Analysis of the hydrolysis solution showed beryllium equivalent to 66.6% di-*t*-butylberyllium or, including the ether, a total of 102.7% of the original sample. On a molar basis the sample was about 51% di-*t*-butylberyllium.

Several points deserve comment. First, isobutene was always evolved on hydrolysis. If its origin is the decomposition of di-*t*-butylberyllium, a corresponding amount of hydrogen should be observed. Although hydrogen was occasionally found, it was not observed in this instance. Second, the discrepancies in material balance are probably within experimental error, since the individual analyses are accurate, at best, to only 1%. It was observed in each of five different preparations that the ether content was slightly less than 50 mole %.

2. **Hydrolysis of Beryllium Hydride Prepared by the Pyrolysis of Di-*t*-butylberyllium Etherate.**—A sample (approximate weight 19 mg.) of the best preparation of beryllium hydride from di-*t*-butylberyllium etherate was found on hydrolysis to liberate hydrogen equivalent to 81% BeH_2. Analysis of the hydrolysis solution showed beryllium equivalent to 79% BeH_2. The check between the beryllium found and the hydrogen observed is within the expected analytical error, so the major impurity is not a beryllium compound and is probably ether. In this sample the hydrolysis gases were not analyzed for ether and isobutane. In other samples both ether and isobutane in varying ratios were found in addition to the hydrogen. The purity of most preparations was between 76 and 80%.

3. **Combustion Analysis of Beryllium Hydride Prepared by the Pyrolysis of Di-*t*-butylberyllium Etherate.**—A sample (weight 33 mg.) on combustion gave CO_2 equivalent to an ether content of 21%. The hydrogen (determined as water) in excess of the stoichiometric amount required for ether corresponded to a BeH_2 content of 76%. Analysis of this material by the hydrolysis procedure also indicated a BeH_2 content of 76%. The ether and BeH_2 calculated in this manner account for 97% of the original sample weight.

4. **Hydrolysis of Di-*t*-butylberyllium.**—Hydrolysis of a sample of the best di-*t*-butylberyllium (weight 225.2 mg.) gave isobutane and isobutene (molar ratio 60:1) equivalent to 101% di-*t*-butylberyllium. (Half as much hydrogen was observed as isobutene.) Analysis of the hydrolysis solution showed an equivalent amount of beryllium (17.5 mg. found, 16.8 mg. expected).

5. **Hydrolysis of Beryllium Hydride Prepared by Pyrolysis of Di-*t*-butylberyllium.**—A sample weighing 17.9 mg. gave, on hydrolysis, hydrogen equivalent to 80.5% BeH_2 and isobutane equivalent to 17.8% di-*t*-butylberyllium, giving a total of 98.3% of the sample. Analysis of the hydrolysis solution showed beryllium equivalent to 99% of the beryllium calculated from the gas analysis (the di-*t*-butylberyllium contributes a minor amount of beryllium to the solution). This is the best sample of beryllium hydride prepared by pyrolysis of ether-free di-*t*-butylberyllium.

Properties of Beryllium Hydride.—The density of the product was estimated from the fact that it sank in liquid ethane at −110°, but floated at lower temperatures. The density of ethane is 0.561 g./cc. at −100°,[9] and the density of the product is estimated to be 0.57 ± 0.02 g./cc. at −110°. Since the product is 97 mole % BeH_2, it is probable that the density of pure BeH_2 would not differ significantly.

Beryllium hydride prepared by pyrolysis is relatively inert to laboratory air. A 26-mg. sample containing 76% BeH_2 gained 0.8 mg. on exposure to laboratory air for eight days and the BeH_2 content decreased to 72%. The product reacts slowly with water but vigorously with dilute mineral acid.

The product prepared from ether-free reagent was not altered by treatment with ethereal $LiAlH_4$.

A microscopic examination of the product prepared from the etherate showed it to be heterogeneous, consisting of optically isotropic grains, with refringence near 1.58, which contained optically anisotropic inclusions with much lower refringence, densely but non-uniformly distributed. The grain size of the inclusions was several tenths of a micron. The two constituents appeared to be present in approximately equal amounts.

