**Reaction of 1,1-Dichloro-2-ethoxy-3,3-dimethylcyclopropane (V) with *n*-Butyllithium.**—The chloride V (20.0 g, 0.11 mole) was dissolved in 30 ml of dry ether and cooled to −30°. An ethereal solution (1.3 *M*) of *n*-butyllithium (100 ml, 0.13 mole) was added dropwise with stirring during 1 hr. The reaction mixture was stirred for another 0.5 hr while the bath temperature rose to 10°. Water was added, and the ether layer was separated. The aqueous layer was extracted with a small amount of ether, and the combined ether layers were dried ($Na_2CO_3$). Evaporation of the ether and fractionation of the residue gave 7.3 g (59%) of impure 1-ethoxy-3-methyl-1,2-butadiene (XVI), bp 55–57° (65 mm), $n^{25}$D 1.4344. Redistillation gave a purer sample: bp 51° (60 mm); $n^{20}$D 1.4400; $\nu_{max}$ 1960, 1120 $cm^{-1}$.

*Anal.* Calcd for $C_7H_{12}$: C, 74.95; H, 10.78. Found: C, 73.30; H, 10.68.

The allene readily formed a 2,4-dinitrophenylhydrazone, which recrystallized from ethyl acetate as red needles, mp 187° (lit.[46] mp 179° for the 2,4-dinitrophenylhydrazone of β-methylcrotonaldehyde).

*Anal.* Calcd for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.94; H, 4.66; N, 21.14.

It is also interesting that V underwent a slow reaction with methyllithium at room temperature, yielding the allene XVI, as evidenced by the band at 1960 $cm^{-1}$ in the infrared spectrum of the crude product

**Reaction of 1,1-Dichloro-2-ethoxy-3-methylcyclopropane (IV) with *n*-Butyllithium.**—The chloride IV was treated with *n*-butyllithium as described for the homolog V. The infrared spectrum of the total distilled reaction product showed no appreciable absorption in the 2000–1900-$cm^{-1}$ region, but strong bands at 2750, 1700, and 1650 $cm^{-1}$ characteristic of an α,β-ethylenic aldehyde.

The mixture gave a 2,4-dinitrophenylhydrazone, mp 187–188°, undepressed on admixture with that of crotonaldehyde.

**Kinetic Measurements.**—The kinetic runs were carried out in a flask inserted in a constant-temperature bath, accurate within 0.1°. At time intervals aliquots were removed, quenched with water, and titrated with hydrochloric acid using phenolphthalein as indicator. A typical run, as that of the compound V in 95% ethanol with 0.01 *M* sodium ethoxide as base, is given in Table III. The rate constants used for calculations of relative rates were an average value of three or more runs. When the base concentration was varied from 0.01 to 0.5 *M*, the rate constant of V decreased by a factor of 2.

TABLE III

KINETIC MEASUREMENT AT 70°

| Time, min | 0.01 *N* HCl, ml | $10^3k$, $min^{-1}$ |
|---|---|---|
| 0 | 5.00 | |
| 15 | 4.50 | 7.03 |
| 60 | 3.26 | 7.13 |
| 90 | 2.45 | 7.92 |
| 120 | 2.06 | 7.39 |
| 150 | 1.63 | 7.47 |
| 175 | 1.39 | 7.32 |

$k = (1.23 \pm 0.08) \times 10^{-4}\ sec^{-1}$

**Acknowledgment.**—The author thanks Dr. E. B. Whipple for helpful discussions of the nmr spectra and Mr. G. G. Vrambout for technical assistance.

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[46] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

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# Study of Epoxy Compounds. VII.[1,2] Base-Catalyzed Reaction of Substituted Phenyl Glycidyl Ethers with Benzoic Acid

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The base-catalyzed reaction of substituted phenyl glycidyl ethers (PGE) with benzoic acid in the presence of dimethyldodecylamine was studied in various nonaqueous solvents such as xylene and mono- and *o*-dichlorobenzene, and nitrobenzene. The reaction in these solvents was found to be third order, being first order in each of the three reactants. Etherification, hydrolysis, and diesterification did not appear to occur under these conditions. The reaction constant, ρ, is positive and is smaller at higher temperature and larger in the solvents of higher polarity.

A considerable number of ring-opening reactions of epoxides with compounds having an active hydrogen have been studied kinetically. Kinetic studies of various epoxides in basic or neutral solutions have been carried out as for the reactions with water,[3-7] ammonia,[8-13] and various amines.[7,11,13-17] The acid-catalyzed reactions with water[3,4,18-21] and amines[22,23] have been studied for a series of epoxides. Boyd and Marle[24] studied the reaction of substituted phenols with ethylene oxide in the presence of corresponding sodium phenoxides in ethyl alcohol, and proposed an ionic mechanism. Patat[25,26] studied the same reaction

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[1] This work was first presented at the 12th Annual Meeting of the Society of Polymer Science, Tokyo, May 1963.

[2] Part VI: Y. Tanaka and H. Kakiuchi, *J. Polymer Sci.*, **A2**, 3405 (1964).

[3] J. N. Brønsted, M. Kilpatrick, and M. Kilpatrick, *J. Am. Chem. Soc.*, **51**, 428 (1929).

[4] A. M. Eastham and G. A. Lathremouille, *Can. J. Chem.*, **30**, 169 (1952).

[5] H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.*, **44**, 905 (1948).

[6] J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **79**, 2365 (1957).

[7] L. Smith and T. Nilsson, *J. Prakt. Chem.*, **162**, 63 (1943).

[8] F. Berbé, *Chim. Ind.* (Paris), **63**, 492 (1950); *Chem. Abstr.*, **47**, 4286 (1953).

