443. *The Kinetics of the Interactions of Sodium Hydroxide with Penta- and Hexa-chloro- and -bromo-ethanes in Aqueous Ethyl-alcoholic Solution.*

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THE carbon–halogen bond may undergo rupture in the presence of hydroxyl or ethoxyl groups in a number of ways, rendering certain apparently simple reactions difficult of interpretation on an electronic basis (see Robinson, " Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry, 1932, p. 35). Although the results of kinetic studies are sometimes ambiguous (see, *e.g.*, Ward, J., 1930, 2143), nevertheless, in the hope that they would aid in elucidating the mode of halogen displacement, they have now been applied to penta- and hexa-halogenoethanes.

An almost instantaneous elimination of one molecule of halogen acids results when sodium hydroxide reacts with either *s*.-tetra-chloro- or -bromo-ethane in ethyl-alcoholic solution (Ward, *loc. cit.*), and the pentahalogeno-compounds are now found to behave similarly, although they are stable in the absence of the alkali. Of these four eliminations, that from *s*.-tetrachloroethane takes place most slowly, but is complete within less than two seconds. Pentachloro- and pentabromo-ethane had previously been studied under similar conditions by Gowing-Scopes (*Analyst*, 1914, **39**, 385) and by Petrenko-Kritschenko (*Ber.*, 1928, **61**, 845) respectively; although our results are not inconsistent with those of the former author, they differ markedly from those of the latter.

On the assumption that the reactions of these four substances with sodium hydroxide are of the same order, the relative values of the velocity coefficients have been found. Either of the chloroethanes was allowed to compete with either of the bromoethanes for a limited amount of sodium hydroxide in ethyl-alcoholic solution; the halogenated ethanes and ethylenes were removed by appropriate methods, and the total resulting sodium bromide and chloride was analysed. The competitive method has been discussed fully by Ingold and Ingold (J., 1931, 2354), and the necessary experimental conditions prescribed by them have been observed. We have used the integrated equation

$$k_B/k_A = [\log b - \log (b - y)]/[\log a - \log (a - x)],$$

where a and b denote the initial concentrations of the halogen compounds A and B, and x and y, the respective concentrations destroyed by sodium hydroxide. Two independent sets of measurements were taken at 20°, and the results summarised below.

$$k_{C_2H_2Br_4}/k_{C_2H_2Cl_4} = 10{\cdot}8; \quad k_{C_2H_2Br_4}/k_{C_2HCl_5} = 2{\cdot}2; \quad \text{hence } k_{C_2HCl_5}/k_{C_2H_2Cl_4} = 4{\cdot}9;$$
$$k_{C_2HBr_5}/k_{C_2H_2Cl_4} = 17{\cdot}3; \quad k_{C_2HBr_5}/k_{C_2HCl_5} = 3{\cdot}5; \quad \text{hence } k_{C_2HCl_5}/k_{C_2H_2Cl_4} = 4{\cdot}9.$$

Ward (*loc. cit.*) has shown that the fairly rapid reaction of sodium hydroxide with tribromoethylene in ethyl alcohol at 25° is bimolecular, although there is a fall in the value of k in the early stages of the reaction. On the reasonable assumption that the four reactions under discussion are bimolecular, it was hoped, by using tribromoethylene and tetrachloroethane in competition, to measure the absolute values of the velocity coefficients, but the disparity in velocity was too great for the method to be applied.

Halogen is displaced slowly, under similar conditions from hexabromoethane, and still more slowly from hexachloroethane; the only products isolated were the corresponding tetrahalogenoethylenes, which react so slowly with sodium hydroxide as not materially to affect the kinetic results. Two halogen atoms, without associated hydrogen, are eliminated from compounds C_2X_6 and C_2X_4 in these experiments, and oxidation of the solvent alcohol must therefore occur; in spite of this, it was decided to use ethyl alcohol because of the solubility of sodium hydroxide in this liquid and for purposes of comparison with other compounds $C_2H_{6-n}X_n$ which had already been studied. The yellow to brown colour of aldehyde resin slowly develops in the hexachloroethane reaction liquid, and after a longer period with tetra-bromo- and -chloro-ethylene (cf. Nef, *Annalen*, 1896, **298**, 332). Possibly sodium hypohalite is first formed, but it could not be detected: alkaline phenolphthalein is not bleached when added to the reaction liquid, and alkaline solutions of sodium hypohalite added to a large excess of ethyl alcohol are immediately and completely reduced.

