0.74	1.0	8.2	6.0
0.194	0.68	0.91	1.2	9.6	7.1
0.340	1.1	1.4	1.9	9.6	7.3
0.608	2.7	3.4	4.6	9.4	7.6
0.699	4.1	5.3	7.1	9.8	8.0
0.823	9.4	12	16	9.6	8.3
0.954	42	51	61	6.6	6.5
1.000[a]	15 (−60 °)	110 (0 °)	350 (30 °)	4.6	5.8

a) Rate measured at temperatures as indicated in parentheses, because of a great reaction rate and low activation energy in pure isooctane.

Discussion

Reaction Sequence. A possible main reaction sequence for the reaction of DPPH with bivalent phenols can be given by

$$\mathrm{QH_2 + DPPH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} QH\cdot + DPPH_2} \qquad \begin{array}{l}(1)\ \text{(foward reaction)},\\ (1')\ \text{(reverse reaction)}\end{array}$$

$$\mathrm{QH\cdot + DPPH \xrightarrow{k_2} Q + DPPH_2} \qquad (2)$$

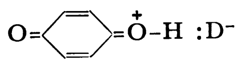
$$\mathrm{2QH\cdot \xrightarrow{k_3}} \text{ Combination, Disproportionation}^{12-15)} \qquad (3)$$

$$\mathrm{QH\cdot + O_2 \xrightarrow{k_4}} \text{ Peroxide}^{16)} \qquad (4)$$

where $\mathrm{QH_2}$ and Q denote the bivalent phenols and the corresponding quinones, respectively, and QH· the phenoxy radical.

For hydroquinone and catechol, Reactions 1′ and 4 can be neglected on the basis of experimental evidence. In order to be consistent with the rate equation and the reaction products, Reaction 3 could also be neglected as compared with Reaction 2. This may be rationalized by the following consideration: The termination constants for unhindered phenoxy radicals have been measured by flash photolysis[14,15] and ESR[12] techniques. The reported values are 10^6—10^9 $\mathrm{M^{-1}\,s^{-1}}$ depending on substituent and solvent. If we assume that $k_3 \approx 10^9$ $\mathrm{M^{-1}\,s^{-1}}$ (diffusion-controlled rate constant), then it can be shown that Reaction 3 can be neglected only when k_2 is approximately larger than 10^7 $\mathrm{M^{-1}\,s^{-1}}$. Since DPPH has been used as a radical scavenger, a value as large as $\approx 10^7$ $\mathrm{M^{-1}\,s^{-1}}$ is not surprising.

The free energy of activation for Reaction 2 would be favored by the resonance contribution such as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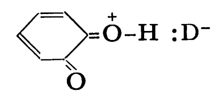

in the transition states for hydroquinone and catechol, where D denotes DPPH. Using the data given by Ayscough and Russell[13] and Mahoney *et al.*,[17] the heat of reaction of DPPH with hydroquinone was calculated to be $\Delta H = -12.3$ kcal/2 mol of DPPH. Since the heat of reaction of 1 can be estimated to be *ca.* 26 kcal/mol from the difference in the dissociation energy of N–H and O–H bonds, the driving forces of Reaction 2 must be the large exothermicity ($\Delta H = -38.3$ kcal/mol) and probably a low activation energy of this step. It can thus be concluded that the rate-determining step is involved in Reaction 1.

The rates for hydroquinone and catechol are of the same order of magnitude.* This indicates that the first abstracted hydrogen atom for catechol is the one which is not intramolecularly H-bonded. For resorcinol, the phenoxy radicals may be consumed *via* competition reactions (1′, 2, 3, and 4) making kinetic analysis difficult. The existence of opposing reaction (Reaction 1′) might be responsible for the upward deviation from the pseudo first-order plot and the retardation by $\mathrm{DPPH_2}$ (Fig. 1), as suggested for other phenols.[6] The fact that a small increase in rates in aerated solutions was observed for resorcinol (Table 1) seems to suggest the importance of Reaction 1′.

An alternative explanation for the retardation effect of $\mathrm{DPPH_2}$ is to assume complex formation between DPPH and $\mathrm{DPPH_2}$; it was introduced to explain the kinetics of the reaction of DPPH with amines and solvents.[2,18] It cannot be excluded since we found that the absorbance of DPPH–$\mathrm{DPPH_2}$ mixture at 520 nm is slightly smaller than that expected from the additivity rule. However, if any complex formation were to occur, it would not exert remarkable effect on the reaction rate, since no retardation was observed for hydroquinone and catechol.