[9] P. Ferrero, F. Berbé, and L. R. Flamme, *Bull. Soc. Chim. Belges*, **56**, 349 (1947).

[10] S. Andersson, *Nord. Kemistmötet, Helsingfors*, **7**, 172 (1950); *Chem. Abstr.*, **48**, 7405 (1954).

[11] J. Hansson, *Svensk Kem. Tidskr.*, **60**, 183 (1948); *Chem. Abstr.*, **43**, 926 (1949).

[12] C. Potter and R. R. McLaughlin, *Can. J. Res.*, **25B**, 405 (1947).

[13] L. Smith, S. Mattsson, and S. Andersson, *Kgl. Fysiograf. Sällskap. Lund, Handl.*, **42**, No. 7, 1 (1946); *Chem. Abstr.*, **41**, 6458 (1947).

[14] N. G. Barker and N. H. Cromwell, *J. Am. Chem. Soc.*, **73**, 1051 (1951).

[15] A. M. Eastham, B. de B. Darwent, and P. E. Beaubien, *Can. J. Chem.*, **29**, 575 (1951).

[16] J. Hansson, *Svensk Kem. Tidskr.*, **67**, 246 (1955); *Chem. Abstr.*, **49**, 12935 (1955).

[17] J. Hansson, *Svensk Kem. Tidskr.*, **67**, 263 (1955); *Chem. Abstr.*, **49**, 12936 (1955).

[18] J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 2667 (1956).

[19] W. L. Petty and P. L. Nichols, *ibid.*, **76**, 4385 (1954).

[20] L. Smith, G. Wode, and T. Widhe, *Z. Physik. Chem.* (Leipzig), **130**, 154 (1927).

[21] G. Wode, *Svensk Kem. Tidskr.*, **40**, 221 (1928); *Chem. Abstr.*, **23**, 2344 (1929).

[22] A. M. Eastham and B. de B. Darwent, *Can. J. Chem.*, **29**, 585 (1951).

[23] A. M. Eastham, *J. Chem. Soc.*, 1936 (1952).

[24] D. R. Boyd and E. R. Marle, *ibid.*, **105**, 2117 (1914).

[25] E. Patat, *Monatsh.*, **83**, 322 (1952).

[26] E. Patat, E. Cremer, and O. Boblester, *J. Polymer Sci.*, **12**, 489 (1954).

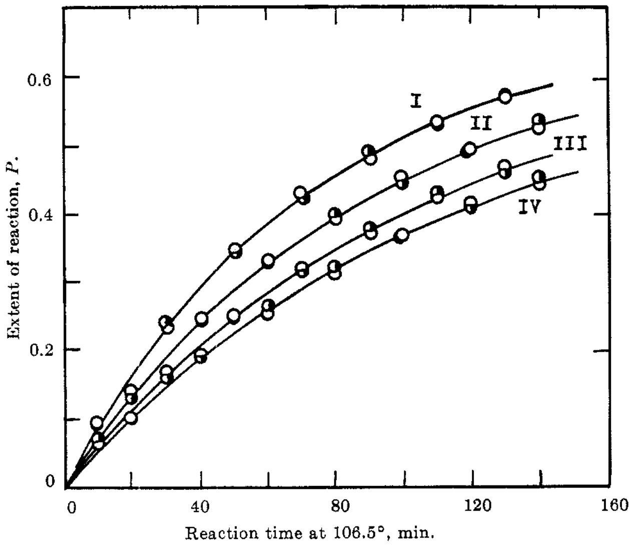


Figure 1.—Reaction of phenyl glycidyl ether and benzoic acid with dimethyldodecylamine in various solvents at 106.5°. The initial concentrations of phenyl glycidyl ether, benzoic acid, and dodecyldimethylamine are $2.7 \times 10^{-1}$, $2.7 \times 10^{-1}$, and $2.3 \times 10^{-2}$ *M*, respectively. I, in nitrobenzene; II, in *o*-dichlorobenzene; III, in chlorobenzene; IV, in xylene. ○, phenyl glycidyl ether; ◑, benzoic acid.

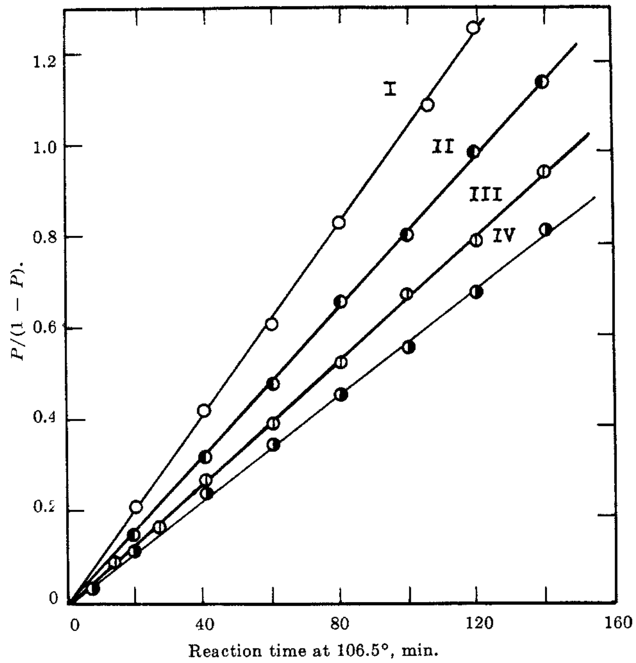
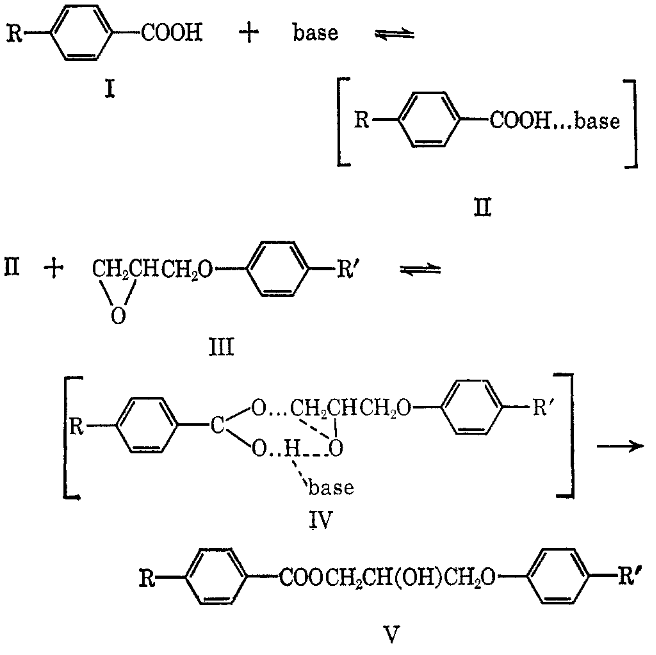


