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Study of Epoxy Compounds. XI.*1 Solvent Effects in the Reaction of Benzoic Acid with Phenyl Glycidyl Ether by a Basic Catalyst

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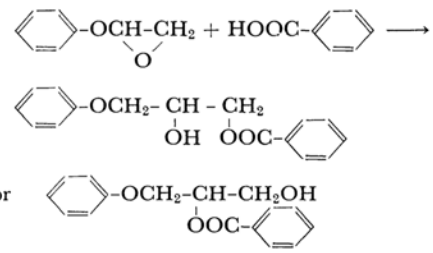
The rates of reaction between benzoic acid and phenyl glycidyl ether in the presence of pyridine in toluene, nitrobenzene, various ethers, and mixed solvents as reaction solvents, are measured kinetically, and the following results obtained: (1) The rates are proportional to the concentrations of benzoic acid, phenyl glycidyl ether, and pyridine. (2) Plots of log k *vs.* the concentration of benzoic acid give a linear relation in toluene-nitrobenzene, but not in nitrobenzene-dioxane. (3) The energies and entropies of the activation increase as dioxane increases in the mixed solvents, toluene-dioxane and nitrobenzene-dioxane. (4) This reaction follows the isokinetic relationship in the mixed solvents. (5) The plots of the rate constants, k_3 *vs.* the pK_b of the ethers indicate a straight-line relation. (6) Both the complex ion and the free ion participate in the reaction; the contribution of the free ion to this reaction is proportional to the dielectric constants of the solvents.

The reaction between *p*- or *m*-substituted benzoic acids and phenyl glycidyl ether, and the reaction between benzoic acid and *p*- or *m*-substituted phenyl glycidyl ethers, have previously been investigated,[1,2] and it has been reported that the initial rate of the reaction is proportional to the concentrations of phenyl glycidyl ether, benzoic acid, and the catalysts.



This paper will describe detailed kinetic studies of this reaction using pyridine as a catalyst in order to investigate the solvent effect in this reaction and clarify the reaction mechanism.

Experimental

Reagents. Phenyl glycidyl ether was dried over calcium hydride and distilled at reduced pressure. A distillate with a epoxy content of 10.65% (calcd, 10.67%) was used. Benzoic acid, pyridine, and the solvents were purified by the usual methods.

Procedure. The reaction procedure has been described previously.[3]

a) Analytical Method. Benzoic acid was titrated with a 0.1 N methanolic potassium hydroxide solution. Phenyl glycidyl ether was titrated with a 0.1 N hydrogen bromide - acetic acid solution.[4]

b) Measurement of the Dielectric Constant. The dielectric constant was measured by an instrument made by the Ando Electric Co.

c) Measurement of the Electric Conductivity. The electric conductivity was measured by an instrument made by the Takeda Riken Co.

Results and Discussion

a) Reaction Order. Figures 1 and 2 show the kinetic behavior of the reaction of benzoic acid with phenyl glycidyl ether, using pyridine as a catalyst, in toluene, nitrobenzene, ether, or their mixtures. The rates of decrease in the concentrations of epoxide and benzoic acid were equal. When 1/[BzOH] or 1/[PGE] was plotted against the reaction time, a good linear relationship was observed, and the second-order reaction rate constant, k_2, was obtained from the slopes of the straight lines. Figures 1—4 show the data from typical experiments used in the determination of the reaction order. It was also found that the values of k_2 are proportional to the concentration of the catalyst.

Therefore, the rate equation of this reaction is found to be as follows:

$$-\frac{d[BzOH]}{dt} = -\frac{d[PGE]}{dt} = k_3[BzOH][PGE][Py] \quad (1)$$

*1 Part X in this series, to be published in *J. Macromol. Chem.*

1) Sakai and Y. Ishii, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 2159 (1961).

2) Y. Tanaka and H. Kakiuchi, *J. Polymer Sci., Part A*, **2**, 3405 (1964).

3) Y. Tanaka and H. Kakiuchi, *J. Appl. Polymer Sci.*, **7**, 1063 (1963).

4) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

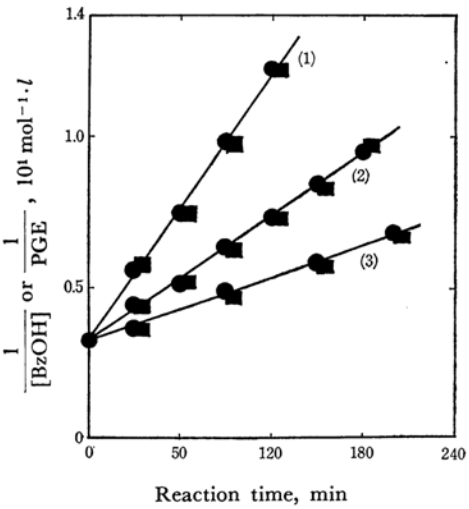


Fig. 1. Reaction of phenyl glycidyl ether (PGE) and benzoic acid (BzOH) using pyridine as a catalyst at 108°C.
- ● Benzoic acid (BzOH)
- ■ Phenyl glycidyl ether (PGE)

