

**135.** *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XVI. Mechanism of the Thermal Decomposition of Quaternary Ammonium Compounds.*

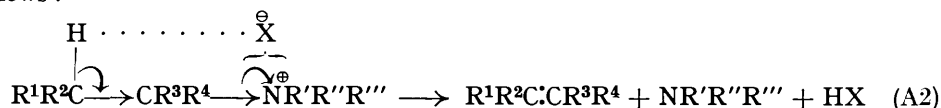
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ALTHOUGH the general theory of the two main modes of decomposition of quaternary ammonium compounds



has not been treated in this series since the appearance of Part I (Hanhart and Ingold, J., 1927, 997), yet the point of view underlying the more recently recorded experiments has developed appreciably in the meantime.

*Reaction (A).*—The conception of reaction (A) advanced in Part I may be symbolised as follows :



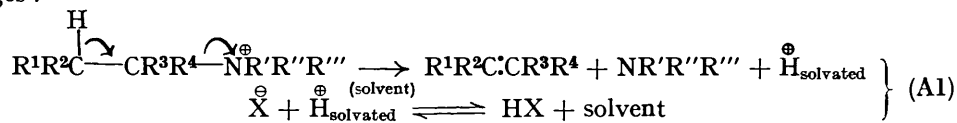
The equation depicts, first, predisposition towards reaction arising from the incipient ionisation of the  $\beta$ -hydrogen atom induced by the electron-attraction of the ammonium pole; and, secondly, the actual process whereby the  $\beta$ -proton is extracted by the anion with the assistance of octet-preserving displacements of electron-duplets towards the pole of the cation. Wide variations in the structure of the ammonium compound have been shown to affect the reaction in the manner demanded by this mechanism.

The above description requires that reaction (A) be of the first order with respect to each of the participating ions and therefore of the second order with respect to the ammonium compound. The numerical part of the description (A2) is intended to symbolise this dynamical character (*vide infra*).

In Part XV (preceding paper) it is shown that the dynamics of the decomposition of  $\beta$ -phenylethyltrimethylammonium hydroxide (reaction A) conform to the requirements of mechanism (A2); and we regard this demonstration as indirect evidence that second-order dynamics govern the decomposition (reaction A) of all ammonium compounds in which the incipient ionisation of the  $\beta$ -hydrogen atom is not greater, and the basicity (proton-affinity) of the anion is not less, than in  $\beta$ -phenylethyltrimethylammonium hydroxide. For example, the formation of any purely aliphatic mono-olefin from a quaternary ammonium hydroxide or alkoxide (Part XII, this vol., p. 68) may be considered to proceed according to mechanism (A2).

Starting from any of the ammonium compounds referred to in the last paragraph, we now imagine progressive changes of structure which (a) increase the hydrogen-polarisation in the cation, and (b) decrease the proton-affinity of the anion. Evidently a state will

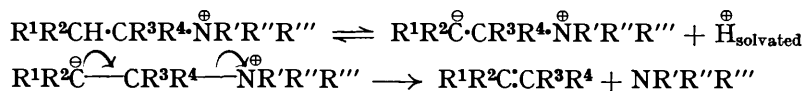
ultimately be reached in which the anion (a) is not required, and (b) is structurally unable, to assist effectively in the extraction of the β-proton. In these circumstances reaction (A) must be a two-stage process such that the cation and anion are concerned in separate stages :



Thus we are led to envisage a second mechanism, here designated (A1), which is of first order with respect to the cation, of zero order with respect to the anion, and thus of order unity with respect to the ammonium compound.

Examples illustrating this mechanism are given in Part XV (*loc. cit.*). Starting from β-phenylethyltrimethylammonium hydroxide, the hydrogen-polarisation in the cation is increased by the introduction of a nitro-group and the basicity of the anion is decreased by replacing it by a halide ion. The decompositions (reaction A) of the resulting β-*p*-nitrophenylethyltrimethylammonium bromide and iodide were each found to be unimolecular with respect to the appropriate salt, and both salts gave the same velocity coefficient.

In relation to these examples, the first stage of mechanism (A1) may require subdivision by the introduction of a hypothetical, and presumably unstable, intermediate betaine; the ammonium cation would then be regarded as a definite acid of which the betaine is the conjugate base and the immediate precursor of the olefin :



If  $k_1$  and  $k_2$  are velocity coefficients representing respectively the rate of dissociation and of formation of the acid, whilst  $k_3$  similarly specifies the speed of fission of the base, then the experimental unimolecular coefficient,  $k$ , has the form,  $k_1k_3/(k_2[\text{H}^+] + k_3)$ . A definite dependence of  $k$  on  $[\text{H}^+]$  has been observed and its direction is consistent with the formula given. This is the reason for the suggested sub-division, which, however, is not regarded as necessarily a general feature of mechanism (A1).

