

Kinetic Studies on Solvolysis. VI. Kinetic Evidence of the Distinct Rôle of the Hydrogen Atom of Hydroxylic Solvent Molecules as an Attacking Center at the First Ionization Stage

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Acceleration by hydroxylic groups has been well known for solvolytic reactions of several secondary and tertiary halides¹⁾, and it was previously pointed out^{1a,2)} that this kind of

acceleration would be a specific driving force by hydrogen-bonding to the leaving halide ion and that it was superimposed on the acceleration by general solvent effect which was assumed to be proportional to the reciprocals of dielectric constants of the solvents²⁾. However, previous investigations^{1,2)} have not given any evidence of the distinct rôle of the hydrogen atom as a reactive center in the

1) a) For the review see A. Streitwieser, Jr., *Chem. Revs.*, **56**, 622 (1956). b) Y. Pocker, *J. Chem. Soc.*, **1959**, 1179.

2) Part IV. H. Shingu and K. Okamoto, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78**, 558 (1957).

hydroxyl group. In the present investigation linear catalysis by ortho- and para-substituted phenols, mono- and di-hydric alcohols and several polar molecules in acetolysis of *tert*-butyl bromide has been examined in order to see if the intramolecularly fixed, or chelated, hydrogen atom of the hydroxyl group would lose its accelerating function as a hydrogen-bonding center, and also to ascertain if there was co-operating acceleration by two adjacent hydroxylic groups in a molecule. Furthermore, the solvolysis rates of *tert*-butyl bromide in phenol-carbon tetrachloride mixtures have been quantitatively discussed from the point of view that the hydrogen atoms of the various species of "associated" phenol molecules would be operative as the key atoms at the first ionization stage of the solvolysis in these phenolic solvents.

When *tert*-butyl bromide was subjected to acetolysis in acetic acid-carbon tetrachloride mixture (1:3 by vol.) in the presence of sodium acetate, it was found that several

TABLE I. CATALYTIC CONSTANTS OF PHENOLS, ALCOHOLS AND SEVERAL POLAR AND NON-POLAR COMPOUNDS IN ACETOLYSIS OF *tert*-BUTYL BROMIDE IN ACETIC ACID-CARBON TETRACHLORIDE MIXTURE (1:3 BY VOL. AT 25.0°C) AT 70.0°C

| Accelerating substance | $10^5 \times \text{Catalytic constants}^*$ $\text{sec}^{-1} \text{M}^{-1}$ |
|-----------------------------------|---|
| Phenol | 2.53 |
| <i>p</i> -Cresol | 4.44 |
| <i>o</i> -Cresol | 2.90 |
| <i>p</i> -Chlorophenol | 5.34 |
| <i>o</i> -Chlorophenol | 2.52 |
| <i>p</i> -Nitrophenol | 11.75 |
| <i>o</i> -Nitrophenol | 0.925 |
| Hydroquinone | 10.8 |
| Catechol | 8.34 |
| Carbon tetrachloride | -0.100 |
| Dioxane | -0.745 |
| Acetone | 1.38 |
| Acetic acid | 1.15 |
| Water | 5.41 |
| Methanol | 2.63 |
| Ethanol | 1.41 |
| Ethylene glycol | 7.69 |
| Cyclohexanol | 0.90 |
| <i>cis</i> -1,2-Cyclohexanediol | 3.04 |
| <i>trans</i> -1,2-Cyclohexanediol | 3.09 |
| Benzene | 0.440 |
| Toluene | 0.370 |
| Chlorobenzene | 0.810 |
| Nitrobenzene | 0.955 |

* Initial concentration of sodium acetate, 0.0500 N; standard rate constant k_1° , 6.72×10^{-6} (sec^{-1}).