Although hexachloroethane and alcoholic sodium hydroxide give aldehyde resin, solutions of sodium hypochlorite and alcoholic sodium hydroxide do not, in whatever proportion they are mixed, but cause chlorination of acetaldehyde. The equilibrium $NaClO + NaCl + H_2O \rightleftharpoons 2NaOH + Cl_2$ may be assumed, and chlorination may be ascribed to free chlorine, whilst oxidation is effected by the hypochlorite ion. If, as in the hexachloroethane reaction, the concentration of hypochlorite ions at any time is extremely small and that of hydroxyl ions is relatively large, the reaction will proceed mainly towards the left, with consequent oxidation of the alcohol and formation of aldehyde resin. On passing chlorine continuously and in very small quantities into concentrated alcoholic sodium hydroxide, the resin was, in fact, formed.

The velocity of halogen displacement from hexachloroethane was measured in aqueous ethyl-alcoholic solution for $M/10$- and $M/100$-solutions. The only method of calculation of k to give reasonably constant values was that in which a modified bimolecular form was used. The following mechanism is in accordance with these results:

$$C_2Cl_6 + OH' \longrightarrow C_2Cl_5OH + Cl' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$C_2Cl_5OH \longrightarrow C_2Cl_4 + HClO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$HClO + EtOH + NaOH \longrightarrow CH_3{\cdot}CHO + NaCl + 2H_2O \quad . \; . \; . \; . \quad (3)$$

The aldehyde would then undergo a slow resinification in presence of hydroxyl ions. On this basis, stage (1) is the time reaction, and stages (2) and (3) are rapid. Stages (1) and (2) may possibly be considered as a single step, $C_2Cl_6 + OH' \longrightarrow C_2Cl_4 + Cl' + HClO$. If c and d are the initial concentrations of sodium hydroxide and hexachloroethane respectively, and x is the concentration of sodium hydroxide removed in time t, then $dx/dt = k(c - x)(d - x/2)$, whence $k = 4{\cdot}605/t(c - 2d) \,.\, \log_{10} d(c - x)/c(d - x/2)$. Values of k in all experiments are thus calculated, and are but little affected by dilution.

In the early stages of the reaction the amount of resin gradually increases, as shown by the intensity of colour, and the formation is attended by a gradual decrease in the values of k. This is followed by a gradual diminution in the intensity of colour, visible coagulation of the resin, and a gradual rise in the values of k. The variation in the values of k is not due to increased viscosity of the liquid, for this is sensibly constant. [From a separate study of its formation in alkaline ethyl alcohol containing acetaldehyde, the resin appears to be a negative colloid: sodium ions coagulate it slowly, and hydrogen ions rapidly.]

This view as to the cause of the decrease in the value of k was confirmed by dissolving hexachloroethane in a resin sol 14 days old; the value of k was lower, and showed far less diminution with time. It appears that k is approximately inversely proportional to the concentration of aldehyde resin. Attempts were made to avoid the complications by introducing urea or sodium bisulphite to remove the oxidising material formed, but the resin still resulted, and the values of k were very irregular.

Hexabromoethane, unlike hexachloroethane and tetra-chloro- and -bromo-ethylene, reacts instantly with acetaldehyde in presence of sodium hydroxide, no resin being formed although it is readily obtained by the interaction of sodium hypobromite and alcoholic sodium hydroxide. The experimental evidence supports the view that reaction proceeds between hexabromoethane and hydroxyl ions as in the case of hexachloroethane, but that the aldehyde formed is then very rapidly brominated and oxidised :

$$\mathrm{CH_3{\cdot}CHO + NaOH + C_2Br_6 \longrightarrow CH_2Br{\cdot}CHO + C_2Br_4 + NaBr + H_2O} \quad . \quad (4)$$

$$\mathrm{CH_2Br{\cdot}CHO + NaBrO + NaOH \longrightarrow CH_2Br{\cdot}CO_2Na + NaBr + H_2O} \quad . \quad . \quad (5)$$

Hence, the molecular ratio of hexabromoethane and sodium hydroxide destroyed in stages (1), (2), and (3) (p. 2004) will be 2 : 4, and in stages (4) and (5) it will be 1 : 2, *i.e.*, the ratio in any time interval is 1 : 2. The rate of reaction will, therefore, be governed by the equation used for hexachloroethane, and this was found best to fit the experimental values. For comparison with the results for hexachloroethane, two-thirds of this value was taken. The slow displacement of bromine from sodium bromoacetate introduces a further complication which causes an upward drift in the values of k.

