138. *The Formation and Decomposition of Quaternary Ammonium Salts in Solution.*

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The rates of combination of tertiary amines and alkyl halides have been extensively studied in many solvents. The decomposition of ammonium salts in solution, however, has received scant attention. The apparent autoracemisation of solutions of optically active ammonium salts (Pope and Harvey, J., 1901, **79**, 831; Jones, J., 1904, **85**, 229; Wedekind, *Z. Elektrochem.*, 1906, **12**, 330, 515; *Ber.*, 1908, **41**, 1029) was shown by von Halban (*Z. Elektrochem.*, 1907, **13**, 57; *Ber.*, 1908, **41**, 2417; *Z. physikal. Chem.*, 1909, **67**, 129; 1911, **77**, 719; 1913, **84**, 129) to be due to the decomposition of the salt into amine and alkyl halide. Von Halban also showed that other higher ammonium salts, not necessarily having all the groups attached to the nitrogen atom different, decomposed in this way. Velocity coefficients were calculated from the equation for a complete unimolecular change, and, where speeds of formation of such salts were calculated, the equation for a complete bimolecular reaction was used. The coefficients thus obtained often show decided drifts, as would be expected, since equilibria are certainly involved. In the present work the ammonium salt equilibrium in aqueous acetone and in chloroform has been investigated, and rates of formation and decomposition have been calculated by using the appropriate corrected equations. The salts used were the *p*-halogenophenyldimethylallylammonium bromides. Previous determinations of the equilibrium constants of -onium salt equilibria (Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882, formation of phenyltrimethylammonium iodide in nitrobenzene; Corran, *Trans. Faraday Soc.*, 1927, **23**, 605, decomposition of triethylsulphonium bromide in benzyl alcohol–glycerol mixtures; Williams, Perrin, and Gibson, *Proc. Roy. Soc.*, 1936, *A*, **154**, 684, decomposition of phenylbenzylmethylallylammonium bromide in chloroform) were made at only one initial concentration, and only one direction of the reaction was investigated.

EXPERIMENTAL.

Materials.—Dimethylaniline, purified by treatment with acetic anhydride, was fractionated. *p*-Fluoro- and *p*-chloro-dimethylaniline were prepared from *p*-fluoro- or *p*-chloro-aniline by the following method. A mixture of the substituted aniline (1 mol.), methyl iodide (2 mols.), sodium hydroxide (2 mols.), and methyl alcohol (10 mols.) was heated at 140° for 6 hours in an autoclave. The solvent was expelled, and the residue steam-distilled. The base was warmed with acetic anhydride, and the mixture steam-distilled. *p*-Fluorodimethylaniline, yield 45%, had m. p. 35° (Schiemann and Winkelmüller, *Ber.*, 1933, **66**, 727, gave 25°). *p*-Chlorodimethylaniline, yield 70%, had m. p. 35·5°.

p-Bromodimethylaniline was purified by steam-distillation and recrystallisation from alcohol. *p*-Iododimethylaniline was prepared by slight modification of Weber's method (*Ber.*, 1875, **8**, 715; 1877, **10**, 763).

Commercial allyl bromide was treated with calcium chloride and fractionally distilled; b. p. 69·4—70·0°/747 mm.

The ammonium salts were prepared by warming under reflux for 8 hours at 40° a mixture of the substituted dimethylaniline (10 g.), allyl bromide (30—40 g.), and ether (30 c.c.). The mixture was kept for 12 hours, and the salt filtered off, washed with ether, and recrystallised from alcohol–ether. p-*Fluorophenyldimethylallylammonium bromide* (Found: Br, 30·7. $C_{11}H_{15}NBrF$ requires Br, 30·7%), unlike the following salts, is highly hygroscopic. The p-*chloro*-analogue forms rectangular plates, m. p. 153° (Found: Br, 30·0. $C_{11}H_{15}NClBr$ requires Br, 28·9%), the *p*-bromo-compound rectangular prisms, m. p. 162° (to a red liquid), and the p-*iodo*-compound flat-ended needles, m. p. 150—160° (to a dark red liquid) (Found: Br, 21·8. $C_{11}H_{15}NBrI$ requires Br, 21·7%).

