LV.—*Reactivity of the Halogens in Organic Compounds. Part IX. Interaction of Alkalis and Alkali Bromoacetates and Bromopropionates in Ethyl-alcoholic Solution.*

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IN a previous paper (T., 1915, **107**, 1070), the action of alkalis on alkali bromoacetates and bromopropionates respectively in methyl alcohol and in mixtures of methyl alcohol and water was discussed, and it was shown that Madsen's conclusions (T., 1913, **107**, 965) as to the order of the reactions required modification in certain important respects. In agreement with Madsen, it was found that in mixtures of methyl alcohol and water both hydroxy-acids and alkyloxy-acids are formed, as was to be expected from the fact that in the mixed solvent an equilibrium is established represented by the equation:

and that sodium methoxide and sodium hydroxide act simultaneously on the alkali salt of the bromo-acid, forming salts of the hydroxy-acid and alkyloxy-acid respectively. A remarkable feature of the reactions is that under equivalent conditions a much larger proportion of alkyloxy-acid than of hydroxy-acid is formed. The simplest explanation of these observations is that when water and methyl alcohol are present in equivalent proportions the amount of sodium methoxide present is greater than that of sodium hydroxide (compare Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 41, 311).

In the present paper, the results of a corresponding investigation with solutions in ethyl alcohol and in mixtures of ethyl alcohol and water are described. As already pointed out (*loc. cit.*, p. 1080), sodium bromoacetate is only sparingly soluble in ethyl alcohol, and it was therefore impossible to measure the speed of the reaction between sodium bromoacetate and sodium ethoxide. A series of

measurements in mixtures of ethyl alcohol and water in various proportions shows that the rate of displacement of bromine increases with increasing proportion of alcohol, so far as the measurements could be carried. The reaction, as in methyl alcohol, is pseudo-bimolecular in character; in any one solution velocity coefficients in good agreement with the assumption that the reaction is bimolecular are obtained, but with different initial concentrations of the reacting substances, the velocity coefficients increase faster than the concentration of the sodium ethoxide. It is remarkable that the bromine is displaced about six times as fast in 90 per cent. ethyl alcohol as in 90 per cent. methyl alcohol. The proportion of ethoxy-acid in the final product was estimated by Zeisel's method, and it was found that in solutions containing up to 40 per cent. alcohol the proportion of ethoxy-acid formed is greater than that of the alcohol present in the solution.

The action of ethyl alcohol on sodium bromopropionate is comparable in speed with that of sodium ethoxide, so that the reaction does not correspond with any simple order. The rate of displacement of bromine attains a maximum in mixtures containing about 25 per cent. ethyl alcohol.

The bearing of the results summarised in the last two paragraphs is briefly discussed in later sections of the paper.

EXPERIMENTAL.

The method of experiment has been fully described in the previous paper, as well as the tests used in establishing the purity of the materials. The results were calculated by the usual formula for a bimolecular reaction, $a-x$ representing the number of c.c. of approximately $N/10$ -sulphuric acid required to neutralise 20 c.c. of the reaction mixture after the latter had been heated for a definite period at constant temperature. The titration value at the time, $t=0$, is not that at the commencement of the reaction, but a measurement made after the mixture had been so long in the thermostat that the temperature was assumed to have become constant.

For estimating the proportion of ethoxyl present by Zeisel's method, a slight modification of Hewitt and Moore's apparatus (T., 1902, **81**, 318) suggested by one of us (H. Wood) was found to give excellent results. The modification consists in using as decomposition vessel a flask with a side-tube, into which the fractionating column is inserted. By this arrangement, only singly bored corks are used, and complete tightness is easily secured. The arrangement will be clear from the diagram without further description.

The hydriodic acid used in the Zeisel determinations was purified by adding a little red phosphorus and heating for three to four hours on a water-bath in an atmosphere of carbon dioxide, in a flask provided with an air condenser. The liquid was then allowed to cool while a slow stream of carbon dioxide was maintained, and then filtered through an asbestos plug under pressure of carbon dioxide from a Kipp's apparatus.

Reaction between Sodium Bromoacetate and Ethoxide in Mixtures of Ethyl Alcohol and Water.

This reaction is represented quantitatively by the equation:

As already mentioned, it was not found possible to determine the rate of reaction between sodium bromoacetate and sodium ethoxide in ethyl alcohol alone, owing to the sparing solubility of the salt in this solvent. Measurements were made using as solvent mixtures containing varying proportions of ethyl alcohol and water. The results of typical experiments in 90 per cent. and 50 per cent. alcohol by volume are given in the accompanying table.

