[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE ALCOHOLYSIS AND HYDROLYSIS OF SOME ALKYL HALIDES IN NEUTRAL SOLUTION

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It might be not unreasonable to expect that the reactions of alkyl halides would be among the simplest to interpret with which organic chemistry has to deal. The extensive literature of the subject,[2] which cannot be reviewed here shows that this expectation is by no means justified.

A tempting start in the interpretation of these reactions as a class would be to correlate relative reaction rates with polarity of the halogen involved. Now, on the basis of almost any polar theory, one of the striking differences to be expected would be that between primary and secondary halides. For practical purposes the suggested comparison would have to be based on the relative reactivities of propyl and *iso*propyl iodides, as these constitute the only suitable pair for which any considerable variety of determinations is available.

Propyl iodide reacts more rapidly than *iso*propyl iodide with sodiomalonic ester, with triethylamine, with sodium ethylate, with sodium phenolate, with sodium benzylate[2] and with sodium thiosulfate.[3] In the case of the chlorides, the same order is observed[4] for reaction with potassium iodide. In fact, with the exception of the work of Brussoff[5] on the velocity of olefin formation with alcoholic potash, which is open to a variety of interpretations, we have found recorded but one reaction in which *iso*propyl iodide reacts more rapidly than the normal iodide. This is the reaction of the halides with silver nitrate in alcohol solution, studied by Burke and Donnan,[6] who found that the chief change taking place was not ethyl nitrate formation, but alcoholysis of the halide. The reaction was catalyzed both by silver nitrate and silver halide.

The present paper describes measurements of the rate of reaction of the four halides propyl bromide and iodide and *iso*propyl bromide and iodide with ethyl alcohol containing varying small amounts of water. The results may be considered to supplement those of Burke and Donnan in giving a measure of the uncatalyzed alcoholysis. They also permit the calculation of relative rates of hydrolysis under the same conditions.

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[1] The material here presented was used by Donald R. Stevens in partial fulfilment of the requirements for the Ph.D. degree, University of Chicago, August, 1924.

[2] For a partial summary see Haywood, *J. Chem. Soc.*, **121**, 1904 (1922).

[3] Slator and Twiss, *J. Chem. Soc.*, **95**, 95 (1909).

[4] Conant and Hussey, THIS JOURNAL, **47**, 477 (1925).

[5] Brussoff, *Z. physik. Chem.*, **34**, 129 (1900).

[6] (a) Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904); (b) *Z. physik. Chem.*, **69**, 148 (1909).

Experimental Part

An accurately weighed portion of the halide was dissolved in sufficient alcohol of the chosen concentration to give 150 cc. of solution. The solutions were 0.33–0.35 molar. This solution was now transferred to the reaction flask, which contained 4 g. of powdered calcium carbonate,[7] and rapidly heated to boiling under efficient reflux. At the end of chosen periods, usually 2, 4, 6, 8 and 10 hours, samples were removed, cooled to 25° and suitable volumes measured for analysis.

For the analysis the samples were submitted to rapid steam distillation until all of the organic halide was removed and the non-volatile halide was then titrated by the Volhard method with $N/30$ silver nitrate.

Due to the large excess of alcohol, and in most cases of water also, which was present, velocity constants were calculated by the usual equation for reactions of the first order. The K so obtained is a combination of the constants of the two competing reactions, hydrolysis and ethanolysis. A typical run is illustrated in Table I.

Table I

Results of a Typical Run

*Iso*propyl iodide (0.330 M) in 96.08%[a] alcohol

Time, hours	% Reaction	$K \times 10^3$ (hours)
2	4.9	25.1
6	14.4	26.0
8	18.8	26.1
10	23.2	26.4
	Average	25.9
	Average variation	0.4

[a] All alcohol concentrations are in per cent. by weight.

The variation in the constants calculated for other runs was approximately the same as for the one shown. For the sake of brevity, the remaining series of experiments on the four halides are represented in Table II only by the average values of K obtained in similar runs. The columns headed "% reaction (10 hours)" is included to show how far the reaction had progressed at the time measurements ceased. Laboratory regulations made it impracticable to continue the runs for longer periods.