Thus the original conception of reaction (A), represented in mechanism (A2), is now generalised by the contemplation of a graded range of mechanisms, (A2)—(A1), of which the extremes have been illustrated.

*Reaction (B).*—In the representation of this reaction advanced in Part I (*loc. cit.*) two stages are distinguished : it is assumed that the cation suffers fission without the direct intervention of the anion, which only subsequently unites with the ejected radical :



This mechanism, designated (B1), represents a reaction which is of first order with respect to the cation, of zero order with respect to the anion, and therefore of first order with respect to the ammonium compound. It has afforded a consistent explanation of many phenomena, but recent investigation, both by von Braun and his collaborators and by ourselves, has revealed four difficulties in its general application.

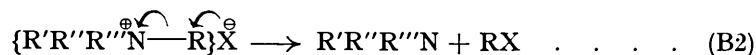
First, von Braun *et al.*, studying the decomposition of trimethyl-*n*-decylammonium hydroxide in dilute solution at constant volume, found that the ratio of the quantities of methyl alcohol and decylene eliminated in the same experiment did not depend on the initial concentration of the ammonium hydroxide (*Annalen*, 1929, 472, 121; cf. *Ber.*, 1931, 64, 2610). This result shows that reactions (A) and (B) are, in this instance, of the same order, but it does not determine the order. We combine it, however, with our dynamical study of reaction (A) (Part XV, *loc. cit.*), which, as the previous section shows, requires the elimination of decylene to be bimolecular. It follows that the elimination of methyl alcohol is bimolecular, contrary to the reaction order required by mechanism (B1).

Secondly, an investigation into the decomposition of benzhydryltrimethylammonium hydroxide in dilute solution at constant volume has shown (Part XIII, this vol., p. 69) that the ratio of the quantities of benzhydrol and methyl alcohol eliminated in the same experiment is strongly dependent on the initial concentration of the ammonium hydroxide. The ratio is also changed by the initial addition of extraneous hydroxide ions. Both results are indicative of the existence of simultaneous reactions of different orders, and a satisfactory interpretation was found to follow from the assumption that the elimination of benzhydrol and methyl alcohol are reactions of the first and second order respectively. Once again the elimination of methyl alcohol exhibits dynamics contrary to the demands of mechanism (B1).

The third difficulty is that, although until recently all the available observations concerning the relative facility with which those groups which cannot appear as an olefin become eliminated as alcohols from quaternary ammonium hydroxides were consistent (Part I, *loc. cit.*) with mechanism (B1), yet one clear case contrary to this mechanism has been observed (Part XI, this vol., p. 67) in the exclusive formation of methyl alcohol and the complementary amine from trimethylneopentylammonium hydroxide; for mechanism (B1) requires that the group with the greater tendency to separate as a cation should preferentially be eliminated as alcohol, and evidently electron-release from the *tert.*-butyl portion of the neopentyl radical should facilitate the formation of the corresponding cation, wherefore neopentyl alcohol rather than methyl alcohol should have been eliminated.

The fourth and last point has reference to the widely observed phenomenon that, when the decomposition of an ammonium salt with a feebly basic anion (*e.g.*, a chloride) is compared with that of a corresponding compound having the same cation but a much more strongly basic anion (*e.g.*, the hydroxide), reaction (A) assumes considerably greater relative importance in the latter case. This is consistent with the operation of the combination of mechanisms (A2) and (B1) (*cf.* Part I, *loc. cit.*), and whilst the hydroxide ion remained the most basic of those investigated in this connexion no difficulty with this interpretation arose. But an extension of the comparison by the inclusion of alkoxide ions (Part XII, this vol., p. 68) has revealed that the suppression of reaction (B) in favour of (A) does not continue when the basicity of the anion is increased beyond that of the hydroxide ion. This effect cannot be ascribed to the operation, over the extension in the range of anions, of the combination of mechanisms (A1) and (B1), for it will be clear from the preceding section that any increase in the basicity of the anion must tend to strengthen the retention of mechanism (A2). The effect referred to must therefore be attributed to some failure of mechanism (B1).