Figure 2.—Plot of $P/(1 - P)$ *vs.* reaction time in the reaction of phenyl glycidyl ether and benzoic acid with dimethyldodecylamine in various solvents at 106.5°. I, in nitrobenzene; II, in *o*-dichlorobenzene; III, in chlorobenzene; IV, in xylene.

without any solvent and confirmed Boyd's conclusion. Recently, however, Patat[22] proposed a new modified mechanism, in which an activated complex composed of phenol, phenoxide, and ethylene oxide was assumed to play an important role at a transition state. Ishii, *et al.*,[28-30] determined the rate of successive addition of ethylene oxide to phenol and proposed a mechanism *via* a complex for this reaction.

SCHEME I



a, R = R′ = H
b, R = R′ = $CH_3$
c, R = $CH_3O$; R′ = $C(CH_3)$
d, R = R′ = Cl
e, R = $C_2H_5COO$; R′ = $NO_2$
f, R = $NO_2$; R′ = $CH_3O$
g, R′ = $CH_3OCO$
h, R′ = $C_6H_5$

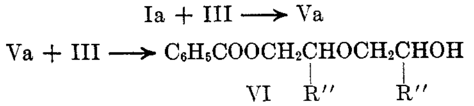
The base-catalyzed reaction of phenyl glycidyl ether (IIIa) and substituted benzoic acids (I) in a nonpolar solvent such as xylene was studied and discussed by Sakai, *et al.*[31] They proposed the similar mechanism in which the first step is an equilibrium reaction between a base and a benzoic acid (I) to produce an activated complex (II) (see Scheme I). The complex II formed reacts with phenyl glycidyl ether (IIIa) through an activated complex or a transition state species (IV) to produce the monobenzoate of 3-phenoxy-1,2-propylene glycol (V). They also showed that the reaction mechanism was affected by the reaction conditions such as temperature, solvent, and substituents of benzoic acid (I).

In this paper we studied the reaction of substituted phenyl glycidyl ethers (III) with benzoic acid (Ia) in the presence of a tertiary amine in such solvents as xylene, mono- and *o*-dichlorobenzene, and nitrobenzene, estimated the effect of substituents of phenyl glycidyl ether and of solvents, and discussed the reaction mechanism.

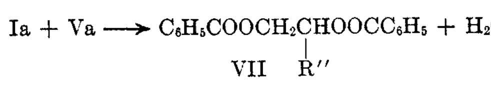
## Results

The following five reactions might occur in a mixture of the epoxide III and benzoic acid (Ia).

$$\text{Ia} + \text{III} \longrightarrow \text{Va} \qquad (1)$$



$$\text{Va} + \text{III} \longrightarrow \underset{\text{VI}}{C_6H_5COOCH_2\underset{R''}{\underset{|}{C}}HOCH_2\underset{R''}{\underset{|}{C}}HOH} \qquad (2)$$



$$\text{Ia} + \text{Va} \longrightarrow \underset{\text{VII}}{C_6H_5COOCH_2\underset{R''}{\underset{|}{C}}HOOCC_6H_5} + H_2O \qquad (3)$$

$$\text{III} + H_2O \longrightarrow \underset{\text{VIII}}{CH_2(OH)CHR''(OH)} \qquad (4)$$

$$\text{Va or VII} + H_2O \longrightarrow \text{Ia} + \text{VIII} \qquad (5)$$

$$R'' = CH_2OC_6H_4R'$$

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[27] E. Patat and B. Wojtech, *Makromol. Chem.*, **37**, 1 (1960).

[28] Y. Ishii, Y. Nishikawa, and H. Kato, *Kogyo Kagaku Zasshi*, **63**, 2177 (1960).

[29] S. Sakai and Y. Ishii, *ibid.*, **61**, 358, 1473 (1958); **62**, 413 (1959).

[30] S. Sakai, T. Sugiyama, and Y. Ishii, *ibid.*, **67**, 333 (1964).

[31] S. Sakai, K. Ueta, and Y. Ishii, *ibid.*, **64**, 2159 (1961).

Figure 1 gives the data of a typical experiment to determine the reaction rate and shows that the rates of the reaction between the epoxide and benzoic acid hardly changed whether the solvent is xylene, mono- or *o*-dichlorobenzene, or nitrobenzene. Since the disappearance of benzoic acid was completely accounted for by the appearance of ester and hydroxyl groups by infrared spectral analysis, the reactions shown by eq 2–5 may be ignored in these conditions. This is contrary to the findings of Malkemus and Swan[32] and Wrigley, *et al.*,[33] who studied the addition reaction of ethylene oxide and fatty acids and found that reactions 2–5 did occur.

