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DIELECTRIC AND HYDROGEN-BONDING EFFECTS OF SOLVENTS ON THE BASE-CATALYSED REACTION OF PHENYL GLYCIDYL ETHER WITH BENZOIC ACID

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Abstract—The effect of the dielectric character of a solvent on the pyridine-catalyzed reaction between phenyl glycidyl ether and benzoic acid was studied in various pure and mixed aromatic hydrocarbons such as toluene, monochlorobenzene, *o*-dichlorobenzene, nitrotoluene, nitrobenzene, and toluene–nitrobenzene mixtures at temperatures ranging from 80 to 108°, and is discussed in terms of the modified Kirkwood's expression. The hydrogen-bonding effect of the solvent was also investigated for this reaction in toluene–dioxan and nitrobenzene–dioxan mixtures at temperatures ranging from 80 to 100° and in various ethers such as tetrahydrofuran, anisole and di-n-butyl ether at 65·0°. A linear relationship was found between the logarithm of the third order rate constants and pK_a values of solvents, and can be described by the proposed rate equation. These show that in aromatic hydrocarbons the nonspecific electrical interactions are predominant, while the hydrogen-bonding character of the solvent can explain reasonably the rate data in solvents containing ethers, and should also suggest that the activated complex or the transition state species proposed previously plays an important role for this reaction in these solvents.

INTRODUCTION

IN PREVIOUS papers,[1,2] it was shown that a hydrogen-bonded complex (III) of a tertiary amine (I) and benzoic acid (II), and an activated complex or a transition species of the type V (see Scheme I) should play an important role for the tertiary amine catalyzed reaction of phenyl glycidyl ether (IV) and benzoic acid. The rate of this reaction was suggested to depend on the structural alteration of the hydrogen-bond due to the structural changes of the amine[2] and of benzoic acid,[3] and was also discussed the proton transfer from the hydrogen-bonded complex III to the epoxide IV through the activated complex V.

Active species such as III may be solvated in liquid phase and in some media the same ionic species may exist in two or more states of solvation. The nature of the solvent determines the type of solvation and hence a change of medium may profoundly affect the course of the reaction. For the elucidation of mechanism responsible for the occurrence of reaction from kinetic data, the dependence of reaction rate on dielectric constant of the medium gives valuable information, on which no extensive data for this reaction exist in the literature.

The present paper reports the data on the influence of dielctric constant on rate constant of this reaction. Moreover, the phenomenon of specific solvation or solvent sorting in the immediate vicinity of solute species in binary solvent mixtures will be considered and emphasis will be placed on the effect of this phenomenon as it is revealed in the activation parameters for this reaction in solution.

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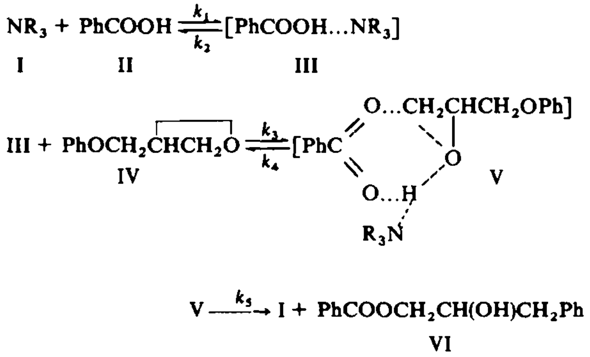
SCHEME I



RESULTS

The dielectric constants of the solvents such as benzene, chlorobenzene, *o*-dichlorobenzene and nitrobenzene were determined at various frequencies (1, 10, 100 Kc, and 1, 3 Mc) at 25·0°, and were found to be independent of the frequency (2.26, 5·63, 9·84 and 34·9, respectively) and to be coincident with those (2·25, 5·65, 9·82 and 34·8) in the literature.[4] The dielectric constants of benzoic acid solutions (0·200 M) at 10 Kc, and 1 and 3 Mc were found to be slightly dependent on the frequency: 2·46, 2·47 and 2·50 in toluene, and 34·98, 35·00 and 35·10 in nitrobenzene at 25·0°. As shown in Table 1, the dielectric constants of the reaction media were not largely affected by adding benzoic acid and phenyl glycidyl ether, and hardly changed during the course of reaction. Therefore, the dielectric constants of the solvents used can be regarded as those of the reaction media through the course of the reaction.

