# 361. *The Kinetics of the Interactions of Sodium Hydroxide with the Bromoethanes in Ethyl-alcoholic Solution. The Mechanism of Olefin Formation in Such Systems.*

By William Taylor.

Hughes and Ingold (this vol., p. 246) have discussed the two types of mechanism—$S_N1$ and $S_N2$—for substitution of the nucleophilic hydroxyl ion at a saturated carbon atom. An entirely distinct mechanism (see p. 1516) is now brought forward to explain olefin formation when hydroxyl ion reacts with bromo- (and other halogeno-) ethanes.

The present paper describes an examination of the kinetics of the elimination of bromine by ethyl-alcoholic sodium hydroxide from those members of the bromoethane series not already studied. Grant and Hinshelwood (J., 1933, 258) worked with ethyl bromide, Ward (J., 1930, 2143) with *s.*-tetrabromoethane, and Taylor and Ward (J., 1934, 2003) with penta- and hexa-bromoethanes. The results obtained (see Table I) indicate that the work of Petrenko-Kritschenko (*Ber.*, 1928, **61**, 845), who kept *N*/20-solutions of compounds 1, 2, 4, 7, 8, and 9 at 60° with ethyl-alcoholic (95%) *N*/20-potassium hydroxide for 30 mins., was superficial.

In no case is bromine eliminated in the presence of ethyl alcohol alone, *i.e.*, mechanism of type $S_N1$ does not operate at all in this series. Where the reaction between any of these compounds and caustic alkali proceeds with measurable speed, it is bimolecular for any one run, but the coefficients so obtained vary in different experiments according to the conditions (see p. 1518). Certain considerations (p. 1518) suggest that the reaction takes place essentially between the hydroxyl (or ethoxyl) ion and the bromoethane.

*Mechanism of Olefin Formation.*—Olefinic compounds are formed to the exclusion of hydroxy-compounds with pentabromoethane, *s.*- and *as.*-tetrabromoethanes, ααβ-tribromoethane, and with ethylene dibromide to the extent of 79·5% (see Table II, which shows the reactions that occur with the six compounds investigated in the present work). Except the last, these five elimination reactions are immeasurably fast, and all can be classified as "rapid" (see Table I). Substitution of bromine by hydroxyl occurs, to the almost complete exclusion of olefin formation, with the remaining four compounds (although with hexabromoethane the hydroxy-compound presumed to be first formed decomposes to the olefinic tetrabromoethylene in a secondary change; Taylor and Ward, *loc. cit.*); these four reactions can be classified as "slow." In Table I values of *k* are expressed in g.-mols./

l./min.; $k_1$ and $k_2$ refer respectively to the elimination of the first and second bromine atoms.

TABLE I.

| Compound. | $k_1$. | $k_2$. | % Changed.* |
|---|---|---|---|
| | *Olefin Formation. Class R* (= *Rapid*). | | |
| 8. Pentabromoethane | Inst. (25°) | $k_{25^\circ} = 6\cdot2 \times 10^{-5}$ | 19·0 |
| 7. *s.*-Tetrabromoethane | Inst. (25°) | $k_{25^\circ} = 1\cdot86 \times 10^{-1}$ | 73·1 |
| 6. *as.*-Tetrabromoethane | Inst. (25°) | $k_{25^\circ} = 1\cdot86 \times 10^{-1}$ | — |
| 4. $\alpha\alpha\beta$-Tribromoethane | Inst. (25°) | $k_{55^\circ} = 2\cdot34 \times 10^{-2}$ | 37·1 |
| 2. Ethylene dibromide | $k_{55^\circ} = 1\cdot42$<br>$k_{25^\circ} = 4\cdot34 \times 10^{-2}$ | $k_{55^\circ} = 1\cdot58 \times 10^{-3}$ | 46 |
| | *Hydroxyl Substitution. Class S* (= *Slow*). | | |
| 9. Hexabromoethane | $k_{25^\circ} = 4\cdot57 \times 10^{-2}$ | $k_{25^\circ} = 4\cdot57 \times 10^{-2}$ | 27·2 |
| 5. $\alpha\alpha\alpha$-Tribromoethane | $k_{55^\circ} = 16\cdot6$ | $k_{55^\circ} = 0\cdot886$ | — |
| 3. Ethylidene bromide | $k_{25^\circ} = 1\cdot21 \times 10^{-4}$ | $k_{25^\circ} = 1\cdot21 \times 10^{-4}$ | — |
| 1. Ethyl bromide | $k_{25^\circ} = 3\cdot60 \times 10^{-3}$ | — | 24 |

* From Petrenko-Kritschenko's results.

Grant and Hinshelwood (*loc. cit.*) think it possible that the measured rate of interaction between hydroxyl ion and ethyl bromide "is determined by a single primary reaction between hydroxyl and the halide and that the proportions of alcohol and ethylene depend upon processes subsequent to the initial act: *e.g.*, activated alcohol molecules may be formed, a certain proportion of which decompose into ethylene and water," and later state that this "simple hypothesis gives a coherent interpretation of the results," since these accurately satisfy the Arrhenius equation. We will consider this suggested theory of olefin formation by applying it to the case of another bromoethane, *viz.*, $\alpha\alpha\beta$-tribromoethane; the hydroxyl ion would presumably attack the positive carbon atom and olefin formation would result as follows:

$$OH^{\ominus} + \overset{+}{C}HBr_2\cdot\overset{-}{C}H_2Br \longrightarrow CHBr(OH)\cdot CH_2Br \longrightarrow CHBr\colon CHBr,$$

but actually *as.*-dibromoethylene is formed. Hence, Grant and Hinshelwood's suggestion does not hold for this case. Further, it fails entirely to explain the extreme difference in the rates of reaction ($k_1$ in Table I) for the two pairs of isomeric bromoethanes, 4 and 5, and 2 and 3, since by this theory the first of the two stages in the suggested consecutive mechanism should operate more quickly (*i.e.*, the disappearance of hydroxyl ion should be more rapid) for the more unsymmetrical molecules, whereas actually the converse is found to occur.

TABLE II.

