134. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XV. Dynamics of the Elimination of Olefins from Quaternary Ammonium Compounds.*

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The work now reported appears to constitute the first direct dynamical investigation of this reaction. We show that decomposition may follow either of two modes, characterised as unimolecular and bimolecular respectively.

The examples described, which are of the form

$$\{R\cdot CH_2\cdot CH_2\cdot NMe_3\}^{\cdot}X' \longrightarrow R\cdot CH{:}CH_2 + NMe_3 + HX,$$

were selected to fulfil certain theoretical conditions (following paper), and also the obvious practical requirements of convenient speed, analytical feasibility, and the absence of side reactions. Except where otherwise noted, the solvent was water and the temperature 100°.

The decomposition of β-phenylethyltrimethylammonium hydroxide ($R = C_6H_5$; $X = OH$) was bimolecular, as shown by the form of the reaction–time curves and the inverse proportionality between the time of half-destruction of the ammonium compound and its initial concentration. Further, by observing the effect on speed of the introduction of extraneous hydroxide, it was shown that the bimolecular character of the reaction arises from first-order dependence on each of the participating ions.

The decomposition of β-p-*nitrophenylethyltrimethylammonium iodide* ($R = C_6H_4\cdot NO_2$; $X = I$) was proved by the reaction–time relation to be unimolecular, and this was confirmed by the observation that the half-change period of the ammonium compound is independent of its initial concentration. The addition of extraneous iodide showed that the reaction was of order zero with respect to this ion, and therefore of order unity with respect to the ammonium cation. Unimolecular decomposition was also established in the case of β-*p*-nitrophenylethyltrimethylammonium bromide ($R = C_6H_4\cdot NO_2$; $X = Br$), and the circumstance that the velocity coefficient was identical with that obtained for the iodide under the same conditions is consistent with the conclusion that the reactions of these salts are of order zero with respect to their anions. These decompositions are retarded by acids, unaffected by neutral salts, and accelerated by alkalis; their dependence on the solvent is indicated by the retardation observed when water as medium was replaced by aqueous *n*-propyl alcohol.

The interpretation of these observations is considered in Part XVI (following paper).

EXPERIMENTAL.

Preliminary Observations.—The kinetics of the decomp. of $\{\mathrm{NEt_4}\}^{\cdot}\mathrm{OH'}$ could not be studied in ordinary glass apparatus because, at the temps. required for a convenient speed of reaction, the vessels were attacked and the decomp. was therefore in part that of an ammonium silicate. Of other quaternary ammonium hydroxides known to decompose quant. in the direction leading to an olefin, β-phenylethyltrimethylammonium hydroxide appeared to be the simplest that had not the disadvantage indicated.

β-*Phenylethyltrimethylammonium Hydroxide.*—The iodide, m. p. *ca.* 225° (decomp.) (Found: C, 45·2; H, 6·3; N, 4·5; I, 43·0. Calc.: C, 45·3; H, 6·2; N, 4·8; I, 43·6%), was prepared by complete methylation of $\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2Ph}$ with MeI, a modification of Decker and Becker's process (*Ber.*, 1912, **45**, 2404).

The hydroxide soln., prep. by means of $\mathrm{CO_3''}$-free $\mathrm{Ag_2O}$, was made up to a known vol. and standardised acidimetrically. Portions of 5·00 c.c. were separated, enclosed in sealed tubes, and heated at 100° for various periods; the tubes were then quickly cooled and opened. The styrene extracted with $\mathrm{CHCl_3}$ and washed with $\mathrm{H_2O}$ and dil. $\mathrm{H_2SO_4}$ was estimated by the addn. of standard $\mathrm{Br_2}$ in $\mathrm{CHCl_3}$ soln. and subsequent iodometric determination of the excess of halogen. The results are in Table I, in which time, t, is given in mins.; absorbed $\mathrm{Br_2}$ is recorded in terms of c.c. of 0·1*N*-$\mathrm{Na_2S_2O_3}$; x is the concn. of the products, and k_2 is the bimol. const. $x/ta(a-x)$.

