70. *The Displacement of Bromine from Mono- and Di-bromoethylbenzenes.*

By William Taylor.

Halogen may be displaced from alkyl halides dissolved in dry or wet alcohol or wet acetone in three ways. Two of these are substitution reactions which have been discussed by Gleave, Hughes, and Ingold (J., 1935, 237), one being apparently unimolecular and the other bimolecular. The third, also bimolecular, consists in the elimination of hydrogen halide, resulting in olefin formation (Olivier, *Rec. trav. chim.*, 1934, **53**, 1093; Hughes, *J. Amer. Chem. Soc.*, 1935, **57**, 708; Taylor, J., 1935, 1514; Hughes, Ingold, and Shapiro, J., 1936, 225; see also *Chem. and Ind.*, 1936, **55**, 275, 312, 383, 422). Recently Hughes, Ingold, and Scott (*Nature*, 1936, **138**, 120) have found that a unimolecular olefin reaction operates in sulphur dioxide, and this constitutes a fourth way by which halogen may be displaced from alkyl halides in solution. It is possible that the thermal dissociation of such compounds (no solvent being present), which commonly results in olefin elimination, resembles the fourth method.

In the present investigation the displacement of bromine from four of the five (side-chain brominated) mono- and di-bromoethylbenzenes in dry and in aqueous ethyl alcohol was studied. The fifth, ββ-dibromoethylbenzene, could not be prepared sufficiently pure for kinetic purposes from phenylacetaldehyde, and one attempt to obtain it from benzylmagnesium bromide and bromoform yielded dibenzyl instead. The results for the four compounds can be briefly stated : (1) the unimolecular olefin reaction was never observed; (2) αα-dibromoethylbenzene underwent the unimolecular substitution reaction only; and (3) the other three compounds suffered bromine displacement by all the first three methods, resembling *iso*propyl bromide in this respect (Hughes, Ingold, and Shapiro, *loc. cit.*). However, except αα-dibromoethylbenzene, only α-bromoethylbenzene displayed any large proportion of the unimolecular displacement. The nature and proportions of the products formed are shown in Table I, and the kinetic details of the two bimolecular processes in Table II.

The values of the first-order velocity coefficient for α-bromoethylbenzene in dry ethyl alcohol, constant over approximately the first 50% of change, then show a downward drift. The alcoholysis of the whole molecule, judged by the acidity of the solution, is never completed, and it might appear that the system is reversible. However, after a relatively long time, there is actually a considerable decrease in the acidity of the solution, and this at least cannot be due to the reversibility of the system. Similar observations on the decrease in acidity are true also for αα-dibromoethylbenzene in dry ethyl alcohol. Ward (J., 1927, 2285) found by a titration method that benzhydryl chloride, dissolved in ethyl alcohol, suffered a unimolecular displacement of chlorine. Norris and Morton (*J. Amer. Chem. Soc.*, 1928, **50**, 1795), using a conductance method, concluded that the reaction was reversible, *i.e.* :

$$CPh_2HCl + EtOH\ (excess) \rightleftharpoons CHPh_2{\cdot}OEt + HCl.$$

It is probable that the apparent reversibility was due to esterification of the dry ethyl alcohol (water greatly retards such esterification; cf. Hinshelwood, J., 1935, 599) by hydrogen halide (see, however, Kny-Jones and Ward, *J. Amer. Chem. Soc.*, 1935, **57**, 2394). That is the explanation now offered for these two systems in which hydrogen bromide is liberated, since it was discovered that the rate of disappearance of hydrogen

TABLE I.

Products from the bimolecular reactions in dry ethyl alcohol, with [KOH or NaOEt] ~ 0·2.

(No olefin was formed in dry alcohol alone, at 55° or 25°.)

Compound.	Olefinic product.	Substitution product.	Olefin, %, at 25°.	55°.
1. Ph·CBr$_2$Me	None	Acetophenone diethylacetal	0	0
2. Ph·CBrH·CH$_2$Br	α-Bromostyrene	β-Bromo-α-phenyldiethyl ether (?)	86·6	86·5 ± 1·4
3. Ph·CBrHMe	Styrene	α-Phenyldiethyl ether	19·3	20·7 ± 0·6
4. Ph·CH$_2$·CH$_2$Br	Styrene	β-Phenyldiethyl ether	91·1	91·9 ± 1·2

TABLE II.

Details of the above bimolecular processes.

[KOH or NaOEt] ~ 0·2; k_2 is expressed as g.-mol./l./sec.; $\sigma_{A,B} = 5 \times 10^{-8}$ cm.

Compound.	Reaction.	*E* (cals.).	$PZ \times 10^{-12}$.	$k_2 \times 10^4$. Obs.	Calc.	*P*.
Ph·CBrH·CH$_2$Br	Both	16,850	10·2	450	84·7	5·3
Ph·CBrH·CH$_3$	Substitution	22,400	1·70	0·618	0·00719	86*
	Olefin	22,600	1·46	0·385	0·00521	74*
Ph·CH$_2$·CH$_2$Br	Substitution	21,600	0·0495	0·185	0·0739	2·5
	Olefin	21,000	1·47	1·90	0·0256	74

* These values are only approximate because of uncertainty regarding the values of *E* (see p. 349).

bromide in initially dry ethyl alcohol was, for all practical purposes, unaffected by the presence of α-phenyldiethyl ether or acetophenone diethylacetal, the "immediate" end-products of the two reactions.

The possibility of a minute but actual reversibility under the given experimental conditions still remains.