" AnalaR " chloroform was shaken with concentrated sulphuric acid, washed with water, dried over calcium chloride, and fractionally distilled from phosphoric oxide; b. p. 60·5—60·9°/754 mm. It was kept in the dark and gave no indication of the presence of free hydrochloric acid throughout the duration of the experiments.

" AnalaR " acetone, purified by Norris and Prentiss's method (*J. Amer. Chem. Soc.*, 1928, **50**, 3042), and distilled, had b. p. 55·4—56·0°/743 mm.

Densities of Solvents.—Chloroform: $d_{4^\circ}^{14^\circ}$ 1·500; $d_{4^\circ}^{18^\circ}$ 1·492; $d_{4^\circ}^{35^\circ}$ 1·461; $d_{4^\circ}^{45^\circ}$ 1·442; $d_{4^\circ}^{50^\circ}$ 1·433; $d_{4^\circ}^{55^\circ}$ 1·423; $d_{4^\circ}^{60^\circ}$ 1·414; $d_{4^\circ}^{65^\circ}$ 1·404. 5% Aqueous acetone (5 vols. of water made up to 100 vols. with acetone): $d_{4^\circ}^{18^\circ}$ 0·8121; $d_{4^\circ}^{35^\circ}$ 0·7927; $d_{4^\circ}^{55^\circ}$ 0·7696; $d_{4^\circ}^{65^\circ}$ 0·7585. 10% Aqueous acetone: $d_{4^\circ}^{13^\circ}$ 0·8352; $d_{4^\circ}^{18^\circ}$ 0·8280; $d_{4^\circ}^{35^\circ}$ 0·8098; $d_{4^\circ}^{50^\circ}$ 0·7928; $d_{4^\circ}^{55^\circ}$ 0·7868; $d_{4^\circ}^{65^\circ}$ 0·7745. 15% Aqueous acetone: $d_{4^\circ}^{18^\circ}$ 0·8461; $d_{4^\circ}^{55^\circ}$ 0·8030; $d_{4^\circ}^{65^\circ}$ 0·7915.

Velocity Measurements.—Solutions of the base and halide, or of the ammonium salt, were made by diluting weighed amounts to a known volume at room temperature. Knowledge of the density of the solvent at various temperatures then enables the initial concentration to be calculated for any temperature.

Several procedures were adopted in carrying out the reactions. (*a*) *Sealed tube method.* This method was used when the reaction temperature was near or above the b. p. of the solvent, or with very slow reactions. The standard solutions of base and halide were mixed, and known volumes of this mixture, or of the ammonium salt solution, were transferred to test-tubes with constricted necks, which were then immediately sealed. The sealed tubes were placed in the thermostat, the instant of immersion being taken as zero time. At suitable intervals a tube was removed, and its contents washed into light petroleum, which was then repeatedly extracted with water. The aqueous extract was titrated against 0·025*N*-silver nitrate, with potassium chromate as indicator. (*b*) *Reaction vessel method.* The method described by Davies and Lewis (J., 1934, 1599) was used when the reaction temperature was rather below the b. p. of the solvent and when the reaction was fast. (*c*) *Stoppered bottle method.* For very dilute solutions in decomposition experiments, the reaction vessel consisted of a glass bottle with a well-ground glass stopper. Samples were removed by a pipette warmed to the temperature of the reaction and calibrated at that temperature. Greater accuracy was obtained by using one stoppered bottle for each determination in a reaction; in this case a weighed quantity of the salt was added to a known volume of solvent contained in the bottle in the thermostat, and after the desired interval, the contents of the bottle were washed into light petroleum, extraction being done as described above.