TABLE I.

t.	Abs. $\mathrm{Br_2}$.	x.	k_2.		t.	Abs. $\mathrm{Br_2}$.	x.	k_2.	
			(a=0·330)	(a=0·318)				(a=0·165)	(a=0·158)
(Initl. concn. hydroxide = 0·330*N*)					(Initl. concn. hydroxide = 0·165*N*)				
10	3·50	0·0350	0·0359	0·0389	40	3·05	0·0305	0·0344	0·0379
20	6·30	0·0630	0·0355	0·0389	90	5·50	0·0550	0·0337	0·0376
40	10·60	0·1060	0·0358	0·0393	150	7·50	0·0750	0·0337	0·0382
60	13·70	0·1370	0·0358	0·0397	210	8·85	0·0885	0·0334	0·0384
90	16·85	0·1685	0·0351	0·0394	300	10·30	0·1030	0·0336	0·0395
120	19·15	0·1915	0·0349	0·0398	∞	15·80	0·1580	—	—
180	21·90	0·2190	0·0332	0·0385					
240	23·75	0·2375	0·0324	0·0387					
300	25·15	0·2515	0·0324	0·0397					
∞	31·80	0·3180	—	—					

A minor complication arose through the partial polymerisation of styrene under the influence of the alkali, and owing to this cause there is a 4% discrepancy between the value of a determined acidimetrically, and what should be its equivalent, *viz.*, the final value of x measured bromometrically (polymerised styrene does not absorb Br under the conditions used). In Table I the bimol. const. k_2 is calculated from both the acidimetric and the bromometric value of a. The two sets differ slightly, and in the expected sense, since the error caused by polymerisation must be negative in the former set and positive in the latter. The small downward drift with time shown by the set dependent on the acidimetric value of a is also to be expected.

The expts. with the 0·330*N*-hydroxide solution show the time of half-destruction to be 86 min. In the second series of expts., with 0·165*N*-hydroxide, the corresponding time is 175 min. (calc. for bimol. reaction, 172 min.).

A value of k_2 which should be free from the error caused by polymerisation may be obtained by extrapolating to zero time the consts. calc. from the acidimetric value of a. The first series of expts. (a = 0·330) then gives k_2 = 0·036, and the second series (a = 0·165) gives k_2 = 0·035.

More extensive polymerisation was experienced in expts. in which a considerable concn. of KOH was added to the hydroxide soln. before decomp. The bimol. velocity coeffs., k_2', show a large downward drift with time (Table II), but the value obtained by extrapolation to zero time, k_2' = 0·037, is substantially identical with the above values of k_2.

The product of such an expt. on extraction with $\mathrm{CHCl_3}$ yielded the polymerised styrene as an amorphous gum having no action on $\mathrm{Br_2}$ in $\mathrm{CHCl_3}$ at room temp.

β-p-*Nitrophenylethyltrimethylammonium Salts.*—Excess of MeI was cautiously added to an EtOH soln. of β-*p*-nitrophenylethylamine in the presence of suspended $\mathrm{Na_2CO_3}$. The reaction,

TABLE II.

Initial concn. of quaternary ammonium hydroxide = 0·160N.
Concn. with respect to added potassium ,, = 0·240N.

a = Initial concn. with respect to hydroxide ion = 0·400.
b = ,, ,, ,, ,, ,, ammonium ion = 0·160.

$k_2' = 2{\cdot}303/t(a - b)\,.\log_{10} b(a - x)/a(b - x)$.

t.	Abs. Br_2.	x.	k_2'.	t.	Abs. Br_2.	x.	k_2'.
10	2·00	0·0200	0·0343	120	10·50	0·1050	0·0264
30	4·70	0·0470	0·0309	150	11·50	0·1150	0·0258
60	7·30	0·0730	0·0283	180	12·25	0·1225	0·0255
90	9·10	0·0910	0·0270	210	13·00	0·1300	0·0253

which took place with evolution of heat, was completed on the water-bath, and the salts were completely pptd. with dry Et_2O and collected. The carbonates were neutralised with HI, and the quaternary ammonium *iodide* which separated was collected, washed with acetone and Et_2O, and crystallised from EtOH. It formed feathery, lemon-yellow leaflets, m. p. 199° (decomp.), insol. in most non-hydroxylic solvents, moderately sol. in H_2O, EtOH, and hot acetone, but much more sol. in aq. acetone than in either solvent alone (Found : C, 39·4; H, 5·1; N, 8·0; I, 37·7. $C_{11}H_{17}O_2N_2I$ requires C, 39·3; H, 5·1; N, 8·3; I, 37·8%). The *picrate*, needles, m. p. 147° (decomp.), sparingly sol. in H_2O but sol. in EtOH and acetone, was crystallised from aq. EtOH (Found : C, 46·7; H, 4·3; N, 15·7. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·3; N, 16·0%). Owing to the instability of the hydroxide solution, the bromide was prepared *via* the carbonate. The iodide in cold aq. suspension was shaken for a few min. with excess of Ag_2CO_3, and the soln. was filtered, tested for I′ (negative), made faintly acid with HBr, and evaporated to dryness. The bromide was washed well with cold EtOH, Et_2O, and acetone, and crystallised once from EtOH–acetone and once from $C_5H_{11}{\cdot}OH$, and thus obtained as small colourless (contrast iodide) needles, m. p. 222° (decomp.), extremely sol. in H_2O.