Commencing with any case to which mechanism (B1) applies, let us imagine changes of structure which (*a*) decrease the cationic stability of the eliminated group, and (*b*) increase the basicity, or, more generally, the nucleophilic tendencies, of the anion. Eventually a state must be reached in which the intervention of the anion (*a*) is necessary for, and (*b*) is effective in, the elimination of the group. The process will now occur in one stage as in the scheme :



According to this mechanism reaction (B) is of the first order with respect to each ion, and hence bimolecular with respect to the ammonium compound, wherefore the mechanism receives the designation (B2). Thus arises the possibility of a generalisation of the mechanistic theory on the lines already illustrated in relation to reaction (A).

Before pursuing this conception, it is necessary to refer to the alternative suggestion by von Braun *et al.* (*loc. cit.*) that reaction (B) is a decomposition of the un-ionised ammonium hydroxide molecule :



Two series of special experiments, relating to the decomposition of trimethyl-*n*-decylammonium hydroxide, were held to support this view. First, it was found that the addition of glycerol to the ammonium hydroxide decreased the proportion of decylene formed and

thus augmented the proportion of methyl alcohol; and it was argued that the glycerol, by repressing the ionisation of the ammonium hydroxide, should favour the molecular reaction (B) at the expense of the ionic reaction (A), though possible disturbance through the formation of ammonium glyceroxides was admitted. Secondly, it was observed that the addition of potassium hydroxide increased the proportion of decylene and decreased that of methyl alcohol; and the argument on this point was that, although extraneous hydroxide ions, by repressing ionisation, must facilitate reaction (B), yet, because the concentration of the molecular ammonium hydroxide is in any circumstances small, therefore this effect must be small in comparison with the direct, accelerative effect of the added hydroxide ions on the ionic reaction (A).

We accept Sidgwick's principle whereby the formation of an un-ionised quaternary ammonium hydroxide is impossible, and accordingly regard all decompositions of ammonium compounds as exclusively ionic. Concerning the effect of added glycerol, we concur in the suggestion relating to the formation of glyceroxides. Regarding the effect of added potassium hydroxide we would remark, first, that the argument based on this effect is contrary to the mass law, and secondly, that von Braun and his co-workers themselves have shown that in aqueous solution reactions (A) and (B) are *equally* affected by hydroxide ions. Furthermore, we imagine that the un-ionised molecule is expected to be more plentiful in the fused ammonium hydroxide than in dilute aqueous solution; wherefore, according to scheme (B'), the proportion of reaction (B) might be expected to be greater in the former case, contrary to the observations. The foregoing comments will not obscure the circumstance that von Braun's scheme (B') requires the same reaction order as our scheme (B2).

Returning to the consideration of mechanism (B2), we first observe that, in each of the cases in which the application of scheme (B1) has led to inconsistencies, the *ad hoc* introduction of its alternative (B2) would interpret the observations. It provides the dynamics which are required in relation to the elimination of methyl alcohol. It accords with reaction inhibition by electron release, and thus interprets the case of the *neopentyl* group ( $\text{Me}_3\text{C}\text{---}\text{CH}_2\cdot$ ), since polarisation in this direction must oppose the address of the anion. Also, mechanism (B2), like (A2), depends on the basicity of the anion, and this circumstance accommodates the observed absence of any marked change in the direction of decomposition on replacing the hydroxide ion by the more basic alkoxide ion.

On the other hand, it is equally evident that no *general* application of mechanism (B2) is possible; for the reasons which led originally to the proposal of mechanism (B1) still hold, and in addition we now have direct evidence for unimolecular dynamics in the elimination of benzhydrol, and indirect evidence for the same mechanism in the case of the elimination of triphenylcarbinol (Hughes, Part XIV, this vol., p. 75). Both mechanisms must be envisaged [this was done in Part I, but (B2) was not regarded as important].

The circumstances which theoretically should determine the replacement of one of these mechanisms by the other are clear. In the molecule  $\{\text{RR}'\text{R}''\text{R}'''\text{N}^{\oplus}\text{X}^{\ominus}\}$ , if either (a) the cationic stability of R is progressively increased, or (b) the basicity of  $\text{X}^{\ominus}$  is progressively decreased, then a stage should be reached at which mechanism (B2) becomes superseded by (B1). It remains to show that this theoretical relation corresponds to known experimental data.