(1) Nitrobenzene (2) Toluene (3) Dioxane

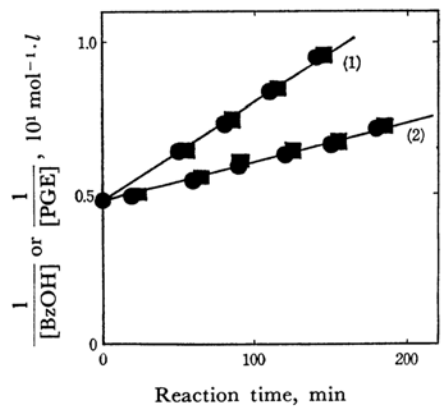


Fig. 2. Reaction of phenyl glycidyl ether [PGE] and benzoic acid [BzOH] in mixed solvent at 98°C.
- ● Benzoic acid [BzOH]
- ■ Phenyl glycidyl ether [PGE]

(1) [BzOH], [PGE]; 0.202 mol/l, [Py]; 1.24×10^{-2} mol/l, nitrobenzene 50 vol%, dioxane 50 vol%

(2) [BzOH], [PGE]; 0.202 mol/l, [Py]; 1.24×10^{-2} mol/l, toluene 50 vol%, dioxane 50 vol%

where k_3 is the observed third-order rate constant. Furthermore, Eq. (1) is also consistent with the reactions in mixed solvents, such as toluene-dioxane, and nitrobenzene-dioxane, and with the reactions containing unequal concentration of [BzOH] and [PGE] (for example, BzOH=0.1 mol/l and PGE =1 mol/l, or BzOH=1 mol/l and PGE=0.1 mol/l).

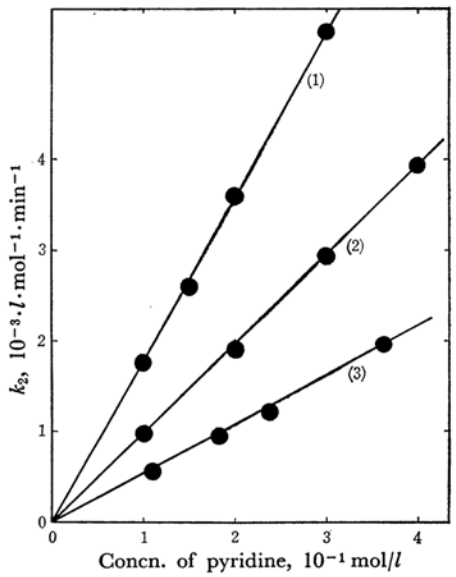


Fig. 3. The observed second-order rate constant k_2 *vs.* the concentration of pyridine.
(1) Nitrobenzene (2) Toluene (3) Dioxane

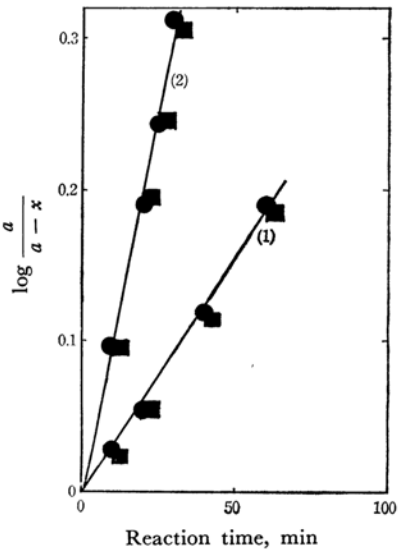


Fig. 4. Reaction of phenyl glycidyl ether [PGE] and benzoic acid [BzOH] with pyridine [Py].
- ● [BzOH]=2.42 mol/l, [PGE]=0.242 mol/l
- ■ [BzOH]=0.242 mol/l, [PGE]=2.42 mol/l

(1) [Py]=2.49×10^{-2} mol/l

(2) [Py]=1.245×10^{-1} mol/l

b) The Dielectric Constants of the Reaction Media. The dielectric constants of the reaction media hardly changed at all during the course of the reaction, as is shown in Table 1. The dielectric constants of the solvents can be regarded as the dielectric constants of the reaction media. The dielectric constants of the mixed-solvents were calculated according to Eq. (2):

TABLE 1. DIELECTRIC CONSTANTS OF SOLVENTS IN THE PRESENCE OF REACTANT SPECIES (MEASURED AT 25°C AT 1Mc) ([BzOH]≒0.2 mol/l)

Solvent	[PGE] mol/l	[Py] mol/l	$D^{1)}$	$D^{2)}$
Toluene	0.985	1.23×10^{-2}	2.45	2.42
Toluene	1.970	9.83×10^{-2}	2.45	2.43
Toluene	3.940	3.94×10^{-1}	2.36	—
Nitrobenzene	0.985	4.93×10^{-2}	35.20	—
Nitrobenzene	1.97	9.83×10^{-2}	35.20	35.05
Nitrobenzene	3.94	1.97×10^{-1}	35.55	35.15