A study of the decomp. of aq. solns. of the hydroxide at room temp., and of the iodide at 100°, showed that the products in the former case were NMe_3 (Found for hydrobromide : Br, 57·0. Calc. : Br, 57·1%) and *p*-nitrostyrene (m. p. and mixed m. p. of dibromide), and in the latter case NMe_3,HI (Found for methiodide : I, 63·1. Calc. : I, 63·2%), *p*-nitrostyrene, and (largely) a *polymeride* of *p*-nitrostyrene. The last substance, originally isolated as a glassy solid, became microcryst. on digestion with acetone; it was washed with hot H_2O, acetone, and $CHCl_3$ [Found : C, 64·0; H, 4·8; N, 9·0. $(C_8H_7O_2N)_x$ requires C, 64·4; H, 4·7; N, 9·4%].

Weighed portions of the iodide or bromide were separately enclosed in sealed tubes each with 5·00 c.c. of H_2O. The tubes were heated at 100° for known periods, cooled, and opened, and the iodides extracted with warm H_2O. The quaternary ammonium salt was then pptd. and weighed as its sparingly sol. picrate. The results are in Table III, t being in hrs., x being the concn. of the products, and $k_1 = 2{\cdot}303/t\,.\log_{10}a/(a - x)$.

TABLE III.

t.	Wt. picrate, g.	Decompn., %.	x.	k_1 (hr.$^{-1}$).
	Salt decomp. : iodide; initl. concn. = 0·300M = a.			
2	0·485	25·4	0·076	0·146
4	0·372	42·8	0·128	0·139
5	0·323	50·3	0·151	0·140
6	0·269	58·6	0·176	0·147
7	0·230	64·6	0·194	0·148
8	0·205	68·5	0·205	0·143
10	0·135	79·2	0·238	0·158
	Salt decomp. : iodide; initl. concn. = 0·600M = a.			
5	0·652	49·8	0·299	0·138
10	0·276	78·8	0·473	0·155

t.	Wt. picrate, g.	Decompn., %.	x.	k_1 (hr.$^{-1}$).
	Salt decomp. : iodide; initl. concn. = 0·300M = a.			
	Substance added : NMe_3,HI; concn. = 0·53M.			
4	0·364	44·0	0·132	0·145
8	0·191	70·6	0·212	0·153
	Salt decomp. : iodide; initl. concn. = 0·300M = a.			
	Substance added : NMe_4I; concn. = 0·30M.			
3	0·425	34·6	0·104	0·142
9	0·176	72·9	0·219	0·145
	Salt decomp. : bromide; initl. concn. = 0·300M = a.			
2	0·492	24·3	0·073	0·139
6	0·264	59·4	0·178	0·150

The first two series of measurements show that the unimol. velocity coeff. for the iodide is 0·145. When a = 0·300, the decompn. after 5 hr. is 50·3%, and when a = 0·600 the decompn. after the same time is 49·8%, so that the period of half-destruction of the ammonium iodide is evidently independent of its initial concn. The third and fourth series show that the velocity is affected neither by NMe_3,HI (a product of the reaction) nor by NMe_4I. The last series shows that the bromide decomposes at the same rate as the iodide. These results are supplemented by qual. observations, which show that the speed of decomposition of the iodide is greatly reduced by acids (*e.g.*, 0·5*N*-HCl) and greatly increased by bases (*e.g.*, 0·1*N*-NMe_3 or OH′ derived from Ag_2O). The effect of replacing H_2O by aq. $Pr^{\alpha}OH$ as solvent is to reduce the speed of the change as indicated below :

Temp. 100°. Initial concn. of iodide = 0·300*N*.

Proportion of $Pr^{\alpha}OH$ in medium, % by vol.	0	70	90
Time of half-change, hours	5·0	18	29

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