phenols, glycols, and some other polar molecules showed linear catalysis, as has previously been known in the case of the unimolecular reaction in nitromethane^{1b}. In Table I the catalytic constants of these hydroxylic molecules are compared. The catalytic constants of the ortho-substituted phenols in which the hydroxyl groups are intramolecularly fixed by a hydrogen bridge are smaller than those of corresponding para-derivatives, as evidenced by the data for nitro-, chloro-, hydroxy- and methyl derivatives of phenols. Among them the effect of the *o*-nitro group is particularly striking in that the catalytic constant of *o*-nitrophenol is the smallest and comparable to that of nitrobenzene, while that of *p*-nitrophenol is the largest one. These observations may lead to the conclusion that the hydrogen atom in the free, or non-chelated, hydroxyl group is the center of reaction in the first ionization stage of the S_N1 -type solvolysis.

For this acetolysis the catalytic order of the substituted phenols is qualitatively, but not quantitatively, the same as the acidity order, while for the solvolysis in nitromethane^{1b} this correlation was found to be quantitatively applicable. This inconsistency would probably be due to the complexity resulting from the hydrogen-bonding interaction between these phenols and acetic acid.

In this connection it is noteworthy that even non-hydroxylic polar molecules, e. g., toluene, chlorobenzene, nitrobenzene, and acetone, and also benzene could give small but definitely positive catalytic constants which were comparable to that of acetic acid per se. This may be explained on the basis that these molecules would modify the self-hydrogen-bonding interaction of the acetic acid molecules to the extent that a certain increase of their free hydrogen atoms and, therefore, relative enhancement of ionizing power of acetic acid would result.

The negative catalytic constant for dioxane can be explained on a basis similar to the above consideration by suppression of the catalytic action of acetic acid due to the hydrogen-bonding, or hydrogen-accepting, nature of dioxane.

A further evidence of the necessity of free hydroxyl groups is revealed by the following fact: that in intramolecularly hydrogen-bonded methyl salicylate solvent, *tert*-butyl bromide did not show any hydrogen bromide evolution for 4.0 hr. at 70°C, while in phenolic solvent this bromide was easily solvolysed even at room temperature.

For dihydroxylic compounds, like 1,2-cyclohexanediols, ethylene glycol, catechol and water, the catalytic constants are greater than

TABLE II. VALUES* of S_n 's AND k 's IN EQUATION 1: $k = \sum_{n=1}^n S_n k_n$

| Phenol concn. M | Phenolysis rate const. k , sec ⁻¹ | S_1 | S_2 | S_3 | S_4 | S_5 | S_6 | S_7 | S_8 | S_9 | S_{10} | $S_{>10}$ ** |
|-----------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|--------------|
| 3.4 | 1.0×10^{-4} | 31 | 22 | 15 | 10 | 7.1 | 5.1 | 3.7 | 2.5 | 1.7 | 1.2 | 3.4 |
| 3.0 | 6.6×10^{-5} | 30 | 21 | 14 | 9.9 | 6.6 | 4.5 | 3.0 | 2.1 | 1.5 | 0.9 | 2.4 |
| 2.5 | 4.1×10^{-5} | 28 | 19 | 13 | 8.2 | 5.5 | 3.8 | 2.3 | 1.6 | 1.1 | 0.8 | 1.7 |
| 2.25 | 3.3×10^{-5} | 27 | 18 | 12 | 7.7 | 5.0 | 3.2 | 1.9 | 1.3 | 0.9 | 0.6 | 1.3 |
| 2.0 | 2.7×10^{-5} | 27 | 17 | 11 | 7.4 | 4.4 | 2.6 | 1.7 | 1.0 | 0.7 | 0.4 | 1.0 |
| 1.75 | 2.2×10^{-5} | 26 | 17 | 10 | 6.5 | 3.9 | 2.3 | 1.2 | 0.8 | 0.5 | 0.2 | 0.6 |
| 1.5 | 1.6×10^{-5} | 26 | 17 | 9.0 | 5.6 | 3.0 | 1.8 | 1.1 | 0.6 | 0.3 | 0.2 | 0.4 |
| 1.25 | 1.1×10^{-5} | 24 | 14 | 7.9 | 4.6 | 2.5 | 1.3 | 0.7 | 0.3 | 0.3 | 0.1 | 0.1 |
| 1.0 | 7.0×10^{-6} | 23 | 12 | 6.3 | 3.3 | 1.6 | 0.8 | 0.4 | 0.3 | 0.1 | 0.1 | 0.1 |
| 0.75 | 4.2×10^{-6} | 21 | 9.7 | 4.5 | 2.2 | 1.1 | 0.5 | 0.2 | 0.1 | — | — | — |
| 0.50 | 2.2×10^{-6} | 18 | 7.0 | 2.8 | 1.2 | 0.5 | 0.2 | 0.1 | — | — | — | — |