Calculations.—(1) For the complete unimolecular reaction $AB \longrightarrow A + B$, $k_1 = 1/t . \log_e a/(a - x)$, where a is the initial concentration of AB at the temperature of the reaction, and x the concentration of A and of B formed after an interval of t minutes (concentrations are expressed throughout in g.-mols./l. at the temperature at which the reaction is being investigated). The concentration of AB (ammonium salt) remaining after t minutes is $a - x = y/40 \times v$, where y is the volume (c.c.) of 0·025N-silver nitrate required by v c.c. of reaction mixture measured at the temperature of the experiment. In procedure (*a*) the volume of mixture used has to be corrected for change from the temperature of the room to that of the experiment in order to give v, but in procedures (*b*) and (*c*) the volume removed is known directly at the reaction temperature.

(2) For the complete bimolecular reaction $A + B \longrightarrow AB$, with initial concentrations of A and B equivalent and equal to a, $k_2 = x/at(a - x)$, where x is the concentration of AB (ammonium salt) after an interval of t minutes and is equal to $y/40 \times v$.

(3) In reversible uni-bi-molecular reactions, $AB \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} A + B$,

$$k_1' = \frac{1}{t\,.\,\sqrt{1 + 4aK}} \log_e \frac{(1 - \sqrt{1 + 4aK})(2Kx + 1 + \sqrt{1 + 4aK})}{(1 + \sqrt{1 + 4aK})(2Kx + 1 - \sqrt{1 + 4aK})}$$

where $K = k_2'/k_1' = (a - n)/n^2$, n being the concentration at equilibrium of A or B, and a and x have the same significance as in (1).

(4) For the opposing reaction in (3),

$$k_2' = \frac{1}{t\,.\,\sqrt{K'^2 + 4aK'}} \log_e \frac{2a^2 - x[(2a + K') - \sqrt{K'^2 + 4aK'}]}{2a^2 - x[(2a + K') + \sqrt{K'^2 + 4aK'}]}$$

where $K' = k_1'/k_2' = (a - n)^2/n$, n is the concentration of AB at equilibrium, and a and x are as in (2). When the initial concentrations of A and B are unequal, *viz.*, a and b respectively, the following equation holds

$$k_2' = \frac{1}{t\,.\,\sqrt{(a - b)^2 + K'(K' + 2a + 2b)}} \times \log_e \frac{2ab - x[(a + b + K') - \sqrt{(a - b)^2 + K'(K' + 2a + 2b)}]}{2ab - x[(a + b + K') + \sqrt{(a - b)^2 + K'(K' + 2a + 2b)}]}$$

Generally, k_1' and k_2' were obtained separately by investigating the reaction from both sides, and only in a few cases was the relation $K = k_2'/k_1'$ used to determine a velocity coefficient.

DISCUSSION OF RESULTS.

(A) *Aqueous Acetone Solutions.*—The equilibrium position of the reversible reaction between *p*-bromophenyldimethylaniline and allyl bromide lies at *ca.* 50% yield of ammonium salt in 10% aqueous acetone at 50—60°, the same equilibrium being reached from either side. On the assumption that the salt-formation reaction is bimolecular and the reverse reaction is unimolecular, it is possible to obtain values of k_1' and k_2' for the separate reactions by using the equations in (3) and (4). Constant velocity coefficients are obtained throughout the major portion of the reactions. Table I gives an example in detail. The experiments given in Table II show that the assumptions regarding the orders of the reactions used in calculating the separate velocity coefficients are justified. In the salt formation, use of a large excess of either amine or allyl bromide gives good pseudo-unimolecular constants (calculated for a complete reaction), so this reaction is of the second order. The order of the decomposition reaction was found to be unimolecular by isolating it in chloroform solution at or above 55° (see Table V).