TABLE 1. DIELECTRIC CONSTANTS OF SOLUTIONS OF REACTANTS AT 25·0°

Solvent	Benzoic acid	Phenyl glycidyl ether	Pyridine	Dielectric constant	
				Initial	Final[a]
Toluene	0·201M	0·983M	0·0125M	2·45	2·43
Toluene	0·200	1·98	0·0986	2·44	2·42
Toluene	0·198	3·97	0·391	2·46	2·44
Nitrobenzene	0·204	0·984	0·0496	35·21	35·07
Nitrobenzene	0·201	1·96	0·0984	35·20	35·05
Nitrobenzene	0·203	3·98	0·197	35·53	35·15

[a] Measured after the reaction was completed (85–90% conversion).

The dielectric constant of the mixed solvent was evaluated by

$$D = \sum_i D_i f_i \qquad (4)$$

where D is the dielectric constant of a mixed solvent, f_i and D_i are the mole fraction and the dielectric constant of a solvent *i*, respectively, and $\sum_i f_i = 1$. For the benzonitrile-, anisole-, and chlorobenzene-benzene systems, there are linear variations of the dielectric constant with mole fraction. It has been shown, however, that many mixed solvent systems such as tetrahydrofuran-,[6] phenol-,[5] benzyl alcohol-,[5] bromobenzene-,[5] aniline-,[5] and nitrobenzene-benzene,[5] and dioxan-,[7] and diethyl ether-chloroform[7] systems can not be evaluated by Eq. 4, and that the last has a maximum dielectric constant value at the composition of about 45 mole % of ether. In the systems of dioxan-[8] and petroleum-[9] tetrahydrofuran, the curves for plots of the dielectric constant *vs* volume per cent of a component are found to be monotonic and virtually linear, and, thus, no linear relationship, Eq. 4, may be obtained between the dielectric constant data, D, and mole fraction, f_i, of a component, because the mole fraction is not proportional to the volume fraction.

As shown in Table 2, our findings on the toluene–nitrobenzene system are not consistent with Eq. 4. This indicates that nitrobenzene should form specific aggregates such as dimer which has been found by Sadek and Fuoss,[10] and Bury and Jenkins,[11] and is called the multipolar complex by Taft *et al.*[12]

TABLE 2. PHYSICAL PROPERTIES OF TOLUENE-NITROBENZENE MIXTURES

Mole fraction of toluene	n_D^{20}		Dielectric constant	
	Obs.	in Lit.	Obs. at 25·0°	Calc.[a]
1·00	1·4965	1·49693[b]	2·40	2·38[b]
0·900	1·5027	—	4·91	5·62
0·800	1·5084	—	7·19	8·86
0·750	1·5112	—	8·90	10·48
0·600	1·5193	—	12·9	15·35
0·500	1·5256	—	15·8	18·59
0·400	1·5312	—	19·1	21·83
0·250	1·5386	—	25·0	26·70
0·100	1·5472	—	30·6	31·56
0·000	1·5521	1·55257[c]	34·9	34·82[c]

[a] By Eq. 4 in Text. [b] In Ref 16*b*. [c] In Ref 16*e*.

The dielectric constant of a medium varies with the temperature, and many workers[13–16] have attempted to account for the observed activation energy behavior for rate processes in terms of the temperature dependence of dielectric constant and have measured, or computed, isodielectric activation energies. Hyne[17] has shown, however, that this explanation can, at best, account for only part of the devious variations of the activation energy. In this study, then, are used the dielectric constant values at 25·0°C.

The product (VI) was obtained in yield of 80–90% of theoretical and the disappearance of benzoic acid was completely accounted for by the appearance of ester and hydroxyl groups by IR spectrum analysis. Similarly as in the previous papers,[1, 2] the reaction of phenyl glycidyl ether and benzoic acid in the presence of pyridine at various temperatures and in various solvents which were pure or mixed was in good agreement with second-order kinetics.