* Calculated from interpolated values of α_n 's using Eq. 2.

** For phenol polymer species with more than eleven phenol molecules. The average number of n was assumed to be thirteen.

twice those of monohydroxylic compounds, like cyclohexanol, ethanol, phenol and methanol, respectively (cf. Table I). Although some electronic effect, especially in the dihydroxylic phenols, might be responsible for these results, the marked acceleration would be mostly attributed to the sterically co-operating attack of two adjacent hydroxyl groups in these molecules.

On the basis of the foregoing discussion, it appears to be reasonable to reconsider the solvent effect of hydroxylic compounds from the point of view that the ionization is controlled by the co-operating attack of hydroxyl groups of the various species of associated hydroxylic molecules. For a discussion of this problem the data for the association degree of those compounds are required. Fortunately the calculated results for the distribution of various associated phenol species in carbon tetrachloride at 20.0°C are available³⁾. Therefore, the solvolysis rates of *tert*-butyl bromide in various phenol-carbon tetrachloride mixtures were measured in the presence of sodium phenolate at 20.0°C and after suitable correction for the initial concentrations of sodium phenolate (see Experimental) the data were tested by the following equations which were derived in order to correlate the observed solvolysis rates with the concentrations of the various species of associated phenol molecules.

Provided that reacting phenols are short-lived polyhydroxylic polymers with various degrees of association, the total rate of the solvolysis may be expressed in the Eq. 1,

$$\text{rate} = \left(\sum_{n=1}^n k_n [S_n] \right) [\text{RX}] = k [\text{RX}] \quad (1)$$

where S_n represents the time-average con-

centration of a phenol polymer species n , and k_n represents the rate constant for the phenol polymer species n . Furthermore, the S_n in the Eq. 1 is expressed by Eq. 2,

$$S_n = (\text{Phenol concn.}) \times \alpha_n / n \times 100 \quad (2)$$

where α_n represents the percentage of the number of the phenol molecules forming polymer species n to the total number of the phenol molecules. Thus, using the values of α_n 's given by Kempter and Mecke³⁾ and of the observed rate constants for the corresponding phenol-carbon tetrachloride mixtures, we can estimate the approximate values for k_n 's. In Table II the values for the coefficients of k_n 's, i.e., the values of S_n 's in Eq. 1, are shown along with the corresponding eleven interpolated values of observed total rate constants.

In examining the relation between the observed total rate constants and the S_n 's in eleven simultaneous equations obtained from the values in Table II, it is obvious that an increasing series of values for k_n 's is required for good agreement between the observed total rate constants and those calculated from the right side of Eq. 1, and one of such series for the k_n 's is shown in the following: $k_1, k_2 = 0.05 \times 10^{-4}$, $k_3, k_4 = 0.1 \times 10^{-4}$, $k_5, k_6 = 0.3 \times 10^{-4}$, $k_7, k_8 = 1 \times 10^{-4}$, $k_9, k_{10} = 6 \times 10^{-4}$, $k_{>10} = 18 \times 10^{-4}$ (sec⁻¹). Using these k_n 's the calculated values for the total rate constants are compared with the observed ones in Fig. 1.

