92. *The Formation of Quaternary Ammonium Salts from Dihalogenoparaffins, etc., in Aqueous Acetone Solution.*

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The reaction between trimethylamine and methylene, ethylene, and trimethylene dibromide in aqueous acetone is bimolecular and leads to the formation of a monoquaternary ammonium salt. When, however, the base is in excess of that required for the above reaction, a consecutive reaction leading to the formation of a diquaternary ammonium salt proceeds. The formation of the latter salt from the former has been separately investigated. The reaction between trimethylene dibromide and trimethylamine has been fully examined, and the velocity coefficient for the primary reaction has been obtained corrected for the incidence of the subsequent formation of diquaternary salt. The results are compared with the reactivities of other organic halides with trimethylamine, and discussed with reference to the mechanism of formation of ammonium salts.

According to Schmidt and Litterschied (*Annalen*, 1904, **337**, 67), methylene dibromide and di-iodide react with trimethylamine in alcoholic solution at room temperature thus: $CH_2X_2 + NMe_3 = CH_2X{\cdot}NMe_3\}X$; at 100°, excess of the amine reacts with methylene di-iodide to give the same product, together with formaldehyde and tetramethylammonium iodide. Trimethyl-β-bromoethylammonium bromide is obtained from ethylene dibromide and aqueous or alcoholic trimethylamine below 50°, but with excess of alcoholic amine at 100°, a variety of products, including the mono- and the di-ammonium salt, is obtained (Schmidt and Kleine, *ibid.*, p. 81). Lucius (*Arch. Pharm.*, 1907, **245**, 246), however, obtained triethyl-β-bromoethylammonium bromide and ethylenebistriethylammonium bromide from the interaction between triethylamine and ethylene dibromide. The mono- and di-ammonium salts were also prepared from the interaction between trimethyl- or triethyl-amine and trimethylene dibromide. These results suggest that the formation of the diammonium salts from methylene and ethylene dihalides is attended with difficulty.

The reactions between a number of organic dihalides and trimethylamine have now been studied kinetically, in order to find out the extent of the diammonium salt formation and to investigate the factors affecting the formation of quaternary ammonium salts. Except for von Braun and Lemke's semi-quantitative observation (*Ber.*, 1922, **55**, 3546) that αδ-dibromo-Δ^{β}-butene affords a bistrimethylammonium bromide much more rapidly than does αδ-dibromobutane, no comparative quantitative measurements have yet been carried out on reactions of this type.

EXPERIMENTAL.

Materials.—The solutions of trimethyl- and triethyl-amine in aqueous acetone were made by adding the anhydrous bases to the solvent and checking the concentration by titration with standard hydrochloric acid.

Methylene and ethylene dichloride and dibromide, αβ- and αγ-dibromopropane were washed with water, treated with calcium chloride, and fractionally distilled. αδ-Dibromo-Δ^{β}-butene was readily purified by sublimation at 55°. *trans*-αβ-Di-iodoethylene, obtained from acetylene by Biltz's method (*Ber.*, 1897, **30**, 1207), formed colourless crystals from alcohol, m. p. 73°.

Semenow's method (*Jahresber.*, 1864, 483) was used to prepare ethylene di-iodide, and the alcoholic solution was shaken with a little purified mercury to remove traces of iodine. The colourless crystals obtained had m. p. 82°, and as the compound was unstable, it was prepared immediately before use.

Solvent. " AnalaR " Acetone was purified by the method of Norris and Prentiss (*J. Amer. Chem. Soc.*, 1928, **50**, 3042), dried over potassium carbonate, and distilled. The aqueous acetone was made by diluting 10 vols. of water to 100 vols. with acetone, and had the following densities: $d_{4^\circ}^{16^\circ}$ 0·8317; $d_{4^\circ}^{35^\circ}$ 0·8098; $d_{4^\circ}^{45^\circ}$ 0·7983; $d_{4^\circ}^{55^\circ}$ 0·7868.