It was also found that the observed second-order rate constant, k, was expressed as

$$k = k''(\text{amine}) + k' \qquad (5)$$

where k'' is the third-order rate constant, k' is the second-order rate constant at the zero concentration of the catalyst, and (amine) is the initial concentration of the

TABLE 3. THIRD-ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES, ARRHENIUS PARAMETERS, AND HEAT AND ENTROPY OF ACTIVATION FOR REACTION OF PHENYL GLYCIDYL ETHER (IV) AND BENZOIC ACID (II) IN TOLUENE–NITROBENZENE MIXTURES[a]

Mole-% of Toluene	D^b	$k'' \times 10^3$, $l^2 . mole^{-2} sec^{-1}$				E^A Kcal/mole	log A	$\Delta H^{\ddagger}_{298}$ Kcal/mole	$\Delta S^{\ddagger}_{298}$ eu	$\Delta G^{\ddagger}_{298}$ Kcal/mole
		108°	100°	87·0°	80·0°					
100	2·40	13·3	8·51	3·60	2·34	17·4	8·11	16·2	−25·4	23·8
75	8·90	15·9	10·6	4·63	3·04	16·4	7·61	15·2	−27·7	23·4
50	15·8	19·9	13·5	6·17	4·13	15·6	7·25	14·4	−29·3	23·1
25	25·0	23·1	15·9	7·42	5·20	15·0	6·97	13·8	−30·6	22·9
0	34·9	27·6	19·8	9·50	6·55	14·6	6·83	13·4	−31·2	22·7

[a] The initial concentrations of II, IV and pyridine are 0·240, 0·240, and 0·0108M, respectively. The physical properties of the media are shown in Table 2.

[b] Observed at 25·0° (Table 2).

TABLE 5. THIRD-ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES, ARRHENIUS PARAMETERS, AND HEAT AND ENTROPY OF ACTIVATION FOR REACTION OF PHENYL GLYCIDYL ETHER (IV) AND BENZOIC ACID (II) IN DIOXANE–TOLUENE AND DIOXANE–NITROBENZENE MIXTURES[a]

Mole fraction of dioxan	$k'' \times 10^3$, $l^2 . mole^{-2} sec^{-1}$			E^A Kcal/mole	log A	$\Delta H^{\ddagger}_{298}$ Kcal/mole	$\Delta S^{\ddagger}_{298}$ eu	$\Delta G^{\ddagger}_{298}$ Kcal/mole
	100°	87·0°	80·0°					
Dioxan–Toluene								
0·200	3·09	1·16	0·709	19·5	8·89	18·3	−21·8	24·8
0·300	2·41	0·881	0·533	20·0	9·08	18·8	−21·0	25·0
0·400	2·08	0·741	0·439	20·5	9·32	19·3	−19·8	25·2
0·500	1·87	0·658	0·390	20·7	9·37	19·5	−19·6	25·3
0·600	1·66	0·572	0·336	21·1	9·54	19·9	−18·8	25·5
0·700	1·47	0·491	0·283	21·8	9·92	20·6	−17·1	25·7
0·900	1·23	0·397	0·226	22·5	10·2	21·3	−15·8	26·0
Dioxan–Nitrobenzene								
0·120	15·3	6·92	4·69	15·7	7·36	14·5	−28·8	23·2
0·230	9·96	4·32	2·85	16·6	7·71	15·4	−27·2	23·5
0·550	6·92	2·79	1·77	18·1	8·43	16·9	−23·9	24·0
0·830	3·61	1·33	0·813	20·0	9·26	18·8	−20·2	24·8

[a] The initial concentrations of II, IV and pyridine are 0·240, 0·240, and 0·0108M, respectively.

amine. Furthermore, the Eq. 5 was also observed for the reactions in mixed solvents such as nitrobenzene–toluene, nitrobenzene–dioxan and toluene–dioxan under the various concentrations of benzoic acid (0·1–1·0M) and phenyl glycidyl ether (0·1–1·0M) at various temperatures from 65·0 to 120°. In Tables 3, 4 and 5 are shown, with the observed or calculated dielectric constant of the solvent, the rate constants at various temperatures, the activation energies, and the frequency factors of this reaction in various solvents. The rate constants of this reaction in some mixed solvent systems containing dioxan are especially lower and their activation energies and frequency factors are correspondingly larger than those estimated with the dielectric constants of the reaction media (Table 5).