Thus, on the basis of Mecke's polymer distribution values³⁾ for phenol polymer species in carbon tetrachloride, we may conclude that

3) H. Kempter and R. Mecke, Z. physik. Chem. Abt. B, 46, 229 (1946).

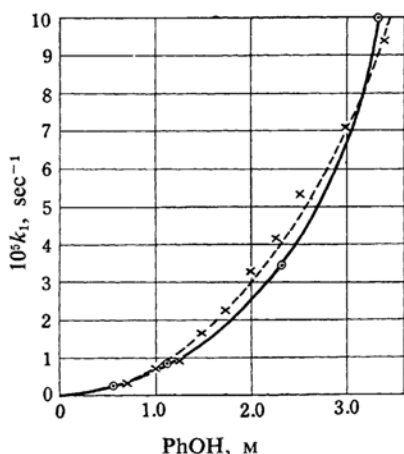


Fig. 1. Phenolysis rate of *tert*-butyl bromide in phenol-carbon tetrachloride mixtures at 20.0°C.

○ Observed × Calcd. from Eq. 1

the phenol polymer species with higher association degree should show more effective acceleration presumably because of their co-operative action as a kind of polyhydroxylic molecule. This would be a more detailed expression of the "polymolecular"⁴⁾ acceleration in solvolysis.

Experimental⁵⁾

Materials.—*tert*-Butyl bromide⁶⁾, *cis*-⁷⁾ and *trans*-⁸⁾ cyclohexanediol were prepared by published procedures. Sodium phenolate was previously prepared⁹⁾. Sodium acetate⁹⁾, dioxane⁹⁾, phenol⁹⁾ and acetic acid¹⁰⁾ were purified by a previously reported method. All the reagents employed were of reagent grade quality, and purified by fractional distillation or by recrystallization. *o*-Cresol, m. p. 30.0~31.0°C; *p*-cresol, m. p. 33.0~34.0°C; *p*-nitrophenol, m. p. 113.0~114.0°C; *o*-nitrophenol, m. p. 44.0~45.0°C; *p*-chlorophenol, m. p. 41.0~42.0°C; catechol, m. p. 104.0~105.0°C; hydroquinone, m. p. 172.0°C; *cis*-1,2-cyclohexanediol, m. p. 97.5~98.0°C; *trans*-1,2-cyclohexanediol, m. p. 103.5~104.0°C; *tert*-butyl bromide, b. p. 73.0°C; methanol, b. p. 64.0~65.0°C; ethanol, b. p. 78.0°C; phenol, b. p. 180.0~181.0°C; cyclohexanol, b. p. 161.0°C; ethylene glycol, b. p. 197.0~198.0°C; *o*-chlorophenol, b. p. 175.0~176.0°C; benzene, b. p. 80.0°C; toluene, b. p. 110.0°C; acetone, b. p. 56.0°C; dioxane, b. p. 101.0°C; carbon tetrachloride, b. p.

76.0°C; chlorobenzene, b. p. 132.0°C; nitrobenzene, b. p. 210.0~211.0°C; acetic acid, b. p. 117.0°C.

The solvent for the kinetic determinations of the acetolysis rates consisted of one volume of acetic acid and three volumes of carbon tetrachloride at 25.0°C. The solvents for the phenolysis were prepared at 25.0°C.

Rate Measurements.—A) *Acetolyses in Carbon Tetrachloride-Acetic Acid (3:1 by vol.)*.—A sealed-ampoule technique was used. The reaction mixtures were prepared by mixing the weighed amounts of *tert*-butyl bromide and aliquots of solutions of known concentrations of sodium acetate and of hydroxylic compounds in carbon tetrachloride-acetic acid mixture at 25.0°C. Each ampoule contained 1.000 cc. of aliquot of the reaction mixture. The thermostat was controlled to $\pm 0.01^\circ$ at 70.0°C. After reaction for appropriate lengths of time, the ampoules were cooled. Each sample was run into a flask and after being rinsed with about 5 cc. of acetic acid the unchanged sodium acetate was titrated with 0.050 N perchloric acid solution in acetic acid with crystal violet indicator. Rate constants were calculated graphically assuming that the reaction was of the first order. Decrease of sodium acetate associated with solvolysis of *tert*-butyl bromide in each run obeyed good first-order kinetics, this being illustrated graphically in Fig. 2 for several runs.