Quaternary Ammonium Salts.—The following general method was used for the preparation of the monoammonium salts from the dihalides : 5 g. of anhydrous trimethylamine were added to a cold solution of excess of the organic dihalide (about 40 g.) in 50 c.c. of anhydrous ether. The container was then tighly stoppered and set aside for 1 week. The precipitated salt was collected on a filter, washed with ether, and recrystallised. Trimethylbromomethylammonium bromide melted at 155° (from alcohol) and trimethyl-β-bromoethylammonium bromide at 243° (decomp.). Trimethyl-γ-bromopropylammonium bromide, m. p. 95° (from alcohol–ether), appears to suffer some decomposition in boiling alcohol.

A solution of trimethyl-β-bromoethylammonium bromide in aqueous acetone treated with excess trimethylamine gave some ethylenebistrimethylammonium bromide, m. p. 247° (decomp.). The products from a similar experiment with trimethylbromomethylammonium bromide are being investigated. The purity of all the salts employed was checked by iodide-ion determinations.

Velocity Measurements.—From a knowledge of the density of the solvent at various temperatures, the initial concentrations of the reactants at the temperature at which the reaction was conducted were calculated. Equal volumes of the solutions of base and halide were transferred to the mixing vessel of an automatic pipette. After thorough mixing, measured volumes (5·74 c.c. at 16°, 5·91 c.c. at 35°, 6·01 c.c. at 45°, 6·08 c.c. at 55°) of the reaction mixture were run into test-tubes with constricted necks, which were then immediately sealed and placed in the thermostat. At convenient intervals a sealed tube was withdrawn, opened, and the contents treated in one of the following ways: (i) They were washed with water into 20 c.c. of light petroleum, which was then repeatedly extracted with water; the aqueous extract was titrated against N/40-silver nitrate, with potassium chromate as indicator. (ii) The contents were washed with water into a titration flask, diluted to about 150 c.c., and titrated against standard hydrochloric acid, the indicator being light-filtered methyl-red (1·25 g. of methyl-red and 0·825 g. of methylene-blue in 1 l. of 90% alcohol). The reaction-vessel method (Davies and Lewis, J., 1934, 1599) was also used in the more rapid reactions at 35° and 45°.

Calculations.—For the complete bimolecular reaction $A + B \longrightarrow AB$,

$$k_2 = [1/(a-b)t]\log_e b(a - x)/a(b - x),$$

where a and b are the initial concentrations of A (organic halide) and B (tertiary base), respectively, and x is the concentration of AB (ammonium salt) formed after an interval of t mins. Concentrations are expressed in g.-mols./l. at the temperature at which the reaction is being carried out. The concentration of ammonium salt formed after t mins. is either (i) $x = y/40v$, where y is the volume (c.c.) of N/40-silver nitrate required by v c.c. of reaction mixture (contents of a sealed tube, volume measured at the temperature of the experiment), or (ii) $x = b - z/20v$, where z is the volume (c.c.) of N/20-hydrochloric acid required by

v c.c. of reaction mixture. In reactions carried out with a large excess of the halide A, $k_2 = (1/at)\log_e b/(b - x)$. In all except the very slow reactions, where the time of immersion of the reaction mixture in the thermostat was taken as the zero time, an initial time correction was applied. This was obtained in the usual way from the time–concentration measurements.

Trimethylamine and Organic Dihalides.—The reaction between ethylene dibromide and trimethylamine is bimolecular: $CH_2Br{\cdot}CH_2Br + NMe_3 \longrightarrow CH_2Br{\cdot}CH_2{\cdot}NMe_3\}Br$. When the halide is in excess (Table I), the velocity coefficients obtained by methods (i) and (ii) agree closely, showing that secondary reactions are absent. When, however, equivalents of the base and halide are taken (Table II, Nos. 2 and 3), the velocity coefficients tend to drift slightly, and the mean coefficient obtained by method (ii) is rather higher than that obtained by method (i). In No. 5, where the base is in excess, the coefficients drift seriously, and halide ion in excess of that required for monoammonium salt formation is ultimately produced. Hence, excess of halide is necessary to prevent formation of diammonium salt, $Br\{NMe_3{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3\{Br$, and if it is in very large excess (Table II, No. 8), the order of the reaction is pseudo-unimolecular, constant velocity coefficients being obtained. The mean value of k_2 is lower than in the other cases, probably bacause the solvent, now containing large excess of ethylene dibromide, is different.

Similar results were obtained in the reaction between methylene or trimethylene dibromide and trimethylamine (Table III).

TABLE I.

