uct, a mixture of dichloride and chloroether, distilled over a very narrow temperature and refractive index range, and could not be separated by fractionation through a glass helix packed, total-condensation, partial take-off type column, the packed section having the dimensions 33 × 1.5 cm. Percentage composition of the product was determined by analysis for total chlorine and this was checked by extraction of the chloroether with concentrated sulfuric acid in which the dichlorides are not soluble.

The following procedures for the hypochlorite reactions illustrate the various modifications used.

Preparation of β-Chloroisopropyl Methyl Ether.—The apparatus consisted of a wide mouthed bottle of about 500 ml. capacity, equipped with a dropping funnel, a reflux condenser, a thermometer which extended to within 3 cm. of the bottom and a gas diffuser which extended to the bottom of the bottle. One-half gram p-toluenesulfonic acid was dissolved in 64 g. (2 moles) of methyl alcohol and the solution placed in the bottle. Propylene was then passed into the solution while 54.2 g. (0.5 mole) of t-butyl hypochlorite was added slowly through the dropping funnel. The solution was not allowed to become very yellow (concentration of hypochlorite kept low) and the temperature was kept at 10°. After all the hypochlorite was added and no more propylene would dissolve, the reaction mixture was poured into a large excess of water, the whole extracted with ether, the ether layer washed with water, dilute sodium carbonate solution, and dried over calcium chloride. The ether was removed by distillation and the residue fractionated through the column described above.

Preparation of 3-Chloro-4-acetoxyhexane.—A solution of 100 g. of acetic acid and 84 g. (1 mole) 3-hexene was placed in a 1-liter, 3-necked, round-bottom flask equipped with a liquid-seal stirrer, a reflux condenser and a dropping funnel. Over a period of two hours 108.5 g. (1 mole) of

t-butyl hypochlorite was added to this solution, with stirring, and the temperature maintained at 30° by external cooling. The reaction mixture was treated as described above except that extraction with ether was not necessary.

Preparation of β-Chloroisopropyl Phenyl Ether.—A solution of 47 g. (0.5 mole) of phenol in 225 ml. of dry benzene was prepared and placed in the apparatus described for the preparation of β-chloroisopropyl methyl ether. Propylene was passed into the solution and 54.2 g. (0.5 mole) of t-butyl hypochlorite added over a period of seven to eight hours. After no more propylene would dissolve, the product was poured into water and the benzene layer separated. The benzene extract was washed repeatedly with water, four times with 15% sodium hydroxide, dried over calcium chloride and fractionated.

Miscellaneous.—The other experiments were conducted on a 0.5 to 1.0 mole scale. Reaction temperatures varied from about 5 to 60° depending on the reactive solvent used; cooling was used for the vigorous reactions and heat supplied for those which seemed to be slow. The solvent was used in considerable excess (2 to 6 moles per mol of olefin) while the hypochlorite was always the theoretical amount.

Summary

t-Butyl hypochlorite has been found to be an effective reagent for the preparation of chlorohydrin ethers and esters by reaction with olefins and alcohols, phenol or acetic acid. Twenty products are described.

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Solvent Effects in Addition Reactions. II. Addition of Hydrogen Bromide and Chloride to α-Pinene

BY G. F. HENNION AND CARL F. IRWIN

Introduction

In a previous communication[1] it was shown that the character of the solvent influences tremendously the relative rates at which hydrogen bromide and chloride add to cyclohexene and 3-hexene. Under comparable conditions of concentration and temperature these reactions are exceedingly rapid in non-donor solvents and very slow in solvents which act as electron donors. This may be taken to mean that the reactions are most rapid in those solvents in which the hydrogen halides are least soluble.

It was thought of interest to repeat these studies with a more reactive olefin. α-Pinene was selected for this purpose since it is known to react (upon heating) even with ammonium chloride, forming bornyl chloride with release of ammonia.[2]

Solutions of hydrogen bromide (approximately 0.15 M) in seven solvents were prepared and these treated with stoichiometric amounts of α-pinene. Relative reaction rates were determined by periodic analyses of the solutions.

In the order of decreasing reaction rates the solvents arrange themselves as follows: chloro-

(1) O'Connor, Baldinger, Vogt and Hennion, THIS JOURNAL, **61**, 1454 (1939).