Discussion of Results

The assumption that two reactions, hydrolysis and alcoholysis, are involved, and that these alone take place, requires some justification. This is found, primarily, in the degree of agreement (shown in the last three columns of Table II) between observed values of K and those calculated

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[7] The calcium carbonate was necessary to prevent the accumulation of halogen acids in the solution. Without it there was definite evidence of the disappearance of HBr or HI by reaction with the solvent alcohol. The constancy of the results obtained indicates that the carbonate caused no serious disturbance. While its use had the theoretical disadvantage that water was formed in the solution ($CaCO_3 + 2HX = CaX_2 + H_2O + CO_2$) during the reaction, calculation will show that the effect was quantitatively of little importance under the conditions actually employed.

TABLE II

REACTION RATES OF ALKYL HALIDES IN NEUTRAL ALCOHOL

Water, % by wt. in alcohol	% Reaction (10 hours)	$K \times 10^3$ (hours), found	$K \times 10^3$ (hours), calcd.	Diff., %
*Iso*propyl iodide (0.330 *M*)				
0.15	16.22	17.4	17.44	0.2
1.05	18.39	19.7	19.5	−1.0
1.73	...	20.8	21.06	1.2
3.92	23.20	25.9	26.06	0.6
9.85	34.04	39.8	39.75	−0.1
$Ka = 17.1 \times 10^{-3}$		$Kw = 246 \times 10^{-3}$		
Propyl iodide (0.339 *M*)				
1.12	5.75	5.88	5.85	−0.6
1.92	6.06	6.18	6.25	1.1
2.68	...	6.66	6.63	−0.4
7.84	8.83	9.23	9.22	−0.1
$Ka = 5.28 \times 10^{-3}$		$Kw = 55.6 \times 10^{-3}$		
*Iso*propyl bromide (0.355 *M*)				
0.74	7.06	7.31	7.33	0.3
2.04	8.17	8.47	8.50	0.3
2.92	8.89	9.19	9.29	1.0
7.84	13.05	13.84	13.71	−1.0
$Ka = 6.66 \times 10^{-3}$		$Kw = 96.7 \times 10^{-3}$		
Propyl bromide (0.365 *M*)				
0.35	4.13	4.19	4.19	0.0
1.12	4.39	4.47	4.56	2.0
2.50	5.35	5.40	5.21	−3.5
7.55	...	7.49	7.61	1.6
$Ka = 4.03 \times 10^{-3}$		$Kw = 51.3 \times 10^{-3}$		

when it was assumed (see above) that the observed rates were made up of two linear components proportional, respectively, to the concentrations of alcohol and of water present in each series.

The reaction of alcoholysis involves ether formation. In the experiments tabulated, the isolation of the ethers would have been excessively difficult and their quantitative determination practically impossible. A special experiment, in which a larger proportion of *iso*-amyl iodide was refluxed for several days with absolute alcohol containing an excess of calcium carbonate, did however result in the isolation of several grams of *iso*-amylethyl ether. The reaction of alcoholysis does, then, take place under such conditions as have been employed. We have not attempted as yet to show the absence of olefin formation under these conditions but we do not know of any case in which this reaction has been observed in dilute, essentially neutral solutions.

Again, the use of the equation for a reaction of the first order in calculating the results given appears at first sight anomalous. In the most extreme case (line 1, Table II) the solution contained 0.330 mole of *iso*propyl iodide and only 0.065 mole of water. It contained, however, 17.0 moles of alcohol, and the proportion of *iso*propyl iodide reacting with water to that reacting with alcohol in any given time would thus have been (see values of Ka and Kw and discussion below) $(0.246 \times .065)/(0.0171 \times 17.0) = 0.57$. As the amount of *iso*propyl iodide which had reacted at the close of the experiment was $0.1622 \times 0.330 = 0.0536$ mole, the amount reacting with water would have been $0.0536 \times 0.057 = 0.0036$ mole, or 5.6% of the water present. As this is much the most extreme case of low water concentration considered, the policy of neglecting changes in the concentration of water during reaction is thought to be justified.