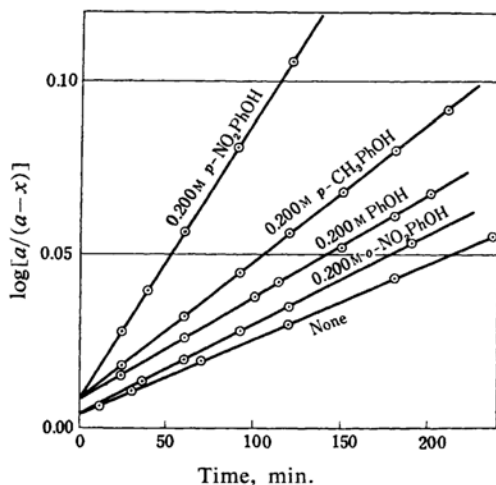


Fig. 2. Rates of acetolyses of *tert*-butyl bromide in acetic acid-carbon tetrachloride (1:3 by vol., at 25.0°C) in the presence of phenols at $70.0 \pm 0.01^\circ\text{C}$, 0.100 M *t*-BuBr, 0.0500 N NaOAc.

B) *Solvolyses in Phenol-Carbon Tetrachloride Mixtures*.—A weighed amount of *tert*-butyl bromide and an aliquot of the solution of a known concentration of sodium phenolate in an appropriate mixture of phenol and carbon tetrachloride were mixed in a measuring flask placed in a thermostat kept at $20.0 \pm 0.01^\circ\text{C}$. At appropriate time intervals, aliquot portions (1.000 cc.) were pipetted into 2 cc. of cold acetic acid at 15°C and the solutions were titrated according to the method described in section A. Rate constants were calculated from the first

4) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York (1940), p. 169.

5) Melting points are not corrected.

6) K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1937, 1185.

7) S. Winstein, H. V. Hess and R. E. Buckles, *J. Am. Chem. Soc.*, 64, 2796 (1942).

8) A. Roebuck and H. Adkins, "Organic Syntheses", Coll. Vol. 3 (1955), p. 217.

9) H. Shingu and K. Okamoto, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, 81, 111 (1960).

10) H. Shingu, K. Okamoto and E. Ajisaka, *ibid.*, 78, 554 (1957).

TABLE III. SUMMARY OF RATE CONSTANTS FOR ACETOLYSIS OF *tert*-BUTYL BROMIDE IN ACETIC ACID-CARBON TETRACHLORIDE MIXTURE (1:3 BY VOL. AT 25.0°C) AT 70.0°C