TABLE I.

*Sodium Bromoacetate, 0.1N.**Sodium Ethoxide, 0.1N.*

90 per cent. Alcohol.			50 per cent. Alcohol.		
<i>t.</i>	<i>a - x.</i>	<i>k.</i>	<i>t.</i>	<i>a - x.</i>	<i>k.</i>
0	16.95	—	0	19.7	—
30	13.45	0.00050	30	18.25	0.000134
60	11.1	0.00052	60	17.1	0.000129
120	8.3	0.00051	120	15.1	0.000129
180	6.5	0.00052	185	13.4	0.000129

As the figures given in the third and sixth columns show, the reaction is strictly bimolecular in these dilutions, and this was also found to be the case in all the mixtures used as solvent. This is a remarkable result when account is taken of the marked alteration in the nature of the solvent, ranging from pure water to 90 per cent. alcohol. The velocity coefficients for different initial concentrations of sodium ethoxide in 90 per cent. alcohol are given in Table II. The temperature throughout was 40.2°.

TABLE II.

Sodium ethoxide.	Sodium bromoacetate.	<i>k</i> × 10 ³ .
0.1 <i>N</i>	0.1 <i>N</i>	0.51
0.15 <i>N</i>	0.1 <i>N</i>	0.57
0.2 <i>N</i>	0.1 <i>N</i>	0.76
0.3 <i>N</i>	0.1 <i>N</i>	0.82

If the rate of reaction is proportional to the concentration of the sodium salt (ethoxide and hydroxide) the coefficients in the last column should be the same, whereas they are greater the greater the concentration of the sodium salt. As this result might possibly be due to the greater reactivity of non-ionised sodium ethoxide, which is present in relatively larger proportion than the C_2H_5O' ion in the more concentrated solutions, the effect of sodium bromide, which increases the proportion of non-ionised salt, was examined. In *N*/10-solution of the bromoacetate and ethoxide with 0.2*N*-sodium bromide, the velocity coefficient is 0.00084, whereas in the absence of the latter salt, the coefficient is 0.00051. The interpretation of this result is discussed later (p. 686).

The velocity coefficient with *N*/10-potassium ethoxide in 90 per cent. alcohol is 0.00056, as compared with 0.00051 for the sodium salt under equivalent conditions, so that in this case also the potassium salt is slightly more reactive (compare T., 1915, 107, 1074).

It has already been mentioned that the proportion of ethoxy-

acid in the products of the reaction was determined for mixtures containing varying proportions of alcohol. The results of these determinations, together with the velocity coefficients in the various mixtures, are given in the accompanying table.

TABLE III.

Sodium Bromoacetate, N/10.
Sodium Ethoxide (Hydroxide), N/10.

Proportion of Alcohol by volume	100	90	75	50	25	10	0 (NaOH only)
Velocity Coefficient $\times 10^3$...	—	0.51	0.24	0.13	0.10	—	0.082
Proportion of Ethoxy-acid in product	90.8	81.6	69.0	48.0	31.0	14.3	—

These results show that the rate of displacement of bromine increases regularly as the proportion of alcohol increases, and that, at least in the more dilute solutions, the proportion of ethoxy-acid formed is greater than the proportion of ethyl alcohol present.

The reason why the proportion of ethoxy-acid is less than 100 per cent. in alcohol alone has not been satisfactorily elucidated. As already mentioned, the bromoacetate is only sparingly soluble in ethyl alcohol at 40°, and the mixture had to be heated either at a much higher temperature to complete the decomposition of the bromoacetate, or at the lower temperature in presence of undissolved salt, so that a secondary product of some character was probably formed in small amount.

The velocity coefficient for the action between sodium bromoacetate and sodium methoxide in 90 per cent. methyl alcohol is 0.30×10^{-3} at 52.4°, and as the temperature coefficient for 10° for this reaction is 2.8, the coefficient at 40.2° would be about 0.08×10^{-3} , which is about one-sixth of the rate of the corresponding reaction in ethyl alcohol. The relatively great velocity of the reaction between sodium ethoxide and sodium bromoacetate doubtless accounts for the regular increase in the velocity coefficients as the proportion of alcohol is increased (Table III).