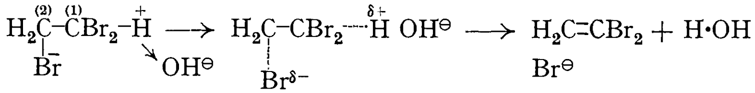
*Products with* EtOH–NaOH.

| Compound. | Olefin formed on displacement of one bromine atom. | Hydroxyl-substitution products. |
|---|---|---|
| 7. $CH_2Br\cdot CBr_3$ | $CHBr\colon CBr_2$ | None found |
| 4. $CH_2Br\cdot CHBr_2$ | $CH_2\colon CBr_2$ | None found |
| 5. $CH_3\cdot CBr_3$ | 2·8% Olefin | $CH_3\cdot CO_2Na$ |
| 3. $CH_3\cdot CHBr_2$ | Very small proportion | $CH_3\cdot CHO$ |
| 2. $CH_2Br\cdot CH_2Br$ | $CH_2\colon CHBr$ (79·5%) | $CH_2(OH)\cdot CH_2\cdot OH$ (18·5%) |
| 1. $CH_3\cdot CH_2Br$ | $CH_2\colon CH_2$ (1·3%) | EtOH |

Scrutiny of the kinetics of the interaction of hydroxyl ion with polybromoethanes reveals that the mechanism of olefin formation is distinct from that of hydroxyl substitution. During the first process 1 equiv. of hydroxyl ion reacts either instantaneously ($k_1$) or very quickly, and then follows a relatively very slow reaction ($k_2$) corresponding to the elimination of a second molecule of hydrogen bromide. During hydroxyl substitution, on the other hand, several equivalents of hydroxyl ion are consumed either simultaneously or consecutively at rates which are of a similar order of magnitude (see Table I). Values of $k_1$ during olefin formation are constant, but those for mechanism $S_N2$ exhibit a drift which is sometimes considerable.

A further difference is seen on comparing the energies of activation (from $k_1$) of the only pair of isomerides—2 and 3—for which this is possible: $E_2 = 22{,}750$ cals., $E_3 = 26{,}340$ cals., which shows that olefin formation takes place more easily than does substitution by hydroxyl.

The theory now brought forward to explain the facts of olefin formation in systems such as those under discussion is that the primary change is the reciprocal attraction between the hydroxyl ion and an initially positively-charged hydrogen atom attached to one of the two carbon atoms [$C_{(1)}$] in the bromoethane molecule. The attraction ends finally in the removal of the hydrogen as a proton to give a molecule of water by union with the hydroxyl ion. This change is essentially gradual, and can only occur if it is accompanied simultaneously by the gradual extrusion of a bromide ion from the other carbon atom [$C_{(2)}$]. Expulsion of bromine will naturally take place from $C_{(2)}$ and not from $C_{(1)}$ because of the proximity of the relatively large negative charge on the hydroxyl ion to the bromine atoms attached to $C_{(1)}$. Olefin formation is thus visualised as being brought about by electronic displacements in the ethane molecule effected by the approach of the hydroxyl ion, the $C_{(1)}$–H link and the $C_{(2)}$–Br link both being gradually and simultaneously extended until, beyond a certain critical point again reached simultaneously by both links, they are ruptured, and water, olefin, and bromide ion result as in the scheme * below, which scheme is similar to that developed by Ingold for olefin formation resulting from the decomposition of quaternary ammonium bases and by Drake and McElvain (*J. Amer. Chem. Soc.*, 1934, **56**, 1810) for the reaction between piperidine and ethyl β-bromopropionate.



$$\mathrm{H_2}\underset{\mathrm{Br}}{\overset{(2)}{\mathrm{C}}}\text{–}\overset{(1)}{\mathrm{C}}\mathrm{Br_2}\text{–}\overset{+}{\mathrm{H}}\ \searrow\mathrm{OH^{\ominus}} \longrightarrow \mathrm{H_2}\underset{\mathrm{Br^{\delta-}}}{\mathrm{C}}\text{–}\mathrm{CBr_2}\cdots\overset{\delta+}{\mathrm{H}}\ \mathrm{OH^{\ominus}} \longrightarrow \mathrm{H_2C{=}CBr_2} + \mathrm{H{\cdot}OH} \quad \mathrm{Br^{\ominus}}$$

It must be emphasised that, according to this theory, complete repulsion by the hydroxyl ion of electrons from the hydrogen atom is only possible if there is an electrophilic atom (or possibly radical) such as a halogen, attached to $C_{(2)}$ to act as a sink for other electrons displaced from $C_{(2)}$ simultaneously with those from the hydrogen atom.

Whether this mechanism will operate to any large extent or not will depend primarily on the magnitude of the positive charge on the hydrogen atom of the $C_{(1)}$–H link, since this will determine whether or not the hydroxyl ion will be attracted to this atom at the expense of any positively-charged carbon atom. Further, it is clear that the rate of olefin formation will depend secondarily and to a large extent on the polarisabilities of the $C_{(1)}$–H, $C_{(1)}$–$C_{(2)}$, and $C_{(2)}$–X links (X = halogen). If the polarisabilities of $C_{(1)}$–H and $C_{(1)}$–$C_{(2)}$ be taken as sensibly constant, then for a given initial positive charge on the hydrogen atom, the rate, and hence the proportion of olefin formation, will be increased with increasing polarisability of the $C_{(2)}$–X link. On this mechanism, then, the rate of olefin formation is proportional to (*a*) the initial positive charge on the hydrogen atom, *i.e.*, the polarisation of $C_{(1)}$–H, and (*b*) the polarisability of $C_{(2)}$–X. Hence, if factor (*b*) is constant, as in the bromoethanes—$C_{(2)}$–Br being the same—then the rate of olefin formation is proportional to factor (*a*) only. This is illustrated by the relative rates of olefin formation from the compounds pentabromoethane (17·3), *s*.-tetrabromoethane (10·8), ααβ-tribromoethane (1·3), and *as*.-tetrabromoethane (0·55), as found by using *s*.-tetrachloroethane as the standard substance in the competitive method (Taylor and Ward, *loc. cit.*). On the other hand, if factor (*a*) is constant, a state of affairs which, in practice, cannot be accurately realised, then the rate of olefin formation is proportional to factor (*b*) alone. This explains the high proportion of olefin formation from aliphatic iodides (see Brussoff, *Z. physikal. Chem.*, 1900, **34**, 129), and also the higher rates of elimination of hydrogen halide from pentabromo- as compared with pentachloro-ethane and from *s*.-tetrabromo- as compared with *s*.-tetrachloro-ethane (Taylor and Ward, *loc. cit.*); the polarisabilities decreasing in the order C–I>C–Br>C–Cl.

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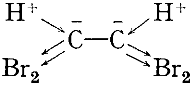
* Any explanatory scheme such as $\mathrm{CH_2Br{\cdot}CHBr_2} + \mathrm{OH'} \longrightarrow \mathrm{CH_2Br{\cdot}CBr_2'} + \mathrm{H{\cdot}OH} \longrightarrow \mathrm{CH_2{:}CBr_2} + \mathrm{Br'}$, is untenable, for otherwise there is no apparent reason why ethylidene bromide should not remove instantaneously one equivalent of OH′.

