CCLXXV.—*Investigations on the Bivalency of Carbon. Part IV. Halogen Displacements from* s-*Tetrabromo- and -chloro-ethane and Tri-bromo- and -chloro-ethylene.*

By Allan Miles Ward.

The collected evidence in previous parts of this series (J., 1927, 2285; 1929, 1541; this vol., p. 535) shows that mechanisms involving bivalent carbon are untenable for halogen displacements from systems CR_1R_2HX. It becomes of interest to examine halogenated ethylenes similarly, to determine if substituted acetylidenes or acetylenes are formed. Lawrie (*Amer. Chem. J.*, 1906, **36**, 487), continuing the work of Nef (*Annalen*, 1897, **298**, 332; 1899, **308**, 264), considered that tribromoethylene by reaction with alcoholic potash yielded dibromoacetylidene, $CBr_2{:}CHBr \longrightarrow HBr + CBr_2{:}C$ (see also Demole, *Ber.*, 1878, **11**, 1310). If this be correct, kinetic experiments might show the displacement to be a unimolecular reaction in ethyl-alcoholic solution, both alone and in the presence of hydroxyl or ethoxyl ions. The experiments now to be described demonstrate, however, that this is not the case, for there is no reaction in ethyl alcohol at 15·0° and 25·0°, but a rapid displacement takes place in the presence of sodium hydroxide or ethoxide, the reactions being bimolecular. The final titrations were somewhat greater than those required for the displacement of one bromine atom. This is probably due to the ease of oxidation of the products of reaction or of the tribromoethylene, for this substance with atmospheric oxygen yields dibromoacetyl bromide (Demole, *Ber.*, 1878, **11**, 315).

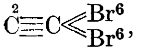
In view of the instability of tribromoethylene, experiments were carried out on tetrabromoethane. It is possible that halogen displacement from tetrabromoethane might proceed thus: $CHBr_2{\cdot}CHBr_2 \longrightarrow HBr + CHBr_2{\cdot}CBr{<}$, with subsequent rearrangements of this phase to give tribromoethylene. No bromine displacement takes place, however, from tetrabromoethane in ethyl-alcoholic solution at 15·0° and at 25·0°, but one bromine atom is displaced instantaneously at these temperatures in the presence of sodium hydroxide or ethoxide, tribromoethylene being formed. The same velocity coefficients should therefore be obtained by using tetrabromoethane and tribromoethylene; this was the case, but agreement between the observed and the calculated final titrations was better in the tetrabromoethane experiments, probably because a purer specimen of tribromoethylene resulted for the subsequent reaction.

Corresponding experiments were made on *s*-tetrachloroethane and trichloroethylene; the latter is much more stable than tribromoethylene and can be kept without undergoing decomposition. No reaction took place between these substances and ethyl alcohol at 15·0° and 25·0°. One chlorine atom was displaced instantaneously from *s*-tetrachloroethane by sodium hydroxide or ethoxide in ethyl-alcoholic solution at these temperatures, but further displacement was very slow. The extreme slowness of the reactions was confirmed with trichloroethylene, and kinetic experiments therefore were not carried out.

Although the kinetic results are not in accordance with the simple mechanism put forward by Nef and Lawrie, it is still possible that the reaction might at least pass through a phase involving bivalent carbon, if an intermediate stage as follows be assumed in their mechanism :

$$\mathrm{CBr_2{:}CHBr} + \overset{\ominus}{\mathrm{OH}} \longrightarrow \mathrm{H_2O} + \mathrm{CBr_2{:}C}\overset{\ominus}{\mathrm{Br}} \longrightarrow \mathrm{CBr_2{:}C} + \overset{\ominus}{\mathrm{Br}}$$

The first stage would presumably be slow, and the dibromoacetylidene formed might polymerise. Possibly Nef and Lawrie visualised such an intermediate step in the mechanism they proposed. Alternatively, the kinetic results would agree with intermediate compound formation taking place between tribromoethylene and hydroxyl or ethoxyl ions, possibly, for example, through phases containing singlet linkages (Robinson, *Chem. and Ind.*, 1925, **44**, 457; Ingold and Ingold, J., 1926, 1314; Sugden, J., 1927, 1182). Addition might occur at either carbon atom, and the elimination of bromide ion, with simultaneous transformation of the singlets by which the hydroxyl or ethoxyl was attached to nonpolar bonds, would yield compounds from which the removal of water or ethyl alcohol would give the brominated acetylene. According to the carbon atom at which addition took place, either dibromoacetylene or dibromoacetylidene would result. The kinetic results alone cannot therefore provide the necessary evidence for a decision to be made between these formulæ.