Reaction between Ethylene Dibromide (2 Mols.) and Trimethylamine (1 Mol.).

Temp.: 55°. Solvent: 90% acetone.

$[C_2H_4Br_2]_{55°} = 0{\cdot}2290$; $[NMe_3]_{55°} = 0{\cdot}1145$.

N/20-HCl,			N/20-HCl,			N/40-AgNO$_3$,			N/40-AgNO$_3$,		
t, mins.	c.c.	100k_2.	*t*, mins.	c.c.	100k_2.	*t*, mins.	c.c.	100k_2.	*t*, mins.	c.c.	100k_2.
65	10·45	2·06	285	4·85	2·02	85	7·9	1·86	305	18·5	1·97
144	7·9	1·96	327	4·27	2·02	225	15·45	1·88	347	19·5	1·95
245	5·49	2·03	371	3·7	2·04	265	17·35	1·99	Mean 100k_2 = 1·93		
			Mean 100k_2 = 2·02								

TABLE II.

Reaction between Ethylene Dibromide and Trimethylamine.

Temp.: 55°. Solvent: 90% acetone.

			100k_2.					100k_2.	
No.	$[C_2H_4Br_2]_{55°}$.	$[NMe_3]_{55°}$.	Method (i).	Method (ii).	No.	$[C_2H_4Br_2]_{55°}$.	$[NMe_3]_{55°}$.	Method (i).	Method (ii).
1	0·0712	0·0712	—	2·30	5	0·0703	0·1407	—	4·27—2·76
2	0·0882	0·0882	2·17	2·51	6	0·2806	0·1409	—	2·01
3	0·1763	0·1763	2·00	2·36	7	0·2290	0·1145	1·93	2·02
4	0·3038	0·3038	—	2·14	8	1·827	0·1762	1·25	1·38

TABLE III.

Reactions between Trimethylamine and Methylene, Ethylene, and Trimethylene Dibromides. Summary of Results in 90% Acetone.

			Methylene dibromide.				
Temp.	[Bromide]$_{t°}$.	[NMe$_3$]$_{t°}$.	$k_2 \times 10^3$.	Temp.	[Bromide]$_{t°}$.	[NMe$_3$]$_{t°}$.	$k_2 \times 10^3$.
35°	0·0694	0·1502	4·2 *	45°	0·1131	0·1131	9·38
45	1·470	0·1457	7·42	55	0·1407	0·1407	21·0
			Ethylene dibromide.				
35	1·471	0·1472	3·51	45	1·456	0·1457	7·76
,,	0·0871	0·0870	5·6	,,	0·1467	0·1467	10·7
,,	0·07494	0·1502	5·6 *				
			Trimethylene dibromide.				
			100k_2.				100k_2.
35	0·1199	0·1446	3·1—4·8	45	1·456	0·1457	4·41
,,	0·2295	0·1147	2·79	,,	0·2261	0·1131	5·99
				55	0·2235	0·1115	11·5

* Slight drift.

The reaction between triethylamine and ethylene dibromide was too slow to be convenient for detailed study, but at 35°, 0·1458N- and 1·461N-solutions, respectively, gave $100\,k_2 = 0{\cdot}0107$ by method (ii), showing that the reaction mechanism is similar; there was a slight downward drift in the velocity coefficients.

Reaction between the solvent and the organic halides was negligible under the conditions of the kinetic measurements.

Trimethylamine and the Monoammonium Salts derived from Organic Dihalides.—Both trimethyl-bromomethyl- and -β-bromoethyl-ammonium bromides reacted with trimethylamine. The rate was slow, and the bimolecular velocity coefficients drifted slightly. Trimethylamine reacted more readily with trimethyl-γ-bromopropylammonium bromide. The bimolecular velocity coefficients were constant over the greater part of the reaction. Table IV gives a detailed example and a summary of the results obtained.

TABLE IV.

Reaction between Trimethylamine and Trimethyl-β-bromoethylammonium Bromide.

Temp.: 55°. Solvent: 90% acetone.