The proportions of any bromoethane changed either by mechanism $S_N2$ or by the olefin mechanism outlined above will thus depend, not only on the relative intrinsic rates of the two mechanisms, but also on the relative magnitudes of the positive charges on the carbon and hydrogen atoms in the ethane molecule. That the olefin mechanism is intrinsically rapid relative to $S_N2$, as witness the values of $E$ and $k$ for the isomeric dibromoethanes, may be because the hydrogen atom attacked is on the outside of the molecule, whereas the carbon atom which is the seat of the attacks in mechanism $S_N2$ is inside the molecule. Alternatively, the difference may lie in the structural differences of the hydrogen and carbon atoms. If the $C_{(1)}$–$C_{(2)}$ link is highly polarised, as, *e.g.*, in $H_3\overset{-}{C}{\cdot}\overset{+}{C}\rightrightarrows Br_3$, whereas the C–H link is only feebly polarised as in the same molecule, then mechanism $S_N2$ should predominate. This actually occurs, for the proportion of olefin formed from this substance is only 2·8%. If the conditions of the links are reversed as in *s.*-tetrabromoethane,  then olefin formation is dominant. It is significant that with all polybromoethanes containing the group $CHBr_2$, in which C–H is presumably highly polarised, elimination of hydrogen bromide is instantaneous if only there is a bromine atom attached to the adjoining carbon atom to serve as an outlet for the electron displacements initiated by the hydroxyl ion. With ethylidene bromide, which has no such bromine atom, olefin formation by initial attack of the hydrogen atom of the $CHBr_2$ group is impossible (that a small amount of olefin is formed is due to the attack of a hydrogen atom of the methyl group—see below). When there is a $\cdot CH_2Br$ group in the molecule of the bromoethane, *i.e.*, where C–H is still polarised to some extent, olefin formation will again predominate over hydroxyl substitution if the necessary bromine atom is to be found on the adjoining carbon atom, as in the case of ethylene dibromide.* With ethyl bromide, as there is no such bromine atom, the case is analogous to that of ethylidene bromide (above). With *as.*-tetrabromoethane the group $\cdot CBr_3$ presumably increases the polarisation of C–H in the adjoining $\cdot CH_2Br$ group to such an extent that olefin formation is instantaneous, but it is noteworthy that $k_{s.\text{-}C_2H_2Br_4}/k_{as.\text{-}C_2H_2Br_4} = 10{\cdot}8/0{\cdot}55$. Olefin formation is still possible by attack of the hydrogen of the methyl group in a bromoethane, for the C–H link must be polarised to a small extent by the presence of the bromine attached to the adjacent carbon atom, but the probability is that in such a molecule, the $\overset{+}{C}\text{–}\overset{-}{C}$ link being relatively highly polarised, the hydroxyl ion will attack the positive carbon in preference to one of the hydrogen atoms of the methyl group. The proportion of olefin formed should therefore be small, and is actually found to be so.

Facts which this theory explains are the remarkable changes in the nature of the products and the enormous difference in the rates of reaction with the hydroxyl ion brought about by introduction of a bromine atom into the methyl group of ethylidene bromide to give ααβ-tribromoethane, or of ααα-tribromoethane to give *as.*-tetrabromoethane, or by the introduction of a hydrogen atom into the $\cdot CBr_3$ group of hexabromoethane to give pentabromoethane. The theory also indicates for any substituted aliphatic hydrocarbon whether olefin formation or hydroxyl substitution may be expected to predominate.

*The Different Rates of Hydroxyl Substitution in Ethyl Bromide, Ethylidene Bromide, and ααα-Tribromoethane.*—A fact brought to light in measuring the rates of hydroxyl substitution in these three substances is that, although with the increasing positive change of $C_{(2)}$ in this series one would expect a steady fall in the energy of activation and probably a concomitant steady rise in the velocity of substitution, yet this is not found to be the case. In Table III, $k_{25^\circ}$ is expressed in g.-mols./l./min., and $P$ is obtained from the equation $k = PZe^{-E/RT}$. The data show that the value of the velocity constant does depend on $E$. The values of $P$ vary with those of $E$, a correlation similar to that obtained by Hinshelwood

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* That hydroxyl substitution operates to a considerable extent with ethylene dibromide, in spite of there being no initial polarisation of the C–C link, is due to there being an initial positive charge on each carbon atom since each is linked to a bromine atom, this positive charge being of comparable magnitude with that existing initially on each of the hydrogen atoms.

and Legard (this vol., p. 592) for the process of esterification. The rapid reaction is therefore slower, and the slow reaction quicker, than it should be on the simple collision theory.

TABLE III.

| Compound. | *E.* | $k_{25^\circ}$. | *P.* |
|---|---|---|---|
| Ethyl bromide ........................ | 20,460 | $3{\cdot}60 \times 10^{-3}$ | $0{\cdot}5$ |
| Ethylidene bromide .................... | 26,340 | $1{\cdot}21 \times 10^{-4}$ | $3{\cdot}8 \times 10^{2}$ |
| $\alpha\alpha\alpha$-Tribromoethane ................ | 11,670 | $2{\cdot}70$ | $1{\cdot}4 \times 10^{-4}$ |

*Effect of Changing Conditions on the Value of* k.—The value of the velocity constant increases with the dilution of the alkali in all cases where the variation has been investigated; moreover, it is independent of the concentration of the bromoethane where examined (see ethylene dibromide, p. 1522, and ethyl bromide, Grant and Hinshelwood, *loc. cit.*), it decreases on addition of relatively large amounts of sodium bromide (see ethylene dibromide, p. 1522), and is decreased by addition of water (see Tables IV, V, and VI). The approximate agreement in the values of the velocity constant and the energy of activation whether sodium or potassium hydroxide reacts with ethylene dibromide, a similar agreement for ethyl bromide, and the marked similarity in the effect of dilution of these alkalis on the values of the velocity constants for the reactions with these two bromo-compounds, suggest that the reactions take place essentially between the hydroxyl ion and the bromoethane. It is, however, possible that, by alcoholysis, the reagent is ethoxyl ion, although the effect on the value of $k_{s.\text{-}C_2H_4Br_2}$ of dilution of sodium ethoxide (see p. 1522) is different from that of dilution of sodium hydroxide.

The value of the velocity constant is approximately doubled by 100-fold dilution; this is similar to the results obtained for reactions between alkyl iodides and sodium ethoxide (Hecht, Conrad, and Brückner, *Z. physikal. Chem.*, 1889, **4**, 272) and sodium naphthoxides (Cox, J., 1918, **113**, 666; 1920, **117**, 443). Sodium bromide produces only a negligible reduction in the velocity coefficient for ethylene dibromide unless it is present in very high concentration, so the salt formed in the course of the reaction does not measurably affect the values of this coefficient.