Interaction between allyl bromide and aqueous acetone. A simultaneous reaction which might complicate the reactions studied is that between the solvent and the allyl halide. That this reaction is relatively unimportant may be inferred from the fact that the velocity coefficients obtained in both the formation and the decomposition of the ammonium salt are constant throughout the course of the reactions. Further, von Halban and Gast (*Z. physikal. Chem.*, **1916**, **91**, 593) gave the unimolecular velocity coefficient at 65° for the action of 8·7—8·9% aqueous acetone as solvent on allyl bromide (initial concentration 0·78—1·62 g.-mol./l.) as $k_1 = 7 \times 10^{-6}$, which is much lower than the velocity coefficients for the reaction in either direction. However, when the equilibrium mixture of *p*-bromo-

TABLE I.

p-*Bromophenyldimethylallylammonium Bromide.*

Solvent : 10% aqueous acetone. Temp. 65°. (A) Decomposition : $[\text{Salt}]_{65^\circ} = 0{\cdot}09354$. (B) Formation : $[C_6H_4Br{\cdot}NMe_2]_{65^\circ} = [C_3H_5Br]_{65^\circ} = 0{\cdot}09354$. Method (*a*) ; 5·345 c.c. at 65°.

A. *Decomposition.*

t.	*y.*	*a* − *x.*	$k_1' \times 10^4$.
90	18·4	0·08606	9·35
120	17·9	0·08373	9·39
180	17·0	0·07950	9·34
245	16·1	0·07530	9·40
300	15·5	0·07249	9·26
360	14·8	0·06923	9·48
460	14·0	0·06548	9·39
485	13·8	0·06455	9·47
∞	11·8	0·05520	—

Mean $k_1' \times 10^4 = 9{\cdot}39$

$K^* = 37{\cdot}54$; $k_2'/k_1' = 37{\cdot}27$.

B. *Formation.*

t.	*y.*	*x.*	$100k_2'$.
29	1·7	0·0080	3·46
62	3·3	0·0154	3·53
120	5·3	0·0248	3·44
150	6·3	0·0295	3·60
179	6·85	0·0320	3·48
273	8·5	0·0398	3·50
297	8·9	0·0416	3·58
340	9·3	0·0435	3·50
390	9·7	0·0454	3·45
475	10·3	0·0482	3·47
∞	11·8	0·0552	—

Mean $100k_2' = 3{\cdot}50$

$K'^* = 0{\cdot}02664$.

* *K* and *K'* throughout the paper refer to the equilibrium constants calculated from the concentrations of the substances at equilibrium.

TABLE II.

Formation of p-*Bromophenyldimethylallylammonium Bromide.*

Solvent : 10% aqueous acetone. Temp. 65°. Method (*a*) ; 10 c.c. at 18°.

A. $[C_6H_4Br{\cdot}NMe_2]_{18^\circ} = 1{\cdot}0$;
$[C_3H_5Br]_{65^\circ} = 0{\cdot}0468$.

t.	*y.*	*x.*	$100k_1$.
9	3·7	0·00865	2·27
17	6·75	0·0158	2·42
25	9·0	0·0211	2·40
31	10·45	0·0244	2·38
40	12·45	0·0291	2·43
48·5	13·7	0·0320	2·37
55	14·55	0·0340	2·36
65	15·9	0·0372	2·44

Mean $100k_1 = 2{\cdot}38$

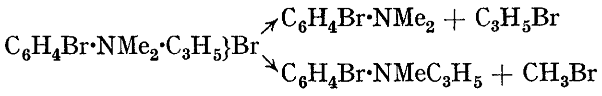
B. $[C_3H_5Br]_{18^\circ} = 1{\cdot}0$;
$[C_6H_4Br{\cdot}NMe_2]_{65^\circ} = 0{\cdot}0468$.

t.	*y.*	*x.*	$100k_1$.
9	4·1	0·00959	2·55
21	8·25	0·0193	2·53
28	10·35	0·0242	2·60
35	11·9	0·0278	2·58
40	13·1	0·0306	2·65
48	14·25	0·0333	2·59
85	17·85	0·0418	2·63
130	20·0	0·0468	—

Mean $100k_1 = 2{\cdot}59$

dimethylaniline, allyl bromide, and the ammonium bromide in aqueous acetone is kept for a long time there is a slow increase in the bromide titre corresponding to the above simultaneous reaction. During the times required for attainment of equilibrium, however, the increase in titre is hardly perceptible, so there is usually no difficulty in fixing the values to be taken as the concentrations at equilibrium.