$[\mathrm{Br{\cdot}(CH_2)_2{\cdot}NMe_3Br}]_{55°} = 0{\cdot}0827$; $[\mathrm{NMe_3}]_{55°} = 0{\cdot}0973$.

t, mins.	356	1367	2816	4243	5674	8563	11456	18658
N/20-HCl, c.c.	10·04	8·38	6·81	5·85	5·15	4·11	3·43	2·50
$k_2 \times 10^3$	6·16	3·76	3·38	3·22	3·14	3·22	3·37	3·95

Summary of Results.

Temp.	$[\mathrm{Br{\cdot}(CH_2)_2{\cdot}NMe_3Br}]_{t°}$.	$[\mathrm{NMe_3}]_{t°}$.	$k \times 10^3$.	Temp.	$[\mathrm{Br{\cdot}(CH_2)_3{\cdot}NMe_3Br}]_{t°}$.	$[\mathrm{NMe_3}]_{t°}$.	$k \times 10^3$.
35°	0·0851	0·100	0·6	35°	0·1124	0·1128	24·3
	$[\mathrm{Br{\cdot}CH_2{\cdot}NMe_3Br}]_{t°}$.			55	0·1111	0·1114	84·5
55	0·107	0·107	3·2				

Reaction of Trimethylene Dibromide with Trimethylamine.—This reaction is a convenient one in which to investigate more thoroughly the effect of excess of base, since both halogen atoms are readily attacked and the rate of formation of the di- from the mono-ammonium salt can be accurately measured. Ritchie's formula (J., 1931, 3112) for the saponification of di-esters can be applied to the determination of the rate of formation of the monoammonium salt, corrected for that of diammonium salt. Let the velocity coefficient for the primary reaction be k_2', that for the secondary reaction k_2'', and the initial concentrations of dibromide and base be a and b g.-mols./l. respectively. Then, if w is the concentration of base used in t mins., we have

$$2a - w - [(1 - m)/k_2''(b - w)]\mathrm{d}w/\mathrm{d}t = a^m\left[\frac{1 - m}{2m - 1}\right]^{1-m}\left[\frac{\mathrm{d}w/\mathrm{d}t}{k_2''(b - w)} - (2a - w)\right]^{1-m}$$

where $m = (k_2' - k_2'')/k_2'$. The values of m at each value of t can be found as follows. Experimental values of w [from method (ii)] are plotted against t, so that $\mathrm{d}w/\mathrm{d}t$ can be obtained for any value of t. There is a slight uncertainty in the value of $\mathrm{d}w/\mathrm{d}t$ so obtained. For a given value of w and the corresponding value of $\mathrm{d}w/\mathrm{d}t$, the left-hand side of the equation is plotted for different values of m, giving a straight line. The right-hand side is plotted similarly and is represented by a curve. The intersection (other than that at $m = 0$) gives the required value of m, and hence of k_2', for k_2'' is accurately known from a separate experiment.

TABLE V.

Reaction between Trimethylamine and Trimethylene Dibromide.

Temp.: 35°. Solvent: 90% acetone.
$a = 0{\cdot}12$; $b = 0{\cdot}145$ (at 35°); $k_2'' = 2{\cdot}4 \times 10^{-2}$.

				$100k_2'$.						$100k_2'$.	
t, mins.	w.	$10^6\mathrm{d}w/\mathrm{d}t$.	m.	Corr.	Uncorr.	t, mins.	w.	$10^6\mathrm{d}w/\mathrm{d}t$.	m.	Corr.	Uncorr.
60	0·0258	351	0·065	2·57	3·07	210	0·0673	205	0·056	2·54	3·79
90	0·0354	314	0·048	2·52	3·10	255	0·0754	175	0·038	2·50	4·02
130	0·0472	279	0·067	2·57	3·16	325	0·0862	140	0·030	2·47	4·49
								Mean $100k_2' = 2{\cdot}53$			

Table V shows that this correction of the coefficients obtained by the ordinary bimolecular formula affords constant velocity coefficients for the monoammonium salt formation. The mean value of k_2' (corr.), $2{\cdot}53 \times 10^{-2}$, is in tolerable agreement with the mean bimolecular velocity coefficient obtained in the reaction between 1 mol. of base and 2 mols. of dibromide, *viz.*, $2{\cdot}79 \times 10^{-2}$, where the formation of the diammonium salt is sufficiently repressed to yield constant bimolecular velocity coefficients.