1) Dielectric constant measured before the reaction started.
2) Dielectric constant measured after the reaction finished.

$$D = \frac{D_1 f_1 + D_2 f_2}{f_1 + f_2} \qquad (2)$$

f: mole fraction of the solvent
D: dielectric constant

It has been reported that the observed value for ethyl ether - tetrahydrofuran[5] and benzene-nitrobenzene are consistent with Eq. (2). Our findings on toluene-nitrobenzene are also consistent with Eq. (2), as Table 2 shows.

c) Solvent Effect. Table 2 shows the reaction rate constants (k_3), the energies of activation (E), and the entropies of activation ($\Delta S^{\neq}$) of the reaction run in toluene-nitrobenzene. It is known that linear relationships between $\log k$ and $1/D$ hold for ion-ion and ion-dipole reactions, and that linear relationships between $\log k$ and $(D-1)/(2D-1)$ hold for dipole-dipole relations. Plots of our findings deviated from the straight lines mentioned above, and the rate constant increased as the mole fraction of nitrobenzene increased. However, as is shown in Fig. 5, a linear relationship was observed between the apparent rate constants in toluene-nitrobenzene and the dielectric constants of the media. On the other hand, no such linear relationship was observed in dioxane-nitrobenzene, perhaps because

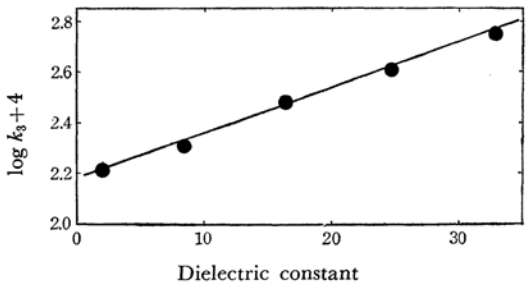


Fig. 5. Rate constant *vs.* dielectric constant in mixed solvent toluene-nitrobenzene.
[BzOH]=[PGE]=0.3 mol/l
Reaction temp. 108°C

of the specific solvating power of dioxane. Table 3 shows the rate constants and the E and $\Delta S^{\neq}$ values for the toluene-dioxane and nitrobenzene-dioxane, reactions. The relationship between polarity as an abstract concept and its concrete effect on reactions has not yet been well established, but it has been generally recognized that solvation by a solvent plays an important role in the chemical reaction. It was found that the values of E and $\Delta S^{\neq}$ increased with the molar ratio of nitrobenzene over toluene. The activated complex (including the ion pairs) at the transition state will be coordinated by solvent molecules with the solvating power. In such a system, the entropies of activation will be very small and will have a negative value. We must, however, consider that solvent molecules solvate not only to the activated complex, but also to the substrates, to the reactants, and to the products.

Various examples of solvations are known. Tokura[6] has classified the solvations into three categories; (A) the electrophilic solvation, (B) the nucleophilic solvation, and (C) the bephilic solvation. The reactions in media containing dioxane will belong to (A) as a result of the nucleophilic character of dioxane, itself resulting from the formation of a hydrogen-bonded solvation

TABLE 2. THE RATE CONSTANT AND ACTIVATION PARAMETERS FOR THE REACTION OF [BzOH] AND [PGE] IN TOLUENE-NITROBENZENE

Mole fraction of toluene	$D^{1)}$ (obs)	$D^{2)}$ (calc)	$k_3\times10^{-4}$ (l^2/mol^2·sec) 80°C	87°C	100°C	108°C	E kcal/mol	$\Delta S^{\neq}$ e. u.
1	2.40	2.38	0.35	0.67	1.60	2.62	17.2	−16.5
0.75	8.90	8.85	0.37	0.80	1.76	2.85	16.3	−17.2
0.50	15.80	16.30	0.41	0.90	1.90	3.92	15.5	−17.8
0.24	25.00	24.81	0.40	1.04	3.02	4.54	14.9	−18.5
0	34.50	34.80	0.55	1.21	3.27	5.43	14.5	−19.0

1) Dielectric constants measured at 25°C.
2) Dielectric constants calculated from Eq. (2).

5) A. Zilkha, *J. Polymer Sci., Part A*, **1**, 1813 (1963).
6) S. Tokura, *Kagaku*, **15**, 2 (1960).