In Figure 2, $P/(1 - P)$ is plotted against the reaction time; $P$ is the extent of the reaction, defined by

$$P = (C_i - C_t)/C_i = 1 - C_t/C_i$$

The slope of the best line drawn through the points is $k_2C_i$, the product of the observed second-order reaction rate constant and the initial concentration of the two reactants. As is seen in Figure 2, the base-catalyzed reaction is in good agreement with second-order kinetics, according to

$$P/(1 - P) = k_2C_it = k_2't \quad (k_2C_i = k_2')$$

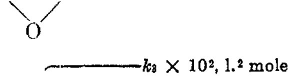
The order of reaction with respect to the tertiary amine was determined through a series of experiments with constant initial concentrations of the epoxide and the acid ($2.70 \times 10^{-1}$ $M$) and with varied concentrations of dimethyldodecylamine (from 1.20–6.70 $\times$ $10^{-2}$ $M$). The various values of the rate constant, $k_2$, were plotted against the concentrations of the tertiary amine, and a straight line was obtained as shown in Figure 3. This shows that the observed second-order rate constant, $k_2$, was proportional to the concentration of the tertiary amine as the catalyst. The rate equation, then, is expressed as

$$-\mathrm{d(epoxide)}/\mathrm{d}t = -\mathrm{d(acid)}/\mathrm{d}t = k_3\mathrm{(amine)(acid)(epoxide)} \quad (6)$$

where $k_3$ is the third-order rate constant. The results are shown in Tables I and II.

Table I

Third-Order Rate Constants and Hammett's ρ Values for the Reaction of Substituted PGE (III) with Benzoic Acid in Xylene at Various Temperatures[a]



$CH_2CHCH_2OC_6H_4R'$ (III)

| III | R' | $k_3 \times 10^2$, l.$^2$ mole$^{-2}$ sec$^{-1}$ 80° | 106.5° | 120° | 130° |
|---|---|---|---|---|---|
| e | $p$-$NO_2$ | 0.356 | 2.00 | 4.08 | 8.36 |
| g | $p$-$CO_2CH_3$ | 0.323 | 1.82 | 4.00 | 7.96 |
| d | $p$-Cl | 0.246 | 1.67 | 3.60 | 7.24 |
| a | H | 0.231 | 1.54 | 3.48 | 7.09 |
| b | $p$-$CH_3$ | 0.211 | 1.40 | 3.33 | 6.77 |
| f | $p$-$OCH_3$ | 0.175 | 1.28 | 2.89 | 6.61 |
| Hammett's ρ value | | 0.26 | 0.17 | 0.13 | 0.097 |
| Correlation coefficient[b] | | 0.989 | 0.996 | 0.982 | 0.992 |

[a] The initial concentrations of PGE (III), benzoic acid (Ia), and dimethyldodecylamine are 0.270, 0.270, and 0.0230 $M$, respectively. [b] See ref 35.

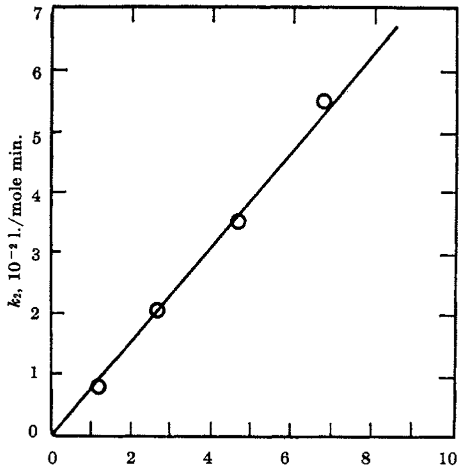


Figure 3.—Effect of concentration of dimethyldodecylamine, $C_A$, on the observed second-order rate constant, $k_2$, in the reaction of phenyl glycidyl ether and benzoic acid in xylene at 106.5°. The initial concentrations of phenyl glycidyl ether and benzoic acid are $2.7 \times 10^{-1}$ $M$.

Table II

Third-Order Rate Constants and Hammett's ρ Values for the Reaction of Substituted PGE (III) with Benzoic Acid in Various Solvents at 106.5°[a]

| III | $k_3 \times 10^2$, l.$^2$ mole$^{-2}$ sec$^{-1}$ $NO_2C_6H_5$ | $o$-$Cl_2C_6H_4$ | $ClC_6H_5$ |
|---|---|---|---|
| e | 4.31 | 3.20 | 2.52 |
| g | 4.03 | 2.86 | 2.32 |
| d | 3.14 | 2.41 | 1.92 |
| a | 2.80 | 2.18 | 1.79 |
| b | 2.52 | 2.04 | 1.71 |
| f | 2.40 | 1.88 | 1.58 |
| Hammett's ρ value | 0.26 | 0.22 | 0.19 |
| Correlation coefficient[b] | 0.992 | 0.996 | 0.991 |

[a] The initial concentrations of PGE (III), benzoic acid (Ia), and dimethyldodecylamine are 0.270, 0.270, and 0.0230 $M$, respectively. [b] See ref 35.