X-Ray examination of the product prepared from di-*t*-butylberyllium gave no lines attributable to BeH_2.

Acknowledgments.—The authors wish to express their appreciation to J. F. Lemons for his encouragement and helpful suggestions; C. Apel, A. W. Mosen, and G. Warren for chemical analyses; F. H. Ellinger for X-ray analyses; E. Staritzky for microscopic analyses; and P. Fain, R. Kandel and E. D. Loughran for mass spectrometric analyses.

(9) "Handbook of Chemistry and Physics," 30th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1948, p. 790.

LOS ALAMOS, N. M.

[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL OF CANADA]

Electrolyte Catalysis. III. The Cleavage of Benzyl Phenyl Ether by Hydrogen Bromide in Nitrobenzene, Chloroform and Carbon Tetrachloride

BY A. Y. DRUMMOND AND A. M. EASTHAM

RECEIVED AUGUST 27, 1956

The kinetics of the cleavage of benzyl phenyl ether by hydrogen bromide in nitrobenzene and chloroform have been determined and the effects of five substituted ammonium bromides on the rate of reaction in these solvents examined. The rate of cleavage in carbon tetrachloride solution is negligibly small but is subject to heterogeneous catalysis by several solid salts. Mechanisms are suggested for the cleavage and its catalysis by electrolytes.

Earlier work in this Laboratory[1,2] showed that several reactions involving the cleavage of a C–O bond were catalyzed by electrolytes in non-aqueous solvents. The salts had considerable specificity in their catalytic powers and it was suggested that the electrolyte facilitated the charge transfers which occurred during the reaction.

In order to obtain more information about this type of catalysis, the cleavage of ethers by hydrogen bromide has now been studied. Walvekar, *et al.*,[3] have reported that this reaction is catalyzed by amine salts in carbon tetrachloride and *n*-hexane. It was first necessary to establish the kinetics of the uncatalyzed reaction for, although the similar cleavage by hydrogen iodide is widely used, little work has been done on the mechanism of this type of reaction.[4]

Since cleavage of ethers by hydrogen bromide is much slower than that by hydrogen iodide, benzyl

(1) A. M. Eastham, *J. Chem. Soc.*, 1936 (1952).

(2) A. M. Eastham, E. L. Blackall and G. A. Latremouille, THIS JOURNAL, **77**, 2182 (1955); E. L. Blackall and A. M. Eastham, *ibid.*, **77**, 2184 (1955).

(3) S. P. Walvekar, N. L. Phalnikar and B. V. Bhide, *J. Ind. Chem. Soc.*, **20**, 131 (1943).

(4) R. L. Burwell, *Chem. Revs.*, **54**, 689 (1954).

phenyl ether was used throughout the work in order to obtain a convenient rate of reaction. The solvents nitrobenzene and chloroform were chosen for their widely different dielectric constants and good solvent properties. The salts used as catalysts were necessarily all bromides in order to avoid uncertainty as to the acid species present.

Experimental

Materials.—Technical nitrobenzene was steam distilled from 2 *N* sulfuric acid, washed with water and dried over calcium chloride. After standing for 12 hr. over phosphorus pentoxide it was filtered and distilled rapidly at *ca.* 10 mm. pressure. The distillate was shaken with dry activated alumina for 8 hr. and filtered before carefully fractionally distilling at *ca.* 5 mm. The product was pale yellow and did not darken on standing over phosphorus pentoxide for 24 hr., $n^{25}D$ 1.5499–1.5500.

C.P. chloroform was shaken with a large amount of calcium chloride. After filtering, it was refluxed over phosphorus pentoxide in an atmosphere of dry nitrogen for 2–3 hr. and was allowed to cool with nitrogen bubbling through. It was then decanted on to fresh phosphorus pentoxide and, after flushing out very thoroughly with nitrogen, was fractionally distilled. The pure chloroform was collected and stored in blackened vessels under nitrogen. The infrared and mass spectra showed no trace of ethanol. After removing the ethanol present in C.P. chloroform it is essential to keep the liquid out of contact with air; accordingly, all vessels were thoroughly flushed out with dry nitrogen before being used with chloroform solutions.