Table 3. The rate constant and activation parameters for the reactoin of [BzOH] and [PGE] in the presence of toluene-dioxane and nitrobenzene-dioxane as solvent
[BzOH], [PGE]; 0.24 mol/l

Toluene-dioxane

Mole fraction of toluene	E kcal/mol	$\Delta S^{\neq}$, e.u. 298°K	$k_3\times10^{-2}$ 98°C l^2/mol^2·min
1.000	17.2	−16.5	2.41
0.80	18.1	−14.1	1.41
0.71	—	—	1.22
0.62	18.8	−12.8	1.14
0.54	—	—	1.05
0.45	19.2	−11.8	0.97
0.29	20.3	− 9.3	0.80
0.14	21.7	− 5.9	0.73
0	23.3	− 1.8	0.56

Nitrobenzene-dioxane

Mole fraction of nitrobenzene	E kcal/mol	$\Delta S^{\neq}$, e. u. 298°K	$k_3\times10^{-2}$ 98°C l^2/mol^2·min
1.000	14.5	−19.0	9.46
0.88	15.4	−17.2	8.15
0.77	16.5	−14.9	5.56
0.45	18.6	−10.8	5.07
0.18	20.8	− 6.0	2.67
0	23.3	− 1.8	0.50

with dioxane by reaction in PGE. In that reaction it is expected that the energies of activation (E) increase as the mole fraction of dioxane increases. Furthermore, it is considered that the entropies of activation ($\Delta S^{\neq}$) increase as the quantity of dioxane increases, because there is little difference between the ground state and the transition state in dioxane solvation, as compared with toluene and nitrobenzene; consequently, $\Delta S^{\neq}$ makes little contribution to this reaction.

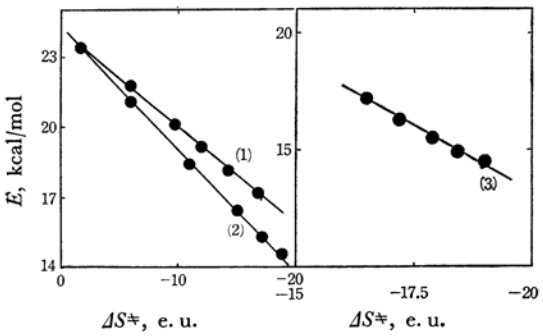


Fig. 6. Plot of activation energy (E) *vs.* activation entropy for the reaction of [PGE] and [BzOH] with pyridine as catalyst in mixed solvent.
(1) Toluene-dioxane
(2) Nitrobenzene-dioxane
(3) Toluene-nitrobenzene

As a result, the reaction rate diminishes as the amount of dioxane increases.

The reaction mechanism does not seem to very in media of various solvent compositions, because a plot of E *vs.* $\Delta S^{\neq}$ gives a good linear relationship in the mixed solvent systems of toluene-nitrobenzene, toluene-dioxane and nitrobenzene-dioxane, as is shown in Fig. 6.

Table 4. Rate constant of [BzOH] with [PGE] in ethers and pK_b values for various ether as solvent [BzOH], [PGE]; 2.42×10^{-2} mol/l [Py]; 2.45×10^{-3}—2.42×10^{-2} mol/l Reaction temp., 64.5°C

Ether	pK_b[7]	log k_3+2
Tetrahydrofuran	16.15	0.55
Dioxane	17.27	0.62
Diisopropyl ether	18.38	0.75
Di-*n*-butyl ether	19.47	0.85
Anisole	20.54	1.04
Benzene	—	1.06
Cyclohexane	—	1.67

The examination of the relationship between E, $\Delta S^{\neq}$ and the mole fraction of the solvents in toluene-dioxane and in nitrobenzene-dioxane reveals peculiar points when the mole fractions of toluene and nitrobenzene are in the vicinity of 0.45 and 0.18 respectively, as is shown in Figs. 6 and 10. The difference in the mole fractions where the peculiar points occurred may have something to do with the fact that nitrobenzene is more polar than toluene; that is to say, a smaller mole fraction of nitrobenzene than toluene plays a major part in this reaction. Therefore, dioxane participates to this reaction until the mole fractions reach the values corresponding to the peculiar points.

In order to investigate the effect of the solvation due to H-bonding between benzoic acid and ethers, the reactions of [BzOH] with [PGE] in various ethers were studied; their rate constants are given in Table 4.

It has been suggested that the ethers solvate toward protons or cations. The strong solvation of ethers toward cations is demonstrated by the fact[7] that the decomposition of optically-active secondary alkyl chlorosulfites in dioxane yields optically-active chlorides. The retention of the steric configuration has been ascribed to the solvation of dioxane toward the cation. In addition, Hart *et al.*[8] have reported that the nuclear alkylation of phenol by *t*-butyl chloride is inhibited by dioxane, the decrease in the reaction rate being proportional to the concentration of dioxane. This phenomenon has also been ascribed to the solvation of dioxane to phenol.

7) C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 308 (1952).
8) H. Hart *et al.*, *ibid.*, **76**, 1639 (1954).