Under suitable experimental conditions alcohols and ethers react with hydrogen halides to give alkyl halides, and it has been found (Bennett and Reynolds, J., 1935, **134**, for alcohols and hydrogen bromide; Hinshelwood, *loc. cit.*, for methyl and *tert.*-butyl alcohols and hydrogen chloride; Ghaswalla and Donnan, J., 1936, **1341**, for phenolic ethers and hydrogen halides) that these reactions may be represented as proceeding in two stages: (*a*) the formation of a complex and (*b*) the elimination of R·OH, where R = aryl radical or hydrogen, *i.e.*, $\text{ROAlk} + \text{HX} \longrightarrow \text{ROAlk,HX} \longrightarrow \text{AlkX} + \text{ROH}$. Reverse processes, such as the unimolecular hydrolysis or alcoholysis of alkyl halides, may reasonably be supposed to follow the reverse path and both stages might, under favourable conditions, be "slow." The first stage would be pseudo-unimolecular because of the huge excess of the solvent ROH, and the second would also be unimolecular, so making the whole process kinetically of the first order and the rate proportional to the concentration of the alkyl halide, which coincides with experimental results. Evidence of the formation and decomposition of such a complex in the reverse processes is found in the high values of *P* shown in Table III, where the activation energy (Arrhenius) has been increased by Q' of the equation $-d\log_e\eta/dT = Q'/RT^2$, and the calculated velocity coefficient has been obtained from $k = Be^{-E/RT}$, where $B = 3\pi N\eta\sigma(M_A + M_S)/2M_AM_S$ (Glasstone, "Recent Advances in General Chemistry," 1936, 292). These high values are comparable with those calculated in a similar manner from the observations of von Halban (*Ber.*, 1908, **41**, 2417; *Z. physikal. Chem.*, 1909, **67**, 129), Fletcher and Hinshelwood (J., 1935, 596), and Hinshelwood (*loc. cit.*) on the unimolecular decompositions of phenylbenzylmethylallylammonium bromide, triethylsulphonium bromide, diphenyliodonium bromide, and the presumed methoxonium chloride respectively. In the light of these results, it is probable that the value of $P \sim 1$ for the hydrolysis of substituted benzyl halides in aqueous ethyl alcohol (50%), calculated by Moelwyn-Hughes ("The Kinetics of Reactions in Solution," 1933, p. 161) from the work of Olivier (*Rec. trav. chim.*, 1922, **41**, 301, 646; 1923, **42**, 516, 775), is due to the instability of the complex, so that the second stage is rapid. The increase in the velocity of such unimolecular reactions of alkyl halides brought about by partially substituting water for alcohol as the solvent (see Table III) is in keeping with the mechanism now proposed, since

Bennett and Reynolds, Hinshelwood, and Ghaswalla and Donnan (*locc. cit.*) have noted the retarding effect of water on the direct reaction, and hence this solvent would, on this scheme, be expected to facilitate the reverse reaction. The present intermediate "complex" hypothesis for the unimolecular substitution reaction of alkyl halides is distinct from the "ionisation" mechanism of Gleave, Hughes, and Ingold (*loc. cit.*) since the *direct* intervention of the solvent in the rate-determining stages of the reaction is here postulated.

TABLE III.

Details of the unimolecular process in dry and in aqueous alcohol.

(Q' has been calculated from Intl. Crit. Tables; σ is the geometric mean diameter of the solute molecule; k_1 is expressed as sec.$^{-1}$.)

Compound.	EtOH, % by vol.	Temp.	σ $\times 10^8$, cm.	E, cals.	Q', cals.	E, corr.	PZ $\times 10^{-14}$.	k_1 $\times 10^5$, obs.	k_1 $\times 10^8$, calc.	P $\times 10^3$.
CHBrPhMe	100	25°	6·1	21,640	3,480	25,120	0·185	0·685	1·92	0·357
	80	25	6·1	21,670	4,520	26,190	25·5	15·4	0·552	27·8
CHClPhMe *	80	25	5·9	21,380	4,520	25,900	0·996	1·00 †	0·931	1·07
CHMe$_2$Br ‡	80	50	5·2	23,160	4,320	27,480	0·0561	0·134	1·12	0·120
	60	50	5·2	22,690	4,910	27,600	0·202	0·411	1·24	0·333
CMe$_3$Cl §	80	25	5·9	23,060	4,520	27,580	11·5	0·914	0·0605	15·1
	50	25	5·9	22,920	5,450	28,370	1780	36·6	0·0255	1960
CBr$_2$PhMe	100	25	7·2	22,580	3,480	26,060	7·65	5·68	0·436	13·3
	80	25	7·2	18,620	4,520	23,140	1·96	211	110	1·92
CCl$_2$PhMe	100	25	6·7	24,120	3,480	27,600	9·32	0·525	0·0324	16·2

* From Ward (J., 1927, 445).

‡ From Hughes, Ingold, and Shapiro (*loc. cit.*).

† Value obtained by extrapolation.

§ From Hughes (J., 1935, 255).

EXPERIMENTAL.