C.P. carbon tetrachloride was passed down silica and alumina columns and was fractionally distilled.

Anhydrous hydrogen bromide was obtained both from a cylinder (The Matheson Co.) and by dropping bromine into dry tetralin. It was stored in solution or in a cold trap at −180°. Benzyl phenyl ether (m.p. 38.9°) was prepared in the usual way[5] from reagent grade phenol and benzyl chloride.

Pyridinium bromide was prepared as previously described.[1] Tri-*n*-butylamine hydrobromide and tetra-*n*-butylammonium bromide were recrystallized from ethyl acetate (m.p. 75.2–75.9° and 117–118°, respectively). Tetra-*n*-propylammonium bromide was recrystallized from ethyl acetate containing 10% absolute ethanol. (*Anal.* Calcd. for $C_{12}H_{28}NBr$: C, 54.15; H, 10.53; N, 5.26; Br, 30.06. Found: C, 54.10; H, 10.58; N, 5.31; Br, 30.09.) Tetraethylammonium bromide was recrystallized from absolute ethanol. (*Anal.* Calcd. for $C_8H_{20}NBr$: C, 45.73; H, 9.59; N, 6.66; Br, 38.03; Found: C, 45.65; H, 9.61; N, 6.70; Br, 38.05.)

Analytical Methods.—Samples of solutions of hydrogen bromide in organic solvents were taken from a buret with the tip held under the surface of 30–40 ml. of aqueous alcohol (60–70% ethanol). They were titrated with standard alkali (brom cresol green indicator) or silver nitrate solution (Ag/AgCl electrode; Fisher Titrimeter). In the latter method alcohol was added during the titration to prevent separation of the solvent. The alkali titration was not affected by small amounts of phenol but the bromide estimation was the more reliable in the presence of appreciable amounts of amine salts.

Kinetics Measurements.—The kinetics of the reaction were determined by measuring the initial rate of consumption of hydrogen bromide. The reaction vessel consisted of a 25-ml. buret fitted with a jacket through which water circulated from a thermostat controlled to within ±0.005°. This buret was sealed to a capillary tube and glass joint with reduced ends, so that it could be filled from the mixing vessel.

Reaction mixtures (30 ml.) were made up in a small flask fitted with a ground joint to take the buret, the solution of ether being in a small sealed bulb. This flask was attached to the elongated buret tip by the ground joint, zero time was taken on breaking the sealed bulb and, after stirring magnetically, the solution was forced up into the reaction buret by nitrogen pressure.

Samples were taken by running out 2 ml. of the solution from the buret. Immediately before sampling, 0.5 ml. of solution was run out and discarded to ensure that the sample came from the main thermostated body of the solution. The first reading was taken after 5 min. and a total of 9 samples was analyzed during the first 5–10% reaction. The initial concentration of hydrogen bromide [HBr] was determined by extrapolating the (straight) line through the experimental points back to zero time. The slope of this line was taken as the initial rate of reaction.

In some experiments in carbon tetrachloride solution a solid salt was placed between two plugs of glass wool at the bottom of the reaction buret. When filling the reaction vessel, all the solution came in contact with the salt. By withdrawing a sample normally, solution which had been standing in contact with the salt was obtained while discarding 2.5 ml. of solution before sampling gave a solution which had had only a short time of contact with the salt. For other experiments with this solvent, the flask in which the reactants were mixed was modified to permit filtering the reaction mixture through sintered glass while forcing it into the buret.

In order to test the quantitative nature of the reaction 22.9 g. of benzyl phenyl ether in nitrobenzene (2.38 *M*) was saturated with hydrogen bromide and left 3 weeks. The solution was extracted with alkali and the phenol estimated by bromide–bromate titration; 6.7 g. of phenol (equivalent to 13.1 g. ether) was found. The organic layer was distilled under reduced pressure yielding 3 fractions: (a) mainly nitrobenzene, (b) 7.9 g. of benzyl phenyl ether, (c) 2.1 g. of high boiling residue. 21 g. (92%) of the original ether was thus found and the remainder was presumed to be in fraction (c). Phenol was therefore formed essentially quantitatively. The other expected product, benzyl bromide, which was detected by its lachrymatory effects, would have distilled in fraction (a) and was not estimated.