Substituent Effects. The reaction between DPPH and resorcinol proceeds much more slowly, the activation energy being *ca.* 5 kcal/mol higher than that for other bivalent phenols. Since the activation energies of univalent phenols are between 4.8 and 16.1 kcal/mol,[6] the difference in the rate is considered to be due to the substituent effects rather than the change in mechanism. Hogg *et al.*[6] studied the dependence of the rate on substituents and obtained a linear relation with a break point at σ nearly equal to 0.2 in the normal Hammett plot. On the other hand, McGowan *et al.*[4] found that the relative rates of the reactions in carbon tetrachloride are very close to those for the solvolysis of α,α-dimethylbenzyl chlorides, and suggested an ionic mechanism involving the abstraction of a hydride ion from phenols.

The polar effect arguments[19–21] in hydrogen abstraction reactions by radicals have been introduced to rationalize the substituent effects in the radical reactions. It was found that the correlation is better when log (relative-reactivity) is plotted against σ^+-values than against σ-values.[22–26] The contribution of polar mesomeric structures for the interpretation of radical reactions has been recognized to be useful.[19,27] It may

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* The apparent rate constant for hydroquinone in Table 1 should be divided by two for comparison with other univalent phenols and catechol. Catechol reacts about three times faster than hydroquinone.

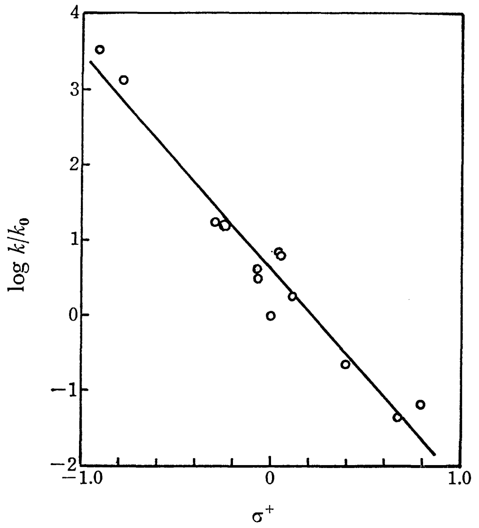
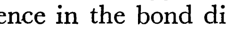


Fig. 3. Corelation of the rate constants for the reaction between DPPH and phenols with σ^+-values; in benzene at 30 °C.

be worthwhile to reexamine the polar effect in this reaction series. Using the data of Hogg *et al.*[6] and those in the present study, log k/k_0 is plotted against σ^+ (Fig. 3). ρ is calculated to be −2.8 by the least-squares method. The correlation coefficient $r=-0.970$ of the σ^+-plot is much better than for the normal Hammett σ-plot ($r=-0.883$). It is noted that ρ has a very large negative value as compared with that for other H-abstraction reactions with more reactive radicals than DPPH.[22–26] Mahoney and DaRooge[10] reported that $\rho=-2.8$($\rho\sigma^+$-plot) for the reaction of 2,4,6-tri-*t*-butylphenoxyl with substituted phenols. We also found that $\rho=-3.1$($\rho\sigma^+$-plot, $r=-0.993$) for the reaction of 2,6-di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-*p*-tolyloxyl (galvinoxyl) with substituted phenols.[28] Such high selectivity would be caused by the extremely stable and electrophilic nature of these radicals. Thus the large ρ-value in this reaction series is not regarded as exceptional. The existence of a better correlation with σ^+-substituent constants and the very large negative value indicate that the contribution of the resonance structures such as II, III, and IV virtually plays an important role in stabilizing the transition state. Hence DPPH acts as an electrophile as in the case of aromatic amines.[4)]



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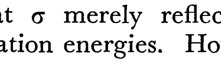
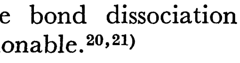
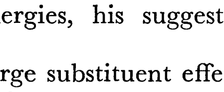


II



III



IV

Zavitsas[29,30)] suggested that σ merely reflects the difference in the bond dissociation energies. However, since the reaction rates are not always directly related to the bond dissociation energies, his suggestion is questionable.[20,21)]

In order to interpret the large substituent effect, we might assume the formation of a CT-complex between the phenols and DPPH, followed by a slow proton transfer. However, we have no spectroscopic evidence. Addition of picryl chloride has no effect on the rate. The kinetic data are not in line with the assumption. Thus such a CT-complex may exist, if any, only as a transient species.