Products of decomposition of an ammonium salt. There are two possible modes of decomposition of *p*-bromophenyldimethylallylammonium bromide, *viz.*,



$$C_6H_4Br{\cdot}NMe_2{\cdot}C_3H_5\}Br \begin{cases} \nearrow C_6H_4Br{\cdot}NMe_2 + C_3H_5Br \\ \searrow C_6H_4Br{\cdot}NMeC_3H_5 + CH_3Br \end{cases}$$

It has been shown that the first of these reactions predominates; for example, 100 c.c. of a solution of the salt (*M*/20) in 10% aqueous acetone were kept in a sealed tube at 65° for 7 days, the acetone then expelled, the residue dissolved in dilute hydrochloric acid, and the mixture neutralised with sodium carbonate. The precipitate, m. p. 54°, mixed m. p. with *p*-bromodimethylaniline, 54·5—55°, weighed 0·327 g. (calc. 0·504 g.). The low yield is mainly accounted for by the difficulty in the separation of the amine after precipitation with sodium carbonate.

Effect of temperature on the ammonium salt equilibrium. Table III summarises the results obtained on the effect of temperature on the formation and decomposition of *p*-chloro- and *p*-bromo-phenyldimethylallylammonium bromide in aqueous acetone, the initial concentration of salt or of amine and allyl bromide being denoted by *a*. The values of the activation energies are similar to those given in analogous reactions. It will be noted that the substitution of a chlorine for a bromine atom in the *p*-position of the aryl group increases the speed of formation and the yield of ammonium salt, but retards the speed of decomposition of the latter.

TABLE III.

Formation and Decomposition of p-*Chlorophenyldimethylallylammonium Bromide in 10% Aqueous Acetone.*

Temp.	*a*.	$k_1' \times 10^4$	$100k_2'$.	*K*.	Yield of salt at equilm., %.
55°	0·0475	1·94	2·31	111·6	65
65	0·04677	7·19	4·21	58·0	55

E_1 = 28,920 cals. E_2 = 13,250 cals.

Formation and Decomposition of p-*Bromophenyldimethylallylammonium Bromide in 10% Aqueous Acetone.*

Temp.	*a*.	$k_1' \times 10^4$	$100k_2'$.	*K*.	Yield of salt at equilm., %.
50	0·04747	1·15	1·54	129·7	67
55	0·04709	2·40	2·01	79·68	60
65	0·04677	9·95	3·57	35·92	49

$\log_{10} k_1' \times 10^4 = 21{\cdot}237 - 6842/T$, whence E_1 = 31,300 cals.
$\log_{10} k_2' \times 10^2 = 8{\cdot}479 - 2679/T$, whence E_2 = 12,260 cals.
$\log_{10} K = 4034/T - 10{\cdot}374$, whence the heat absorbed in the decomposition of the salt or the heat evolved in its formation is Q_v = 18,450 cals.

Factors influencing the yield of ammonium salt. The effect of temperature and of initial concentration on the yield of ammonium salt in the formation reaction is given in Tables III and VII. The reversibility of ammonium-salt formation is more common than is generally realised. It is therefore incorrect to heat the mixture of generators, as is often done, with the object of obtaining a good yield of salt. Moreover, the drifts obtained in the bimolecular velocity coefficients (calculated by assuming the formation to be complete) reported by certain workers may be due to the reversibility of the reaction.

Whereas in 10% aqueous acetone at 50° the yield of *p*-bromophenyldimethylallylammonium bromide is 67% (both reactants = *M*/20), in chloroform under the same conditions it is only 1·25%. Increase in the proportion of water in the aqueous acetone has an important effect, augmenting the yield of salt by accelerating its formation and retarding its decomposition (see Table IV). Such effects were predicted by Hughes and Ingold (J., 1935, 244) on the basis of their mechanism for these reactions.