Vapor Pressure Measurements.—A modification of the apparatus of Howland, Miller and Willard[6] was used. An all-glass system which could be thoroughly evacuated was constructed and hydrogen bromide was supplied from a cold trap. The solvent was stirred magnetically and surrounded by a water-bath at 10.0 ± 0.06°.

Samples were taken into a sealed, evacuated trap which was attached to the solvent flask by a ground joint. This trap had a calibrated stem in which the volume of solution was measured. The solvent and hydrogen bromide were frozen in liquid nitrogen, the trap removed and excess standard alkali was placed over the sample. After melting, the hydrogen bromide was determined by back titration.

Results

The Reaction in Nitrobenzene at 25.0°.—At least in its initial stages the cleavage of benzyl phenyl ether is second order with respect to the concentration of hydrogen bromide and first order with respect to the concentration of ether. The kinetics of the reaction are expressed by the equation

$$-\frac{d[HBr]}{dt} = k[HBr]^2[C_6H_5OCH_2C_6H_5]$$

in which, at 25°, $k = 0.058 \pm 0.002$ l.^{2} mole^{-2} min.$^{-1}$.

Figure 1 shows the vapor pressure of hydrogen bromide at 10.0° over pure solvent and over solutions of pyridinium, tetra-*n*-propyl- and tetra-*n*-butylammonium bromides. A stable complex MBr·HBr is formed with each salt and these complex salts have distinct "salting-in" effects on the "free" hydrogen bromide in the solution. Within the limits of experimental error, the vapor pressure of hydrogen bromide over solutions of benzyl phenyl ether (up to 0.25 *M*) is the same as that over pure solvent. The salt complex, MBr·HBr, in the ab-

(5) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1950, p. 91.

(6) J. J. Howland, D. R. Miller and J. E. Willard, THIS JOURNAL, **63**, 2807 (1941).

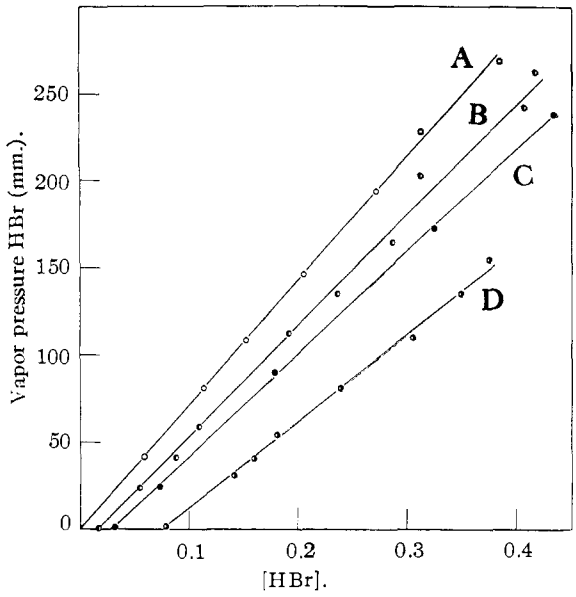

Fig. 1.—Vapor pressure of HBr over nitrobenzene: B, 0.018 *M* tetra-*n*-propylammonium bromide; C, 0.031 *M* pyridinium bromide; D, 0.075 *M* tetra-*n*-butylammonium bromide; A, no added salt.

sence of free HBr reacts only very slowly, if at all, with the ether.

At constant salt concentration the kinetics of the catalyzed cleavage of the ether have the same form as before, *i.e.*

$$-\frac{d[HBr]}{dt} = k'[HBr]^2[C_6H_5OCH_2C_6H_5]$$

where [HBr] is taken as the concentration of hydrogen bromide, outside the MBr·HBr complex. The dependence of k' on the electrolyte concentration is shown in Fig. 2. The catalytic effects of the five salts increase in the order: $C_5H_5NHBr \cong n\text{-}Bu_3NHBr < n\text{-}Bu_4NBr < n\text{-}Pr_4NBr < Et_4NBr$.