Reactions between Trimethylamine and Organic Chlorides.—Vincent and Chappuis (*Bull. Soc. chim.*, 1886, **45**, 502) showed that trimethylamine combined with methyl chloride to give tetramethylammonium chloride. Other organic chlorides, with the possible exception of allyl chloride, are not very reactive towards tertiary bases in solution (Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589). We have now followed the course of the reaction between several organic chlorides (in great excess) and trimethylamine in aqueous acetone, and shown that a reaction of bimolecular mechanism takes place.

Reaction between Organic Chlorides and Trimethylamine.

Solvent: 90% acetone. Temp.: 55°.

			Mean $k_2 \times 10^4$.	
	a.	*b.*	Method (i).	Method (ii).
Ethyl chloride	1·434	0·1405	—	29·2
Methylene dichloride	1·435	0·1428	6·08	6·06
Ethylene dichloride	1·430	0·1430	—	2·80

The velocity coefficients obtained were satisfactorily constant over the greater part of the reaction. There was a tendency for a slight drift in the coefficients in the case of methylene dichloride, but the similarity of the results obtained by the two methods of titration led to the conclusion that secondary reactions are of minor importance.

When trimethylamine and excess of methylene or ethylene dichloride were mixed in ether, a small quantity of a white precipitate was formed in about 1 week. These products, especially that from methylene dichloride, were very hygroscopic, and determinations of halide ion, although low, left no doubt that they were trimethyl-chloromethyl- and -β-chloroethyl-ammonium chlorides, respectively.

Reactions between Ethylene Di-iodide and Trimethylamine.—In our usual procedure, the rapidity of the salt-forming reactions and the separation of iodine prevented a full examination. Although iodine separates slowly from solutions of ethylene di-iodide in aqueous acetone, the presence of trimethylamine promotes this change (Slator, J., 1904, **85**, 1697, found that the dissociation $C_2H_4I_2 \rightleftharpoons C_2H_4 + I_2$ was catalysed by iodide ion). We believe that there are two fast, consecutive reactions leading to the formation of the mono- and di-ammonium iodides, as well as the catalysed dissociation.

The Reaction of Trimethylamine with αβ-Dibromopropane.—Roth (*Ber.*, 1881, **14**, 1351) stated that αβ-dibromopropane did not react with trimethylamine, but Schmidt and Kleine (*loc. cit.*) obtained α-bromo-Δ^{α}-propylene, trimethyl-Δ^{α}-propenylammonium bromide, and dimethylamine and trimethylamine hydrobromides when the reactants were heated in alcoholic solution for 6 hours at 100°. In our investigation of the reaction at 55° in 90% acetone between trimethylamine (0·1407 g.-mol./l.) and αβ-dibromopropane (0·1118 g.-mol./l.), the bimolecular velocity coefficients were reasonably constant over a large part of the reaction at a mean value of $k_2 \times 10^3 = 1{\cdot}73$, but the initial values were high.

When a mixture of the dibromide, in excess, and trimethylamine with no solvent was kept for several days, a solid separated. The substance, m. p. 245—247° (decomp.), is difficult to recrystallise, since it is decomposed by boiling with alcohol. The bromide-ion content (Found: Br′, 32·5%) indicated that the salt was either (I) or (II) (Calc.: Br′, 30·6%), and not a salt in which elimination of a molecule of hydrogen bromide had taken place.

(I.) $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}NMe_3\}Br$ $CH_2Br{\cdot}CHMe{\cdot}NMe_3\}Br$ (II.)

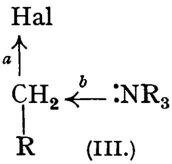
It is concluded that primarily αβ-dibromopropane reacts normally with trimethylamine, but the salts formed may readily lose hydrogen bromide and undergo other transformations, especially at higher temperatures in alcohol.

Reactions of Trimethylamine with some Unsaturated Organic Halides.—No trace of precipitate appeared in sealed tubes containing trimethylamine and excess of vinyl bromide or *trans*-αβ-di-iodoethylene diluted with ether and kept for several months. In addition, a mixture of the tertiary base and di-iodoethylene in aqueous acetone kept at 55° gave no indication of iodide ion and there was no decrease in the trimethylamine content at the end of 10 days. In approximately 3 minutes all the base had reacted in an equimolar mixture of trimethylamine and αδ-dibromo-Δ^{β}-butene (0·073 g.-mol./l.) in aqueous acetone at room temperature. A corresponding amount of bromide ion was produced. Separation of crystalline salt from the mixture during reaction prevented the calculation of accurate velocity coefficients.