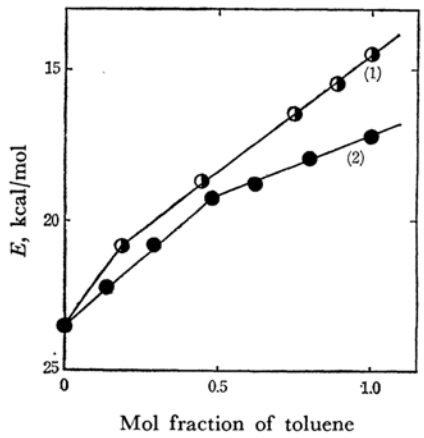


Fig. 7. Plot of activation energy (E) *vs.* mol fraction of toluene.
(1) Nitrobenzene-dioxane
(2) Toluene-dioxane

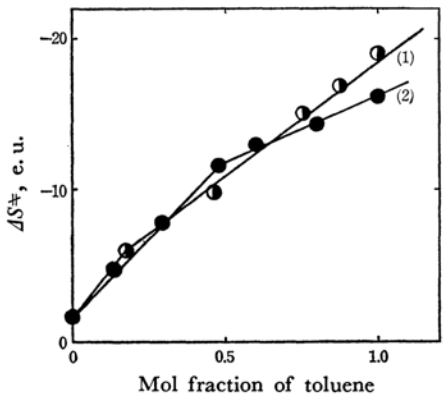


Fig. 8. Plot of activation entropy ($\Delta S^{\neq}$) *vs.* mol fraction of toluene.
(1) Nitrobenzene-dioxane
(2) Toluene-dioxane

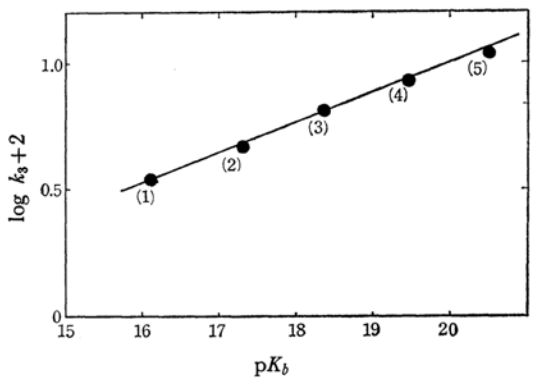


Fig. 9. Plot of $\log k_3$ *vs.* pK_b of ethers for the reaction of [PGE] and [BzOH] with pyridine as catalyst in ethers [BzOH]=[PGE]=2.42×10^{-1} mol/l at 64.5°C.
(1) Tetrahydrofuran (2) Dioxane
(3) Diisopropyl ether (4) *n*-Dibuthyl ether
(5) Anisole

In order to investigate the effect upon this reaction of the solvation of dioxane to benzoic acid, the relationship between the rate constants and the basicity of ethers[9] has been examined; a linear relationship was obtained between $\log k$ and pK_b, as is shown in Fig. 9. Such a decrease in the reaction rate can best be explained by assuming that the formation of the complex ($BzOH\cdot Py$) or of the free ions (BzO^-, PyH^+) is hindered by H-bonding between benzoic acid and ethers.

Furthermore, the rate constant in anisole was found to be almost the same as that in benzene (because the fact is considered to be solvated to benzoic acid by the π-electron in anisole), and the rate constant in benzene was smaller than that in cyclohexane.

Reaction Mechanism

The relationship between the apparent rate constant, $\bar{k}$, and the equilibrium constant, K, is expressed as Eq. (3), according to Acree[10]:

$$\bar{k} = k' + k''(K/c^*)^{1/2} \qquad (3)$$

where k' indicates the rate constants for ion pairs,

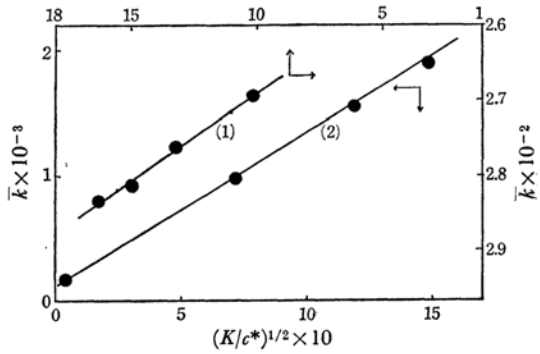


Fig. 10a. Plot of $\bar{k}$ *vs.* $(K/c^*)^{1/2}$ for the reaction using toluene and nitrobenzene as solvent.
(1) Nitrobenzene (2) Toluene

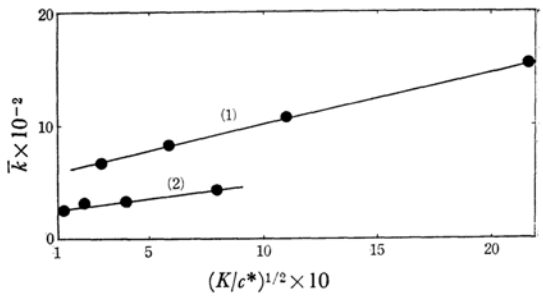


Fig. 10b. Plot of k *vs.* $(K/c^*)^{1/2}$ for the reaction using benzonitrile and chlorobenzene as solvent.
(1) Benzonitrile (2) Chlorobenzene

9) "Progress in Physical Organic Chemistry," Wiley Publishers, New York, p. 289.
10) S. F. Acree, *Am. Chem. J.*, **1912**, 37.