The effects of substituents of phenyl glycidyl ether (PGE) on the reaction of PGE–benzoic acid–dimethyldodecylamine (0.270:0.270:0.0230 $M$) at various temperatures and in various solvents are shown in Tables I and II. Hammett plots of the logarithms of the observed third-order reaction rate constants, $k_3$, *vs.* σ are given for the reaction at various temperatures in xylene and at 106.5° in the other solvents. The best straight lines for these reactions have been found by the least-squares method, and, from the slopes, ρ values are found to be +0.26, 0.17, 0.13, and 0.097 at 80, 106.5, 120, and 130° in xylene, as shown in Table I, and to be +0.26, 0.22, and 0.19 in nitrobenzene and *o*-di- and monochlorobenzene at 106.5°, as shown in Table II. The σ values used in these plots or calculations have been taken from Jaffé's review.[34] The fact that ρ values are positive indicates that electron-withdrawing substituents enhance the rate and that the reaction is that of S$_N$2 type. Phenyl glycidyl ethers substituted by electron-releasing groups had lower rate constants as shown in Tables I and II, larger activation energies, $E_A$, and larger frequency factors, as shown in Table III.

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[32] J. D. Malkemus and J. D. Swan, *J. Am. Oil Chemists' Soc.*, **34**, 342 (1957).

[33] A. N. Wrigley, D. F. Smith, and A. J. Stirton, *ibid.*, **36**, 34 (1959).

[34] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

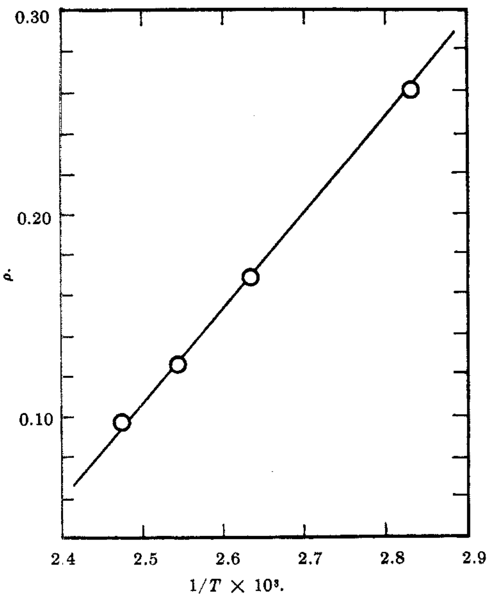


Figure 4.—Temperature dependence of ρ value in the reaction of phenyl glycidyl ether and benzoic acid with dimethyldodecylamine in xylene.

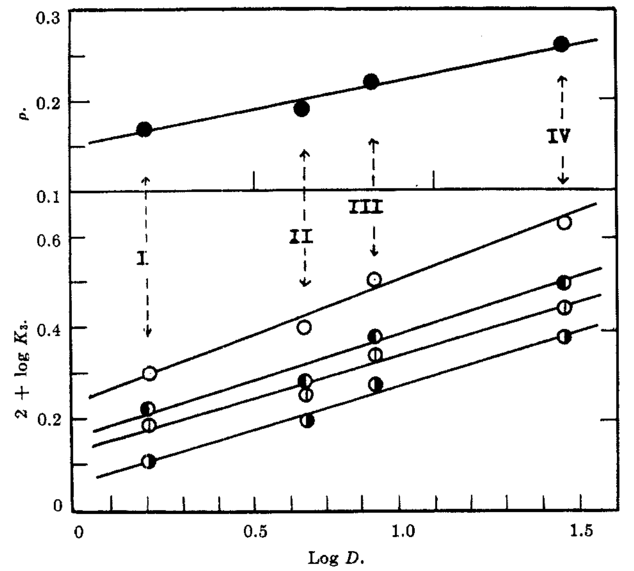
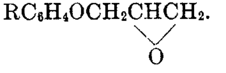


Figure 5.—Plot of ρ and log $k_3$ *vs.* log *D* in the reaction of *para*-substituted phenyl glycidyl ethers and benzoic acid with dimethyldodecylamine in various solvents at 106.5°. I, in nitrobenzene; II, in *o*-dichlorobenzene; III, in chlorobenzene; IV, in xylene. ○, $NO_2$; ◐, Cl; ⦶, H; ◑, $CH_3O$. Symbols are R from



$RC_6H_4OCH_2\underset{\diagdown\,O\,\diagup}{CHCH_2}$.

TABLE III

ARRHENIUS PARAMETERS AND HEAT AND ENTROPY OF ACTIVATION FOR REACTION OF SUBSTITUTED PGE WITH BENZOIC ACID IN XYLENE

| III | $E_A$, kcal/mole | Log *A* | $S^*_{298}$, eu | $H^*_{298}$, kcal/mole | $G^*$, kcal/mole |
|---|---|---|---|---|---|
| e | 17.3 | 8.30 | −24.4 | 16.1 | 23.3 |
| g | 17.7 | 8.47 | −23.6 | 16.5 | 23.5 |
| d | 18.7 | 9.04 | −21.5 | 17.5 | 23.9 |
| a | 18.9 | 9.09 | −20.9 | 17.7 | 23.9 |
| b | 19.2 | 9.25 | −20.2 | 18.0 | 24.0 |
| f | 19.5 | 9.37 | −19.6 | 18.3 | 24.6 |

The Arrhenius parameters and the enthalpies and the entropies of activation are obtained from eq 7–9 and are collected in Table III.

$$k = (KT/h)e^{\Delta S^*/R}e^{-\Delta H^*/RT} \tag{7}$$

$$\Delta H^* = E_A + (\Delta n^* - 1)RT \tag{8}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{9}$$

where *k*, *K*, *h*, *R*, and *T* are the observed rate constant, Boltzmann's constant, Planck's constant, the gas constant, and the absolute temperature, respectively, and $\Delta H^*$, $\Delta S^*$, $\Delta G^*$, and $\Delta n^*$ 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 the reactants, respectively.

Sakai, *et al.*,[31] showed that there was a little steric effect for the reactions of substituted benzoic acids (I) with PGE in the presence of trimethylbenzylammonium hydroxide in such solvents as xylene and nitrobenzene. In this case, however, there may be no steric effect of substituents of PGE, since the substituents are further away from the site of reaction.