Preparation of Materials.—α-Bromoethylbenzene (15 g.) was prepared by the method of Ashworth and Burkhardt (J., 1928, 1791) from styrene (10 g.) and a cold solution of dry hydrogen bromide (27 g.) in glacial acetic acid (50 c.c.); b. p. 105°/30 mm. (Found : Br, 43·5. Calc. : Br, 43·2%). It was also obtained by passing (2 hrs.) dry hydrogen bromide through styrene (18 g.) cooled in carbon dioxide–ether. No trace of purple colour developed (contrast the preparation of αα-dibromoethylbenzene); excess hydrogen bromide was promptly removed by dry carbon dioxide (½ hr.). Distillation gave two fractions : (1) b. p. 104°/26 mm. (3·5 g.), (2) b. p. 94°/14 mm. (28 g.), which was α-bromoethylbenzene. This was hermetically sealed in small glass tubes, for exposure to air soon caused cloudiness. In this preparation all hydrogen bromide must be promptly removed before distillation, for in an experiment in which it was not completely removed, the pressure during distillation was not sufficiently reduced for some 3 hours, during which the temperature was 180°; two fractions of equal bulk were then obtained : (1) b. p. 100—101°/20 mm. (α-bromoethylbenzene); (2) b. p. 185—190°/15 mm., a colourless oil with a blue fluorescence which slowly disappeared. The latter was presumably "liquid distyrene," since Erlenmeyer (*Annalen*, 1865, **135**, 122) obtained it by heating styrene for many hours with hydrochloric acid (*d* 1·12) at 170°, and it had b. p. 310° at ordinary pressure.

β-Bromoethylbenzene, prepared by refluxing β-phenylethyl alcohol with constant-boiling hydrobromic acid, had b. p. 105—106°/18 mm. (Found : Br, 43·0. Calc. : Br, 43·2%).

The preparation of αα-dibromoethylbenzene presented difficulties (see this vol., p. 304). The addition of phenylacetylene (8 g.) to an ice-cold solution of dry hydrogen bromide (27 g.) in glacial acetic acid (50 c.c.) produced after 3 days acetophenone (1·5 g.), styrene dibromide (0·2 g.), and dypnone (4·5 g.) (oxime, m. p. and mixed m. p. 131—133°). When, however, dry hydrogen bromide was passed for 2 hours through phenylacetylene (20 g.) cooled in carbon dioxide–ether, a deep purple colour developed, which disappeared on removal of the excess of hydrogen bromide by dry carbon dioxide, and on distillation three fractions were obtained : (1) b. p. 70—100°/15 mm. (22 g.), (2) b. p. 100—115°/11 mm. (5 g.), (3) b. p. 116—118°/10 mm. (16 g.). Fractions (1) and (2) had the odour of α-bromostyrene. Fraction (3) was the αα-dibromoethylbenzene used in the kinetic experiments (although α-bromostyrene was present as an impurity, this difficulty was immaterial, for the effect of its presence was always examined). It was a pale yellow, fairly pungent-smelling liquid, which fumed slightly in air and became cloudy within 1 minute; therefore it was immediately sealed in glass tubes (Found : Br, 56·4. Calc. : Br, 60·6%). A further amount was obtained by passing dry hydrogen bromide for

1 hour through fraction (1) surrounded by ice-salt, the same procedure as above then being followed. No purple colour developed. Two fractions were collected : (1*a*) b. p. 100—118°/15 mm. (13 g.), (1*b*) b. p. 118—120°/15 mm. (7 g.); (1*b*) contained Br, 60·0% and was similar in properties to (3). The αα-dibromoethylbenzene was identified by keeping a solution of fraction (3) (*ca.* 3 g.) in alcohol (70 c.c.) and water (30 c.c.) at 55° for 16 hours and then refluxing it for 1 hour with semicarbazide hydrochloride (1·5 g.) and sodium acetate (5 g.); acetophenone semicarbazone (1·7 g.) was obtained, m. p. 196° (after recrystallisation from alcohol) and mixed m. p. 196—197°. The b. p. of the liquid precluded it from containing much, if any, styrene dibromide, which, according to Anschütz (*Annalen*, 1886, **235**, 328), has b. p. 139—141°/15 mm., and kinetic experiments showed that none of this isomer was present.

αα-Dichloroethylbenzene was prepared in a similar manner by adding dry hydrogen chloride to phenylacetylene (3 g.); the mixture became purple and finally deep green and a colourless liquid (4·5 g.) was obtained (Found : Cl, 35·6. Calc. : Cl, 40·6%). This liquid, which fumed in air and became cloudy within a few minutes, was hermetically sealed; after a day or so it became bright green and then brown. Its identity was established by the preparation (from 2·5 g.) of acetophenonesemicarbazone (2·2 g.), m. p. 195° after recrystallisation from alcohol.

αβ-Dibromoethylbenzene, obtained by Glaser's method (*Annalen*, 1870, **154**, 154), had m. p. 73°. Acetophenone diethylacetal was prepared by Claisen's method (*Ber.*, 1907, **40**, 3908).

Products of Reactions of α-Bromoethylbenzene.—(a) *With ethyl alcohol.* α-Bromoethylbenzene (4 g.), dissolved in dry ethyl alcohol (100 c.c.), was kept at 55° for 16 hrs. A slight excess of solid potassium carbonate was added to neutralise the liberated hydrogen bromide, the alcohol distilled off, dry ether added, and the potassium bromide filtered off. Only α-phenyldiethyl ether, b. p. 69—71°/13 mm., was obtained (Found : OEt, 29·0. Calc. : OEt, 30·0%). Quantitative analysis of the product for styrene (see p. 347) showed that it was absent.