TABLE IV.

Formation and Decomposition of p-*Bromophenyldimethylallylammonium Bromide in Aqueous Acetone.*

Temp.: 65°. Initial concn. of base and halide or of salt at 65° = 0·0467 g.-mol./l.

Solvent.	$k_1' \times 10^4$.	$k_2' \times 10^4$.	*K*.	Yield of salt at equilibrium, %
5% Aqueous acetone	17·5	127	6·21	19
10% ,, ,, ...	9·95	357	35·92	49
15% ,, ,, ...	2·42	562	234·1	74

(B) *Chloroform Solutions.*—The decomposition of *M*/20-*p*-bromophenyldimethylallylammonium bromide in chloroform solution is complete at or above 55°. At 50°, from equivalent quantities of the generators (*M*/20) the yield of salt is 1·25%, and at 35° it is 5%. The decomposition is of the first order, and no correction is necessary for the reverse reaction even at 35° (Table V). The results obtained at an initial salt concentration of approximately *M*/20 for the decomposition reaction are summarised in Table VI.

Change of the nuclear halogen substituent affects the stability of the salt, the order of stability being F>Cl>Br. This should be compared with the order, Cl>Br>I, of decreasing reactivity of the halogenophenyldialkylamines towards alkyl halides (Davies and Lewis, *loc. cit.*). Examination of Table VIII shows that, in spite of the great effect which

TABLE V.

Decomposition of p-*Bromophenyldimethylallylammonium Bromide in Chloroform.*

Initial concn.: 0·04897 at 35°; 0·04739 at 60°. Method (*a*).

35° (10·21 c.c. portions).

t.	*y*.	$a - x$.	$k_1 \times 10^4$. (1).*	$k_1 \times 10^4$. (2).*
1050	13·2	0·03232	3·96	3·97
1490	11·2	0·02743	3·90	3·92
2640	6·8	0·01665	4·09	4·20
2985	6·0	0·01469	4·03	4·17
4980	2·9	0·00710	3·88	4·30
∞	1·0	0·00245	—	—
		Mean $k_1 \times 10^4$ =	3·97	4·11

* (1) Calculated for the reaction going to completion; (2) corrected for the reverse reaction: K = 1·131.

60° (10·55 c.c. portions).

t.	*y*.	$a - x$.	$100k_1$.
15	16·6	0·03933	1·24
30	13·7	0·03246	1·26
45	11·3	0·02678	1·27
60	9·4	0·02227	1·26
75	7·6	0·01801	1·29
90	6·4	0·01517	1·27
105	5·4	0·01279	1·25
120	4·4	0·01042	1·26
140	3·4	0·00806	1·27
160	2·6	0·00616	1·28
180	2·0	0·00474	1·28
		Mean $100k_1$ =	1·27

TABLE VI.

Decomposition of p-*Halogenophenyldimethylallylammonium Bromides in Chloroform.**

Temp.	*a*.	$k_1 \times 10^3$.
p-*Fluoro*-.		
55°	0·04772	2·97
65	0·04697	11·4
E_1 = 29,680 cals.		
p-*Chloro*-.		
55	0·04772	5·87
65	0·04697	24·0
E_1 = 31,090 cals.		

Temp.	*a*.	$k_1 \times 10^3$.	
p-*Bromo*-.			
35°	0·04897	0·397	
45	0·04832	1·62	
50	0·04801	3·05	
55	0·04758	6·24	Method (*b*)
,,	0·04687	6·25	Method (*a*)
,,	0·04758	6·21 †	
60	0·04739	12·7	
65	0·04786	24·6	

$\log_{10} k_1 \times 10^4 = 20{\cdot}472 - 6120/T$, whence E_1 = 28,000 cals.

* *p*-Iodophenyldimethylallylammonium bromide was almost insoluble in chloroform, and no measurements could be carried out with it.

† This reaction was carried out in a bottle packed with soda glass.

initial concentration has on the value of the unimolecular velocity coefficient, the *p*-chloro-salt remains slightly more stable than the *p*-bromo-salt in a range of dilution of 20—300 l./g.-mol.