The formulation for dibromoacetylidene,  $\overset{2}{\mathrm{C}}≣\mathrm{C}\lll^{\mathrm{Br}^6}_{\mathrm{Br}^6}$, using the notation proposed by Main Smith (see J., 1927, 1174), involves electronic groups which are not met with in other carbon compounds. The results of Hammick, New, Sidgwick, and Sutton (this vol., p. 1876) show that carbon in carbon monoxide has a lone pair of electrons, as in the formula above, but no evidence appears to exist for carbon in combination having other than a completed octet. Physical measurements analogous to those of Sidgwick and his collaborators on carbon monoxide and the *iso*nitriles should decide definitely between this formula for dibromoacetylidene and that for dibromoacetylene, which would be formulated $\mathrm{Br^6{=}C\overset{\equiv}{\equiv}C{=}Br^6}$.

EXPERIMENTAL.

Preparation of Materials.—The *s*-tetrabromoethane, *s*-tetrachloroethane, and trichloroethylene were materials of constant boiling points distilled from commercial products. Tribromoethylene was prepared from tetrabromoethane by reaction with dry ammonia in alcoholic solution (Elbs and Newmann, *J. pr. Chem.*, 1898, **58**, 245). It was also made by adding aqueous sodium hydroxide (2*N* approx.) to a solution of tetrabromoethane (200 g.) in methylated spirit (500 c.c.) containing phenolphthalein, until the solution was pink: this was then made faintly acid with hydrochloric acid, about a litre of cold water was added, and the oil separated from the aqueous-alcoholic emulsion. The crude product (130 g.) was dried over calcium chloride and fractionally distilled; the main portion was redistilled and yielded tribromoethylene (75 g.), b. p. 166—167°/763 mm. A further 15 g. of pure tribromoethylene was obtained from the aqueous emulsion by extraction with light petroleum. Tribromoethylene decomposes on keeping, and then fumes strongly. It was therefore redistilled immediately before use.

Ethyl alcohol was dried by refluxing and distilling it over lime and then over aluminium amalgam. The second distillation was made in an atmosphere of nitrogen, and the solvent was stored in contact with this gas. Ethyl-alcoholic solutions of sodium hydroxide or ethoxide were prepared from this solvent, and stored in contact with an atmosphere of nitrogen.

Apparatus.—The apparatus previously described (Ward, J., 1929, 1546) was used and all the experiments were carried out in an atmosphere of nitrogen. The ethyl alcohol or ethyl-alcoholic sodium hydroxide or ethoxide (100 c.c. in each case) was placed in A, and the halogen compound of known weight was contained in B. In these experiments, B was a test-tube cut off to give a vessel of about 4 c.c. capacity.

Halogen Compounds and Ethyl Alcohol.—Tetrabromoethane (*M*/10 approx.) was added to ethyl alcohol in the above apparatus at 15·0°

and also at 25·0°, and samples (10 c.c.) were titrated at intervals against $N/10$-sodium hydroxide and phenolphthalein. The titration results corresponded with an immediate displacement of one bromine atom and the successive titres did not then change. It would thus appear that one bromine atom is displaced instantaneously by ethyl alcohol. This is incorrect, however, for the change is only due to the instantaneous reaction with the caustic soda added in the titration, as shown by the fact that if the solution was added to some 150 c.c. of water containing phenolphthalein to which $N/10$-sodium hydroxide had been added in just sufficient amount to give a permanent pink coloration, the colour persisted for a few minutes. It faded slowly, however; one or two drops of the caustic soda solution restored it, but fading again took place. Samples were withdrawn during periods up to 144 hours, and the titration results showed no change. The alcoholic solution of tetrabromoethane formed an emulsion when poured into water, and the fading is no doubt due to the heterogeneous reaction between the tetrabromoethane and sodium hydroxide.

Titration of alcoholic tetrachloroethane with sodium hydroxide gave similar results. The ease of displacement of one halogen atom from these substances has been recorded previously by Gowing-Scopes (*Analyst*, 1914, **39**, 385). Similar experiments to those with tetrabromoethane in which samples of tetrachloroethane were added to very dilute sodium hydroxide solution as above did not cause the colour of the indicator to fade; an emulsion was not formed in this case. With tribromoethylene the solution was distinctly acid; when this acidity was neutralised, the colour faded from the very dilute caustic soda solution; the titres were unchanged with time. Trichloroethylene in ethyl alcohol, added to 150 c.c. of water, behaved as did tetrachloroethane.