(b) *With* 80% *ethyl alcohol.* A mixture of alcohol (80 c.c.), water (20 c.c.), and α-bromoethylbenzene (5 g.) was treated as in (a), except that after addition of potassium carbonate (to remove water), the mixture was filtered; on distillation, a colourless liquid (1·6 g.), b. p. 66—88°/10 mm., was obtained. This contained no styrene (bromine did not give styrene dibromide) and from the b. p. range was presumably a mixture of α-phenyldiethyl ether and phenylmethylcarbinol; Ward (J., 1927, 452) found that α-chloroethylbenzene and 80% alcohol at 50° yielded this mixture.

(c) *With alcoholic potash.* A solution of α-bromoethylbenzene (6·5 g.) in dry ethyl alcohol (300 c.c.) and alcoholic potash (30 c.c.; approx. 2*N*) was maintained at 55° for 4 hours. The liquid was added to water (1 l.); this was extracted with ether, from which were obtained two fractions : (1) b. p. 35—74°/15 mm. (1·2 g.), (2) b. p. 74—76°/15 mm. (2·9 g.). Fraction (1) was dissolved in an equal bulk of chloroform, and bromine added drop by drop; styrene dibromide (0·35 g.) was obtained. Fraction (2) was mainly α-phenyldiethyl ether but contained 7·4% of styrene as found by the method on p. 347.

(d) *With alcoholic sodium ethoxide.* A solution of α-bromoethylbenzene (3 g.) in the reagent (50 c.c., approx. *N*), kept at 55° for 17 hours, gave a liquid of b. p. 30—40°/12 mm., which with bromine yielded styrene dibromide and was mainly styrene. In this case the reaction liquid was much more strongly alkaline than in (c).

Products of Reaction of Alcoholic Potash with β-Bromoethylbenzene.—A solution of β-bromoethylbenzene (6 g.) in dry alcohol (300 c.c.) and alcoholic potash (30 c.c.; approx. 2*N*) was maintained at 55° for 20 hours, and then worked up as in (c), above, giving two fractions : (1) b. p. 44—46°/17 mm. (3·0 g.); (2) b. p. 88—90°/15 mm. (0·4 g.). Fraction (1) was styrene (Biltz, *Annalen*, 1897, **296**, 274, gives b. p. 43°/17 mm.). Fraction (2) was mainly β-phenyldiethyl ether (Found : OEt, 27·6. Calc. : OEt, 30·0%); 0·216 g. of (2) also gave styrene dibromide (0·035 g.). Ashworth and Burkhardt (*loc. cit.*) found styrene as the only product, but the concentration of their alcoholic potash was not stated.

Products of Reactions of αα-Dibromoethylbenzene.—(a) *With ethyl alcohol.* A solution of αα-dibromoethylbenzene (1·4 g.) (Found : Br, 56·4%) in dry alcohol (10 c.c.) was kept at 55° for 1½ hours; distillation afforded, after removal of the alcohol, (1) a liquid of b. p. 80—94°/11 mm. (0·6 g.) (Found : Br, 32·2; OEt, 4·6%), and (2) a white crystalline solid (0·15 g.) (Found : Br, nil), m. p. 170°, very sparingly soluble in alcohol. It is probable that (1) was a mixture consisting mainly of α-bromostyrene, present as impurity in the original αα-dibromoethylbenzene, and some acetophenone diethylacetal (Arbusow, *Ber.*, 1907, **40**, 3303, gave b. p. 103·5—104°/17 mm. for the latter). The solid (2) was *s*-triphenylbenzene (Engler and Dengler, *Ber.*, 1893, **26**, 1445, gave m. p. 169—170°). Claisen (*Ber.*, 1898, **31**, 1020) showed that acetyl chloride reacts vigorously with acetophenone diethylacetal to give *s*-triphenylbenzene, so presumably this compound is obtained here by the interaction of hydrogen bromide on the acetal in *dry* alcohol.

(b) *With* 80% *alcohol.* αα-Dibromoethylbenzene (0·31 g.) (Found : Br, 56·0. Calc. : Br, 60·6%) in dry alcohol (8 c.c.) and water (2 c.c.) were kept at 55° for 74 hours, then neutralised with sodium hydroxide and heated at 55° with a slight excess of semicarbazide acetate ($\frac{1}{2}$ hr.). Acetophenonesemicarbazone (0·06 g.) was obtained.

(c) *With potassium hydroxide and* 80% *ethyl alcohol.* αα-Dibromoethylbenzene (0·24 g.) (Found : Br, 56·0%) in dry alcohol (7 c.c.), alcoholic potash (1 c.c., approx. 2*N*), and water (2 c.c.) were similarly treated, hydrochloric acid being used for neutralisation; 0·04 g. of semicarbazone was obtained. This and the previous experiment indicate the formation of approximately the same proportion of acetophenone with or without alkali in 80% alcohol.

(d) *With alcoholic sodium ethoxide.* αα-Dibromoethylbenzene (4 g.) (Found : Br, 49·0%) in dry alcohol (200 c.c.) containing excess of the ethoxide was heated at 55° for 30 mins., then added to water (500 c.c.) and extracted with ether. A colourless liquid (2 g.), with the odour of acetophenone diethylacetal and of b. p. 90—95°/11 mm., was obtained (Found : Br, 21·0; OEt, 10·0%), but no *s*-triphenylbenzene. The liquid (0·44 g.), refluxed with semicarbazide hydrochloride (0·5 g.) and sodium acetate (0·5 g.) in alcohol (30 c.c.) and water (5 c.c.) for 1 hr., gave no acetophenonesemicarbazone, but an oil. When, however, 1·0 g. was refluxed with a slight excess of semicarbazide hydrochloride in alcohol (30 c.c.) and water (5 c.c.) for 15 mins., followed by heating with sodium acetate for 1 hour, acetophenonesemicarbazone (0·60 g.) was obtained. The liquid was thus a mixture of α-bromostyrene and acetophenone diethylacetal. α-Bromostyrene (0·7 g.), from styrene dibromide, treated in exactly the same way, gave no semicarbazone, but an oil. Hence the semicarbazone derived from the αα-dibromoethylbenzene product is not formed from the α-bromostyrene present as impurity.