The reaction represented by (4) suggests that acetaldehyde is in tautomeric equilibrium with its enolic form in alkaline as well as in acid solution (see Dawson, Burton, and Ark, J., 1914, **105**, 1287). According to Dawson and Carter (J., 1926, 2292), for the enolisation of acetone the ratio $k_{\mathrm{OH}^\ominus}/k_{\mathrm{H}^\oplus}$ is $10/(442 \times 10^{-6})$, the catalytic activity of the hydroxyl ion being more than 20,000 times as great as that of the hydrogen ion. Dawson and Powis (J., 1912, **101**, 1510) show that the addition of small amounts of sodium hydroxide " by reason of the rapid decomposition of the sodium hydroxide (by iodine) cannot throw much light on the nature of the isomeric change in the initial stages or of the occurrence and velocity in neutral or in alkaline solution." Hexabromoethane, on the other hand, reacts with sodium hydroxide only very slowly. It thus appears to be an exceptional reagent for confirming directly the catalytic efficiency of the hydroxyl ion in keto-enol tautomeric changes. From the observed result given in (4), the full scheme of this stage of the reaction may be

$$\mathrm{CH_3{\cdot}CHO \xrightarrow{OH'} CH_2{:}CH{\cdot}OH} \quad (\textit{rapid})$$

$$\mathrm{CH_2{:}CH{\cdot}OH + C_2Br_5{\cdot}Br \longrightarrow CH_2(C_2Br_5){\cdot}CHBr{\cdot}OH} \quad (\textit{rapid})$$

$$\mathrm{CH_2(C_2Br_5){\cdot}CHBr(OH) \longrightarrow CH_2Br{\cdot}HO + C_2Br_4 + HBr} \quad (\textit{rapid})$$

According to Dawson, Burton, and Ark (*loc. cit.*), the first step under the catalytic influence of the hydrogen ion is slow. Propaldehyde reacts in a similar way towards hexabromoethane. Acetone and acetoacetic ester also react instantly but remove approximately 3 and 2 mols. of sodium hydroxide respectively, instead of 1 mol. for the aldehydes.

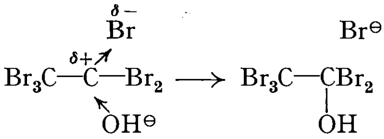
The relatively slow reactions of potassium hydroxide with ethyl chloride, bromide, and iodide in ethyl-alcoholic solution have been shown by Grant and Hinshelwood (J., 1933, 258) to be closely bimolecular, although again there is a fall in the values of k in the early stages of the reaction. Ethyl alcohol is the main product, with very little ethylene. The extreme differences in the rates of elimination of halogen from the two sets of compounds (see Table I, where values are given for k_{25° in g.-mols./l./sec.) are most probably due to the operation of different mechanisms.

TABLE I.

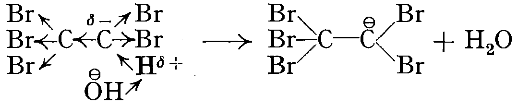
Class S (slow).		Class R (rapid).	
Ethyl bromide	$7{\cdot}63 \times 10^{-5}$	Pentabromoethane	" Instantaneous "
Ethyl chloride	$2{\cdot}86 \times 10^{-6}$	Pentachloroethane	
Hexabromoethane	$2{\cdot}96 \times 10^{-4}$	Tetrabromoethane	
Hexachloroethane	$6{\cdot}31 \times 10^{-6}$	Tetrachloroethane	

The seats of attack in these molecules by the nucleophilic (see Ingold, J., 1933, 1121) hydroxyl ion are the carbon and hydrogen nuclei; the electrophilic halogen nuclei would necessarily repel the hydroxyl ion. For reaction to proceed, there must be a recession of electrons from the space immediately surrounding either of these two nuclei. The presence of halogen atoms in these molecules ensures this state of affairs. In hexa-bromo- and

-chloro-ethanes the carbon nucleus is the only possible seat of attack and the mechanism is probably :