In the decomposition of *p*-bromophenyldimethylallylammonium bromide in chloroform the resulting amine was shown to be *p*-bromodimethylaniline by the following experiment. A solution of 0·4012 g. of the salt in 25 c.c. of chloroform was kept at 55° for 24 hours, and then worked up as for the experiment in aqueous acetone (p. 617). The precipitated *p*-bromodimethylaniline had m. p. 54° (mixed m. p. 54·5°). The amount recovered was 0·238 g. (calc., 0·250 g.).

Formation of p-*bromophenyldimethylallylammonium bromide at* 35° *in chloroform solution.* By working with solutions stronger than $M/20$ it is possible to measure the speed of formation of the salt from its generators. Equation (4) must be used in order to obtain constant velocity coefficients. The mean values are discussed later (see Table IX).

Formation of phenyltrimethylammonium iodide in chloroform. At 45° and with initial concentrations of dimethylaniline and methyl iodide *ca.* $M/10$, good bimolecular velocity coefficients are obtained on the assumption that formation of salt is complete. However, at 65° under similar conditions, the bimolecular coefficients drift seriously, indicating that the reverse reaction is now of considerable importance. Separation of salt prevented a determination of the equilibrium position, but it was determined for less concentrated equivalent solutions:

Temp.	Initial concn.	$k_2 \times 10^3$ (calc. for complete reaction).	% Reaction when salt commenced to separate.
45°	0·0967	3·75	20
65	0·0939	13—5	22
,,	0·0470	Equilm. reached when reaction was *ca.* 7% complete.	No separation.

(C) *Effect of Dilution on Velocity Coefficients and Equilibrium Constants.*—In aqueous acetone, dilution has only a small effect on the velocity coefficients of the formation or dissociation of ammonium salts or on the equilibrium constant (see Table VII), the increase of coefficient with dilution being most evident in the formation of phenyltrimethylammonium iodide, a reaction which goes to completion under the conditions given. On the other hand, the values of the velocity coefficients of the decomposition of an ammonium salt in chloroform depend on the initial concentration of the salt, the coefficient increasing markedly with dilution (see Table VIII). When velocity coefficients are plotted against initial concentration, a straight line is obtained below a concentration of 0·02 g.-mol./l.; *i.e.*, the velocity coefficient is directly proportional to the initial concentration of the salt in very dilute solution. It would appear that in dilute solution the decrease of the speed of decomposition with increase in the initial concentration is due to negative catalysts of concentration proportional to that of the salt. Further, since in a decomposition at any particular initial concentration of salt, the unimolecular velocity coefficients are constant throughout the whole course of the decomposition, it is necessary to postulate that the salt and one of the products of the decomposition act as catalysts. These two catalysts must be of almost identical activity. It seems unlikely that the catalyst is a complex of a reactant or product with the solvent, since the index of catalytic activity, obtained by comparison of velocity coefficients, at 65° is almost identical with that at 55°. From graphs of the results given in Table VIII, values of the velocity coefficients at 55° and 65° at certain dilutions were obtained.

TABLE VII.

Formation and Decomposition of p-*Bromophenyldimethylallylammonium Bromide in 10% Aqueous Acetone at 65°.*

Initial concns.							
Amine.	Allyl bromide.	Salt.	$k_1' \times 10^4$.	$k_2' \times 10^2$.	K.	K'.	Yield of salt at equilm., %.
0·09354	0·09354	0·09354	9·39	3·50	37·54	0·02664	59
0·04677	0·04677	0·04677	9·95	3·57	35·92	0·02784	49
0·02339	0·04677	—	11·5 *	4·15	—	0·02775	55
0·04677	0·02339	—	11·5 *	4·14	—	0·02775	55

* Calculated from K' and k_2'.

Reaction between Equivalent Amounts of Dimethylaniline and Methyl Iodide in 10% Aqueous Acetone at 45°.