Hammett's ρ values for a given reaction depend on the conditions under which the reaction takes place. The higher the temperature becomes, the smaller the ρ value becomes for the reaction in xylene as shown in Table I. In Figure 4, ρ is plotted against the reciprocal of the temperature, $1/T$, for the reaction in which four reaction constants were evaluated under the conditions differing only in the temperature of the experiment. With due allowance for the large uncertainties in reaction constants, the plots appear to be linear. The best straight line has been found by the least-squares method[35] and shown by

$$\rho = -1.054(1 - 440.5/T) \tag{10}$$

The correlation coefficient has been found to be 0.999.

The reaction rates and reaction constants appear to increase with increasing dielectric constant, *D*, of the solvent as shown in Table II. Neither log $k_3$ nor ρ is found to hold a linear relationship with *D*, $(D - 1)/(2D - 1)$, or $1/D$, but a good linear relationship between log $k_3$ or ρ and log *D* has been found as shown in Figure 5. The best straight line has been found by the least-squares method[35] and is shown by eq 11. The slope, *a*, and intercept, *b*, are collected in Table IV.

$$\log k_3 = a \log D + b \tag{11}$$

TABLE IV

CONSTANTS IN THE RELATIONSHIP: LOG $k_3$ = *a* LOG *D* + *b*

| III | *a* | *b* | Correlation coefficient[a] | No. of data used for calcn |
|---|---|---|---|---|
| e | 0.296 | 0.235 | 0.992 | 4 |
| g | 0.305 | 0.190 | 0.996 | 4 |
| d | 0.251 | 0.158 | 0.996 | 4 |
| a | 0.232 | 0.130 | 0.987 | 4 |
| b | 0.227 | 0.100 | 0.992 | 4 |
| f | 0.241 | 0.0565 | 0.995 | 4 |

[a] See ref 35.

## Discussion

Boyd and Marle[24] showed that $C_6H_5O^-$ was an active species directly related to the base-catalyzed reaction between ethylene oxide and phenol in ethanol-water. The ionic mechanism might be a reasonable

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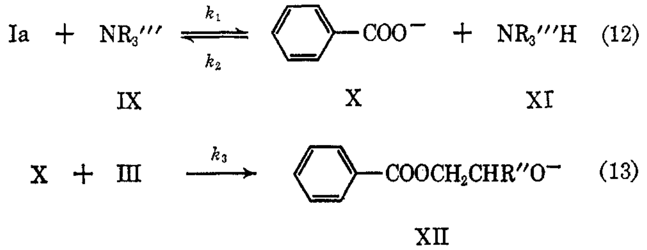
(35) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954.

explanation for the reaction in such a highly polar solvent. Since amine salts of benzoic acid have poor solubilities and small dissociation constants in nonpolar solvents such as xylene, the reaction may not have the same kinetics as in polar solvents such as alcohol and water. The theory in which the $C_6H_5CO_2^-$ ion (X) has a direct relationship with the reaction rate as shown in eq 12–14 cannot account for the fact that the reaction in these solvents was third order, being first order with respect to each of the three reactants, an amine, an acid, and an epoxide, and that the $\rho$ value was dependent on the temperature as shown in Figure 4. Here, IX is dimethyldodecylamine and $k_{1-4}$ are rate constants.



$$\mathrm{XII} + \mathrm{XI} \xrightarrow{k_4} \mathrm{V} + \mathrm{IX} \qquad (14)$$

Briegleb and Bieber[36] showed that the $\rho$ value for the dissociation of substituted benzoic acids in water at 15–50° is independent of the temperature.

Now let us see what kind of rate equation is obtained if eq 12–14 take place. By assuming that (1) $dC_X/dt = dC_{XI}/dt = dC_{XIII}/dt = 0$, and (2) $k_1, k_2 \gg k_3C_{III}$, we obtain

$$dC_V/dt = (k_1k_3^2/k_2)^{1/2}C_{III}(C_{Ia}C_{IX})^{1/2} \qquad (15)$$

Equation 15 disagrees with eq 6, which was found by experiment.

If the reaction proceeds as shown by eq 16–18

$$\mathrm{Ia} + \mathrm{IX} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{II} \qquad (16)$$

$$\mathrm{II} + \mathrm{III} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{IV} \qquad (17)$$

$$\mathrm{IV} \xrightarrow{k_5} \mathrm{V} + \mathrm{IX} \qquad (18)$$

and if $dC_{II}/dt = dC_{IV}/dt = 0$, the rate equation becomes

$$dC_V/dt = k_1k_3k_5C_{Ia}C_{III}C_{IX}/[k_2(k_4 + k_5) + k_3k_5C_{III}] \qquad (19)$$

With a reasonable assumption that $k_2$ is much larger than $k_3C_{III}$, then eq 19 becomes

$$dC_V/dt = (k_1k_3/k_2)C_{Ia}C_{III}C_{IX} \qquad (20)$$

Equation 20 can reasonably explain the experimental results.