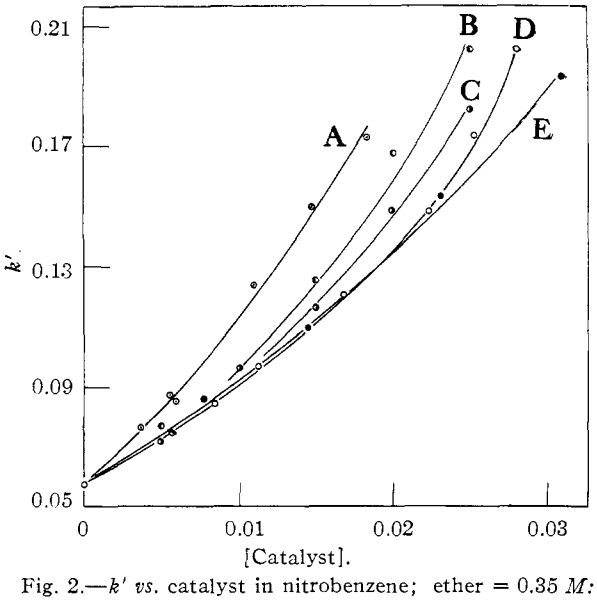

Fig. 2.—k' *vs.* catalyst in nitrobenzene; ether = 0.35 *M*: A, tetra-ethylammonium bromide; B, tetra-*n*-propylammonium bromide; C, tetra-*n*-butylammonium bromide; D, tri-*n*-butylammonium bromide; E, pyridinium bromide.

Water, ethanol and phenol also catalyze the reaction. Phenol, a product of the reaction, is less active than the other compounds and did not cause significant error in the initial rate measurements.

Reaction in Chloroform at 40.0°.—The cleavage is much slower in chloroform than in nitrobenzene and experiments were therefore done at a higher temperature. Initial rates for the uncatalyzed reaction were again first order with respect to the concentration of ether but showed a complex dependence of the initial rate upon the initial concentration of hydrogen bromide. It was impossible, with the experimental method used, to maintain a fixed and reproducible initial concentration of hydrogen bromide, so the initial rates were corrected to a chosen standard concentration of hydrogen bromide. The corrections, which very rarely exceeded 5–10%, were made on the basis of curve A in Fig. 3. The "standard" concentration

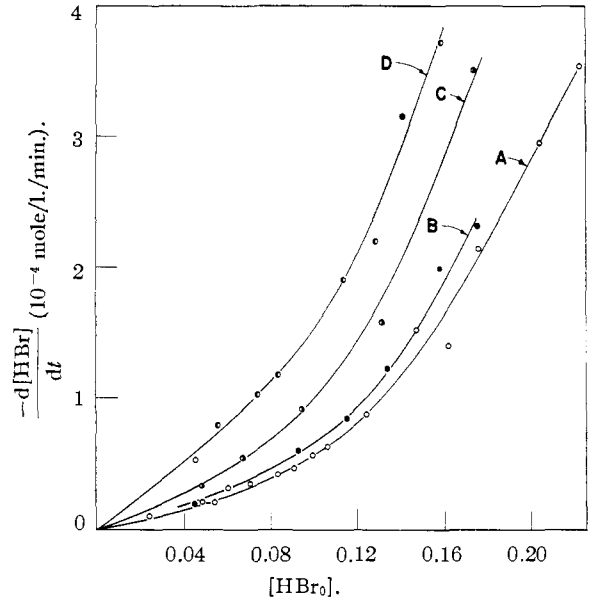

Fig. 3.—Initial rate *vs.* HBr concentration in chloroform; ether = 0.367 *M*, all salts 3.03×10^{-4} *M*: A, no added salt; B, tri-*n*-butylammonium bromide; C, pyridinium bromide; D, tetra-*n*-propylammonium bromide.

of hydrogen bromide was chosen to lie in the most accurate region of the rate *vs.* [HBr] curve. Similar corrections were applied to the results of Fig. 4 on the basis of the experiments of Fig. 3.