Although experiments (a) and (d) do not exclude the possibility of the formation of α-bromostyrene from αα-dibromoethylbenzene, the olefin estimations (p. 348) show conclusively that this compound is not formed either with or without sodium ethoxide in dry alcohol.

Products of Reaction of Alcoholic Potash with αβ-*Dibromoethylbenzene.*—αβ-Dibromoethylbenzene (5 g.) in dry alcohol (200 c.c.) and alcoholic potash (20 c.c.; approx. 2*N*) were warmed at 55° for 10 mins., then poured into water (1 l.) and extracted with ether. A liquid (2·5 g.), b. p. 105—110°/37 mm., 81—86°/9 mm., was obtained (Found : Br, 43·0. Calc. for α-bromostyrene : Br, 43·7%. Calc. for β-bromo-α-phenyldiethyl ether : Br, 34·5%). Ashworth and Burkhardt (*loc. cit.*) found only α-bromostyrene in this reaction. They accounted for Nef's obtaining phenylpropiolic acid on treatment of the product with sodium and carbon dioxide (*Annalen*, 1899, **308**, 273) as being due to the presence of unchanged αβ-dibromoethylbenzene : Nef held that it was due to the presence of β-bromostyrene. From the bromine content, but more particularly from the results of olefin determination (see Table I), it appears probable that β-bromo-α-phenyldiethyl ether is formed, along with α-bromostyrene, in this reaction.

Estimation of Olefin.—Styrene and α-bromostyrene, products from the mono- and one of the di-bromoethylbenzenes respectively, were estimated by bromine addition. The results are given in Table I. There were two difficulties : (1) the rapid bromine substitution of the ethyl ethers (and especially of α-phenyldiethyl ether), also present with the olefins, even at room temperature in daylight, and (2) the slow rate of addition of bromine to α-bromostyrene. The following are the details of a control experiment for the estimation of a relatively small amount of styrene in presence of α-phenyldiethyl ether. To styrene (0·0170 g.; $1·64 \times 10^{-4}$ g.-mol.) and α-phenyldiethyl ether (0·1522 g.; $10·15 \times 10^{-4}$ g.-mol.), dissolved in carbon tetrachloride (20 c.c., 99·9%) in a stoppered bottle fitted with an opaque covering and cooled in ice–salt, was added dropwise and with shaking, standard bromine (AnalaR) in carbon tetrachloride (99·9%). The liquid, still in ice–salt, was left in the dark for 30 mins., treated with excess potassium iodide, and then titrated with sodium thiosulphate. The result showed a quantitative addition of bromine to the styrene, and a similar result was obtained when styrene (0·0209 g.) was mixed with α-phenyldiethyl ether (0·1567 g.). In estimating α-bromostyrene, owing to the marked effect of temperature on the rate of addition of bromine, duplicate experiments were performed on the products from the same reaction liquid over different time intervals at room temperature. Consistent results were accepted as a true measure of the amount of α-bromostyrene.

The following procedure for extraction and estimation of the products from the reaction of α- and β-bromo- and αβ-dibromo-ethylbenzenes was therefore adopted, after control experiments had shown that the method gave quantitative results for styrene. A solution of the compound under investigation, in dry alcohol (10 c.c.) either with or without sodium ethoxide or potassium hydroxide, the reactants being of concentrations similar to those used in kinetic experiments, was maintained at 55° or 25° for a slightly longer time than had been found necessary for the elimination of one bromine atom. The liquid was then added to water (100 c.c.), and twice extracted with carbon tetrachloride (10 c.c. and 5 c.c.). The total extract was washed with water (50 c.c.) and run into a stoppered bottle, this water being finally extracted with a further 5 c.c. of tetrachloride and the extract run into the bottle. In all cases the procedure from this point was exactly as for the control experiment on styrene, except that for bromine addition to the products from αβ-dibromoethylbenzene the time was 3—7 days and the temperature that of the room.

The estimation of possible α-bromostyrene formation from αα-dibromoethylbenzene required separate treatment. The compound as prepared was always associated with α-bromostyrene, and further, acetophenone diethylacetal in the products suffers ready acid hydrolysis to acetophenone (cf. Haworth and Lapworth, J., 1922, **121**, 76) which is easily brominated. The procedure was to extract the products of reaction in dry alcohol, either with or without sodium ethoxide, after elimination of two bromine atoms, exactly as with the other three compounds. The tetrachloride extract (20 c.c.) was shaken at room temperature with *N*/10-hydrochloric acid (25 c.c.) for 30 mins. and then with a saturated sodium bisulphite solution (50 c.c.) for 15 mins. After separation, the aqueous layer was extracted with more solvent (5 c.c.) and the 25 c.c. of tetrachloride were washed with two successive amounts of 50 c.c. of water. Each of these two aqueous liquids was extracted with carbon tetrachloride (5 c.c. each) and the extracts washed. The bromine addition to the resulting extract (35 c.c.) was effected exactly as for the products from αβ-dibromoethylbenzene. From the amount of α-bromostyrene found and that of αα-dibromoethylbenzene used, as estimated by acid or alkali titration, the bromine content of such a mixture was calculated, and it was always in very close agreement with that of the original mixture. Hence, no α-bromostyrene was formed during the reaction of αα-dibromoethylbenzene in dry alcohol, either with or without sodium ethoxide. For example, with αα-dibromoethylbenzene (Found : Br, 53·5%) : (*a*) 10 c.c. of dry alcoholic solution after 30 mins. at 55° gave a titre of 6·60 c.c. of *N*/10-sodium hydroxide, representing αα-dibromoethylbenzene, and finally after bromine addition a difference in titre of 6·95 c.c. of *N*/10-sodium thiosulphate, representing α-bromostyrene, which would mean a bromine content of 53·4% for the supposed mixture; (*b*) 10 c.c. of dry alcoholic solution with [NaOEt] = 0·1260 after 30 mins. at 55° gave a titre of 6·53 c.c. of *N*/10-hydrochloric acid, *i.e.*, 6·07 c.c. represent αα-dibromoethylbenzene, and finally after bromine addition a difference in titre of 6·05 c.c. of *N*/10-thiosulphate, representing α-bromostyrene, which would mean a bromine content of 53·6% for the supposed mixture.