The effect of changes of type (a) in the cation may be illustrated first by reference to alkyl groups. Concerning the series  $\text{CH}_3\cdot$ ,  $\text{AlkCH}_2\cdot$ ,  $\text{Alk}_2\text{CH}\cdot$ ,  $\text{Alk}_3\text{C}\cdot$ , it is known that methyl and *tert.*-butyl groups are readily eliminated as alcohols from quaternary ammonium hydroxides, whilst primary and secondary alkyl groups are not (cf. Parts I and XI, *loc. cit.*); thus the property of facile elimination in the form of alcohol passes through a minimum in the series considered.

The circumstance may be interpreted as follows. From left to right in the series the inductive effect of the alkyl components produces a progressive increase of electron density at the point of attachment of the whole group. This electron density is lowest in the methyl group and it is consistent that this group suffers elimination by mechanism (B2). As explained in connexion with the *neopentyl* group, the first effect of the introduction of

alkyl components in place of hydrogen is to suppress reactivity by mechanism (B2), and, apparently, one alkyl substituent is sufficient to render it immeasurably small. Mechanism (B1), however, as is evident from its nature, must be facilitated by alkyl substitution, so that at some stage in the series reactivity by this alternative mechanism should rise to an appreciable value; and once this mechanism takes control of the decomposition, further alkyl substitution must enhance reactivity. This explains the minimum occurring in the series, and we expect similar conditions to apply in analogous substitution reactions such as the alkaline hydrolysis and alcoholysis of alkyl halides.

The corresponding theory of the araliphyl series  $\text{CH}_3\cdot$ ,  $\text{ArCH}_2\cdot$ ,  $\text{Ar}_2\text{CH}\cdot$ ,  $\text{Ar}_3\text{C}\cdot$  is different because the polar effect of the phenyl substituent is electromeric and duplex, and this group thus adjusts itself to the requirements of the system. In mechanism (B2) it is difficult to state what those requirements are, since at the moment of reaction the aromatic electrons are simultaneously under the opposing influences of the ammonium pole and the attracted anion. In mechanism (B1), however, an integral cationic charge requires dispersal, and accordingly electron release from the aryl groups must be maximal. Hence in reaction by mechanism (B2) progressive substitution by aryl groups is expected to produce comparatively small effects (in either direction), but in reaction by mechanism (B1) each additional aryl group should greatly enhance reactivity. Thus, this series also should contain a point at which mechanism (B1) supplants (B2). The point of supersession need not, however, be associated with minimal reactivity, but it should have the property that the portion of the series to its left should show slight (possibly irregular) effects, and that to its right a large enhancing effect, of the aryl groups on reactivity.

In the series,  $\text{CH}_3$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{CHPh}_2$ ,  $\text{CPh}_3$ , observations are available (cf. Parts XIII and XIV, *loc. cit.*), and the preceding statement faithfully describes them. The point of supersession occurs at  $\text{CHPh}_2$ , and, independently of the indication provided by the observed differences of reactivity, the alteration of mechanism is clearly established by dynamical evidence. The expectation that similar conditions will prevail for other aliphatic substitutions such as the alkaline alcoholysis or hydrolysis of corresponding halides is supported by the observation (Ward, J., 1927, 2285) of a change from second- to first-order dynamics in this reaction on passing from a benzyl to benzhydryl chloride.

Effects of type (b) to be expected from changes in the anion may be illustrated by means of a series such as  $\text{OEt}'$ ,  $\text{OH}'$ ,  $\text{OPh}'$ ,  $\text{OAc}'$ ,  $\text{Cl}'$ , the order being that of decreasing basicity. In general, there will be a point such that, to its left mechanism (B2), and to its right mechanism (B1), controls reaction (B). Assuming that a simultaneous reaction (A) is controlled by mechanism (A2) throughout, then to the left of the point of mechanistic replacement both reactions (A) and (B) are similarly dependent on the anion, changes in which will not much alter the direction of decomposition, whilst to the right of the same point reaction (A) alone will depend on the anion, a decrease in the basicity of which should therefore favour reaction (B). The above will be recognised as a description of the corresponding observations (cf. Parts I and XII), which formerly could not be reconciled.

When the various series can be more fully filled in, what has been described as a "point" of mechanistic change will probably appear as a region, and thus, just as with reaction (A), we now generalise the original conception of reaction (B) by the contemplation of a range of mechanisms, (B1)—(B2), both extremes of which have been experimentally exemplified. Most aliphatic substitutions can with advantage be regarded analogously, and the lines along which this further generalisation would proceed will become evident on comparing the foregoing with a previous discussion of aliphatic substitutions in the side chains of aromatic compounds (Ingold and Rothstein, J., 1928, 1217; cf. Ingold and Patel, *J. Indian Chem. Soc.*, 1930, 7, 95).