Solvent Effects. Although bulk properties such as the dielectric constant of medium are important in radical reactions, specific solvation effect such as H-bonding would be more important. We see from Table 2 that the rate is the greatest in solvents which do not usually form H-bond, and the slowest in aprotic H-accepting solvents. Acetone, dioxane, and diethyl ether act as H-acceptors. Since the reaction involves the abstraction of the H-bonded hydrogen, extra energy is required for desolvation in the transition state. The rates in protic solvents seem to suggest that the solvents act as a proton-donor as well as a proton-acceptor. There is a marked difference between *o*- and *p*-methoxyphenols in reactivity (Table 3). It seems that the difference is too large to be ascribed to the steric and/or electronic effects since the reactivity ratios depend strongly on the nature of solvent. It is reasonable to ascribe the slower rate for *o*-methoxyphenol to the intramolecular H-bonding. In diethyl ether and dioxane, there should be an intermolecular H-bond formation between the *p*-isomer and these solvents. This may be responsible for the pronounced decrease in rates. It is noted that the rates are of the same order as those for the *o*-isomer in benzene and carbon tetrachloride. On the other hand, since the *o*-isomer is already intramolecularly H-bonded, no serious solvent effect is expected for this compound. However, the rates decreased one order of magnitude in dioxane and diethyl ether as compared with benzene and carbon tetrachloride (Table 3). This could be interpreted in terms of the masking effect through partial H-bonding with the solvents. For the *o*-isomer the rates are greater in methanol and 2-propanol than in other solvents. The alcohols would behave as a proton donor as well as a proton acceptor. The hydroxyl group of the solvents would help push out the hydrogen atom being abstracted. The fact that the rate is greater for catechol than for hydroquinone supports this idea. Judging from the experimental results, the pushing effect overwhelms the masking effect for the *o*-isomer. Since the hydroxyl group of this compound is fixed by the neighboring methoxy group, the pushing effect may become predominant. On the other hand, the masking effect is operative for the *p*-isomer. The rate can be determined by a compromise between the two effects.

An alternative interpretation is that a rapid proton exchange in protic solvents results in only a small difference in the rates of the two isomers. In this respect, the comparatively poor reproducibility in the protic solvents (Tables 2 and 3) deserves attention.

Reaction in Binary Mixtures. If the thermodynamic quantities for solvation are known, they can be correlated with the rate factors. If we examine the dependency of the reaction rate on the composition of mixed solvents, with one of which the reactant is solvated, the result would be of interest. Kondo *et al.*[31)] have developed a theory of the reaction rates in binary mixed solvents.

They derived rate equations

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{M}^{\ddagger} \longrightarrow \mathrm{X} + \mathrm{Y} \cdots$$

for a general second-order reaction in mixed solvents which consist of two components denoted by 1 and 4. If only one of the reactants, say B, is solvated in the solvent 4 to form an addition product, the simplified rate equation is given by

$$\ln k_{\mathrm{mix}} = x_1 \ln k_1 + x_4 \ln k_4 + x_4 \ln (K_{\mathrm{x}}+1) - \ln (x_4 K_{\mathrm{x}}+1), \tag{5}$$

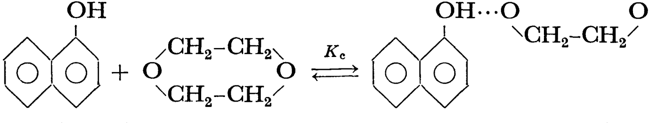
where K_{x} denotes the association constant expressed in terms of mole fractions for the formation of the addition product; x_1 and x_4 are the mole fractions of 1 and 4, respectively. The expression for the activation energy is given by differentiating Eq. 5 with respect to temperature;

$$E_{\mathrm{mix}} = x_1 E_1 + x_4 E_4 - \frac{x_1 x_4 \Delta H^\circ}{(1+1/K_{\mathrm{x}})(x_4+1/K_{\mathrm{x}})}, \tag{6}$$

where ΔH° denotes the heat of formation of the adduct.

In acetone–cyclohexane mixtures, the rate deviates considerably from that expected from an ideal solution (Figs. 4 and 5). Although the deviation is as expected from Eq. 5, the rate in pure cyclohexane and the K_{x}-value could not be obtained in this system.

For examination of Eqs. 5 and 6, we carried out the reaction of DPPH with α-naphthol in isooctane–dioxane mixtures; the results are given in Table 4. The system was chosen since Baba and Suzuki[32] reported that the association constant for the reaction



is $K_{\mathrm{c}}(20\ ^\circ\mathrm{C}) = 20.9\ \mathrm{M}^{-1}$ and the heat of formation is $\Delta H^\circ = -5.4$ kcal/mol. The heat of formation of the adduct agrees with the difference in activation energy for the reaction in pure dioxane and isooctane (Table 4). In the