Kinetic Experiments.

The ethyl alcohol throughout was dried as described (Taylor, *loc. cit.*). In each experiment, 100 c.c. of a solution of the bromo-compound either in dry alcohol with or without potassium hydroxide or sodium ethoxide, or in aqueous alcohol (80% by vol.) with or without potassium hydroxide at the required temperature were taken. In the bimolecular reactions between potassium hydroxide or sodium ethoxide and β-bromo- or αβ-dibromo-ethylbenzenes, where the unimolecular mechanism was negligible, the reaction was stopped by adding 10 c.c. of the reaction liquid to about 50 c.c. of cold water. In all other cases this addition was to benzene (25 c.c.) and water (50 c.c.). The resulting liquid was titrated with *N*/10-aqueous acid or alkali (phenolphthalein).

The equations $k_1 = (2{\cdot}303/t) \,.\, \log_{10} a/(a - x)$ and $k_2 = [2{\cdot}303/t(a - b)] \,.\, \log_{10} b(a - x)/a(b - x)$, where t is the time in mins. (unless otherwise stated), and a and b are respectively the concentrations of bromo-compound and potassium hydroxide or sodium ethoxide in g.-mols./l., were used in calculating the velocity constants for the uni- and the bi-molecular reactions respectively.

α-Bromoethylbenzene.—In dry alcohol alone the earlier values of k_1 for a unimolecular reaction are reasonably constant, but later, esterification of the solvent by the liberated hydrogen bromide causes first a decrease in the values of k_1 and then decrease in acidity, as the following details of an experiment at 55° show.

Expt. 2. $a = 0{\cdot}1020$.

t.	NaOH, c.c.	k_1.	t.	NaOH, c.c.	k_1.	t.	NaOH, c.c.	k_1.	t.	NaOH, c.c.	k_1.
4·85	0·57	0·0119	37·8	3·60	0·0115	114	7·25	0·0109	293	9·10	0·0076
10·9	1·18	0·0113	62·2	5·22	0·0115	178	8·55	0·0102	1267	7·30	—
21·7	2·27	0·0116	71·5	5·55	0·0110						

In dry alcohol containing sodium ethoxide all three reactions operate, as is indicated by an increase in the value of the first-order velocity " constant " ($\mathbf{k}_1$) over that in dry alcohol alone, and by a gradual fall in the values of $\mathbf{k}_1$ and a gradual rise in $\mathbf{k}_2$ during any one run. Thus the displacement of halogen from this compound resembles the corresponding displacement from *iso*propyl bromide (Hughes, Ingold, and Shapiro, *loc. cit.*). Using their notation and their method of calculation of the total second-order constant k_2, for an experiment at 55°, we get (see Table IV) : mean total $k_2 = 0{\cdot}158$ when [NaOEt] $= 0{\cdot}1622$.

TABLE IV.

Expt. 3. $a = 0{\cdot}0760$; $b = 0{\cdot}1622$; $k_1 = 0{\cdot}01165$.

t.	HCl, c.c.	$\mathbf{k}_1$.	$\mathbf{k}_2$.	$k_1/(b-x)$.	$t\,.\,d\mathbf{k}_2/dt$.	Total k_2.
0	16·22	—	—	—	—	—
4·65	15·18	0·0316	0·202	0·0763	0·0170	0·143
10·65	14·05	0·0316	0·210	0·0826	0·0160	0·145
20·9	12·55	0·0316	0·224	0·0924	0·0293	0·161
35·0	11·28	0·0307	0·228	0·1028	0·0350	0·160
52·0	10·16	0·0307	0·252	0·1142	0·0350	0·173
73·8	9·44	0·0302	0·265	0·1240	0·0295	0·171
96	9·10	0·0288	0·264	0·1275	0·0192	0·155
198	8·74	—	—	—	—	—
242	8·72	—	—	—	—	—
5565	8·62	—	—	—	—	—

The value of k_2 increases (see Table V) with increasing dilution of the sodium ethoxide, as would be expected if the ethoxide ion is the actual reagent in both the bimolecular reactions, since its activity coefficient will increase with dilution. The fraction of α-bromoethylbenzene destroyed by the unimolecular reaction has been calculated by the method employed by these three authors. The figures for the velocity constants for the two bimolecular reactions—k_2 (olefin) and k_2 (substitution)—are based on the observed percentages of olefin formation given in Table I and on the calculated fraction of the whole reaction which is due to the unimolecular reaction. In view of the facts that for any one temperature this fraction appears to depend, not only on the concentration of alkali, but also upon the relative concentrations of alkali and bromo-compound, and that the concentrations used were similar to, but not identical with, those for olefin estimation, these figures can only be regarded as approximate.