The values of K obtained with a given halide, when plotted against the water content of the alcohol used, fall near a straight line which may be represented by the equation

$$A + B \text{ (wt. fraction water)} = K$$

Here A and B are constants. Table II shows the calculated values of K determined from such a straight line. If Ka and Kw represent the respective constants for the reactions due to alcoholysis and hydrolysis, then the equation may also be written

$$Ka \text{ (wt. fraction alcohol)} + Kw \text{ (wt. fraction water)} = K$$

$$\text{Here } Ka = A \text{ and } Kw = Ka + B$$

The values of Ka and Kw thus derived are included in Table II. Ka should represent with some accuracy the value of K for 100% alcohol. Kw is rather less accurate and may bear little relation to the rate which would be found in pure water. The ratios of the values of Kw obtained for the different halides should, however, be more significant.

Attention is called to the fact that the rate of reaction found is in each case greater for the secondary halides. The ratio of Ka for *iso*propyl iodide to that for propyl iodide is 3.24; for the bromides this ratio is 1.65. Similar ratios of Kw are 4.42 for the iodides and 1.89 for the bromides. It is certainly a remarkable fact that the secondary halides react the more rapidly in neutral solution and yet the less rapidly in alkaline solution.[2] Pending further data, no explanation is here offered. It is, however, of interest to note that the rate ratios found are greater in the case of the iodides. If the polarities of the halogen atoms are responsble for the variations in rate, one would expect to find the divergence widest in the case of the iodides, since iodine is a less definitely negative element than bromine and should thus be capable of showing a greater variation in polarity under a given stimulus.

Corresponding to the catalytic effect of silver salts reported by Burke and Donnan, it was found that the alcoholysis of the halides studied was markedly catalyzed by the corresponding mercuric halides. Thus 0.34 molar *iso*propyl bromide reacts some 20 times as rapidly in the presence of 0.17 molar mercuric bromide, and the influence of dissolved mercuric iodide on the reaction of *iso*propyl iodide was even greater. Satisfactory constants have not as yet been obtained, but the catalyst appears to be inactivated according to the equation $HgX_2 + 2X^- = HgX_4^{--}$

Summary

1. The rates of alcoholysis and hydrolysis of propyl and *iso*propyl bromides and iodides in boiling alcohol containing definite small amounts of water have been measured.

2. The reactions considered differ from most of those which have been studied with alkyl halides in that the secondary halides show in each case a more rapid reaction than the corresponding primary halides.

3. The reactions are strongly catalyzed by the corresponding mercuric halides.

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ANOMALOUS EFFECT OF ORTHO-PARA ORIENTING GROUPS ON THE MELTING POINTS OF DIHALOGENATED BENZENE DERIVATIVES

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Introduction

The introduction of an additional substituent into the benzene nucleus usually results in the formation of a compound which has a higher melting point than the parent substance. For this reason the observation that symmetrical tribromobenzene has a somewhat higher melting point than its amino derivative led to a study of the melting points of halogenated benzenes and their derivatives. The investigation showed that the melting points of derivatives of halogenated benzene increased with the number of substituents in the nucleus, except in the case of those compounds which are formed by the entrance of a group which causes ortho-para substitution into a para halogenated benzene.

Symmetrical chloro-bromo-iodobenzene and its amino derivatives were prepared in order to show the effect of the introduction of the amino group on the melting points of the trihalogenated benzenes.

Study of the Melting Points

An examination of the melting points of the disubstituted halogen benzene derivatives showed that the amines of the ortho and meta halogen derivatives melted at a higher temperature than the corresponding dihalogenated benzene, whereas the melting points of the amino derivatives of para halogenated benzene are lower. In a similar way the melting point of a derivative of an ortho or meta dihalogenated benzene is raised