The greater reactivity of sodium ethoxide as compared with sodium methoxide has been observed for other reactions. Thus, according to Hecht and Conrad (*Zeitsch. physikal. Chem.*, 1889, **4**, 299), sodium ethoxide reacts with ethyl iodide about four times as fast as does sodium methoxide, and Kremann (*Monatsh.*, 1905, **26**, 279) found that the rate of hydrolysis of ethyl acetate by sodium ethoxide in ethyl alcohol is about 1.4 times as great as

the corresponding reaction with sodium methoxide in methyl alcohol. Kremann was of opinion that this result is to be ascribed to the influence of traces of moisture in the alcohols, which would form a much greater proportion of sodium hydroxide from sodium ethoxide than from sodium methoxide; as sodium hydroxide hydrolyses ethyl acetate several hundred times faster than the alkyloxide, the observed results would thus be accounted for. In this connexion, it is interesting to note that the solvent used in the classical experiments of Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1899, **3**, 450; **4**, 272, 631; 1890, **5**, 289) was 99.8 per cent. alcohol. In the experiments described in this paper, however, as hydroxyl ions act relatively slowly on sodium bromoacetate, the explanation for the relatively great reactivity of sodium ethoxide suggested by Kremann cannot apply, and it is doubtful if the small proportion of water present in Hecht and Conrad's experiments had much effect on the character of the results. In fact, it would probably be found, contrary to the opinion of Kremann, that in the entire absence of water sodium ethoxide would react with ethyl acetate more rapidly than would sodium methoxide.

It is not easy to suggest a satisfactory explanation for the relatively great reactivity of sodium ethoxide. Reactions in methyl alcohol will usually be more rapid than in ethyl alcohol, owing to the higher dielectric constant and smaller viscosity of the former solvent (Menschutkin), so that the true ratio of the chemical activity of sodium ethoxide to methoxide, determined in the same solvent, would probably be greater than the value given above. So far as steric hindrance is concerned, the methoxide might be expected to react more rapidly than the ethoxide. It may be that the methoxy-group takes up more affinity from the sodium than the ethoxy-group, and therefore the sodium atom united with the latter group, having more affinity left over, is able to displace the bromine more rapidly than that attached to the methoxy-group. The effect of sodium bromide in accelerating the action would appear to show that the non-ionised alkyloxide, and not the anion, is the main factor in the change.

As far as the relative proportions of ethoxy-acid obtained from the solvents containing different proportions of alcohol and water are concerned, there is little to add to the discussion in the previous paper (*loc. cit.*, p. 1078). It is there pointed out (p. 1078) that, in drawing conclusions as to the relative proportions of hydroxide and alkyloxide in the mixture from the relative proportions of hydroxy-acid and alkyloxy-acid in the final product, the relative rates of reaction of hydroxide and alkyloxide with the bromo-acid

have to be taken into account. The results now given show, as was to be anticipated, that the equilibrium

is displaced more to the right than in solutions of sodium methoxide under equivalent conditions. The observations cannot be interpreted quantitatively until the above equilibrium has been more accurately investigated, especially by means of electrical conductivity measurements. The suggestion of Kremann (*loc. cit.*) that the proportion of alkyloxide in such mixtures containing 50 per cent. of water is extremely small is not borne out by his own observations, owing to the relatively great effect of even a small proportion of sodium hydroxide on the rate of hydrolysis of ethyl acetate, and is disproved by the results described in the present paper.

Reaction between Sodium Bromopropionate and Ethoxide in Ethyl Alcohol and in Mixtures of Ethyl Alcohol and Water.

As sodium bromopropionate is fairly soluble in ethyl alcohol, it was possible to determine the speed of this reaction in 100 per cent. alcohol, as well as in mixtures of ethyl alcohol and water. As the reaction is much slower than in the case of sodium bromoacetate, the measurements were carried out at 51.4°. The results of typical experiments in 90 and 50 per cent. alcohol are given in Table IV.

TABLE IV.

Sodium α-Bromopropionate, N/10.

Sodium Ethoxide, N/10.