The Arrhenius parameters and the enthalpies and the entropies of activation are obtained from Eqs 6–8

$$k = (KT/h)\exp[(\Delta S^*/R) - (\Delta H^*/RT)] \tag{6}$$

$$\Delta H^* = E_A + (\Delta n^* - 1)RT \tag{7}$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \tag{8}$$

where k, K, h, R, and T are the observed rate constant (in this case, k'), Boltzmann's constant, Planck's constant, the gas constant, and the absolute temperature, respectively, and ΔH^*, ΔS^*, ΔG^*, and Δn^* are the enthalpy, entropy, Gibbs free energy of activation, and the change of moles in activation, defined as the number of molecules of the activated complex minus the number of molecules of reactants, respectively. The parameters, enthalpies, and entropies appear in columns 7–11 of Tables 3 and 4, and 5–9 of Table 5.

The rate constants measured for over-all reaction are all accurate to ±3% or better by the agreement between duplicate determinations. These uncertainties of ±3% in the rate constants correspond to uncertainties in E_A and ΔH^* of 0·4–0·5% Kcal/mole, in log A of 0·3 units, and in ΔS^* of 0·9 units. In spite of the above uncertainties, some effects of solvents are observed significantly.

In pure or mixed aromatic hydrocarbon solvents, the reaction rates and reaction constants appear to increase with increasing dielectric constant, D, of the solvent as shown in Tables 3 and 4. The activation energy or the logarithm of the rate constant, k'', for this reaction is found to hold no linear relationship with D, $(D - 1)/(2D + 1)$, or $1/D$, but a good linear relationship between $\log k''$ and $\log D$ has been found for this reason in various pure and mixed solvents except ethers such as dioxan and tetrahydrofuran, as shown in Fig. 1. This is coincident with the result in the previous paper,[1] in which N,N-dimethyldodecylamine was used as a catalyst. The best straight line has been found by the least-squares method[18] and is shown by Eq. 9. The slope, a, and intercept, b, are collected in Table 6.

$$\log k'' = a \log D + b \tag{9a}$$

$$\Delta H^*_{298} = a \log D + b \tag{9b}$$

DISCUSSION

The relationship between polarity of a solvent as an abstract concept and its concrete effect on reaction in solution has not yet been well established, but it has been generally recognized that the solvation by a solvent molecule plays an important supported by the fact that the dielectric constant is a poor measure of solvating power when the systems being compared are limited to a pure and single chemical type, namely, the aromatic hydrocarbons. (Tables 3 and 4, and Figs 1 and 2).

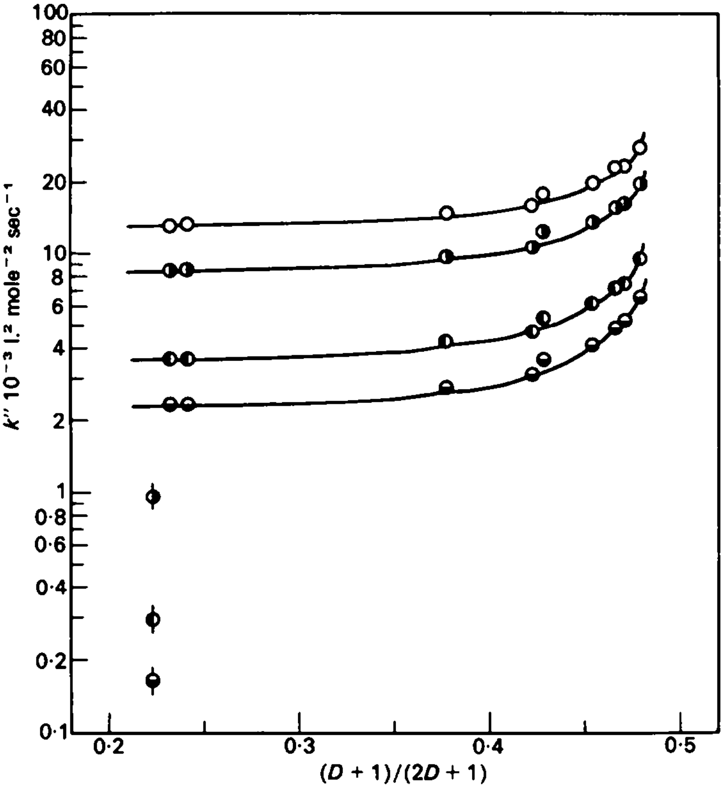


FIG. 2 Plots of log k'' vs. $(D - 1)/(2D + 1)$ in the reaction of phenyl glycidyl ether and benzoic acid with pyridine in various solvents at various temperatures. Symbols are the same as in Fig. 1.