In the presence of a constant amount of a catalyst the cleavage is again a complex function of the concentration of hydrogen bromide as is shown by curves B, C and D of Fig. 3. Experiments in which the concentration of hydrogen bromide was varied also were performed using constant amounts of tetraethylammonium and tetra-*n*-butylammonium bromides as catalysts but the results were too close to those for tetra-*n*-propylammonium bromide to be shown on the graph. At a fixed concentration of hydrogen bromide the initial rate of reaction varies linearly with the amount of catalyst up to 10^{-3} *M* (Fig. 4). The five salts increased in catalytic activity in the order $n\text{-}Bu_3NHBr < PyHBr < n\text{-}Bu_4NBr < n\text{-}Pr_4NBr < Et_4NBr$. It may be noted

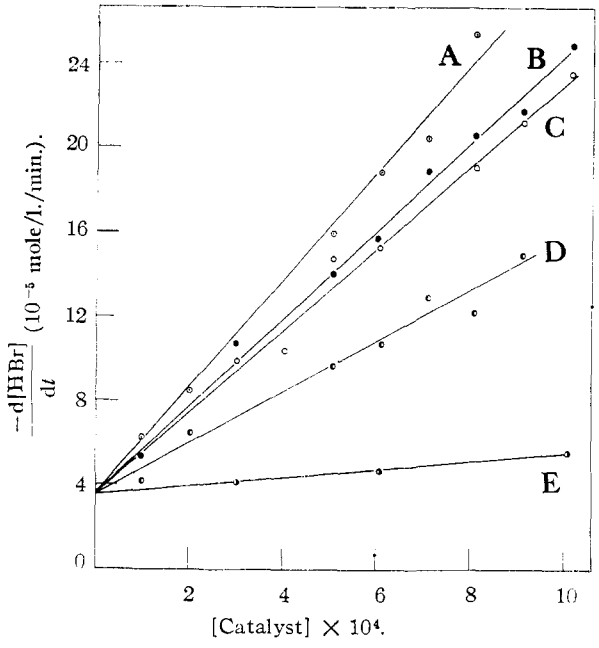

Fig. 4.—Initial rate *vs.* catalyst concentration in chloroform at 40°; ether = 0.367 *M*, HBr = 0.076 *M*: E, tri-*n*-butylammonium bromide; D, pyridinium bromide; C, tetra-*n*-butylammonium bromide; B, tetra-*n*-propylammonium bromide; A, tetraethylammonium bromide.

that in chloroform solution the catalyst concentrations were much lower than those used in nitrobenzene.

The cleavage was also catalyzed by ethanol but phenol, up to 0.02 *M*, had little effect upon the rate of reaction. In a few experiments diethyl ether was examined and was found to react very slowly with hydrogen bromide; the reaction was markedly catalyzed by tetra-*n*-butylammonium bromide.

The Reaction in Carbon Tetrachloride at 2.50°.—Within the limits of experimental error, benzyl phenyl ether does not react with either hydrogen bromide or pyridinium bromide alone in carbon tetrachloride. However, solid pyridinium bromide, which is insoluble in carbon tetrachloride solutions of hydrogen bromide or of benzyl phenyl ether, catalyzes the cleavage of the ether by hydrogen bromide. After stirring a solution of ether and hydrogen bromide with pyridinium bromide for $^1/_2$ hr. and then filtering, the filtrate did not react further but a considerable amount of the hydrogen bromide had reacted during the stirring. The insoluble salts LiBr, NaBr, KBr, NH_4Br, Me_4NBr, LiCl, NaCl, KCl, Na_2SO_4 and K_2SO_4 behave similarly to pyridinium bromide but glass surfaces do not act catalytically. Very finely divided sodium chloride (*ca.* 15 m.^{2}/g.) is a more powerful catalyst than an ordinarily ground specimen. There can be little doubt that in all these experiments in carbon tetrachloride the cleavage of the ether occurred on the surface of the solid salt.