90 per cent. Alcohol.			50 per cent. Alcohol.		
<i>t.</i>	<i>a - x.</i>	<i>k</i> × 10 ³	<i>t.</i>	<i>a - x.</i>	<i>k</i> × 10 ³
0	20.1	—	0	19.75	—
60	18.4	0.076	60	17.75	0.095
120	16.7	0.084	120	16.0	0.099
240	14.1	0.088	240	13.3	0.102
360	12.3	0.088	360	11.2	0.107
480	10.65	0.092	480	9.2	0.121

As the coefficients increase regularly as the reaction proceeds, it is evident that the assumption that the reaction is bimolecular in character is not justified. As a similar result in the case of solutions in methyl alcohol was shown to be due to the fact that the action of sodium methoxide and methyl alcohol on sodium bromopropionate are comparable in speed, the action of ethyl alcohol

on sodium bromopropionate was investigated. The main reaction is presumably that represented by the equation

As it has been found in previous investigations that the rate of formation of bromidion is not always the same as the rate of increase of the acidity of the solution, as would be the case if the above equation adequately represented the course of the reaction, the speed of the change was followed by titrating the solution with *N*/10-silver nitrate, as well as with *N*/10-sodium hydroxide. The results of a typical experiment at 51.4° are given in the accompanying table. The velocity coefficients, *k*, have been calculated for the silver nitrate titrations only by the formula for a unimolecular reaction.

TABLE V.

Sodium α-Bromopropionate, N/10, in Ethyl Alcohol.

<i>t</i> .	c. c. <i>N</i> /10-AgNO ₃ .	c. c. <i>N</i> /10-NaOH.	<i>a</i> - <i>x</i> '	<i>a</i> - <i>x</i> "	<i>k</i> × 10 ³ .
0	0.2	0.2	19.8	19.8	—
60	1.1	0.85	18.9	19.15	0.944
180	2.6	2.00	17.4	18.0	0.774
300	3.85	2.95	16.15	17.05	0.712
510	5.55	4.2	14.45	15.8	0.638
1680	11.1	8.25	8.9	11.75	0.482

When the coefficients in column 6 are divided by 20, to make them comparable with those in table IV, the conclusion that ethyl alcohol and sodium ethoxide act on sodium α-bromopropionate at comparable rates is confirmed.

As shown in the last paper (*loc. cit.*, p. 1075; compare *Ber.*, 1912, **45**, 2318), the difference in the titration values with silver nitrate and sodium hydroxide is due to the intermediate formation of the compound

by the interaction of two molecules of sodium α-bromopropionate. This compound would undergo slow decomposition by ethyl alcohol with the formation of bromopropionic acid and α-ethoxypropionic acid, and the fact that the simultaneous titration values with silver nitrate and sodium hydroxide differ more in ethyl- than in methyl-alcoholic solution doubtless indicates that the intermediate compound is decomposed more rapidly by methyl than by ethyl alcohol. α-Chloroacetoxypropionic acid,

similar in constitution to the above compound, has been prepared in this laboratory by Mr. G. H. Martin by a method described by Blaise (*Bull. Soc. chim.*, 1914, [iv], **15**, 666), and it is intended

at a later stage to give an account of the behaviour of such compounds from the kinetic point of view.

The rapid diminution in the magnitude of the velocity coefficients calculated for a unimolecular reaction is doubtless to be ascribed to the formation of hydrobromic acid during the reaction, whereby the sodium salt is changed to free bromopropionic acid, which reacts more slowly than the salt. Towards the end of the reaction the odour of ethyl α -bromopropionate becomes perceptible.

The relative rates of reaction of sodium methoxide and ethoxide with sodium bromopropionate cannot be determined with any degree of accuracy, as the results are complicated by the action of the alcohols themselves on the salt.

As already mentioned, the rate of displacement of bromine from sodium α -bromopropionate has also been investigated in mixtures of ethyl alcohol and water. The approximate values of the velocity coefficients at different dilutions, calculated by the formula for a bimolecular reaction, are given in table VI.

TABLE VI.

Sodium α -Bromopropionate, 0.1N.
Sodium Ethoxide (Hydroxide), 0.1N.

Proportion of Ethyl } Alcohol by volume }	100	90	75	50	25	10	0
							(NaOH only)
Velocity Coefficient $\times 10^3$...	0.113	0.087	0.098	0.107	0.130	0.115	0.097

It is interesting to note that there is a maximum rate of reaction in the solution containing 25 per cent. by volume of alcohol. As the results given in the present and in previous papers show that the change is a highly complicated one, at least four simultaneous reactions taking place, namely, the action of ethyl alcohol, sodium ethoxide, water, and sodium hydroxide respectively on sodium bromopropionate, there is no advantage in discussing the results more fully at the present stage.

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