The equilibrium reaction shown by eq 16 can be suggested from the formation[37] of association products, $R_3N(RCOOH)_n$ (where $n > 2$), from carboxylic acids and a tertiary amine, and their 1:1 acid–amine salts in nonpolar media. The catalytic effect of the complex II might be suggested from the fact that a quaternary ammonium salt plays an important role on the formation of chlorohydrin ester from epichlorohydrin and a carboxylic acid.[38–42]

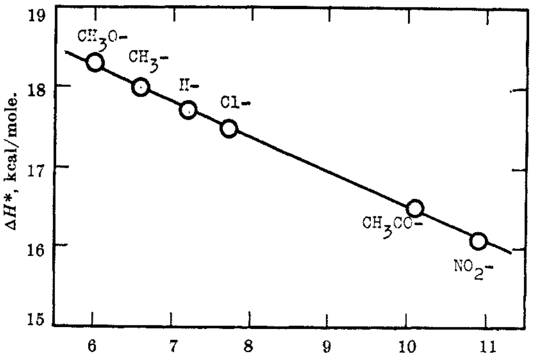


Figure 6.—Isokinetic relationship in the reaction of phenyl glycidyl ether and benzoic acid with dimethyldodecylamine in xylene. Symbols are R from $\mathrm{RC_6H_4OCH_2\underbrace{CHCH_2}_{O}}$.

Table III and Figure 6 show that the isokinetic relationship[43] or the linear enthalpy–entropy relationship, eq 21, holds for this reaction

$$\Delta H^* = \Delta H^*_0 + \beta\Delta S^* \qquad (21)$$

where $\Delta H^*_0 = 27.2$, and $\beta = 450$. The correlation coefficient[35] is 0.999.

Reaction constants for a given reaction depend on the conditions under which the reaction takes place. Hammett[44] proposed that reaction constants can be expressed in the form of the following equation

$$\rho = (B_1/D + B_2)/RTd^2 \qquad (22)$$

where $R$ is the gas constant, $T$ is the absolute temperature, $D$ is the dielectric constant of the solvent, and $d$ is the distance from the substituent to the reaction site. $B_1$ was assumed to depend on purely electrostatic interaction between the reacting benzene derivative and the medium, and $B_2$ was assumed to measure the susceptibility of the reaction toward the changes in the charge density at the reaction site.

The best straight line was obtained between $\rho$ and $1/T$ for the reaction of substituted PGE with benzoic acid in xylene, as shown in Figure 4 and eq 10. Equation 22 satisfactorily explains the temperature dependence of $\rho$, but cannot explain the fact that $\rho$ approached zero as the temperature approached the isokinetic temperature,[45] $\beta$ (in this case, 445°K from the experimental eq 10 or 21), as shown by eq 10.

Leffler and Grunwald[45] proposed that reaction constants can be expressed in the form of the following equation

$$\rho_T = \rho_\infty(1 - \beta/T) \qquad (23)$$

where $\rho_T$ and $\rho_\infty$ are the reaction constants at temperature $T$ and $\infty$, and parameter $\beta$ has the dimension of

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[36] G. Briegleb and A. Bieber, *Z. Elektrochem.*, **55**, 250 (1951); **53**, 350 (1949).

[37] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 2886 (1962).

[38] G. Stein, U. S. Patent 2,224,026 (Dec 3, 1940); German Patent 708,463 (June 12, 1941).

[39] E. C. Shokal, W. Creek, and A. C. Mueller, U. S. Patent 2,895,947 (July 21, 1959).

[40] P. Edwards, U. S. Patent 2,537,981 (Jan 16, 1951).

[41] G. Maerker, J. F. Carmichael, and W. S. Port, *J. Org. Chem.*, **26**, 2681 (1961).

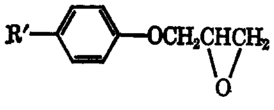
[42] N. Fukugawa, F. Kato, K. Shimomura, and M. Yoshihara, Report, 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1964.

[43] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

[44] L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).

[45] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapters 7, 9.

TABLE V
SUBSTITUTED PHENYL GLYCIDYL ETHERS



| R′ | Bp (mm) or mp, °C | $n^{25}$D | $d^{25}$ | Mol wt Calcd | Mol wt Found[a] | Oxiran oxygen, % Calcd | Oxiran oxygen, % Found | C, % Calcd | C, % Found[b] | H, % Calcd | H, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 100–106 (5) | 1.5288 | 1.1057 | 150 | 147 | 10.67 | 10.58 | 72.06 | 72.07 | 6.73 | 6.86 |
| $CH_3$ | 117–122 (7) | 1.5242 | 1.0773 | 164 | 161 | 9.77 | 9.66 | 73.19 | 72.95 | 7.37 | 7.33 |
| $C(CH_3)_3$ | 144–146 (3) | 1.5130 | 1.0234 | 207 | 199 | 7.74 | 7.52 | 75.72 | 75.61 | 8.74 | 8.73 |
| Cl | 115–118 (3) | 1.5422 | 1.2478 | 185 | 188 | 8.65 | 8.64 | 58.38 | 58.10 | 4.86 | 4.91 |
| $NO_2$[c] | 64–66 | ... | ... | 195 | 193 | 8.21 | 8.16 | 55.38 | 55.27 | 4.65 | 4.68 |
| $OCH_3$ | 46–48 | ... | ... | 180 | 175 | 8.89 | 8.59 | 66.67 | 66.69 | 6.67 | 6.60 |
| $CO_2CH_3$ | 54–56 | ... | ... | 208 | 201 | 7.70 | 7.58 | 63.46 | 63.60 | 5.81 | 5.90 |
| $C_6H_5$[d] | 69–71 | ... | ... | 226 | 216 | 7.08 | 6.93 | 79.62 | 79.45 | 6.19 | 6.24 |

[a] Determined by a cryoscopic method using benzene. [b] Determined with the HCl–DMF method: Y. Tanaka and H. Kakiuchi, *Kobunshi Kagaku*, **20**, 629 (1963). [c] Recrystallized from methanol–water solution. [d] Recrystallized from petroleum ether.

absolute temperature and can be identified as an actual or virtual temperature at which all the differences in the rate or the equilibrium constants will vanish, that is, $\delta_R \Delta G^* = 0$ at $T = \beta$. Equation 23 appears to represent the temperature dependence for this reaction. As Table I shows, the $\rho$–$\sigma$ relationship holds well even when the temperature is changed. This fact can be explained only by eq 23, not by eq 22.