| Exp. No. | Accelerating substance | Concn. M | $10^6 \times k_1^*$ sec ⁻¹ | Exp. No. | Accelerating substance | Concn. M | $10^6 \times k_1^*$ sec ⁻¹ |
|----------|------------------------|----------|---------------------------------------|----------|------------------------------------|----------|---------------------------------------|
| 40 | None | | 6.72 | 27 | Methanol | 0.200 | 11.5 |
| 29 | None | | 6.72 | 53 | Ethanol | 0.100 | 8.23 |
| 14 | None | | 6.72 | 24 | Ethanol | 0.200 | 9.32 |
| 58 | None | | 6.72 | 55 | Ethylene glycol | 0.100 | 14.4 |
| 39 | Phenol | 0.100 | 9.23 | 54 | Ethylene glycol | 0.200 | 22.3 |
| 13 | Phenol | 0.200 | 11.8 | 60 | Cyclohexanol | 0.100 | 7.60 |
| 19 | <i>p</i> -Cresol | 0.100 | 11.2 | 59 | Cyclohexanol | 0.200 | 8.52 |
| 12 | <i>p</i> -Cresol | 0.200 | 15.5 | 66 | <i>cis</i> -1, 2-Cyclohexanediol | 0.100 | 9.98 |
| 52 | <i>o</i> -Cresol | 0.100 | 9.67 | 65 | <i>cis</i> -1, 2-Cyclohexanediol | 0.200 | 12.4 |
| 51 | <i>o</i> -Cresol | 0.200 | 12.5 | 64 | <i>trans</i> -1, 2-Cyclohexanediol | 0.100 | 9.98 |
| 43 | <i>p</i> -Chlorophenol | 0.100 | 12.4 | 63 | <i>trans</i> -1, 2-Cyclohexanediol | 0.200 | 12.5 |
| 16 | <i>p</i> -Chlorophenol | 0.200 | 16.7 | 38 | Nitrobenzene | 0.100 | 7.68 |
| 47 | <i>o</i> -Chlorophenol | 0.100 | 9.25 | 15 | Nitrobenzene | 0.200 | 8.62 |
| 22 | <i>o</i> -Chlorophenol | 0.200 | 11.7 | 20 | Chlorobenzene | 0.200 | 8.34 |
| 18 | <i>p</i> -Nitrophenol | 0.100 | 18.5 | 42 | Toluene | 0.100 | 7.08 |
| 11 | <i>p</i> -Nitrophenol | 0.200 | 30.1 | 21 | Toluene | 0.200 | 7.47 |
| 56 | Hydroquinone | 0.050 | 12.1 | 28 | Acetone | 0.200 | 9.48 |
| 62 | Catechol | 0.100 | 14.0 | 23 | Benzene | 0.200 | 7.60 |
| 61 | Catechol | 0.200 | 25.5 | 32 | Dioxane | 0.200 | 6.23 |
| 49 | Water | 0.100 | 12.1 | 31 | Carbon tetrachloride | 0.200 | 6.52 |
| 26 | Water | 0.200 | 17.6 | 17 | Acetic acid | 0.200 | 7.87 |
| 50 | Methanol | 0.100 | 9.58 | | | | |

* Initial concentrations; *tert*-butyl bromide 0.100 M, sodium acetate 0.0500 N.TABLE IV. SUMMARY OF RATE CONSTANTS FOR PHENOLYSIS OF *tert*-BUTYL BROMIDE IN PHENOL-CARBON TETRACHLORIDE MIXTURES AT 20.0°C

| Exp. No. | Phenol concn. vol. %* | Concn. M | Concn. of sodium phenolate, N | k_1 sec ⁻¹ | k_1 N = ∞ |
|----------|-----------------------|----------|-------------------------------|-------------------------|-----------------------|
| 8 | 50.0 | 5.68 | 0.0456 | 2.35×10^{-4} | 2.70×10^{-4} |
| 9 | 50.0 | 5.68 | 0.0225 | 2.12×10^{-4} | |
| 14 | 40.0 | 4.45 | 0.0754 | 1.45×10^{-4} | |
| 12 | 40.0 | 4.45 | 0.0505 | 1.26×10^{-4} | 1.64×10^{-4} |
| 13 | 40.0 | 4.45 | 0.0251 | 1.15×10^{-4} | |
| 5 | 30.0 | 3.37 | 0.0995 | 8.37×10^{-5} | |
| 6 | 30.0 | 3.37 | 0.0496 | 7.40×10^{-5} | 1.00×10^{-4} |
| 7 | 30.0 | 3.37 | 0.0245 | 6.75×10^{-5} | |
| 17 | 20.0 | 2.33 | 0.0525 | 3.05×10^{-5} | |
| 18 | 20.0 | 2.33 | 0.0257 | 2.80×10^{-5} | 3.39×10^{-5} |
| 16 | 10.0 | 1.11 | 0.0313 | 7.34×10^{-6} | |
| 19 | 10.0 | 1.11 | 0.0157 | 6.71×10^{-6} | |
| 20 | 5.00 | 0.559 | 0.0147 | 1.45×10^{-6} | 8.33×10^{-6} |
| 21 | 5.00 | 0.559 | 0.0104 | 1.21×10^{-6} | |
| | | | | | 2.70×10^{-6} |