DISCUSSION.

The principal results we have obtained regarding the reactivities of organic halides towards trimethylamine are summarised below, the reaction of only one of the halogen atoms (*) being considered.

$$C_2H_5Cl > Cl{\cdot}CH_2\overset{*}{Cl} > Cl{\cdot}CH_2{\cdot}CH_2\overset{*}{Cl}$$
$$CH_3Br > Br{\cdot}CH_2\overset{*}{Br} \sim Br{\cdot}CH_2{\cdot}CH_2\overset{*}{Br}$$
$$Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{*}{Br} > Br{\cdot}CH_2{\cdot}CH_2\overset{*}{Br}$$
$$Br{\cdot}CH_2{\cdot}CH_2\overset{*}{Br} > \overset{-}{Br}\{\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2\overset{*}{Br}$$
$$\overset{-}{Br}\{\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{*}{Br} > \overset{-}{Br}\{\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2\overset{*}{Br}$$
$$Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{*}{Br} = \overset{-}{Br}\{\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{*}{Br}$$



(III.)

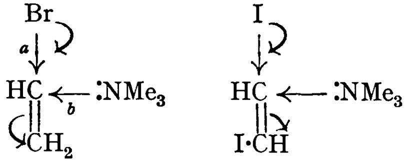
Two factors (Baker, J., 1932, **1148**, and succeeding papers) affect the velocity of formation of an ammonium salt: (*a*) anionisation of the halogen atom of the organic halide, facilitated by an electron accession to the halogen, and (*b*) the co-ordination of the base by means of its unshared electrons to the methylene group of the organic halide, facilitated by an electron recession from the halogen. These are depicted in (III). Although the formation of the salt requires the completion of the cycle, it can be considered that the initiation of the cycle depends on either of the factors (*a*) or (*b*). Substituents in the organic halide determine the probability of initiation by (*a*) or (*b*).

The halogens have complex polar effects, $-I$, $+M$. In the methylene dihalides the $+M$ effect, which increases the ease of anionisation of chlorine, may operate, $\overset{\curvearrowright}{Cl}{-}\overset{\curvearrowright}{CH_2}{-}Cl$, as well as the inductive attractive effect $Cl{\leftarrow}CH_2{-}Cl$. In the ethylene dihalides, however, the former effect is excluded because of the intercalation of the saturated carbon atom. The greater speed of reaction with trimethylamine of methylene dichloride than of ethylene dichloride (the dibromides are of almost equal reactivity) is, therefore, to be expected.

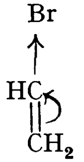
On comparing ethylene and trimethylene dibromides it will be seen that removal of one bromine atom from the other reacting bromine, with a consequent diminution of the attraction ($-I$) of the one for the other, increases reactivity. Substitution of the strongly attractive ($-I$) group $\overset{+}{N}Me_3$ for Br further decreases reactivity in the ethylene derivatives. It will be noted that, whereas the first halogen in ethylene dibromide is replaced much more readily than the second in the monoammonium salt produced, yet in trimethylene dibromide the diammonium salt is produced as readily as the monoammonium salt. This is due to the greater damping out of the polar effect of the halogen or $\overset{+}{N}Me_3$ group as it is moved further away from the reaction centre. Electronic effects ($-I$ in these cases) can be transmitted through only two saturated carbon atoms at the most, and it would be expected, therefore, that the attractive electronic effect of $CH_2Br{\cdot}CH_2{-}$ would be less than that of $\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2{-}$, whereas the attractive effects of $CH_2Br{\cdot}CH_2{\cdot}CH_2{-}$ and $\overset{+}{N}Me_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{-}$ would be approximately equal.

Consideration of these results indicates that initiation of the electron cycle leading to ammonium-salt formation depends on factor (*a*).