Equation 22 also predicts the change of $\rho$ with the dielectric constant of the solvent. However, as Table IV shows, the linear relationship was found to hold between log $k_3$ and log $D$ in nitrobenzene, *o*-dichlorobenzene, monochlorobenzene, and xylene. It was also found that the following relationship held between $\rho$ and log $D$

$$\rho = a \log D + b \tag{24}$$

where $a$ and $b$ are 0.0784 and 0.149, and $D$ is the dielectric constant taken from Lange's handbook.[46] The correlation coefficient[35] is 0.991. Until the significance of the results shown in Table IV is better understood, the significance of eq 24 cannot be interpreted adequately.

The mechanism shown by eq 16–18 can clearly explain the facts that the electron-donating tertiary amine is the effective catalyst for this reaction, and that the $\rho$ value observed for substituted benzoic acids[31] was positive.

## Experimental Section[47]

**Materials.**—Substituted phenyl glycidyl ethers were prepared from epichlorohydrin and corresponding substituted phenols with an aqueous solution of sodium hydroxide by the one-step method of Kuwamura.[48] A modification of this method was necessary in the procedure; the reaction temperature was 50–60° in some cases, *p*-phenylphenol was treated at 70–80° and the methyl ester of hydroxybenzoic acid was treated at 45–55° with a sodium hydroxide solution of lower concentration. This method was similar to those used by others.[49–54] The properties of the epoxides are given in Table V. *p*-Methoxyphenol was obtained from hydroquinone and dimethyl sulfate by the method of Robinson and Smith.[55] Phenols except *p*-methoxyphenol were commercial.

Dimethyldodecylamine and benzoic acid, both reagent grade, were either distilled *in vacuo* or recrystallized before use.

Solvents were purified as usual.[56] Xylene (mixed isomer) was shaken successively with sulfuric acid and a sodium bicarbonate solution, dried with calcium chloride, and then fractionally distilled. A fraction boiling at 137–139° was collected and used. Chlorobenzene was purified[57] by shaking it repeatedly with portions of sulfuric acid until the acid no longer became colored. It was then washed with water and with a dilute sodium bicarbonate solution, dried with calcium chloride, and fractionally distilled through a 40-cm column. A fraction boiling at 131.5° was collected; $n^{20}$D 1.5248. *o*-Dichlorobenzene was distilled through a 60-cm Widmer column and the middle fraction boiling at 179–180° was collected.[58]

**Reaction Procedure.**[59] A reaction flask containing benzoic acid and a solvent was heated to a desired temperature, and to this was added a solution of substituted PGE preheated to the same temperature. The measurement of time was started at the time of mixing in all cases. The lapse of time introduced no detectable error into any of the runs. The reaction mixtures were stirred by bubbling dry nitrogen gas, and the aliquots (3 or 4 ml) of the reaction mixtures were taken out at convenient intervals and analyzed. The epoxide and acid contents of the reaction system were determined by the method of Durbetaki[60] and by the direct neutralization method.[61,62] The initial concentrations of PGE, benzoic acid, and dimethyldodecylamine were $2.70 \times 10^{-1}$, $2.70 \times 10^{-1}$, and $1.20\text{–}6.70 \times 10^{-2}$ $M$. Attempts were made to hold the temperature of the reaction mixtures constant (±0.2°). The extent of reaction, $P$, is defined as

$$P = (C_i - C_t)/C_i = 1 - C_t/C_i \tag{25}$$

where $C_t$ and $C_i$ are the concentrations of reagents in the reaction system at times $t$ and 0, respectively. The rate equation of the second-order reaction is expressed as

$$P/(1 - P) = k_2C_it = k_2't \quad (k_2C_i = k_2') \tag{26}$$

when the initial concentrations of both PGE and benzoic acid are the same.

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(46) N. A. Lange and G. M. Forker, "Handbook of Chemistry," 10th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 1222.

(47) Boiling and melting points are uncorrected. The molecular weights were determined by the cryoscopic method with benzene.

(48) T. Kuwamura, *Kogyo Kagaku Zasshi*, **63**, 595 (1960).

(49) A. Fairbourne, G. P. Gibson, and D. W. Stephens, *J. Chem. Soc.*, 1965 (1932).

(50) D. R. Boyd and E. R. Marle, *ibid.*, **93**, 838 (1908).

(51) E. R. Marle, *ibid.*, **101**, 305 (1912).

(52) K. E. Marple, E. C. Shokal, and T. W. Evans, U. S. Patent 2,260,753 (1941); 2,327,053 (1943); 2,380,185 (1945).

(53) T. W. Evans and E. F. Bullard, U. S. Patent 2,156,724 (1939).

(54) R. Oda, *Kogyo Kagaku Zasshi*, **55**, 673 (1952).

(55) R. Robinson and J. O. Smith, *J. Chem. Soc.*, 393 (1926).

(56) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955, pp 321, 407, 419, 432.

(57) K. B. McAlpine and C. P. Smyth, *J. Chem. Phys.*, **3**, 55 (1935).

(58) E. M. Moore and M. E. Hoobs, *J. Am. Chem. Soc.*, **71**, 411 (1949).

(59) H. Kakiuchi and Y. Tanaka, *Kobunshi Kagaku*, **20**, 619 (1963).

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

(61) E. R. Bishop, E. B. Kittredge, and J. H. Hildebrand, *J. Am. Chem. Soc.*, **44**, 135 (1922).

(62) J. Mitchell, Jr., B. A. Montague, and R. H. Kinsey, "Organic Analysis," Vol. 3, J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 1.