A similar mechanism would be applicable to all compounds in class S—the ethyl halides yield ethyl alcohol. In class R the hydrogen nucleus is the probable seat of attack, the mechanism being



In each class (excluding C_2X_6) it is possible that both types of mechanism are operating, with that type preponderating which is suggested above (cf. Baker, J., 1933, 1129). Grant and Hinshelwood's hypothesis (*loc. cit.*) that " reactions between an organic compound and an ion in solution tend to take place at approximately the rate given by the simple kinetic equation " $k = Ze^{-E/RT}$, which may be written as

$$k = (N/1000)\sigma_{1,2}^{2}[8\pi RT(1/M_1 + M_2)]^{\frac{1}{2}}e^{-E/RT}$$

appears to be fairly true for compounds of class S. Hexachloroethane does not give close agreement, but the critical increment (E) in this case is calculated from kinetic results at two temperatures only. As in the case of hexabromoethane, disturbing factors are obviously involved and the values of the critical increments which have been derived from kinetic data can only be regarded as approximate. Values of k (obs.) and k (calc.), in g.-mols./l./sec. at 25°, are given in Table II; $\sigma_{1,2}$ is taken as 4×10^{-8} cm. throughout, owing to lack of precise knowledge of the size of the hydroxyl ion. From a consideration of tribromoethylene, which may be taken to belong to class R, the reactions of this class appear to be abnormally fast.

TABLE II.

	k (obs.).	E (critical increment).	k (calc.).
*Ethyl bromide	$7{\cdot}63 \times 10^{-5}$	21,000	$7{\cdot}5 \times 10^{-5}$
*Ethyl chloride	$2{\cdot}86 \times 10^{-6}$	23,000	$4{\cdot}35 \times 10^{-6}$
Hexabromoethane	$2{\cdot}96 \times 10^{-4}$	19,000	$7{\cdot}61 \times 10^{-4}$
Hexachloroethane	$6{\cdot}31 \times 10^{-6}$	19,600	$2{\cdot}82 \times 10^{-4}$
†Tribromoethylene	$1{\cdot}86 \times 10^{-3}$	25,100	$2{\cdot}60 \times 10^{-8}$

* Values obtained from Grant and Hinshelwood (*loc. cit.*).

† Values obtained from Ward (*loc. cit.*).

EXPERIMENTAL.

Preparation of Materials.—Commercial pentachloroethane was fractionally distilled, and a constant-boiling fraction collected; b. p. 158°/760 mm. [Thorpe, J., 1880, **37**, 192, gives b. p. 159·1° (corr.)/760 mm.] [Found : Cl (Stepanow), 87·8. Calc. : Cl, 87·6%. Stepanow's method gives low results with these highly halogenated ethanes, unless the liquid, after addition of sodium, is refluxed for at least 20 hours. All other halogen estimations were carried out in this way].

Pentabromoethane was prepared by shaking bromine with tribromoethylene (Elbs and Newmann, *J. pr. Chem.*, 1898, **58**, 249), the reaction being instantaneous and the yield almost theoretical; m. p. 55° (Bourgoin, *Bull. Soc. chim.*, 1875, **23**, 173, gives m. p. 56—57°; Elbs and Newmann, *loc. cit.*, give 55°; Denzel, *Ber.*, 1879, **12**, 2208, gives 54°).

Tetrabromoethylene was prepared by dissolving pentabromoethane (64 g.) in boiling methylated spirits (300 c.c.) and adding 2*N*-aqueous sodium hydroxide until phenolphthalein in the liquid remained slightly pink; boiling must be maintained in order to prevent the separation of either tetrabromoethylene or pentabromoethane. Excess of alkali was neutralised with hydrochloric acid, and then sufficient water was added to cause a slight permanent turbidity. On cooling, almost all the tetrabromoethylene crystallised within 24 hours. The crystals were filtered off, washed with a little methylated spirits and then water, recrystallised from spirits, and dried in a vacuum; yield 96%; m. p. 56° (Biltz, *Ber.*, 1902, **35**, 1530, gives m. p. 56·5—57·5°; Nef, *Annalen*, 1897, **298**, 332, m. p. 56°; Lemoult, *Compt. rend.*, 1903, **136**, 1334, m. p. 55°).