*Solvent Effect.*—The retarding effect of water on substitution reactions such as those for ethyl bromide and ethylidene bromide—type $S_N2$—in alcoholic solution has been discussed by Hughes and Ingold (*loc. cit.*). These authors develop a theory of solvent action based on the assumptions that, where electrical charges are present in a given solvent, (i) solvation will increase with the magnitude of the charge, leading to a reduction of the energy of the " critical complex " in excess of the reduction of the energy of the factors, which excess equals the reduction of the energy of activation, and (ii) solvation will decrease with increasing distribution of a given charge, leading to an increase in the energy of activation. They state that : " We have then only to consider the magnitude and distribution of the charges on the ' critical complex ' in relation to those in the factors, in order to deduce the effect of solvation on the energy of activation and the velocity; and, whatever the direction of the effect may be, its magnitude will be greater in strongly solvating (ionising) than in feebly solvating solvents." Evidently a further important assumption not made explicitly by them is that a decrease in the energy of activation results in an increase in the velocity of reaction and *vice versa*. This assumption is admittedly generally true, but unless the retarding or accelerating effect of water additions to such ethyl-alcoholic solutions can be shown to be proportional to the variations in the energy of activation, this " solvating theory " of solvent action obviously cannot be accepted as a true explanation of the facts. Curiously enough, Hughes later (this vol., p. 256) adduces a fact in direct contradiction to the theory as outlined above. He shows, with *tert.*-butyl chloride, where the mechanism of type $S_N1$ operates, " that, although the velocity constant is decreased 40-fold in passing from 50% alcohol to 80% alcohol, and 200-fold in passing from the former medium to 80% acetone, the value of *E* varies but slightly in the examples studied. The variation is almost entirely accounted for in the $\log_e B$ term " of the Arrhenius equation $k = Be^{-E/RT}$. The variation recorded in the values of *E* is from 22,920 cals. (50% alcohol) to 23,060 cals. (80% alcohol). The big changes noted in the values of the velocity constant for this reaction, and brought about by alteration of the water content, cannot then be due to a corresponding variation of $E$, and this example certainly does not support the "solvating theory." The results now recorded for ethyl bromide (Table VI), ethylidene bromide (Table IV), and ethylene dibromide (Table V), although in this last case the mechanism is only partially one of hydroxyl substitution, show that whereas the values of the velocity constants continuously decrease with continued addition of water (but note the exception of ethyl bromide at 25° up to 25% water), yet $E$ falls to a minimum and then increases very gradually.

In calculating values of $E$, it has been assumed that the reaction in any one system is the same whether the alcohol be wet or dry. This assumption would appear to be justified with ethylene dibromide (see p. 1522) and also with the other two compounds for, with these, the proportions of olefin formation in dry alcohol are negligible and ether formation can possibly be discounted. It is further assumed that the reactions satisfy the Arrhenius equation—this is at least justified for ethylene dibromide (see p. 1523). On the basis of the "solvating theory" the values of $E$ should rise continuously with water addition and thus these results also contravert the theory. It would appear that, in outlining their general theory of solvent action, Hughes and Ingold have neglected to consider the factor $P$ in the equation $k = PZe^{-E/RT}$.

## EXPERIMENTAL.

*Preparation of Materials.*—as.-*Tetrabromoethane.* ααβ-Tribromoethane (13 g.), dissolved in methylated spirits (100 c.c.), was rendered barely alkaline to phenolphthalein by $2N$-aqueous sodium hydroxide, excess of which was neutralised by hydrochloric acid, and the liquid was poured into cold water (1 l.). A colourless oil (*as.*-dibromoethylene) settled out immediately. Bromine (3 c.c.) was added to the oil under the water, and instantaneous and vigorous union took place; yield 12 g.; b. p. 105°/15 mm. (Anschütz, *Annalen*, 1883, **221**, 140, gives b. p. 103·5°/13·5 mm.) [Found: Br (Robertson), 92·8. Calc.: Br, 92·5%. Robertson's method (J., 1915, **107**, 902) is much preferable to Stepanow's in estimating bromine in these compounds. Platinised asbestos must be used, and the complete analysis then takes only 1½—2 hrs., instead of more than 20 hrs. required by Stepanow's method. All other bromine estimations were performed in this way unless otherwise stated].

ααβ-*Tribromoethane.* Vinyl bromide (Swarts, *Bull. Acad. roy. Méd. Belg.*, 1901, 383) was passed into bromine covered with water, and the liquid of b. p. 79°/15 mm. collected (Anschütz, *loc. cit.*, p. 138, gives b. p. 73°/11·5 mm.) (Found: Br, 89·4. Calc.: Br, 89·9%).

ααα-*Tribromoethane.* Wallach's method (*Annalen*, 1893, **275**, 146) of preparing the required carbon tetrabromide was cumbersome and the yield low—only 10 g. from 5 c.c. of acetone. It was improved by adding acetone (5 c.c.) in small amounts and with vigorous shaking to bromine (30 c.c.) previously dissolved in approx. $2N$-aqueous sodium hydroxide (1 l.); yield 20 g.; m. p. 92° (Wallach, *loc. cit.*, gives m. p. 92—93°). In dry ether carbon tetrabromide reacted violently with methylmagnesium iodide, giving mainly iodine, but with the corresponding bromide reaction was quieter, affording, however, dibromopropane, b. p. 75°/15 mm. [Found: Br (Robertson), 79·3; Br (Stepanow), 79·2. Calc. for $C_3H_6Br_2$: Br, 79·2%. Calc. for $C_2H_3Br_3$: Br, 89·9%]. The required tribromoethane was prepared by boiling a mixture of carbon tetrabromide (20 g.), methyl iodide (12 g.), and dry ether (100 c.c.) under reflux over thin sodium wire (5 g.; 0·5 mm. diam.) for 60 hrs. The mixture was filtered, and the ether distilled off, a liquid (4 g.) of b. p. 52°/15 mm. being obtained (Found: Br, 90·2. Calc.: Br, 89·9%). Methyl bromide reacted similarly. Methyl acetate (1 c.c.) accelerated the action without increasing the yield. The vapour of ααα-tribromoethane apparently has a peculiar and harmful effect on the sympathetic nervous system.

*Ethylidene bromide.* This was prepared (see also Wibaut, *Rec. trav. chim.*, 1931, **50**, 316) by leaving a mixture of bromine (90 c.c.) and phosphorus trichloride (140 c.c.) over-night, then adding acetaldehyde (130 c.c.) slowly to the well-cooled solid till an almost colourless liquid was obtained. Finely powdered ice (300 c.c.) was added slowly through the condenser, and the pale golden heavy oil which separated was purified in the usual way, affording a colourless liquid, b. p. 26°/15 mm. (Found: Br, 84·7. Calc.: Br, 85·1%). The yield (50 g.) was greatly diminished by an initial distillation at ordinary pressures, which was accompanied by decomposition. Ethylidene bromide is very lachrymatory.