TABLE V.

Summary of the values of velocity constants in dry ethyl alcohol, with and without sodium ethoxide, and of the percentage of α-bromoethylbenzene destroyed by the unimolecular reaction.

(k_1 is expressed as min.$^{-1}$, and k_2 as g.-mol./l./min.)

Expt.	a.	b.	$10^3\,\mathbf{k}_1$.	$10^3\,\mathbf{k}_2$.	$10^3\,k_1$.	$10^3\,k_2$.	Unimolecular reaction (%).	$10^3\,k_2$ (olefin).	$10^3\,k_2$ (substn.).
				Temp. 55°.					
1.	0·0728	—	—	—	11·7	—	—	—	—
2.	0·1020	—	—	—	11·6	—	—	—	—
3.	0·0760	0·1622	31·6—28·8	202—264	(11·65)	158	39·0	54	104
4.	0·0515	0·0800	24·5—22·9	330—489	(11·65)	237	48·6	96	141
5.	0·0732	0·2167 *	47·4—38·9	—	—	—	—	—	—
				Temp. 25°.					
6.	0·1680	—	—	—	0·410	—	—	—	—
7.	0·0774	—	—	—	0·412	—	—	—	—
8.	0·1213	0·1430	1·12—0·95	8·35—11·1	(0·411)	5·49	50·2	2·13	3·36
9.	0·0327	0·0817	0·942—0·938	11·9—12·6	(0·411)	6·55	49·3	2·49	4·06

* Potassium hydroxide was used in this expt.

When aqueous alcohol (80%) replaced the dry solvent, values of the first-order velocity coefficient k_1 were constant throughout the whole of the displacement, whether potassium hydroxide was present or not. The value of k_1 was the same in both cases, and evidently the use of this solvent medium produced a change from a mixed uni- and bi-molecular reaction to one which was entirely unimolecular. The results are summarised below.

Summary of results in aqueous alcohol (80%).

Expt.	Temp.	a.	b.	k_1.	Expt.	Temp.	a.	b.	k_1.
10	55°	0·0737	—	0·263	12	25°	0·2180	—	0·00925
11	55	0·0746	0·2145	0·264					

β-*Bromoethylbenzene.*—In dry alcohol alone there was no measurable bromine displacement during 24 hrs., but in aqueous alcohol (80%) a unimolecular reaction took place as shown by the following experiment at 55°, where a = 0·1522.

t (hrs.)	5·5	51	96	200	
NaOH, c.c.	0·10	0·90	1·50	3·00	
$10^3 k_1$ (hr.$^{-1}$)	1·17	1·20	1·08	1·10	Mean 1·14

With potassium hydroxide in dry alcohol, constant values were obtained for a second-order velocity coefficient; details of one experiment at 55° are given.

a = 0·1090; b = 0·2470.

t (mins.)	1·95	4·0	7·05	12·5	17·65	24·0	41·5	77	211
HCl, c.c.	23·03	21·82	20·17	18·30	16·91	15·95	14·57	13·95	13·80
k_2	0·369	0·337	0·347	0·341	0·351	0·358	0·371	0·358	—

Mean 0·353

Table VI shows the complete results for alcoholic potash at different temperatures.

Table VI.

Temp.	Solvent.	a.	b.	k_2.	k_2 (olefin).	k_2 (substn.).
55°	EtOH	0·1090	0·2470	0·353	0·323	0·029
55	,,	0·0980	0·1965	0·351	—	—
55	EtOH (80%)	0·0690	0·2110	0·153	—	—
45	EtOH	0·1126	0·2348	0·108	—	—
35	,,	0·1208	0·2365	0·0389	—	—
25	,,	0·0765	0·2099	0·0125	0·0114	0·0011

The values of k_2 (olefin) and k_2 (substitution) are computed from the olefin percentages given in Table I.

αα-*Dibromoethylbenzene.*—This preparation always contained α-bromostyrene, from which alkali caused slow displacement of bromine; further, the hydrogen bromide produced by its alcoholysis was removed (though slowly) by dry alcohol. For these two reasons, the reaction concentration produced by a known weight of αα-dibromoethylbenzene (from any one preparation) in dry alcohol was computed (1) by reference to the hydrolysis of a known weight in aqueous alcohol (80%), and (2) checked by its bromine content (Robertson, J., 1915, **107**, 902). To indicate the variation in the values of the first-order velocity coefficient, details of two runs, both in dry alcohol at 55°, are given (Table VII), one without and the other with sodium ethoxide. The values of k_1 are calculated from the usual equation for a unimolecular reaction (p. 348), x being taken as half the titre (NaOH) or half the difference in titre (HCl); *i.e.*, it is assumed that the two bromine atoms are displaced simultaneously.

Table VII.

a = 0·0305.						a = 0·0245; b = 0·1620.					
t.	NaOH, c.c.	k_1.	t.	NaOH, c.c.	k_1.	t.	HCl, c.c.	k_1.	t.	HCl, c.c.	k_1.
1·55	0·96	0·111	30·9	5·90	0·116	0·55	15·92	0·107	32·8	11·48	0·101
3·05	1·74	0·110	63	6·05	—	1·85	15·32	0·107	248	11·28	—
7·0	3·08	0·107	147	5·90	—	4·45	14·20	0·118	119 (hr.)	9·03	—
10·9	4·35	0·115	46 (hr.)	4·61	—	8·53	13·05	0·106	188 (hr.)	8·15	—
18·1	5·30	0·112	282 (hr.)	2·10	—	16·25	12·00	0·112			
Mean k_1 = 0·112.						Mean k_1 = 0·109.					