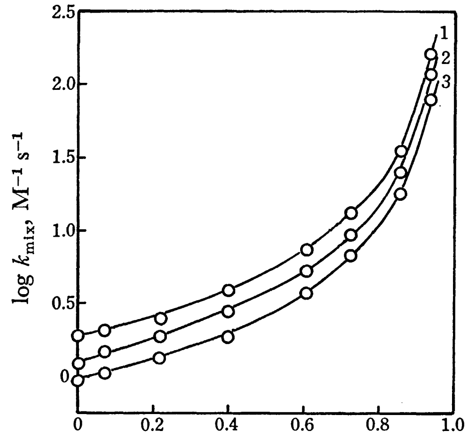


Fig. 4. Plots of log k_{mix} *vs.* the mole fraction of cyclohexane (x_1) for the reaction between DPPH and catechol in cyclohexane–acetone mixed solvent. Temperatures: 1, 30 °C; 2, 25 °C; 3, 20 °C.

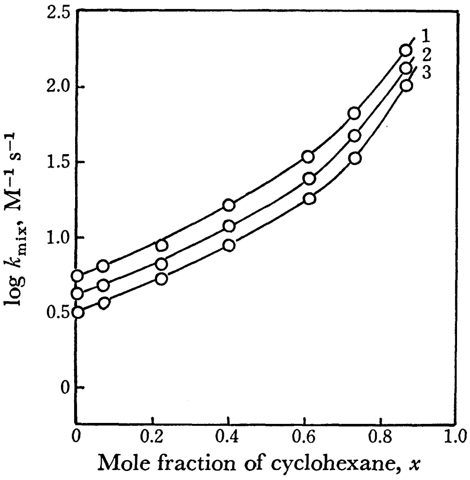
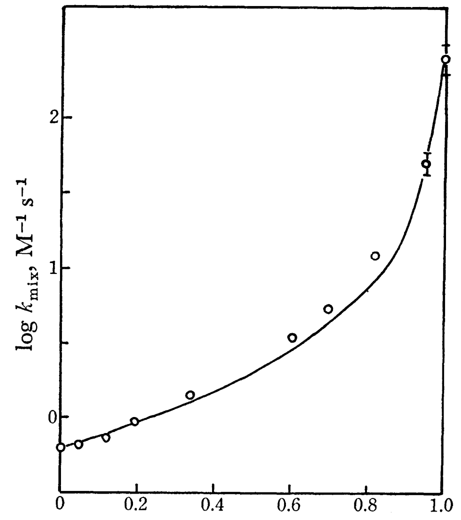
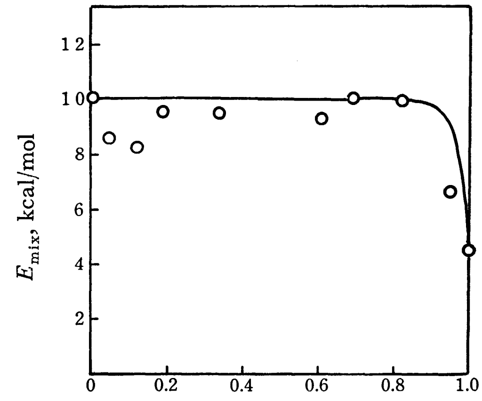


Fig. 5. Plots of log k_{mix} as a function of x_1 for DPPH–hydroquinone system. Temperatures: 1, 30 °C; 2, 25 °C; 3, 20 °C.



Mole fraction of isooctane, x_1

Fig. 6. Dependence of log k_{mix} on the mole fraction of isooctane for the reaction between DPPH and α-naphthol in dioxane–isooctane mixtures at 20 °C.



Mole fraction of isooctane, x_1

Fig. 7. Dependence of the activation energy on the mole fraction of isooctane.

papers of Kondo *et al.*[31] K_x-values were tacitly assumed to be independent of the solvent composition. However, this is not the case generally. In the present case the K_x-value varies from 245 in pure dioxane to 126 in pure isooctane when $K_c=20.9\ M^{-1}$ is used. By means of Eq. 5, the rate constant k_{mix} at any composition can be calculated using the values for k_1 and k_4 (Table 4) and the K_x-values estimated from the K_c-values obtained by Baba and Suzuki. The predicted k_{mix}-values are plotted in Fig. 6 as a function of the mole fraction of isooctane (solid line), together with the experimental points (open circles). It can be seen that the behavior of the specific solvation interaction in the binary dioxane–isooctane system is expressed by this theory. A similar treatment has been carried out for the energy of activation (Fig. 7). As a results of the specific solvation, the energy of activation decreases sharply as the mole fraction of isooctane approaches unity, as predicted by the theory.

It is concluded that in the hydrogen abstraction reaction in this system, the most important factors which govern the reaction rate are the polar mesomeric and H-bonding effects which affect greatly the free energies in the transition and ground states, respectively.

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