Ethylene dibromide was material of b. p. 130°/760 mm. (Found: Br, 84·9. Calc.: 85·1%). Ethyl bromide was material of constant b. p.

*Kinetic Experiments.*—Since water affected the rate of elimination of bromine from these compounds, the ethyl alcohol used in all kinetic experiments was dried over and then distilled from lime, followed by refluxing and distillation over calcium. In each experiment, to 90 c.c. of a solution of the substance in ethyl alcohol, either anhydrous or containing a known percentage of water, were added 10 c.c. of either alcoholic or aqueous sodium hydroxide. The reaction was stopped by adding 10 c.c. of the liquid to about 50 c.c. of cold, carbon dioxide-free water. The resulting liquid was titrated with standard hydrochloric (phenolphthalein). In all the results given below and recorded subsequently, unless otherwise stated, $a$ and $b$ are the concentrations of sodium hydroxide and bromo-compound respectively in g.-mols./l.; $t$ is the time in mins.; and the velocity constant is calculated for a bimolecular reaction from the equation :

$$k = [2{\cdot}303/t(a - b)] \log_{10} b(a - x)/a(b - x)$$

Titres throughout are expressed as c.c. of $N/10$-solution unless otherwise stated. The value of $a$ was obtained by titrating 10 c.c. of a solution prepared by adding 10 c.c. of the sodium hydroxide used to 90 c.c. of ethyl alcohol (dry or wet).

as.-*Tetrabromoethane.* The following are details of an experiment with this compound in dry alcohol at 25° :

$$a = 0{\cdot}2373;\ b = 0{\cdot}0400;\ a - b = 0{\cdot}1973.$$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $t$ | 0 | 1 | 10 | 20 | 36 | 4800 | |
| Titre | 19·73 | 19·58 | 18·70 | 18·05 | 17·38 | 15·00 | |
| $10^3k$ | — | 193 | 155 | 145 | 134 | — | Mean 157. |

Ward (J., 1930, 2146) has emphasised the difficulties involved in this method of examining the elimination of bromine from tribromoethylene. The present work is not concerned with the elimination of the second bromine atom from the molecule of this tetrabromoethane except in so far as the value of the velocity constant thus found (cf. Ward, who gives $k = 186 \times 10^{-3}$) serves to establish the identity of the tribromoethylene.

αα β-*Tribromoethane.* The bimolecular velocity constant for the rate of elimination of hydrogen bromide from *as.*-dibromoethylene at 55° was $234 \times 10^{-4}$. The competitive method at 20° gives $k_{\alpha\alpha\beta\cdot C_2H_3Br_3}/k_{s.\cdot C_2H_2Cl_4} = 1{\cdot}3$.

ααα-*Tribromoethane.* The kinetic results can best be interpreted by the following scheme :

$$\begin{array}{llrcll}
1 & & CH_3{\cdot}CBr_3 + OH' & = & CH_3{\cdot}CBr_2{\cdot}OH + Br' & \text{(slow)} \\
2 & \text{(a)} & CH_3{\cdot}CBr_2(OH) + OH' & = & CH_3{\cdot}CBr(OH)_2 + Br' & \text{(slow)} \\
 & \text{(b)} & CH_3{\cdot}CBr(OH)_2 & = & CH_3{\cdot}COBr + H_2O & \text{(inst.)} \\
 & \text{(c)} & CH_3{\cdot}COBr + C_2H_5{\cdot}OH & = & CH_3{\cdot}CO_2C_2H_5 + HBr & \text{(inst.)} \\
 & \text{(d)} & HBr + OH' & = & H_2O + Br' & \text{(inst.)} \\
3 & & CH_3{\cdot}CO_2C_2H_5 + OH' & = & CH_3{\cdot}CO{\cdot}O' + C_2H_5{\cdot}OH & \text{(slow)}
\end{array}$$

Stages 2(c), 2(d), and 3 were confirmed. Acetyl bromide of a concentration appropriate for the purposes of this investigation reacted instantly with ethyl alcohol as in 2(c); and even when sodium hydroxide (of a concentration used in the kinetic experiments) was present, the same rapid reaction occurred, but it was then followed by a slow removal of hydroxyl ions, presumably due to hydrolysis of the ethyl acetate. The velocity constants for stages 1 and 3 are calculated from the usual bimolecular equation (see above). In stage 2, two hydroxyl ions are removed for every molecule of tribromoethane originally present, and hence the velocity constant for this stage is calculated from the formula $k = [4{\cdot}605/t(a - 2b)] \log_{10} b(a - x)/b(a - x/2)$ (see Taylor and Ward, *loc. cit.*), where $a$, $b$, and $t$ have the same significance as before (above). Details of two experiments at 55° follow, one showing the full decomposition, and the other the bimolecular nature of stage 1.

*Expt.* 1. $a = 0{\cdot}2508;\ b = 0{\cdot}0450.$

| | $t$. | Titre. | $10^4k$. |
|---|---|---|---|
| Stage 1. | 0 | 25·08 | — |
| | 0·5 | 21·27 | 166,000 |
| Stage 2. | 1·0 | 20·42 | — |
| $t_0 = 1{\cdot}75$ | 2 | 18·58 | 12,310 |
| $a = 0{\cdot}1900$ | 4 | 16·71 | 9,300 |
| $b = 0{\cdot}0371$ | 10 | 14·40 | 8,210 |
| Stage 3. | 70 | 11·56 | — |
| $t_0 = 105{\cdot}6 + 1{\cdot}75$ | 150 | 11·15 | 94·8 |
| $= 107{\cdot}35$ | 287 | 10·65 | 89·4 |
| $a = 0{\cdot}1134$ | 360 | 10·50 | 96·3 |
| $b = 0{\cdot}0426$ | 2865 | 6·68 | — |

*Expt.* 2. $a = 0{\cdot}1705;\ b = 0{\cdot}0249.$

| | $t$. | Titre. | $10^4k$. |
|---|---|---|---|
| Stage 1. | 0 | 17·05 | — |
| | 0·42 | 15·39 | 163,100 |
| | 0·92 | 14·80 | 163,900 |
| | 1·42 | 14·61 | 181,300 |
| Stage 2. | 2·45 | 13·84 | 12,570 |
| $t_0 = 2{\cdot}24$ | 4·92 | 12·66 | 10,140 |
| $a = 0{\cdot}1400$ | 6·75 | 12·26 | 8,500 |
| $b = 0{\cdot}0221$ | | | |