Evidently the only process operating here is unimolecular, and the reaction is not sensitive to alkali. The complete results are given in Table VIII and show that, as usual for this type of unimolecular halogen displacement, water produces a marked increase in the value of k_1. In view of this, the value of k_1 obtained from Expt. 5, in which potassium hydroxide in dry alcohol was substituted for the sodium ethoxide used in other experiments, is interesting since it indicates that in such a solution the equilibrium KOH + dry EtOH (solvent) $\rightleftharpoons$ KOEt + H_2O lies far over to the right. Expt. 5 (Table V) supports this observation, as also does the work of Williams and Bost (*J. Chem. Physics*, 1936, **4**, 251).

Two experiments with αα-dichloroethylbenzene and sodium ethoxide in dry alcohol were performed for purposes of comparison with the bromo-compound :

Temp.	a.	b.	k_1.	Temp.	a.	b.	k_1.
55°	0·0260	0·0610	0·0131	25°	0·0370	0·0800	0·000315

TABLE VIII.

Solvent, dry EtOH; [NaOEt] = b; k_1 in min.$^{-1}$.

	Temp. 55°.				Temp. 25°.		
Expt.	*a*.	*b*.	k_1.	Expt.	*a*.	*b*.	k_1.
1	0·0305	—	0·112	6	0·0315	—	0·00338
2	0·0245	0·1620	0·109	7	0·0274	0·0812	0·00344
3	0·0420	0·1620	0·117	8	0·0455	0·1430	0·00341
4	0·0320	0·0806	0·111				
5	0·0340	0·2080 *	0·152				

Solvent, aqueous EtOH (80%).

	Temp. 55°.				Temp. 25°.		
9	0·0903	—	2·19	11	0·0755	—	0·126
10	0·0460	0·1735 *	2·31	12	0·0705	0·1760 *	0·127

* [KOH] = b.

αβ-*Dibromoethylbenzene.*—Details of the unimolecular displacement in aqueous alcohol (80%) at 55° follow; a = 0·0695.

t (hrs.)	5	28	51	96	218	
NaOH, c.c.	0·65	2·90	4·52	5·85	6·95	
$10^2 k_1$ (hr.$^{-1}$)	1·97	1·89	2·06	1·92	—	Mean 0·0196

In dry alcohol at 55° (a = 0·0878), the mean value of k_1 was 0·000471 hr.$^{-1}$.

All other experiments were performed with potassium hydroxide in dry alcohol, and under these conditions the values of the second-order coefficient are sensibly constant for any one run, *i.e.*, the unimolecular displacement is negligible. The reaction is so fast at 55° that details are afforded for one experiment at 25° in order to illustrate how the values of k_2 vary during one such run.

a = 0·0926; b = 0·2070.

t	0·6	1·2	1·9	2·6	3·5	5·0	6·6	10·3	197
HCl, c.c.	18·15	16·51	15·20	14·20	13·42	12·50	12·13	11·70	11·58
k_2	2·78	2·89	2·73	2·80	2·77	2·91	2·73	2·55	—
								Mean k_2 = 2·77	

Full results are tabulated below :

Temp.	42°	35°	25°	25°	15°
a	0·0613	0·0629	0·0926	0·0944	0·0944
b	0·2387	0·1960	0·2070	0·1977	0·1991
Total k_2	12·5	6·79	2·77	2·61	1·00

From Table I it is seen that the percentages of olefin formation at 55° and 25° are almost identical, and hence the temperature coefficients and activation energies for the bimolecular olefin and substitution reactions were calculated from the values of "total k_2."

Examination for Reversibility in Dry Alcoholic Solutions of Reactions of α-Bromo- and αα-Dibromo-ethylbenzenes.—Dry hydrogen bromide was passed (½ hr.) into dry alcohol surrounded by ice–salt, and the solution immediately diluted with dry alcohol until it was approx. $N/5$. The solutions (2) and (3) were made as soon as possible afterwards (5 mins.), and all three solutions were placed in the thermostat at 55° and allowed to attain its temperature (15 mins.).

The method of procedure was the general one employed in the other kinetic experiments, *i.e.*, benzene (25 c.c.) and water (50 c.c.) were used in stopping the reaction; the titre is given in c.c. of $N/10$-sodium hydroxide.

t (hrs.)		0	0·25	1·1	5	23	47	96	150
Titre	(1) Control expt.	19·10	19·05	18·85	17·73	11·40	8·08	4·15	3·60
	(2) [CHPh(OEt)Me] = 0·0310	19·05	19·00	18·80	17·68	11·20	7·90	4·05	3·45
	(3) [CPh(OEt)$_2$Me] = 0·0513	18·90	18·85	18·65	17·60	10·95	7·60	3·90	3·40

SUMMARY.

1. The different modes of displacement of bromine from α- and β-bromo- and αα- and αβ-dibromo-ethylbenzenes in dry and in aqueous ethyl alcohol (80%) have been studied.

2. Evidence is adduced to show that the apparent unimolecular displacement is actually composite, and generally includes the formation and decomposition of an intermediate complex.

THE POLYTECHNIC, REGENT STREET, LONDON, W. 1.

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