The additional influential factor is, in all probability, the same one claimed by Glasstone *et al.*[19] as partially responsible for the deviation from the Kirkwood's expression,[22] namely, the μ^2/r^3-functions. The slope of the plot of ln k against $(D - 1)/(2D + 1)$ in Eq. 10 can be given by

$$\frac{\mathrm{d}\ln k}{\mathrm{d}(D-1)/(2D+1)} = -\frac{1}{KT}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_M^2}{r_M^3}\right) \tag{11}$$

where d-operator can be replaced by Δ-operator; it is then apparent that the plot of the left-hand side of Eq. 11 against $1/T$ should be a straight line for the same reaction in different media. Our plots are shown in Fig. 3 and appear to be linear with due allowance for the large uncertainties in values of the left-hand side of Eq. 11. The slope was found to be positive at any $(D - 1)/(2D + 1)$ value. This fact indicates that the dipole moment of the activated complex V may be large in comparison with the sum of the moments of the reactants (here, the hydrogen-bonded complex III and the epoxide IV), and that the moment of the complex V should increase with increasing dielectric constant, D, of the medium.

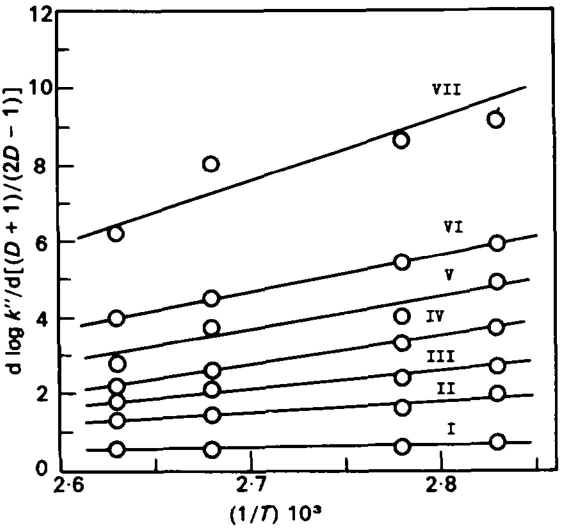


FIG. 3 Temperature dependence of d log k''/d[$(D - 1)/(2D + 1)$] value. I to VII are values at 0·30, 0·41, 0·43, 0·44, 0·45, 0·46 and 0·47 of $(D - 1)/(2D + 1)$.

The dipole moment value measured in solution has been found to be different from values for gases and to be dependent on the solvent.[24] The phenomenon is attributed[25] to the electrical effect of a solute molecule on surrounding solvent molecules. The solution dipole moment will exceed the moment for gas if the solute molecules is ellipsoidal in shape and the axis of the dipole moment coincides with or is close to the long symmetry axis of the molecule. Many substances fit this description,[25] and this may suggest the structure of the activated complex or the transition state species V.

As mentioned above, the linear relationship has been found between log k'' and log D for the reactions in pure or mixed aromatic hydrocarbons (Fig. 1 and Table 6). On the other hand, no such a linear relationship was able to be observed for the reactions in dioxan containing solvents (Table 5). The wide divergence of plots from the general curve for the relationship between log k'' and $(D - 1)/(2D + 1)$ also has been found and perhaps can be explained by the specific solvation of dioxan. When the solvent used is a nucleophile such as dioxan, the solvation of benzoic acid II and the complex III by the solvent may be predominant and the formation of the activated complex V should be thus retarded or inhibited. The larger rate constants or the smaller free energies of activation for the reaction in nitrobenzene–dioxan than those in toluene–dioxan mixtures (Table 5) can be described in terms of the higher dielectric character of nitrobenzene. The measured quantities of the dielectric constant and the dipole moment can describe the orientation of the various dipoles within the functional group and the arrangement of groups in the molecule. Hydrogen-bonding always affects the dipole orientations, but the resulting change in D and dipole moment varies both in direction and magnitude.[26] It is not possible, therefore, to make a simple general statement of the electrical behaviour from the internal hydrogen-bonding.