Tetrachloroethylene was similarly prepared from a cold solution of pentachloroethane (50 g.) in methylated spirits (550 c.c.). After neutralisation, the liquid was added to 1 l. of water, and the oil which slowly separated from the resulting emulsion was dried over calcium chloride and distilled; yield 98%; b. p. 119—120°/780 mm. (Herz and Rathmann, *Chem.-Ztg.*, 1912, **36**, 1417, give b. p. 118·5°/751 mm.).

Hexabromoethane was prepared by Mouneyrat's method (*Bull. Soc. chim.*, 1898, **19**, 177); much tar was produced (see also Elbs and Newmann, *loc. cit.*) and the yield was low, being only 14% of the weight of *s*.-tetrabromoethane (Found : Br, 95·1. Calc. : Br, 95·2%) When heated in a capillary tube, it decomposed into tetrabromoethylene and bromine at 195—196° (Mouneyrat, *loc. cit.*, gives 200—210°). An improved method of preparation was to add bromine (16 c.c.; dried over sulphuric acid) to tetrabromoethylene (15 g.) in carbon disulphide (70 c.c.) solution, using resublimed iodine (0·05 g.) as a catalyst, and refluxing for 50 hours; the hexabromoethane was separated by distilling off the solvent and some bromine and iodine, the remainder being removed on the water-bath. At about 70°, it is solid whereas tetrabromoethylene is liquid and can be decanted off, the last traces being removed by extraction with small quantities of hot methylated spirits. The hexabromoethane was crystallised from carbon disulphide, giving pure material, decomp. 198—199°; yield 7·5 g., 34%. Other solvents and catalysts were ineffective, and the use of bromine dried as above is essential.

Hexachloroethane, recrystallised commercial material, melted in a sealed capillary at 181° [Städel, *Ber.*, 1878, **11**, 1738, gives m. p. 186·85—187·40° (corr.)] (Found : Cl, 90·2. Calc. : Cl, 89·9%).

Kinetic Experiments.—Ethyl alcohol (A) used in preliminary kinetic experiments was ordinary absolute alcohol. Later work was carried out with alcohol (B) which was lime-dried and then distilled from lime, or (C), lime-dried and distilled, followed by refluxing and distilling over aluminium amalgam. For experiments with hexabromoethane, it was especially important that the alcohol should be freed from acetaldehyde, and this was effected by (D) subjecting alcohol (B) to refluxing and distillation over dry silver nitrate alone (Senter, J., 1911, **99**, 96) or together with a little potassium hydroxide (Dunlap, *J. Amer. Chem. Soc.*, 1906, **28**, 395), or by (E) refluxing alcohol (B) over aluminium amalgam and then distilling it in nitrogen and storing it in contact with this gas.

In the actual experiments, to 90 c.c. of approx. $M/10$-solution of the substance in ethyl alcohol, at the required temperature, were added 10 c.c. of approx. $2N$-aqueous sodium hydroxide. Experiments were also made at one-tenth of these concentrations. The reaction was stopped by adding 10 c.c. of the liquid to about 50 c.c. of cold water (previously boiled and cooled out of contact with carbon dioxide for $M/100$-solutions). The resulting suspension was titrated with $N/10$- or $N/100$-hydrochloric acid, with phenolphthalein as indicator. Attempts to determine ionised halide by use of $N/100$-silver nitrate and dichlorofluorescein were not successful. Values of k are calculated from the equation on p. 2004, where t is expressed in hours, and all concentrations in g.-mols./l. The value of c was obtained by titrating, with the standard hydrochloric acid, 10 c.c. of a solution prepared by adding 10 c.c. of the sodium hydroxide used to 90 c.c. of alcohol.

Hexachloroethane. Details of two experiments at 25·0° using ethyl alcohol (C) are given, titres being expressed as c.c. of $N/10$-solution both here and elsewhere unless otherwise specified :

Experiment 1.

$c = 0\cdot2236$; $d = 0\cdot0818$;
$c - 2d = 0\cdot0600$.

t.	Titre.	Colour.	$k \times 10^4$.
0	22·36	Colourless	—
45	20·59	Lemon-yellow	244
140·5	18·88	Orange	166
286·5	17·93	Brown	112
663	14·72	,,	106
888	12·94	,,	117
1172	11·11	Yellow	132
1536	9·42	Pale yellow	152
2009	7·85	V. pale yellow	187
2515	5·44	,, ,,	—

Experiment 2.