Table 5. Equilibrium constants between benzoic acid [BzOH] and pyridine [Py], and rate constants for reaction of [BzOH] with [PGE]

Concn. of benzoic acid, mol/l	Specific conductivity $\Omega^{-1}\cdot cm^{-1}$	Equivalent conductivity $\Omega^{-1}\cdot cm^2/eq.$	Dissociation constant (α)	Equilibrium constant (K) mol/l	Concn. of pyridine c^*, mol/l	$(K/c^*)^{1/2}$	Rate constant $l^2/mol^2\cdot min$
Nitrobenzene							
0.200	0.15×10^{-7}	0.77×10^{-4}	4.05×10^{-2}	3.32×10^{-4}	1.24×10^{-2}	1.64×10^{-1}	0.8×10^{3}
0.100	0.14×10^{-7}	1.47×10^{-4}	7.73×10^{-2}	6.05×10^{-4}	0.62×10^{-2}	3.12×10^{-1}	0.96×10^{3}
0.050	0.11×10^{-7}	2.25×10^{-4}	11.87×10^{-2}	7.10×10^{-4}	0.31×10^{-2}	4.78×10^{-1}	1.25×10^{3}
0.025	0.10×10^{-7}	3.80×10^{-4}	20.00×10^{-2}	10.00×10^{-4}	0.16×10^{-2}	7.90×10^{-1}	1.65×10^{3}
Benzonitrile							
0.200	0.43×10^{-8}	2.15×10^{-5}	0.70×10^{-2}	0.98×10^{-5}	1.24×10^{-2}	2.79×10^{-2}	6.73×10^{2}
0.100	0.42×10^{-8}	4.25×10^{-5}	1.42×10^{-2}	2.02×10^{-5}	0.62×10^{-2}	5.72×10^{-2}	8.25×10^{2}
0.050	0.41×10^{-8}	8.34×10^{-5}	2.78×10^{-2}	3.88×10^{-5}	0.31×10^{-2}	11.20×10^{-2}	10.50×10^{2}
0.025	0.41×10^{-8}	16.60×10^{-5}	5.53×10^{-2}	7.70×10^{-5}	0.16×10^{-2}	21.90×10^{-2}	14.7×10^{2}
Chlorobenzene							
0.200	1.69×10^{-9}	0.85×10^{-5}	4.30×10^{-3}	0.37×10^{-5}	2.48×10^{-2}	1.22×10^{-2}	2.73×10^{2}
0.100	1.26×10^{-9}	1.26×10^{-5}	7.20×10^{-3}	0.52×10^{-5}	1.24×10^{-2}	2.05×10^{-2}	3.02×10^{2}
0.050	0.68×10^{-9}	1.36×10^{-5}	14.20×10^{-3}	1.01×10^{-5}	0.62×10^{-2}	4.07×10^{-2}	3.18×10^{2}
0.025	0.42×10^{-9}	1.68×10^{-5}	2.75×10^{-3}	1.90×10^{-5}	0.31×10^{-2}	7.82×10^{-2}	4.10×10^{2}
Toluene							
0.200	0.17×10^{-11}	0.83×10^{-8}	1.11×10^{-3}	0.25×10^{-6}	2.48×10^{-2}	3.16×10^{-3}	2.65×10^{2}
0.100	0.16×10^{-11}	1.60×10^{-8}	2.13×10^{-3}	0.46×10^{-6}	1.24×10^{-2}	6.08×10^{-3}	2.71×10^{2}
0.050	0.14×10^{-11}	2.81×10^{-8}	3.75×10^{-3}	0.71×10^{-6}	0.62×10^{-2}	10.70×10^{-3}	2.80×10^{2}
0.025	0.12×10^{-11}	4.62×10^{-8}	6.15×10^{-3}	0.95×10^{-6}	0.31×10^{-2}	17.5×10^{-3}	2.94×10^{2}

Table 6. Contribution of free ions in nitrobenzene, benzonitrile, chlorobenzene and toluene [BzOH]=[PGE]=0.2 mol/l

	Nitrobenzene	Benzonitrile	Chlorobenzene	Toluene
k, $l^2/mol^2\cdot sec$	0.8×10^{3}	6.73×10^{2}	2.73×10^{2}	2.65×10^{2}
k', $l^2/mol^2\cdot sec$	5.7×10^{2}	5.56×10^{2}	2.68×10^{2}	2.56×10^{2}
$k''\times(K/c^*)^{1/2}$	2.30×10^{2}	1.17×10^{2}	0.15×10^{2}	0.12×10^{2}
Dielectric constant*	34.8	25.2	5.63	2.37
Contribution of free ions, %	28.8	17.4	5.42	4.52

* These values were given from "Hand Book of Chemistry" edited Lange.

k'' is the rate constant for the free ion, and c^* is the number of active centers, which is equivalent the concentration of the catalyst. The contributions to this reaction of the complexes [BzOH·Pr] and free ions [BzO^-, PyH^+] (to be described later) were estimated by measuring the electric conductivity of benzoic acid in nitrobenzene, benzonitrile, chlorobenzene, and toluene.