Discussion

The results obtained in nitrobenzene are in agreement with those of Mayo, *et al.*,[7] for the cleavage of diethyl ether by hydrogen bromide in toluene or chlorobenzene, and suggest a mechanism of the type

$$R_1CH_2OR_2 + HBr \overset{K}{\rightleftharpoons} \begin{matrix} R_1CH_2 \\ R_2 \end{matrix}\!\!>\!O\cdots\cdots HBr \quad (1)$$

$$\begin{matrix} R_1CH_2 \\ R_2 \end{matrix}\!\!>\!O\cdots\cdots HBr + HBr \xrightarrow{k_1} R_1CH_2Br + R_2OH + HBr \quad (2)$$

which leads to the observed kinetics if K is small. The vapor pressure measurements indicate that K is in fact quite small since no association of ether and acid could be observed. Reaction 2 can be regarded as an SN2 type attack by the second molecule of hydrogen bromide at the $-CH_2-$ group of the ether–hydrogen bromide complex, a view supported by the fact that diphenyl ether apparently is not cleaved by hydrogen halides.[8]

In chloroform solution the observed kinetics are more complex and do not agree with those of Mayo, *et al.*, who found the rate law

$$-\frac{d[HBr]}{dt} = k[HBr]^{1/2}[ether]^{1/2}$$

for the cleavage of diethyl ether. In the present work the apparent order with respect to acid increases with concentration, an effect not due to polymeric molecules of hydrogen bromide since Henry's law is obeyed.[6]

One must suppose that the mechanism suggested for reaction in nitrobenzene would also apply to some extent in chloroform. It seems possible, however, that the ether–hydrogen bromide complex may also decompose in a unimolecular fashion since Hart and Eleuterio[9] have observed retention of configuration in the cleavage of α-phenylethyl phenyl ether by hydrogen chloride in solvents of low dielectric constant and high acid concentration. However, the apparent order with respect to HBr although approximately one at low acid concentrations seems to rise above two at higher concentrations so the mechanism perhaps involves medium effects as well.

Examination of models indicates that the SN2 type reaction should lead to the regeneration of a molecule of hydrogen bromide in which the individual ions are initially some distance apart in the solution. Processes of this type occur readily in solvents such as water which can stabilize the newly-formed ions, but in non-polar solvents they proceed only with difficulty if at all. In the present case solvation of the ions by hydrogen bromide (HCl_2^- is known to be stable[10]) might provide a reaction path which would account for orders in acid greater than one.

The effect of electrolytes upon the reaction is undoubtedly related to this problem of separating charges in non-ionizing solvents. There is little direct information on the dissociation of the salts in these solutions, other than that the constant for tetra-*n*-butylammonium bromide in nitrobenzene is

(7) F. R. Mayo, W. B. Hardy and C. G. Schultz, THIS JOURNAL, **63**, 426 (1941).

(8) W. Hoffmeister, *Ber.*, **3**, 347 (1870).

(9) H. Hart and H. S. Eleuterio, THIS JOURNAL, **76**, 1379 (1954).

(10) H. F. Herbrandson, R. T. Dickenson and J. Weinstein, *ibid.*, **76**, 4046 (1954).

1.6×10^{-2} at 25°.[11] By analogy with other systems, however, it is apparent that the constants for tetra-*n*-propyl- and tetraethylammonium bromide will be successively smaller than this value while those for pyridinium and tri-*n*-butylammonium bromides will be of the order of 10^{-4}. In chloroform the corresponding values of the constant for the two types of salts should be about 10^{-9} and 10^{-14}, respectively.

Since the effectiveness of the salts as catalysts increases with decreasing dissociation constant and dielectric constant, the catalysis probably is not due to free ions in solution. Also, it does not seem to result from an increase in the activity of the reactants since the "salting in" of the hydrogen bromide indicates a decrease in activity which is not likely to be outweighed by an increase in the activity of the ether.