The mean values at 55° are: $k_1 = 16{\cdot}4$, $k_2 = 0{\cdot}886$. Because the three stages represent consecutive reactions, allowance must be made for the concentration of hydroxyl ion removed, *e.g.*, by stage 2 during the time that stage 1 is mainly operative. In Expt. 1, with $k_1 = 16{\cdot}4$, the time for the removal of 1 equiv. of hydroxyl ion by reaction 1 alone is calculated to be 1·75 mins. ($t_0$ for stage 2). By extrapolation from the curve relating titre to time, the concentration of sodium hydroxide at $t = 1{\cdot}75$ is 0·1900, but if stage 1 alone were operating the value at $t = 1{\cdot}75$ would be 0·2058. Hence, it has been assumed that the additional 0·0158 g.-mol./l. of sodium hydroxide has been removed by reaction 2. Therefore at $t = 1{\cdot}75$, $a = 0{\cdot}1900$ and $b = [CH_3{\cdot}CBr_2{\cdot}OH] = 0{\cdot}0371$, and these values have been used in calculating values of $k_2$. The values of $k_1$ at 25° show a very big drift for the first $\frac{1}{2}$ mol. of change, but then become fairly constant (cf. ethyl bromide and ethylidene bromide). This drift is not apparent at 55° because it had finished before the first reading could be taken. The mean value at 25° of $k_1$ is 2·70, from which the temperature coefficient (over 30°) is 6·07 and $E = 11{,}670$ cals. On the basis of the collision theory for chemical activation, $k_{25^\circ}$ (calc.) = 321·5 g.-mols./l./sec., whereas $k_{25^\circ}$ (obs.) = 0·045 g.-mol./l./sec., whence $k$ (obs.)/$k$ (calc.) = $1{\cdot}4 \times 10^{-4}$. The value of $k_3$ for the hydrolysis of ethyl acetate under these conditions is low.

Since the rate of elimination of bromine from this tribromoethane is very rapid but measurable, an attempt was made to use the competitive method to determine the absolute value of the velocity constant for the standard substance *s*.-tetrachloroethane. However, at 20° in ethyl alcohol and in presence of a limited amount of sodium hydroxide, the amount of bromide ion formed is immeasurably small, *i.e.*, chloride-ion formation is exactly equivalent to the amount of sodium hydroxide added.

*Ethylidene bromide.* The kinetic results can best be interpreted by the scheme

$$CH_3{\cdot}CHBr_2 + OH' \longrightarrow CH_3{\cdot}CHBr(OH) + Br' \quad \text{(slow)}$$
$$CH_3{\cdot}CHBr(OH) + OH' \longrightarrow CH_3{\cdot}CHO + H_2O + Br' \quad \text{(inst.)}$$

Values of the velocity constant have been calculated from the modified bimolecular equation (see p. 1520). There follow details of a typical experiment at 55°:

$a = 0{\cdot}2372$; $b = 0{\cdot}0800$; $a - 2b = 0{\cdot}0772$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $t$ | 0 | 310 | 1230 | 1770 | 2790 | 4230 | 5580 | 7080 | 16,140 |
| Titre | 23·72 | 20·56 | 15·89 | 14·64 | 12·98 | 11·30 | 10·40 | 9·60 | 8·07 |
| $10^5k$ | — | 646 | 574 | 509 | 473 | 463 | 447 | 452 | 445 |

The initial values of $k$ at 55° varied with the initial concentration of sodium hydroxide as shown below:

| | | | |
|---|---|---|---|
| [NaOH] | 0·24 | 0·1 | 0·04 |
| $10^5k$ | 682 | 762 | 957 |

Almost identical results were obtained with potassium hydroxide. Variation in the concentration of ethylidene bromide had no effect on the value of $k$.

Table IV shows the effect of adding water to the alcohol, the concentration of sodium hydroxide in all cases being 0·24 ± 0·015 g.-mol./l. To obtain comparable results, curves were drawn relating $k$ to the proportion of ethylidene bromide reacting, and by extrapolation the values of $k$ for 12·5% and 20% reaction of ethylidene bromide were obtained.

TABLE IV.

| $H_2O$, % by vol. | $10^5k$ at 12·5% reaction. | | $10^5k$ at 20% reaction. | | Mean temp. coeff. (for 30°). | $E$ (cals.). |
|---|---|---|---|---|---|---|
| | 55°. | 25°. | 55°. | 25°. | | |
| 0 | 705 | 12·1 | 660 | 11·1 | 58·65 | 26,340 |
| 10 | 504 | 8·68 | 450 | 7·92 | 57·45 | 26,190 |
| 25 | 273 | 5·17 | 255 | 4·67 | 53·70 | 25,770 |
| 50 | 151 | 2·92 | 120 | 2·62 | 50·67 | 25,390 |
| 90 | 116 | — | 100 | — | — | — |

On the collision theory for activation, in dry alcohol, $k_{25^\circ}$ (calc.) = $5{\cdot}36 \times 10^{-9}$ g.-mol./l./sec. Now $k_{25^\circ}$ (obs.) = $2{\cdot}02 \times 10^{-6}$ g.-mol./l./sec., whence $k$ (obs.)/$k$(calc.) = 377.

*Ethylene dibromide.* The much smaller difference between values of $k_1$ and $k_2$ (see Table I) for ethylene dibromide than for other members of Class R is possibly due to the fact that $k_1$ is decreased by the concurrent hydroxyl substitution mechanism whilst $k_2$ is increased by the operation of the same mechanism. The velocity constant is calculated from the usual bimolecular equation (see p. 1520). Details of one experiment, using dry alcohol, at 55° follow:

$a$ = 0·2552; $b$ = 0·0500.

| | *t.* | Titre. | 100*k*. | | *t.* | Titre. | 100*k*. |
|---|---|---|---|---|---|---|---|
| Stage 1. | 0 | 25·52 | — | Stage 2. | 30·0 | 20·50 | — |
| | 2·2 | 22·90 | 140 | $t_0$ = 20·5 | 77 | 20·43 | 0·155 |
| | 4·1 | 21·79 | 144 | $b$ = 0·05 | 1125 | 19·14 | 0·148 |
| | 8·3 | 20·89 | 141 | $a$ = 0·2052 | 2580 | 17·87 | 0·155 |
| | | | | | 5475 | 16·48 | 0·168 |

In calculating values of $k_2$ it has been assumed that there was no elimination of hydroxyl ion by stage 2 until stage 1 was complete, *i.e.*, until $t$ = 20·5, $k_1$ being assumed to be 142 × $10^{-2}$. Values of $k_1$ at any temperature vary with the initial concentration of sodium hydroxide (or ethoxide) and of sodium bromide, but not of ethylene dibromide. Water has a retarding effect. On the other hand, $k$ is remarkably constant in any one experiment, as the following example, using dry alcohol, shows.