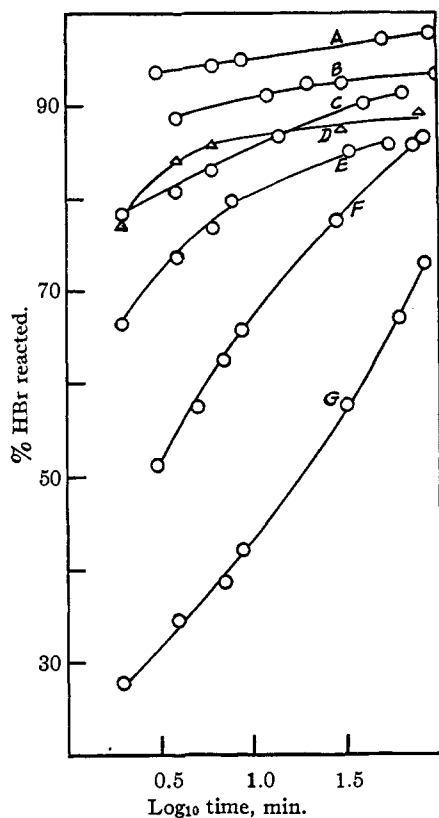(2) Aschan, Översikt Finska Vetenskaps Soc. Förh., **58**, 9 (1919): C. A., **14**, 3654 (1920).

Fig. 1.—A, 0.135 M, chloroform; B, 0.187 M, nitroben-
zene; C, 0.174 M, xylene; D, 0.047 M, heptane; E, 0.135
M, dioxane; F, 0.139 M, Et-O-Bu; G, 0.161 M, ether.

Fig. 2.—A, 0.142 M, chloroform; B, 0.157 M, xylene;
C, 0.143 M, nitrobenzene; D, 0.148 M, methanol; E,
0.167 M, Et-O-Bu; F, 0.141 M, dioxane.

form > xylene > heptane > nitrobenzene > di-
oxane > ethyl n-butyl ether > diethyl ether. In
the first three of these the reactions are so rapid as
to render their above sequence of little significance.

Hydrogen chloride solutions (0.15 M) were
similarly treated. The reactions were exceedingly
rapid in three of the solvents and very slow in the
other four. The rate order is chloroform > xy-
lene > nitrobenzene ≫ methanol > dioxane >
ethyl n-butyl ether > diethyl ether. In the last
instance there was no detectable reaction with
0.126 M hydrogen chloride even after ninety
minutes.

The experimental results are shown in Figs. 1
and 2 for hydrogen bromide and chloride, re-
spectively. Time is plotted as the logarithm to
obtain better distribution of the points. In the
non-donor solvents hydrogen bromide and chlo-
ride add at about equal rates. As shown by the
diagrams hydrogen bromide is considerably more
reactive in donor solvents than is hydrogen chlo-
ride. It must be pointed out that the actual nu-
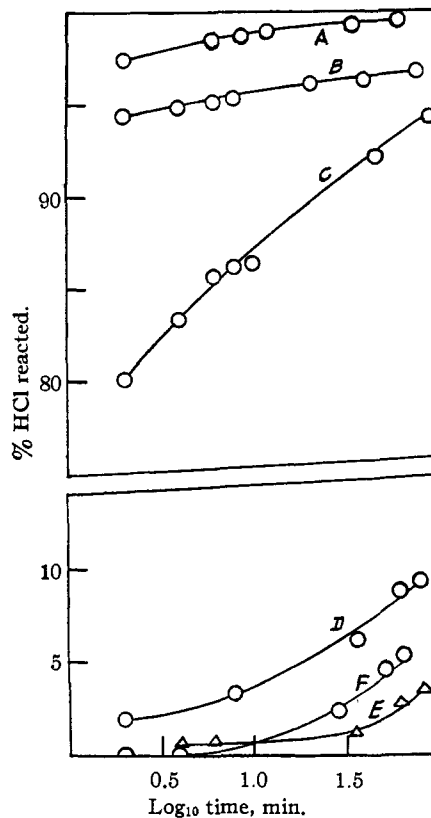merical values are close approximations only.

The technique has not yet been refined sufficiently
to permit use of the data for derivation of reliable
rate expressions. The hydrogen halides are vol-
atilized somewhat from most of the solutions,
particularly when the containers are opened for
analysis. Such losses were always greater in the
experiments with hydrogen chloride than with
hydrogen bromide. Blank experiments showed
hydrogen bromide loss to be less than 3% in all
cases; hydrogen chloride loss was somewhat
higher, especially from chloroform, xylene and
nitrobenzene. In these cases blank solutions
lost 10–15% of the dissolved hydrogen chloride
after containers had been opened four to five
times for analysis.