Initial concn. of base and halide	0·09620	0·04810	0·02405
$100k_2$	4·29	6·20	6·17

TABLE VIII.

Effect of Initial Concentration on the Decomposition of Ammonium Salts in Chloroform Solution.

p-Bromophenyldimethylallylammonium bromide.

Temp. 55°	Initial concn. × 10^3	47·58	23·79	11·90	7·925	6·359	3·179
	$k_1 \times 10^3$	6·24	8·30	12·2	14·3	16·0	18·2

Temp. 65°	Initial concn. × 10^3	47·86	15·65	7·820	3·135
	$k_1 \times 10^3$	24·6	48·0	67·8	79·4

p-Chlorophenyldimethylallylammonium bromide.

Temp. 55°	Initial concn. × 10^3	47·58	23·79	11·90	7·925	6·359	3·179
	$k_1 \times 10^3$	5·83	8·10	11·6	13·4	15·3	17·2

Decomposition of p-*Bromophenyldimethylallylammoninm Bromide in Chloroform Solution: Ratios of* k_1 *at Various Dilutions to* k_1 *at* M/60, *and Values of* E.

Dilution	20	60	120	240	380
55°; k_1/k_1 (M/60)	—	1	1·43	1·73	1·87
65°; ,,	—	1	1·46	1·69	1·80
E, kg.-cals.	28·0	33·4	33·9	32·9	32·6

These values of the activation energies at different initial concentrations of the ammonium salt are of interest. In the most concentrated solution, E is very different from the nearly constant values in the dilute solutions, for which the velocity coefficient is proportional to the initial concentration.

The important part played by complex formation between the solvent and the reactants in determining the mechanism of reactions in solution has been stressed by Moelwyn-Hughes and Sherman (J., 1936, 101). If the reaction $A + B \rightleftharpoons AB$ is considered to proceed through an intermediate stage involving the solvent, or if there is a side reaction in which one of the generators combines with the solvent, then the apparent equilibrium constant $K = [A][B]/[AB]$ would be expected to change in value at different dilutions. This, of course, assumes that an appreciable amount of the solvent–reactant complex is formed at the temperature of the reaction. We were unable to detect the production of chloride ion in solutions of *p*-bromodimethylaniline in chloroform kept for long periods at 35°, but nevertheless there appears to be a possibility of complex formation at this temperature. Our results on the equilibrium constant of the reaction between *p*-bromodimethylaniline and allyl bromide in chloroform at 35° (Table IX) do not lead to an entirely satisfactory conclusion The equilibrium constant increases with dilution, but the velocity coefficients do not alter regularly with dilution. If the value of K' obtained in the most concentrated solution is taken to be the most accurate, values for those velocity coefficients which cannot conveniently be directly determined may be calculated. These are given in parentheses in Table IX, and it will be seen that they compare better with the determined values. Experimental errors in the determination of the equilibrium constant in the dilute solutions are large, but the increase in the constant is slightly too large to be ascribed to this cause. Search is being made for a pair of generators which will give an equilibrium position in chloroform less far displaced towards one side.

TABLE IX.

Initial concn.	$k_1 \times 10^4$.	$k_2' \times 10^4$.	K'.	Amount of salt at equilm., %.
0·1958	3·4 *	6·3	0·541	22
0·0979	5·9 * (4·1)	7·5	0·793	10
0·04897	4·0	4·5 * (7·4)	0·886	5

* Calculated from k_1 or k_2' and K'.

SUMMARY.

1. The formation of certain ammonium salts in solution in aqueous acetone and in chloroform is reversible.

2. The equilibrium constant in aqueous acetone is constant over a range of initial concentrations. In chloroform, however, the equilibrium constant increases with dilution; the effect of complex formation of the participants with the solvent is discussed in this respect.

3. The unimolecular velocity coefficients for the decomposition of ammonium salts in chloroform solution increase with decrease of initial concentration of the salt; in dilute solution the velocity coefficient is proportional to the initial concentration of the salt.

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