It is reasonably expected, in this reaction, that the enthalpy of activation increases as the mole fraction of dioxan increases, because the desolvation must occur when

In order to investigate the effect of the solvation due to hydrogen-bonding between benzoic acid, II, or hydrogen-bonded complex III and various ethers on this reaction rate, this reaction was studied in some ethers and the rate constants are given in Table 8. It is well known that the moment of associated compounds changes when

TABLE 8. THIRD-ORDER RATE CONSTANTS AT 65·0° FOR REACTION OF PHENYL GLYCIDYL ETHER (IV) AND BENZOIC ACID (II) IN VARIOUS ETHERS[a]

Number	Solvent	$k'' \times 10^5$, l^2. mole^{-2} sec^{-1}	pK_a[b]
1	Tetrahydrofuran	2·58	−2·08
2	Dioxan	3·39	−3·22
3	Diisopropyl ether	4·63	−4·30
4	Di-n-butyl ether	5·76	−5·40
5	Anisole	8·40	−6·54
6	n-Amyl phenyl ether	9·80	−7·40
7	Benzene	74·6	−10[c]
8	Cyclohexane	109	[d]

[a] The initial concns of II, IV and pyridine are 0·240, 0·240, and 0·0108M, respectively.

[b] Edward M. Arnett, *Progress in Physical Organic Chemistry* (Edited by Saul G. Cohen, Andrew Streitwieser, Jr., and Robert W. Taft) Vol. I; p. 223. Interscience, New York, N.Y. (1963).

[c] Nitrobenzene, −10·93 or −11·38; *p*-methylnitrobenzene, 10·0 or 10·44 (J. C. D. Brand, W. C. Horning, M. B. Thornley, *J. Chem. Soc.* 1374 (1952); R. J. Gillespie and C. Solomons, *Ibid.*, 1796 (1957); M. A. Paul and F. A. Long, *Chem. Rev.* 57, 1 (1957)).

[d] Cyclohexene, < −4 (H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.* 73, 5198 (1951)).

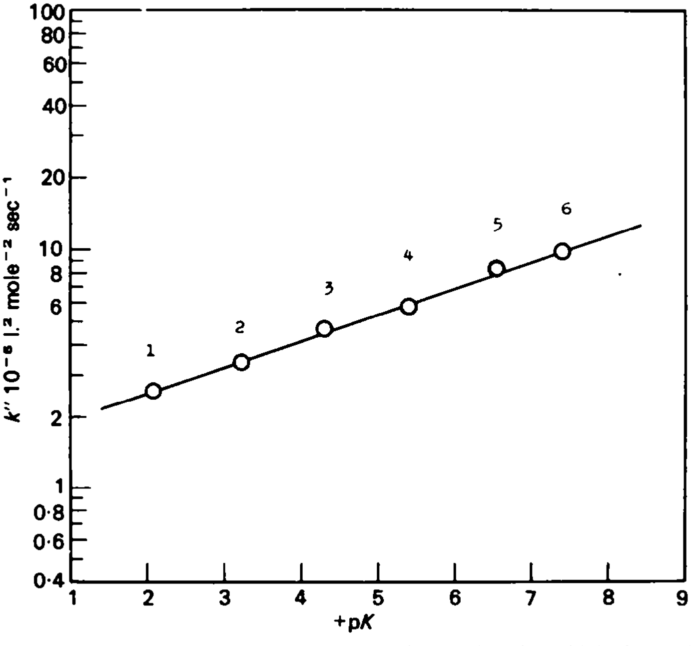


FIG. 4 The relationship between log k'' for the reaction of phenyl glycidyl ether and benzoic acid with pyridine in various ethers at 65·0° and pK_a values of the solvents. Number is the same as in Table 8.

hydrogen-bonding occurs, and that the change is proportional to the electron donating ability of the solvent.[26] In such a system, a linear relationship may be obtained between the rate data and the basicity of the solvent. For this reaction, the rate constants are plotted against the pK_a values in Fig. 4, and, although a linear relationship appears reasonable, there is an uncertainty of the rate data to render the gradient of the line uncertain. This relationship can be explained partly by Eq 17, and should suggest that the formation of the activated complex V is retarded or hindered by hydrogen-bonding of II or III with the solvent molecules. There may be unavoidably an overlap between the effect that can be ascribed to nonspecific electrical interaction and hydrogen-bonding of solute with solvent in the case of aromatic hydrocarbons, because the benzene ring can be mentioned as a proton acceptor.[27] Furthermore, the fact, shown in Table 8, that the rate constant in benzene was smaller than that in cyclohexane shows that the activated complex of the type V should play an important role for this reaction.