* at 25.0°C

** Initial concentration of *tert*-butyl bromide, 0.100 M.

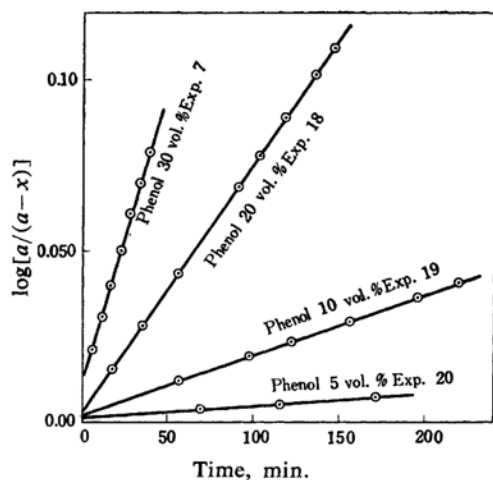


Fig. 3. Rates of phenolyses of *tert*-butyl bromide in phenol-carbon tetrachloride mixtures at 20.0°C, 0.100 M *t*-BuBr, 0.147 ~ 0.0245 N NaOPh.

order rate equation by a graphical method, and satisfactory first order behavior was observed for each run, this being shown graphically in Fig. 3.

Results

The rate constants of acetolyses used for the calculation of catalytic constants of phenols, alcohols, and several polar and non-polar compounds are summarized in Table III. The catalytic constants were calculated by Eq. 3.

$$k_1(\text{obs.}) = k_1^\circ + k_2(\text{Conc. of the accelerating substance}) \quad (3)$$

where k_1° represents the standard rate constant and k_2 represents the catalytic constant.

The first order rate constants for the solvolyses of *tert*-butyl bromide in phenol-carbon tetrachloride mixtures depended on the initial concentrations of sodium phenolate and at high concentrations they increased reaching the maximum values which were previously concluded to be the rates of the first ionization step of *tert*-butyl bromide⁹. According to the total rate expression⁹ for the phenolysis of this compound, these maximum values for the rate of ionization were estimated from the

plots of the reciprocals of observed rate constants vs. those of the initial concentrations of sodium phenolate. In Table IV, the observed rate constants are summarized along with the estimated maximum values for the rate of ionization (k_1 , $N=\infty$).

Summary

The catalytic constants of phenols, alcohols, and several polar and non-polar molecules in acetolysis of *tert*-butyl bromide were measured in acetic acid-carbon tetrachloride (1:3 by vol., at 25.0°C) in the presence of sodium acetate at 70.0°C. Ortho substituted (NO_2 , Cl, CH_3 , OH) phenols gave smaller constants than those of corresponding para derivatives, and among them *o*-nitrophenol gave the smallest one which was comparable to that of nitrobenzene. Dihydroxylic compounds, like 1,2-cyclohexanediols, ethylene glycol, catechol and water, gave constants greater than twice those of the corresponding monohydroxylic compounds, like cyclohexanol, ethanol, phenol and methanol, respectively. It was concluded that, in view of the lack of catalytic action of intramolecularly hydrogen-bridged hydroxylic compounds, the hydrogen atom of those hydroxylic molecules was distinctly the center of attack in the first ionization stage of the solvolysis and that two adjacent hydroxyl groups in dihydric compounds sterically co-operated in this stage. On these bases, similar accelerating action of various species of associated phenol molecules was suggested and illustrated by the analysis of the data of solvolysis rates of *tert*-butyl bromide in phenol-carbon tetrachloride mixtures at 20.0°C. It was shown that phenol polymer species with higher association degree exhibited more effective acceleration.

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