Kinetic Experiments on Tribromoethylene.—Preliminary experiments in which the alcoholic solutions of tribromoethylene and sodium hydroxide or sodium ethoxide were titrated with aqueous hydrochloric acid gave results which were irregular and in excess of those required for the displacement of one bromine atom. Hydrochloric acid was therefore prepared from oxygen-free water in an atmosphere of nitrogen; it was stored and transferred to the burette in contact with this gas. The solution added from the pipette (Ward, J., 1929, 1546) was titrated in an atmosphere of nitrogen against this acid. The final titrations obtained in this way were generally in moderate agreement with those required for the displacement of one bromine atom. Several of the results summarised on pp. 2147, 2148 were obtained by this method.

The resulting aqueous-alcoholic solution reacted very readily with oxygen, for, if after the final titration air was drawn through the solution for a minute or two, the acid formed required some 10 c.c. of $N/10$-sodium hydroxide for its neutralisation. The use of a standard solution of benzoic acid in methylated spirit overcame this difficulty. The reactants (10 c.c.) were transferred to a flask containing somewhat less than the required amount of benzoic acid and titrated with the same acid and phenolphthalein. Oxygen had no effect, for if air freed from carbon dioxide were passed through the solution after titration the colour of the indicator persisted. The results, by this method, of a typical experiment at 25·0° are given below : t is expressed in minutes, and the titre $(b - x)$ in c.c. of $N/10$ strength per 10 c.c. of solution. The velocity coefficients are calculated for a bimolecular reaction, $k = 2{\cdot}3/t(a - b) \,.\, \log_{10} b(a - x)/a(b - x)$.

The initial amounts of tribromoethylene (a) and sodium hydroxide (b) are calculated in terms of $N/10$ strength per 10 c.c. of solution; the titre ($t = 0$) is the theoretical value, based on the amount of sodium hydroxide added.

Tribromoethylene, 0·0986 g.-mol./l.; sodium hydroxide, 0·2416 g.-mol./l.

t.	Titre $(b - x)$.	$k \times 10^5$.	t.	Titre $(b - x)$.	$k \times 10^5$.
0	24·16	—	24	18·31	182
1	23·16	404	38	17·05	171
6	21·68	211	68	15·52	169
11	20·41	196	407	14·16	—
17	19·38	182	1272	13·65	—

The complete results on tribromoethylene at 25·0° are summarised below, the amounts of reactants being expressed in g.-mol./l., and k calculated as above.

C_2HBr_3	0·0988	0·1017	0·1051	0·0986	0·0955
NaOH	—	—	0·1192	0·2416	0·2407
NaOEt	0·2951	0·1710	—	—	—
$k \times 10^5$	183	193	186	185	182

Two experiments at 15·0° gave the following results :

C_2HBr_3,	0·0890 g.-mol./l.	NaOEt,	0·2543 g.-mol./l.	k, 0·000414.
,,	0·0716 ,,	NaOH,	0·2122 ,,	k, 0·000403.

The velocity coefficients are thus identical, as far as can be judged from these results, whether sodium hydroxide or ethoxide is used. The temperature coefficient of the reaction velocity per 10° over the range 15·0° to 25·0° is 4·51.

Kinetic Experiments on s-*Tetrabromoethane*.—The method was as in the experiments with tribromoethylene. Below is a typical set of results at 15·0°.

Tetrabromoethane, 0·0560 g.-mol./l.; sodium hydroxide, 0·2195 g.-mol./l.

t.	Titre $(b - x)$.	$k \times 10^6$.	t.	Titre $(b - x)$.	$k \times 10^6$.
0	16·35	—	128	13·19	447
1	16·01	—	207	12·57	385
20	15·42	573	312	11·82	396
40	14·88	488	412	11·39	409
73	14·11	462	1392	10·72	—

The value of b ($t = 0$) is calculated on the assumption that one atom of bromine is displaced instantaneously; the observed value at $t = 1$ corresponds with a further partial displacement of a second bromine atom; k is calculated as in the series of experiments with tribromoethylene. The complete results are summarised below.

Temp. 25·0°.

$C_2H_2Br_4$	0·0822	0·0724	0·0576	0·0696	0·0623	0·0740
NaOH	0·2529	0·2529	0·1192	—	—	—
NaOEt	—	—	—	0·2414	0·1367	0·1716
$k \times 10^5$	193	189	196	191	207	191

Temp. 15·0°.

$C_2H_2Br_4$	0·0560	0·0661	0·0570	0·0521	0·0637	0·0634
NaOH	0·2195	0·2521	0·2241	—	—	—
NaOEt	—	—	—	0·2423	0·2129	0·2112
$k \times 10^6$	432	414	462	446	444	430

The temperature coefficient per 10°, calculated from the mean of these results, is 4·44.

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