$a$ = 0·2072; $b$ = 0·1111; $a - b$ = 0·0961. Temp. 25°.

| *t.* | Titre. | $k \times 10^4$. | *t.* | Titre. | $k \times 10^4$. | *t.* | Titre. | $k \times 10^4$. |
|---|---|---|---|---|---|---|---|---|
| 0 | 20·72 | — | 31·5 | 18·00 | 434 | 101 | 14·83 | 433 |
| 12 | 19·63 | 425 | 51 | 16·98 | 431 | 177 | 12·88 | 439 |
| 21·5 | 18·80 | 448 | 72 | 15·88 | 442 | 280 | 11·64 | 417 |

The magnitude of the effect of varying the initial concentration of sodium hydroxide in dry and wet alcohol is illustrated below :

(i) *In dry ethyl alcohol at* 55°.

| *a.* | *b.* | *k* (mean). | *a.* | *b.* | *k* (mean). | *a.* | *b.* | *k* (mean). |
|---|---|---|---|---|---|---|---|---|
| 0·4425 | 0·0929 | 1·18 | 0·1159 | 0·2500 | 1·61 | 0·0250 | 0·2482 | 2·22 |
| 0·2000 | 0·2234 | 1·46 | 0·1000 | 0·2482 | 1·67 | 0·0125 | 0·2482 | 2·54 |
| 0·1684 | 0·1045 | 1·50 | 0·0500 | 0·2482 | 1·89 | 0·0015 | 0·0100 | 3·07 |

(ii) *In aqueous alcohol* ($H_2O$ = 10% *by vol.*) *at* 55°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0·2089 | 0·1250 | 1·01 | 0·0418 | 0·1250 | 1·39 | 0·00836 | 0·1250 | 1·88 |

The corresponding effect with varying initial concentrations of sodium ethoxide is as below :

*In dry ethyl alcohol at* 55°.

| [NaOEt]. | *b.* | *k* (mean). | [NaOEt]. | *b.* | *k* (mean) |
|---|---|---|---|---|---|
| 0·2104 | 0·0849 | 0·986 | 0·0526 | 0·1250 | 1·77 |
| 0·1052 | 0·1091 | 1·40 | 0·01052 | 0·1250 | 2·82 |

The effect of varying the initial concentration of sodium hydroxide at different temperatures, in dry ethyl alcohol, was as follows :

| Temp. | *a.* | *b.* | *k.* | Temp. | *a.* | *b.* | *k.* |
|---|---|---|---|---|---|---|---|
| 25° | 0·2072 | 0·1110 | 0·0434 | 45° | 0·2370 | 0·1892 | 0·416 |
| | 0·1146 | 0·2328 | 0·0521 | | 0·1320 | 0·1805 | 0·515 |
| 35 | 0·2146 | 0·1115 | 0·138 | 55 | 0·2000 | 0·2234 | 1·46 |
| | 0·1023 | 0·2337 | 0·173 | | 0·1000 | 0·2482 | 1·67 |

As sodium bromide is sparingly soluble in dry ethyl alcohol, the effect of its initial concentration was studied in 90% alcohol (by vol.) at 55°. In each experiment $a$ = 0·1296, $b$ = 0·1146.

| | | | | |
|---|---|---|---|---|
| [NaBr] ............... | 0 | 0·227 | 0·454 | 0·681 |
| *k* ........................ | 1·25 | 1·00 | 0·875 | 0·746 |

That the velocity constant did not vary with different initial concentrations of ethylene dibromide is shown by the following details of experiments in dry ethyl alcohol at 55°.

| *a.* | *b.* | *k.* | *a.* | *b.* | *k.* | *a.* | *b.* | *k.* |
|---|---|---|---|---|---|---|---|---|
| 0·1159 | 0·25 | 1·59 | 0·1159 | 0·05 | 1·62 | 0·1159 | 0·0125 | 1·61 |

Table V shows the retarding effect of water on the rate of diminution of hydroxyl-ion concentration.

An experiment with sodium ethoxide in dry ethyl alcohol at 25° where [NaOEt] = 0·0526, $b$ = 0·125, gave $k_{25^\circ}$ = 0·0520, from which the temperature coefficient (for 30°) is 34·02. Two

TABLE V.

| $H_2O$, % by vol. | *a.* | $k_{55^\circ}$. | *a.* | $k_{25^\circ}$. | Mean temp. coeff. (30°). | *E* (cals.). |
|---|---|---|---|---|---|---|
| 0 | 0·2000 | 1·46 | 0·2072 | 0·0434 | 33·66 | 23,750 |
| 10 | 0·2089 | 1·01 | 0·2378 | 0·0365 | 27·67 | 21,480 |
| 25 | 0·2317 | 0·452 | 0·2356 | 0·0235 | 19·23 | 19,130 |
| 50 | 0·2317 | 0·252 | 0·2419 | 0·0124 | 20·30 | 19,470 |
| 75 | 0·2517 | 0·123 | 0·2351 | 0·00566 | 21·77 | 19,940 |
| 95 | 0·2325 | 0·0637 | 0·2394 | 0·00272 | 23·42 | 20,410 |

experiments with potassium hydroxide in dry ethyl alcohol, details of which follow, give 32·64 for the same coefficient.

| Temp. | [KOH]. | *b.* | *k.* | Temp. | [KOH]. | *b.* | *k.* |
|---|---|---|---|---|---|---|---|
| 55° | 0·1076 | 0·0849 | 1·84 | 25° | 0·1094 | 0·0909 | 0·0565 |

From the value of *E* (see Table V) for the action of sodium hydroxide in dry ethyl alcohol, assuming the collision theory for activation, $k_{25^\circ}$ (calc.) $= 2{\cdot}32 \times 10^{-6}$ g.-mol./l./sec., but $k_{25^\circ}$ (obs.) $= 7{\cdot}22 \times 10^{-4}$ g.-mol./l./sec.; whence $k$(obs.)/$k$(calc.) = 311 (cf. ethylidene bromide).

*Ethyl bromide.* Grant and Hinshelwood (*loc. cit.*) made a detailed study of the kinetics of the reaction of this compound with ethyl-alcoholic potassium hydroxide. The reaction is bimolecular, addition of water up to 10% having only a small effect. The effect of water on the system containing sodium hydroxide is shown in Table VI.