The equilibrium of reaction 1 in which the ether and hydrogen bromide form a complex involves an increase in the dipole moment associated with the HBr and the presence of other ions and dipoles will tend to increase K and so accelerate the observed cleavage of the ether. However, it is doubtful if such an increase in K would account for more than a small part of the catalysis. Walvekar, *et al.*,[12] found no correlation between the values of K for different ethers and their rates of cleavage as measured by Ghaswalla and Donnan.[13] However, the very slow cleavage of diethyl ether in chloroform is markedly catalyzed by tetra-*n*-butylammonium bromide. Since diethyl ether certainly forms an oxonium complex much more readily than benzyl phenyl ether, it must be stage 2 of the reaction, cleavage of the complex, which is significantly affected by the catalyst.

It seems then that the catalysis is due to the ion pairs in solution accelerating the rate of cleavage of the C–O bond, a process which probably is closely related to the heterogeneous catalysis observed in carbon tetrachloride. The catalysis by ionic crystals is of such a general nature that it must be due primarily to the electrical inhomogeneity of the crystal surface but in solution specific ion effects must be of considerable importance because the catalytic activities of the salts do not seem to be related to the dipole moments. It seems probable therefore that the ion pair of the salt is closely associated with the transition state where it acts as a sort of bridge between the appearing and disappearing ions.

Finally it should be noted that our solubility measurements suggest that Walvekar, *et al.*, were dealing with heterogeneous systems and not solutions.

(11) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

(12) S. P. Walvekar, N. L. Phalnikar and B. V. Bhide, *J. Univ. Bombay*, **11A**, Pt. 5, 69 (1943).

(13) R. P. Ghaswalla and F. G. Donnan, *J. Chem. Soc.*, 134 (1936).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Studies of Some Methyl-substituted Benzhydryl Carbonium Ions

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RECEIVED MARCH 16, 1957

The behavior of the following methylbenzhydrols in 100% sulfuric acid has been studied: 2,2',3,4,5,6-hexamethylbenzhydrol, 2,2',4,6-tetramethylbenzhydrol and 3-methylbenzhydrol. The first two compounds gave fairly stable carbonium ions; the last gave a less stable and more reactive carbonium ion. The properties were investigated utilizing *i*-factors, ultraviolet and near-visible spectra, titration studies, and chemical studies, all using sulfuric acid. Evidence for the steric effect of three *ortho*-methyl groups and the "buttressing" effect of methyl groups in the 3- and 5-positions of the hexamethylbenzhydryl carbonium ion is discussed.

Introduction

It has been shown that many benzhydrols[1-4] ionize in 100% sulfuric acid to give stable carbonium ions. The ionization can be represented as

$$(C_6H_5)_2CHOH + 2H_2SO_4 \longrightarrow (C_6H_5)_2\overset{+}{C}H + 2HSO_4^- + H_3O^+ \quad (1)$$

Actually benzhydrol is rather unstable in sulfuric acid and undergoes rapid polymerization and sulfonation.[1] In the present work it was desired to find out the effect of certain methyl-substitutions on the formation and stabilization of benzhydryl carbonium ions. In addition, it had been noted that benzhydryl carbonium ions with two or less *ortho*-methyl substituents formed benzhydryl ethers, while those with four *ortho*-methyl substituents formed benzhydrols when poured into water. It was therefore of interest to ascertain the behavior of such ions when three *ortho*-methyl substituents were present.

(1) C. M. Welch and H. A. Smith, THIS JOURNAL, **72**, 4748 (1950).

(2) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951).

(3) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(4) H. A. Smith and R. G. Thompson, THIS JOURNAL, **77**, 1778 (1955).

Results

***i*-Factors.**—Table I gives the *i*-factors as extrapolated to zero time for the compounds studied. For the hexamethyl and tetramethyl compounds, solution was rapid, and the first *i*-factors could be determined within 10 or 15 minutes after addition of the benzhydrol to the sulfuric acid. The freezing points slowly changed as sulfonation took place. The *i*-factor of approximately 4.0 obtained by extrapolation to zero solution time is that expected for ionization according to eq. 1. For 3-methylbenzhydrol, however, solution in the sulfuric acid was very slow, for an insoluble polymer was formed which dissolved slowly as sulfonation occurred