EXPERIMENTAL

Materials. Reagent grade benzene, toluene and xylene (mixed isomer) were shaken successively with H_2SO_4 and a $NaHCO_3$aq, dried with $CaCl_2$, and then fractionally distilled. Fractions boiling at 80·0, 110·0–110·5 and 137–139°, respectively, were collected and used. Chlorobenzene was purified[32] by shaking it repeatedly with portions of H_2SO_4 until the acid no longer became colored. It was then washed with water and with a dil $NaHCO_3$aq, dried with $CaCl_2$, and fractionally distilled through a 40-cm column. A fraction boiling at 131·5° was collected; n_D^{20} 1·5249. *o*-Dichlorobenzene was distilled through a 60-cm Widmer column and the middle fraction boiling at 179–180° was collected.[33] A commercial nitrobenzene was dried with $CaCl_2$ and fractionated at reduced press. The nitrobenzene was distilled fresh for each series of measurements, only the middle fraction being used.[34] *o*-Nitrotoluene was purified by the method used for nitrobenzene.[35] Reagent grade anisole was washed with NaOHaq and then with water, dried over $CaCl_2$ and filtered. It was refluxed with Na and distilled. The fraction boiling at 154–155° was collected and used.[36] THF was purified by treating with KOH pellets, Na-wire successively, and distilled under N_2 atmosphere, b.p. 66·0°. Reagent grade *p*-dioxan was purified by the method of Eigenberger;[37] boiled under reflux for 7 hr with 10% of its volume of 1N HCl, a slow stream of air being passed in through the condenser to remove the acetaldehyde formed. The distilled *p*-dioxan was treated with KOH for 1 day and dried by refluxing over Na for several hr. It was then distilled through a 30-cm column from the Na. A fraction boiling at 101·0–101·5° was collected. Aliphatic open-chain ethers such as diisopropyl ether and di-n-butyl ether were shaken with 50% H_2SO_4, NaOHaq and water, dried for 8–15 days over $CaCl_2$ and then with Na-ribbon. The ethers were repeatedly decanted and fresh Na added until evolution of H_2 ceased. They were filtered and distilled, only the middle fractions being used.[38–40] Reagent grade cyclohexane was washed several times in the cold with a mixture of conc HNO_3 and H_2SO_4. After repeated washings with water, it was fractionally distilled over Na;[41] b.p. 80·5°; n_D^{20}, 1·4263.

Reagent grade phenyl glycidyl ether was dried over CaH_2 for several days and distilled at reduced press. The fraction boiling at 103°/6 mm Hg was collected for use. Benzoic acid was recrystallized from its aqueous soln and dried over P_2O_5. The pyridine dried with KOH pellets was distilled under N_2 atmosphere after refluxing with BaO.

Reaction procedure. Reaction apparatus, procedure and analytical methods of the epoxide and the acid for kinetic measurements have been described in previous papers.[1,2] A reaction flask containing benzoic acid and a solvent was heated to a desired temp, and to this were added solns of phenyl ether and of an amine preheated to the same temp. The time was measured from the moment of mixing an amine in all cases. For analysis the aliquots (3 or 4 ml) of the reaction mixtures were taken out at convenient intervals. The acid and epoxy contents of the sample were determined by the direct neutralization method[42] and by the method of Durbetaki.[43] The temp of the reaction mixtures was kept in as constant as ±0·2°. An Ando TR-10C transformer bridge in a TRS-10C Dielectric Loss Measuring Set with a SE-33 Liquid Cell, operating on 1 Kc – 3 Mc, was used in determining the dielectric constants of the mixtures, and the reliability of the measurements was checked by determining the dielectric constants of some pure liquids, including pure toluene and nitrobenzene. The results seem to be accurate within 1% as shown in Table 2.