TABLE VI.

| $H_2O$, % by vol. | *a.* | $k_{55^\circ}$. | *a.* | $k_{25^\circ}$. | Mean temp. coeff. (30°). | *E* (cals.). |
|---|---|---|---|---|---|---|
| 0 | 0·2050 | 0·0851 | 0·2130 | 0·00360 | 23·64 | 20,460 |
| 10 | 0·2307 | 0·0780 | 0·2356 | 0·00370 | 21·81 | 19,950 |
| 25 | 0·2317 | 0·0574 | 0·2441 | 0·00355 | 16·17 | 18,010 |
| 50 | 0·2262 | 0·0339 | 0·2479 | 0·00301 | 11·26 | 15,660 |
| 75 | 0·2309 | 0·0200 | 0·2429 | 0·00174 | 11·50 | 15,810 |
| 95 | 0·2325 | 0·0146 | 0·2407 | 0·00121 | 12·10 | 16,130 |

For purposes of comparison two experiments with potassium hydroxide in dry ethyl alcohol were performed, with the results shown :

| Temp. | [KOH]. | *k.* | Temp. | [KOH]. | *k.* |
|---|---|---|---|---|---|
| 55° | 0·1184 | 0·0974 | 25° | 0·1214 | 0·00406 |

These figures give a temperature coefficient (for 30°) of 24·00, and the values of the velocity constant are rather lower than those obtained by Grant and Hinshelwood who, working with *N*/10-solutions, found for 59·75°, 50·12°, and 24·74°, $k$ = 0·1986, 0·0810, and 0·004578 respectively, whence the temperature coefficient (for 30°) is 25·30, and $E$ = 21,000 cals.

*Examination of Reaction Products.*—From the kinetic results (p. 1520), tribromoethylene is formed mainly, if not wholly, from *as.*-tetrabromoethane; similarly, *as.*-dibromoethylene is the principal, if not the sole, product from ααβ-tribromoethane, as shown by addition of bromine, which produced *as.*-tetrabromoethane (p. 1519).

*Estimation of the proportion of olefin formation from the other compounds of this series.* In estimating olefin in these systems, by addition of halogen, there are two main difficulties, *viz.*, the presence of alcohol, which reacts readily with halogen, and the inhibitory effect of the substituent bromine in the olefin compound on the addition of halogen. The method finally adopted was to add a known amount of ethyl-alcoholic sodium hydroxide to a fairly large excess of an alcoholic solution (10 c.c.) of the substance under investigation. This was done to avoid possible acetylene compound formation. The mixture was then maintained at 55° for a longer time than had been found necessary (kinetic experiments) to complete the reaction. Carbon tetrachloride (10 c.c.) was added in such a way that no vapours could be lost, the resulting liquid was washed with water (150 c.c.) to remove alcohol, and the tetrachloride layer run off into a stoppered bottle containing an appropriate amount of Wijs's solution, which gave more consistent results than standard bromine. The remaining aqueous liquid was extracted with two successive amounts of carbon tetrachloride (5 c.c.), which were also run into the Wijs's solution. The bottle was placed in the dark for 7—8 days, water (400 c.c.) added, and the liquid titrated with standard thiosulphate. A blank experiment upon ethyl alcohol alone (10 c.c.) was performed under exactly the same conditions. The percentage of olefin formation is given in Table

II. It is necessary to indicate, however, that if the olefin formed is sufficiently reactive and if there are suitable molecular species present in the system addition may occur. In these circumstances the analytical results obtained by the above procedure will lead to faulty conclusions as to the percentage of olefin formed initially. With bromo-ethylenes as products and in systems such as those obtaining in this investigation, addition is unlikely and the results given in Table II are therefore probably reliable.

The case of ethylidene bromide requires further discussion because almost exactly 50% of olefin is formed, according to this method of examination. By using precisely the same method of extraction of the reaction products as above, but by adding them to potassium bisulphite solution, followed by back-titration with standard iodine, it was found that 1 mol. of acetaldehyde is produced, so the apparent 50% of olefin is really 100% of acetaldehyde. The result shows that the two bromine atoms of ethylidene bromide are eliminated simultaneously, for otherwise the equivalent of acetaldehyde would not be formed under the experimental conditions, *i.e.*, with a large excess of the bromoethane present. This confirms the scheme given on p. 1516. No acetylene could be detected in these experiments (ammoniacal cuprous chloride), although a trace is formed when sodium hydroxide is present in excess.

*Further examination of the reaction products from ααα-tribromoethane and ethylene dibromide.* The reaction liquid from an experiment with ααα-tribromoethane was evaporated to dryness. The hygroscopic solid residue contained sodium acetate (cacodyl oxide test). By titration with silver nitrate, the proportion of sodium bromide was found to be in moderate agreement with that required for the formation of $3NaBr + CH_3\cdot CO_2Na$.

The olefinic product of the reaction with ethylene dibromide was vinyl bromide, as shown in a separate experiment by distillation of the residual alcoholic liquid into bromine-water, ααβ-tribromoethane separating as a heavy oil, b. p. 186°/760 mm. (Found: Br, 90·1. Calc.: 89·9%). Glycol formation was estimated in dry and in wet alcohol by keeping excess sodium hydroxide and a known amount of ethylene dibromide at 55° for sufficient time for the complete destruction of this compound. The volatile substances (acetylene and alcohol) were distilled off, concentrated nitric acid added, and the liquid evaporated on a water-bath to 3—5 c.c. The oxalic acid formed was precipitated as barium oxalate, which was treated with sulphuric acid and titrated with potassium permanganate. The percentage of glycol varied from 18·2 (0% water) to 18·8 (40% water), showing that the reaction in dry and in wet alcohol followed essentially the same course.

## SUMMARY.

1. The kinetics of the interactions of ethyl-alcoholic sodium hydroxide with *as.*-tetrabromoethane, the two tribromoethanes, and the two dibromoethanes have been investigated, completing the series of the nine bromoethanes. The reactions, where of a measurable rate, are bimolecular.

2. A clear distinction between reactions involving hydroxyl substitution of bromine by Ingold's mechanism $S_N2$, and those involving complete or almost complete olefin formation is revealed. In hydroxyl substitution, several bromine atoms are displaced either simultaneously, or else consecutively at rates which are of a similar order of magnitude. In olefin formation, one bromine atom is displaced instantaneously (or almost so) and then a second one relatively very slowly.

3. A mechanism for olefin formation has been outlined involving a primary mutual attraction of hydroxyl ion and an initially positively charged hydrogen atom, followed by simultaneous extension of the $C_{(1)}$–H link and a $C_{(2)}$–Br link, finally resulting in the simultaneous rupture of the two links and the formation of olefin, water, and bromide ion. On the basis of this theory the rate of olefin formation is proportional to (*a*) the initial polarisation of $C_{(1)}$–H and (*b*) the polarisability of $C_{(2)}$–X, where X is an electrophilic atom (or radical).

4. Results showing the retarding effect of addition of water on both types of reaction are given, and the " solvating theory " of solvent action (Hughes and Ingold) is shown to be untenable for reactions of type $S_N2$.

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