These results are listed in Table 5. A plot of k *vs.* $(K/c^*)1/2$ gave a straight line, as Fig. 10 shows.

The k' and k'' $(K/c^*)^{1/2}$ values and other are summarized in Table 6.

The contribution of the free ions to this reaction was estimated to be 28.8% in nitrobenzene, 17.4% in benzonitrile, 5.42% in chlorobenzene, and 4.52% in toluene.

The degree of the contribution of the free ions to the rate of this reaction is proportional to the dielectric constant and should be taken as the ionizing power as shown in the presence of toluene-nitrobenzene.

The apparent rate constant described above is the initial rate constant. Therefore, it is considered that the concentration of benzoic acid diminishes,

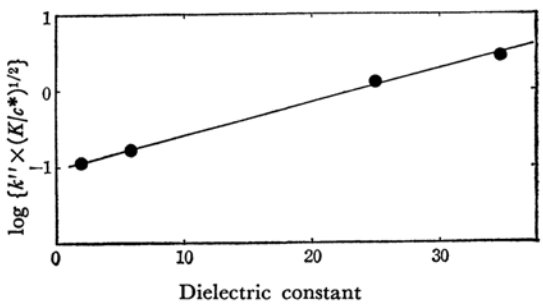


Fig. 11. Dielectric constant *vs.* log $\{k''\}\times(K/c^*)^{1/2}\}$.

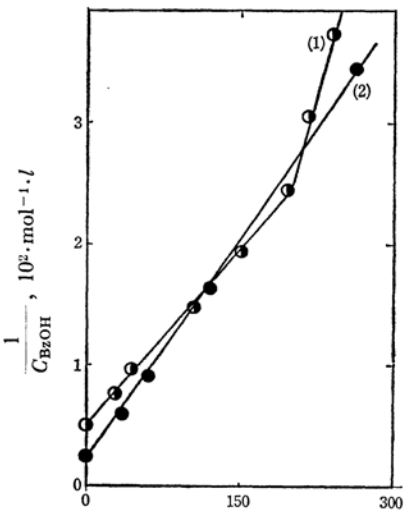
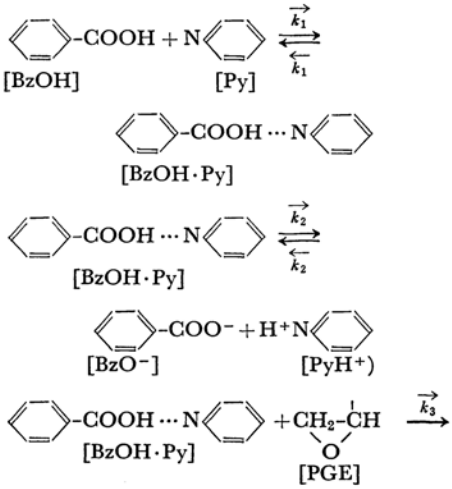
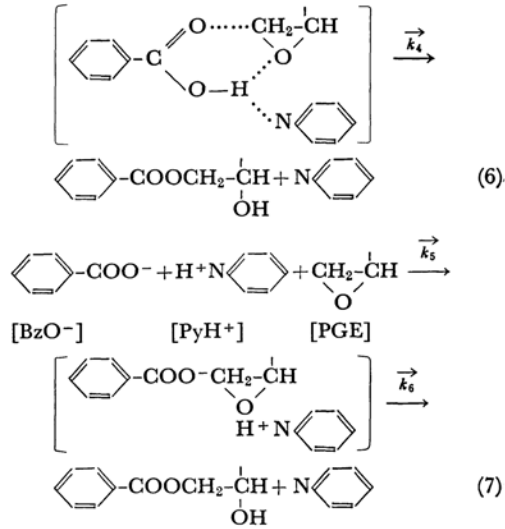


Fig. 12. Plot of $1/C_{BzOH}$ vs. reaction time for the reaction of [PGE] and [BzOH] using nitrobenzene and toluene as solvent at 98°C.
(1) [BzOH], [PGE]; 0.2 mol/l [Py]; 0.9×10^{-1} mol/l, nitrobenzene
(2) [BzOH], [PGE]; 0.4 mol/l [Py]; 1.77×10^{-1} mol/l, toluene

while the dissociation constant increases, as the reaction proceeds.