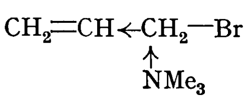
Vinyl bromide and *trans*-αβ-di-iodoethylene are both highly unreactive towards tertiary bases, whereas the related compounds, allyl bromide and αδ-dibromo-Δ^{β}-butene, are very reactive (towards dimethylaniline, allyl iodide is more reactive than methyl iodide; Preston and Jones, J., 1912, **101**, 1930). The vinyl group is considered to have an intrinsic attraction for electrons ($-I$), as well as a possibility when it is in a conjugate system of an electronic displacement ($+T$) (see Dippy, J., 1937, 1008). The non-activity of the first two compounds is, therefore, due to electron movements (IV) retarding anionisation of the halogen. Phase (V) is less important. With allyl bromide (and αδ-dibromo-Δ^β-butene) either of the movements (VI) or (VII) could take place. In (VI) there would have to be a change in the mechanism of the initiation of the cycle leading to formation of the salt, to factor (*b*).



(IV.)

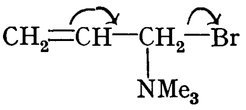


(V.)



(VI.)

$$CH_2{=}CH{\leftarrow}\underset{\underset{NMe_3}{\uparrow}}{CH_2}{-}Br$$



(VII.)

$$CH_2{=}\overset{\curvearrowright}{CH}{-}\underset{\underset{NMe_3}{|}}{CH_2}{-}\overset{\curvearrowright}{Br}$$

The effect of alkyl groups on the speed of the reactions between *p*-substituted benzyl halides and pyridine (Baker and Nathan, J., 1935, 1844) and of *p*-alkyldimethylanilines with methyl iodide (Davies and Hulbert, *J. Soc. Chem. Ind.*, 1938, **57**, 349; J., 1938, 1865), where steric effects can be deemed unimportant, is similar to that found with the reaction between alkyl halides and trimethylamine (Me>Et>Pr^β). Theoretical considerations advanced for the former examples could, therefore, be applied to the simple alkyl halides. An explanation frequently given for this order of the alkyl groups in the reactions of the alkyl halides depends on the steric effects of the groups (see, *e.g.*, Vavon, *Bull. Soc. chim.*, 1931, **49**, 979). Although the present work has not decisively shown the absence of steric effects in the reactions being considered, yet it has been demonstrated that the experimental results can be adequately explained by considering the operation of polar effects alone.

Energy of Activation and Probability Factor.—Values of E and $\log_{10}PZ$, derived from the Arrhenius equation k (time in secs.) $= PZe^{-E/RT}$, are given in Table VI. These values are probably not highly accurate, but they give some useful indications.

TABLE VI.

Formation of Monoammonium Salts from Trimethylamine and Dibromides.

	E, kg.-cals.	$\log_{10}PZ$.		E, kg.-cals.	$\log_{10}PZ$.
(1) CH_2Br_2	16·1	7·3	(3) $CH_2Br\cdot CH_2\cdot CH_2Br$	14·2	6·8
(2) $CH_2Br\cdot CH_2Br$	12·7	5·0			

Formation of Diammonium Salts from Bromo-substituted Monoammonium Salts.

(4) $CH_2Br\cdot CH_2\cdot\overset{+}{N}Me_3\overset{-}{Br}$	18·3	8·0	(5) $CH_2Br\cdot CH_2\cdot CH_2\cdot\overset{+}{N}Me_3\overset{-}{Br}$	12·5	5·5

Winkler and Hinshelwood (J., 1935, 1147) showed that, in the reaction of trimethylamine with alkyl halides, the order of increasing E and of decreasing rate of reaction was MeHal, EtHal, Pr^βHal. The increase in E may be attributed to increasing strength of the C—Hal bond, which might be expected if the initiating factor is a, and the total electronic effect of the alkyl groups is in the order Me>Et>Pr^β. On the other hand, the increase in E might be due to steric hindrance, but the results in Table VI do not support this view. The increase in E from (1) or (2) to (4) can be attributed to strengthening of the C—Hal bond in (4) by substitution of $\overset{+}{N}Me_3$ for Br. The greater similarity of the E values for (3) and (5) is to be expected, for now, the substituents Br and $\overset{+}{N}Me_3$ have less effect on the strength of the C—Hal bond. Comparing (1) and (2), the fall in E is to be expected from the weakening of the electronic effect of the one halogen on the other in (2). A similar explanation serves for the decrease in E in passing from (4) to (5).

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