Experimental

α-Pinene.—A good grade of white turpentine was
fractionated repeatedly from sodium shavings to yield α-
pinene, b. p. 156–157° (746 mm.); d^{20} 0.8780. The α-
pinene was stored in small sealed containers and was
freshly distilled before use.

Solvents.—These were dried and purified by distillation.
Only middle portions were retained and freshly distilled
before use.

Procedure.—The individual experiments were performed essentially as described previously.[1] All experiments were conducted at 25°.

Summary

α-Pinene, in dilute solution, adds hydrogen

bromide and chloride rapidly from non-donor solvents and slowly from donor solvents. As shown previously[1] coördination of halogen halides with a solvent lessens their effectiveness for addition to an olefinic linkage.

The Solubility Effect in Solvents of Low Dielectric Constant. I. The Solubility of Tetrabutylammonium Iodide in Benzene in the Presence of Tetrabutylammonium Picrate and Nitrate

BY ARTHUR A. VERNON, W. F. LUDER AND MARIO GIELLA

I. Introduction

Attacking the problem from three angles, Kraus and Fuoss have been remarkably successful in explaining the properties of electrolytic solutions in solvents of any dielectric constant.[1] Using conductance, freezing point and dielectric constant measurements, they have shown that, where acid–base reactions are not involved, the properties of such solutions depend primarily upon the dielectric constant of the solvent. These properties have been accounted for on the basis of coulomb forces between ions, ion pairs and triple ions.

Higher association is observed in solvents of very low dielectric constant, such as benzene and dioxane. However, the behavior of such solutions is so complex that no quantitative theory is yet available for any but very dilute solutions, and the accumulation of more data will be necessary before an adequate one can be proposed. One approach to the problem in addition to those employed by Kraus and Fuoss seems to be that of an investigation of the effect of a second salt on the solubility of a salt dissolved in solvents of low dielectric constant.

Some work already has been done on the solubility effect in non-aqueous solvents.[2] That of most interest in connection with the present investigation has been done by Seward,[2g] and Seward and Hamblet.[2f] They used ethylene dichloride and acetic acid as solvents. Solvents of

higher dielectric constant than about ten are of little interest since the concentration of single ions is high enough in such solvents so that the familiar solubility effects are observed: namely, a decrease in solubility with a common ion and an increase when no common ion is present.

An investigation is now under way in this Laboratory to obtain data for solvents of dielectric constants varying from that of benzene (2.28) to that of ethylene dichloride (10.23).[3] This paper is the first of a series and presents preliminary results and a discussion of the problem. In solvents of sufficiently low dielectric constant, association is such that the proportion of single ions to ion pairs and higher multiples is exceedingly small. Therefore, it is to be expected that the solubility effects will be different from those usually observed in solvents of higher dielectric constant. This is strikingly demonstrated by the results herewith presented. Even though a common ion is involved, the solubility of tetrabutylammonium iodide in benzene *increases* rapidly as tetrabutylammonium picrate or nitrate is added.

II. Experimental

Materials.—C. P. thiophene free benzene was distilled from calcium oxide onto sodium, the first and last quarters being discarded. It was redistilled from this sodium onto fresh sodium and stored with moisture proof seals.

The salts were prepared and recrystallized according to the method of Cox, Kraus and Fuoss.[4]

The melting points were: for tetrabutylammonium iodide, 148°; for the picrate, 89.5°; for the nitrate, 120°.

(1) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933), and following papers on properties of electrolytic solutions.

(2) (a) Robinson, *J. Phys. Chem.*, **32**, 1089 (1928); (b) Kraus and Seward, *ibid.*, **32**, 1294 (1928); (c) Williams, THIS JOURNAL, **51**, 1112 (1929); (d) Hansen and Williams. *ibid.*, **52**, 2759 (1930); (e) Seward and Schumb, *ibid.*, **52**, 3962 (1930); (f) Seward and Hamblet, *ibid.*, **54**, 554 (1932); (g) Seward, *ibid.*, **56**, 2610 (1934).

(3) Benzene and ethylene dichloride form a thermodynamically ideal solution. One method of obtaining the desired values of dielectric constant will be to choose various proportions of the two liquids. In doing this, the effect of the addition of ethylene dichloride dipoles on the solubility of salts in benzene will also be noted.

(4) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).