We would like to consider why the reaction rate increases and the plot of $1/C_{BzOH}$ *vs.* time deviates from the straight-line relationship. As is shown in Fig. 12, a good linear relationship was obtained in toluene, but the plots deviated from the line in the vicinity of 80% conversion in nitrobenzene. This fact can be explained by assuming that these is a larger participation of free ions as the reaction proceeds in nitrobenzene. On the basis of the reasoning described above, the following elementary reactions are assumed to occur:





The occurrence of Reactions (4) and (5) has been supported by the UV and IR spectra and by the electric conductivity. Reaction (4) was proposed by Ishii[11] and Kakiuchi.[12]

Taking [BzOH], [Py], [BzOH·Py], [BzO^-], [PyH^+], [PGE] and [BzOH·Py·PGE] as the concentrations of benzoic acid, pyridine, the complex of benzoic acid and pyridine as shown in Reaction (5), the carboxylate anion, the pyridinium ion, phenyl glycidyl ether, and an activated complex of three species between benzoic acid, pyridine and phenyl glycidyl ether as shown in Reaction (6) respectively, the following equations are obtained:

$$\frac{d[BzOH\cdot Py]}{dt} = \vec{k}_1[BzOH][Py] - \overleftarrow{k}_1[BzOH\cdot Py] - \vec{k}_3[BzOH\cdot Py][PGE] \quad (8)$$

Since $d[BzOH\cdot Py]/dt=0$ in the stationary state, we obtain:

$$[BzOH\cdot Py] = \frac{\vec{k}_1[BzOH][Py]}{\overleftarrow{k}_1+\vec{k}_3[PGE]} \quad (9)$$

Furthermore, the following equations are obtained from Eqs. (5) and (7):

$$\frac{d[BzO^-]}{dt} = \vec{k}_2[BzOH\cdot Py] - \overleftarrow{k}_2[BzO^-][PyH^+] - \vec{k}_5[BzO^-][PyH^+][PGE] \quad (10)$$

because $d[BzO^-]/dt=0$ in the stationary state:

$$[BzO^-][PyH^+] = \frac{\vec{k}_2[BzOH\cdot Py]}{\overleftarrow{k}_2+\vec{k}_5[PGE]} \quad (11)$$

Therefore, the total reaction rate, V, may be

11) Sakai and Y. Ishii, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan. Ind. Chem. Sect.)*, **66**, 51 (1963); **67** 333 (1964); **64**, 2159 (1961).
12) Y. Tanaka and H. Kakiuchi, *J. Polymer Sci., Part A*, **2**, 3405 (1964).

expressed as follows:

$$V = \vec{k_3}[\mathrm{BzOH\cdot Py}][\mathrm{PGE}] + \vec{k_5}[\mathrm{BzO^-}][\mathrm{PyH^+}][\mathrm{PGE}]$$
$$= \frac{\vec{k_1}\vec{k_3}[\mathrm{BzOH}][\mathrm{Py}][\mathrm{PGE}]}{\overleftarrow{k_1}+\vec{k_3}[\mathrm{PGE}]}$$
$$+ \frac{\vec{k_1}\vec{k_2}\vec{k_5}[\mathrm{BzOH}][\mathrm{Py}][\mathrm{PGE}]}{(\overleftarrow{k_2}+\vec{k_5}[\mathrm{PGE}])(\overleftarrow{k_1}+\vec{k_3}[\mathrm{PGE}])} \quad (12)$$

If $\overleftarrow{k_1} \gg \vec{k^3}$ [PGE] and $\overleftarrow{k_2} \gg \vec{k_5}$ [PGE], then:

$$V = \frac{\vec{k_1}\vec{k_2}}{\overleftarrow{k_1}}[\mathrm{BzOH}][\mathrm{Py}][\mathrm{PGE}]$$
$$+ \frac{\vec{k_1}\vec{k_2}\vec{k_5}}{\overleftarrow{k_2}\,\overleftarrow{k_1}}[\mathrm{BzOH}][\mathrm{Py}][\mathrm{PGE}] =$$
$$\left(\frac{\vec{k_1}\vec{k_2}}{\overleftarrow{k_1}} + \frac{\vec{k_1}\vec{k_2}\vec{k_5}}{\overleftarrow{k_2}\,\overleftarrow{k_1}}\right)[\mathrm{BzOH}][\mathrm{Py}][\mathrm{PGE}] \quad (13)$$

Eq. (13) explains the results of Figs. 1—4 and is consistent with the experimental equation of the reaction rate, Eq. (1).

Summary

(1) The rate of the reaction between benzoic acid and phenyl glycidyl ether in the presence of pyridine in toluene, nitrobenzene, ethers and mixed solvents is proportional to the concentrations of benzoic acid, phenyl glycidyl ether, and pyridine.

(2) Plots of $\log k$ *vs.* $[\mathrm{BzO^-}]$ give a linear relation in toluene-nitrobenzene, but not in nitrobenzene-dioxane.

(3) The energies of activation and the entropies of activation increase as the amounts of dioxane increase in the mixed solvents, toluene-dioxane, and nitrobenzene-dioxane.

(4) This reaction follows an isokinetic relationship in the mixed solvents.

(5) Plots of $\log k_3$ *vs.* the pK_b of ethers gives a straight line relation.

(6) Both the complexes (including ion pairs) and the free ions participate in the reaction; the contribution of the free ions to this reaction is proportional to the dielectric constants of the solvents.