$c = 0\cdot2236$; $d = 0\cdot1191$;
$c - 2d = -0\cdot0146$.

t.	Titre.	Colour.	$k \times 10^4$.
0	22·36	Colourless	—
45	19·89	Yellow	217
140	17·91	Orange	144
286·5	16·21	Brown	108
663	12·32	,,	101
888	9·97	,,	112
1172	8·08	Yellow	120
1536	5·32	Pale yellow	160
2009	3·44	V. pale yellow	198
2515	1·80	,, ,,	289

The mean of seven experiments at 25° gave initial $k_{25^\circ} = 227 \times 10^{-4}$, and that of two experiments at 35° gave $k_{35^\circ} = 676 \times 10^{-4}$, whence the temperature coefficient is 2·99 per 10° and E_A = 19,900 cals. An experiment at 35° with M/100-hexachloroethane gave initial $k_{35^\circ} = 610 \times 10^{-4}$.

That the viscosity of the reaction liquid (c = 0·2034, d = 0·0873) does not alter markedly was shown by measuring the time of flow of 10 c.c. in an Ubbelohde viscometer at 25° : ethyl alcohol (B), which was used as solvent, gave a time of flow of 53·8 secs., whereas during 1155 hours' reaction the times varied only between 76·8 and 75·2 secs.

In an experiment to show that resin formation is responsible for the variation in the values of k, 10 c.c. of aqueous sodium hydroxide were added to 90 c.c. of ethyl alcohol (B) and acetaldehyde, and the mixture was left at 25° for 14 days. Then hexachloroethane was dissolved in the almost black liquid, and 10 c.c. were immediately titrated against N/10-hydrochloric acid : this value is the titre at t = 0. The results are given below :

Experiment 3.

c = 0·1791; d = 0·0868; acetaldehyde = M/10; temp. = 25°.

t.	Titre.	$k \times 10^4$.	t.	Titre.	$k \times 10^4$.	t.	Titre.	$k \times 10^4$.
0	17·91	—	336	16·09	37	1026	13·86	36
20·5	17·64	41	476	15·57	37	2175	9·66	47
165	16·97	41	671	14·99	33			

At the end of the experiment the liquid had become orange-red.

In experiment 1 it may be taken that the concentration of aldehyde which has formed resin is 0·0382 g.-mol./l. at t = 663, and in experiment 3 the corresponding concentration is 0·1000 g.-mol./l. at t = 0. The ratio of these concentrations, *viz.*, 0·382, is very close to the inverse ratio of the corresponding values of k, *viz.*, 106 : 41 = 1 : 0·387. There is not such close agreement between the results of experiments 2 and 3, but it appears that k is approximately inversely proportional to the concentration of aldehyde which has formed resin.

Tetrabromoethylene. Two experiments in ethyl alcohol (C) are detailed. In experiment 4 pentabromoethane was used, and in 5, tetrabromoethylene.

Experiment 4.

c = 0·2907 − 0·0930 = 0·1977;
d = 0·0930; $c - 2d$ = + 0·0117.

t.	Titre.	$k \times 10^5$.	t.	Titre.	$k \times 10^5$.
0	19·77	—	505	17·56	276
67	19·44	357	963	16·17	253
117·5	19·08	373	1411	14·81	263
170	18·95	305	2016	12·46	322
336·5	18·42	249	2492	11·05	328

Experiment 5.

c = 0·2072; d = 0·0906;
$c - 2d$ = + 0·0260.

t.	Titre.	$k \times 10^5$.	t.	Titre.	$k \times 10^5$.
0	20·72	—	505	19·07	309
67·5	20·56	291	1081	18·18	252
115·5	20·22	376	1411	17·21	275
167	20·15	312	2016	14·95	358
337	19·52	318	2492	13·42	408

Initial $k_{C_2Br_4}$ at 25° = 374×10^{-5}.

In each experiment the colour became pale yellow after about 500 hours and then persisted.

Tetrachloroethylene. In an experiment with tetrachloroethylene at 25°, using ethyl alcohol (B), with c = 0·2371, d = 0·1786, the values of $k \times 10^5$ at t = 883, 1368, and 2687 hrs. were 14, 14, and 11 respectively.

Hexabromoethane. Experiments were confined to M/100- or M/200-concentrations owing to the very low solubility in ethyl alcohol. Preliminary experiments with ethyl alcohol (A) revealed a rapid initial displacement of bromine, followed by a comparatively slow displacement, and large drifts were found in the values of k by whatever method they were calculated. The following experiment is typical :

c = 0·01938; d = 0·00685; temp. = 25°.

t, mins.	0	3	7	11	16
Titre, c.c. N/100	19·38	15·72	15·47	15·29	15·10

A solution of hexabromoethane (0·5 g.) and acetaldehyde (0·1 g.) in 100 c.c. of ethyl alcohol (A) was prepared, and 10 c.c. were added to water (50 c.c.), the resulting suspension being titrated with N/100-sodium hydroxide. There was no trace of acidity, showing that hexabromoethane and acetaldehyde do not react in neutral solution.

Standard ethyl-alcoholic (D) solutions of acetaldehyde, prepared by distilling paraldehyde from phosphoric acid (d 1·75), were made, and measured volumes of them were used in determining the effect of acetaldehyde on ethyl-alcoholic (D) solutions of hexabromoethane and sodium hydroxide. In the following experiments at 25° the initial titres were found from alcohol (D)–sodium hydroxide solutions containing the same concentration of acetaldehyde as in the hexabromoethane liquid. (In the following six experiments, t is given in mins., and titres in c.c. of $N/100$.)

$[\mathrm{C_2Br_6}] = 0{\cdot}004786$; $[\mathrm{NaOH}] = 0{\cdot}03056$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}00396$.
$t = 1$, titre $= 26{\cdot}51$; $t = 30$, titre $= 26{\cdot}08$.
[NaOH removed instantly] = 0·00405.

$[\mathrm{C_2Br_6}] = 0{\cdot}00648$; $[\mathrm{NaOH}] = 0{\cdot}02718$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}00099$.
$t = 1$, titre $= 26{\cdot}30$.
[NaOH removed instantly] = 0·00088.

It is clear that the sodium hydroxide consumed instantly is equal to the concentration of acetaldehyde when hexabromoethane is present in excess. The two following experiments similarly show that the converse is also true :

$[\mathrm{C_2Br_6}] = 0{\cdot}00531$; $[\mathrm{NaOH}] = 0{\cdot}03056$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}03962$.
$t = 1$, titre $= 25{\cdot}17$; $t = 30$, titre $= 24{\cdot}00$.
[NaOH removed instantly] = 0·00539.

$[\mathrm{C_2Br_6}] = 0{\cdot}00382$; $[\mathrm{NaOH}] = 0{\cdot}03056$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}03962$.
$t = 1$, titre $= 26{\cdot}59$.
[NaOH removed instantly] = 0·00397.

Hence in the rapid initial reaction equimolecular proportions of hexabromoethane, acetaldehyde, and sodium hydroxide react. For purposes of comparison, experiments were performed with hexachloroethane at 25° in ethyl alcohol (D) : reaction of alkali is only very slight.

$[\mathrm{C_2Cl_6}] = 0{\cdot}00640$; $[\mathrm{NaOH}] = 0{\cdot}03056$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}03962$.
$t = 2$, titre $= 30{\cdot}46$.

$[\mathrm{C_2Cl_6}] = 0{\cdot}07666$; $[\mathrm{NaOH}] = 0{\cdot}1993$; $[\mathrm{CH_3{\cdot}CHO}] = 0{\cdot}1248$.
$t = 1$, titre $= 19{\cdot}83$.

Details of two experiments with hexabromoethane at 25° in ethyl alcohol (E) are given below.

$c = 0{\cdot}00784$; $d = 0{\cdot}00565$; $c - 2d = -\,0{\cdot}00346$.

$c = 0{\cdot}02092$; $d = 0{\cdot}00401$; $c - 2d = +\,0{\cdot}01290$.

t.	Titre, c.c. $N/100$.	$100\,k$.	t.	Titre, c.c. $N/100$.	$100\,k$.	t.	Titre. c.c. $N/100$.	$100\,k$.	t.	Titre, c.c. $N/100$.	$100\,k$.
0	7·82	—	166·83	2·28	193	0	20·92	—	166·6	13·69	177
1·07	7·54	—	214·5	1·76	194	1·33	20·31	—	214·18	13·21	204
22·97	6·41	163	286·5	1·23	196	22·73	18·43	168	286·25	12·99	211
46·8	5·29	168	334	0·86	216	46·52	16·84	164	333·5	12·79	—
113·75	3·41	181				113·67	14·53	168			

Initial k_{25° (by extrapolation to $t = 0$) $= 1{\cdot}60$ g.-mol./l./hr.

The means of two experiments each at 35° and 60° gave initial values : $k_{35^\circ} = 4{\cdot}65$ and $k_{60^\circ} = 63{\cdot}0$, whence the temperature coefficient is 2·89 per 10° and $E_\mathrm{A} = 19{,}300$ calories. The true velocity coefficient (see p. 2005) at 25° is $\frac{2}{3} \times 160 \times 10^{-2}$, *i.e.*, 107×10^{-2}.

Products of the Reaction of Hexachloroethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—Hexachloroethane (2·4 g.) and $2N$-aqueous sodium hydroxide (10 c.c.) were dissolved in ethyl alcohol (A) (90 c.c.) and the solution kept at 35° for a week. The aqueous residue after distillation was homogeneous. The distillate was added to 1 l. of water, and the resulting emulsion settled over-night to an almost colourless oil and traces of a white solid. The oil was washed, dissolved in ether, dried (calcium chloride), the ether removed, and the liquid distilled. Crystals of hexachloroethane sublimed in the side-tube of the distilling flask, and nearly 1 c.c. of a colourless oil was collected. On redistillation the oil boiled at 121°/760 mm. (Herz and Rathmann, *loc. cit.*, give b. p. 118·5°/751 mm. for tetrachloroethylene).

Products of the Reaction of Hexabromoethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—(*a*) To hexabromoethane (2·5 g.), dissolved in ethyl alcohol (A) (500 c.c.), 5 c.c. of $2N$-aqueous sodium hydroxide (equivalent to the displacement of two bromine atoms) were added, and the liquid was left for 3 days at room temperature. It was then poured into 1 l. of water, and the precipitate was filtered off, washed, and dried; yield, 1·5 g. (calc. for $\mathrm{C_2Br_4}$, 1·8 g.); m. p. 55°; mixed m. p. with tetrabromoethylene 55°, with pentabromoethane 19—22°; mixed m. p. of tetrabromoethylene with pentabromoethane 19—22°. (*b*) The same method as above was used with only 2·5 c.c. of alkali; yield, 1·0 g. A m. p. determination with about 5 mm. in depth of the solid gave, at 53°, partial fusion to a clear liquid and a line of solid at the bottom, some solid also remaining on the sides of the tube above the liquid level; at 190—200° this solid decomposed with production of bromine vapour. A similar determination with a mixture of tetrabromoethylene and hexabromoethane gave similar results. A mixture of some of the solid with tetrabromoethylene gave initial m. p. 55°, and with pentabromoethane initial m. p. 20°.

Products of the Reaction of Acetaldehyde and Hexabromoethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—Acetaldehyde (0·22 g.) was dissolved in ethyl alcohol (A) (200 c.c.) and shaken with hexabromoethane (2·5 g.) and 5 c.c. of 2*N*-aqueous sodium hydroxide at room temperature. The hexabromoethane disappeared within an hour. The liquid was distilled on the water-bath, and the distillate gave a white precipitate of tetrabromoethylene (m. p. tests) when diluted with water. The semi-solid residue in the flask was distilled in an oil-bath and a mere trace of neutral liquid with a peculiar odour and of b. p. 80—105°/760 mm. was collected (Fischer and Landsteiner, *Ber.*, 1892, **25**, 2551, give b. p. 80—105°/760 mm. for bromoacetaldehyde). The dry solid remaining after distillation was extracted with water, and the aqueous solution again evaporated to dryness; a neutral, white, slightly hygroscopic solid was obtained (Found, by titration with $AgNO_3$: Br, 60·4. Calc. for NaBr, 77·6%. Calc. for NaBr + $CH_2Br{\cdot}CO_2Na$, 60·7%). Sodium acetate was absent (cacodyl test). When a neutral ferric chloride solution was added to a solution of the solid, there was immediately formed a buff-coloured precipitate, together with a deeply-coloured liquid, which, on being heated, evolved vapours with an odour somewhat resembling that of acetic acid. Sodium bromoacetate responded in an identical manner to these tests.

We are indebted to the Chemical Society for a grant.

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