426. *Mechanism of Elimination Reactions. Part XVI. Constitutional Influences in Elimination. A General Discussion.*

By M. L. DHAR, E. D. HUGHES, C. K. INGOLD, A. M. M. MANDOUR, G. A. MAW, and L. I. WOOLF.

Classical organic chemistry has provided two empirical rules for the orientation of elimination, the Hofmann rule, that tetra-alkylammonium ions give the least alkylated ethylene, and the Saytzeff rule that alkyl halides produce the most alkylated ethylene. These antithetical rules are reconciled on the basis that they signalise different internal processes of electron displacement, which appear at different times during an individual molecular act of elimination, and are energised from independent sources. The detailed theory involves the correlation of orientation with reaction rate and kinetic type, and the fitting of constitutional effects on all these phenomena into the framework of the established mechanisms of elimination.

The Hofmann rule is part of a broader pattern of constitutional effects, which can all be consistently interpreted as the control of elimination by inductive electron-displacement. The effect depends on the polarity of substituents, and their consequent ability to create a positive electrical field at the β-carbon atom. Amongst alkyl compounds, control by the inductive effect is dominating for bimolecular eliminations when the electron-attracting substituent, Y in $HC_{\beta}{\cdot}C_{\alpha}Y$, carries a positive ionic charge. Substituents of sufficient polarity will, however, exert a dominating inductive effect on elimination in any system.

The Saytzeff rule is a part of another general pattern of structural effects, all of which can be consistently interpreted as the control of elimination by electromeric electron-displacement. This effect depends on the unsaturation of substituents, and their consequent ability to conjugate or hyperconjugate with the developing olefinic double bond, $C_{\beta}{:}C_{\alpha}$. Amongst alkyl compounds, control by the electromeric effect is dominating in bimolecular eliminations when the electron-attracting group Y is uncharged; and in all unimolecular eliminations. Substituents of sufficient unsaturation will, however, exert a dominating electromeric effect on elimination in any system.

The inductive effect is a polarisation, exerted from the commencement of reaction; but the electromeric effect is a polarisability effect, which is developed during reaction, and achieves its main kinetic importance in the transition state of olefin formation. The inductive effect is driven by the Coulomb forces of classical electrostatic polarity; but the electromeric effect is energised independently by the quantal resonance of electrons having properties of unsaturation. The polarity and unsaturation of alkyl groups are especially considered, and the concept of hyperconjugation is broadened.

Steric factors may limit the free operation of these polar constitutional influences. The most important steric restriction on elimination is that the β-CH electrons in $HC_{\beta}{\cdot}C_{\alpha}{\cdot}Y$ must enter the octet of C_{α} on the side remote from Y. This applies only to bimolecular elimination; but it then applies no matter whether Y is a formally neutral group, or whether it carries a positive ionic charge. The requirement arises from the need to economise energy by minimising bond-overlap in the transition state of elimination.

This discussion of constitutional effects on heterolytic 1 : 2-elimination is complementary to a discussion of environmental effects already given in Part V and supplemented in Parts VII and VIII.

(1) MECHANISMS OF ELIMINATION.

ANY reaction of the form

$$X\text{—}a\text{—}b\text{—}Y \longrightarrow \overset{+}{X} + a{=}b + \overset{-}{Y}$$

where X separates without the electrons which it shared with *a*, and Y with those which it shared with *b*, X and Y being otherwise unrestricted as to charge, may be designated a heterolytic 1 : 2-elimination. The context admitting no ambiguity, we shall often hereafter refer to such a reaction simply as an elimination.

We are to discuss constitutional effects on heterolytic 1 : 2-eliminations. Any theory of such constitutional effects must be fitted into an established framework of reaction mechanism. Therefore we shall first consider the nature and range of application of the mechanisms known to be available.

(1.1) *Bimolecular Mechanism* (E2).—This was first recognised as a general mechanism of elimination by Hanhart and Ingold in 1927. It is the most widespread of elimination mechanisms. It may be described for the case in which X is a hydrogen, and *a* and *b* are carbon atoms, since this is the most common case, though other possibilities for all these atoms exist as will be mentioned later. In the case specified, a reagent Z possessing nucleophilic (in particular basic) properties extracts the protonic part of a combined hydrogen atom, while an electron-attracting group Y simultaneously separates in possession of its previously shared electrons. A co-operative effect arises in 1 : 2-elimination by this mechanism, since the hydrogen atom and the electron-attractor are bound to adjacent atoms, and therefore atomic electron shells may remain complete throughout the change, without any alteration of the carbon frame. Two bonds are broken, but each fission assists the other, the two together constituting a single synchronised act. The mechanism may be formulated thus.

$$Z + H\overset{\frown}{\text{—}}CR_2\overset{\frown}{\text{—}}CR_2\text{—}Y \longrightarrow ZH + CR_2{:}CR_2 + Y \quad . \; . \; . \; . \; . \; . \; . \quad (E2)$$

the arrows showing how the charges on Z and Y are changed, though for the charges themselves there are several possibilities.

The consequences of the bimolecular mechanism have up to the present been illustrated with respect to the formation of olefins from tetra-alkylammonium salts, certain specially chosen tetra-alkylphosphonium salts, trialkylsulphonium salts, dialkyl and aryl alkyl sulphones, and alkyl halides. The mechanism has also been made probable for alkyl sulphonates and certain alkyl carboxylates. Neutral or negatively charged reagents, varying in basicity from water to ethoxide and amide ions, have been employed :

$$\cdot Y = \cdot\overset{+}{N}R_3,\ \cdot\overset{+}{P}R_3,\ \cdot\overset{+}{S}R_2,\ \cdot SO_2R,\ \cdot Cl,\ \cdot Br,\ \cdot I,\ \cdot O\cdot SO_2R,\ \cdot O\cdot COR$$

$$Z = OH_2,\ NMe_3,\ \overset{-}{O}Ac,\ \overset{-}{O}\cdot C_6H_4\cdot NO_2,\ \overset{-}{O}Ph,\ \overset{-}{O}H,\ \overset{-}{O}Et,\ \overset{--}{CO_3},\ \overset{-}{N}H_2$$

The following reactions are typical of those which have been investigated in this connexion (cf. p. 2096) :

$$NMe_3 + CH_2Ar\cdot CH_2\cdot\overset{+}{N}Me_3 \longrightarrow \overset{+}{N}HMe_3 + CHAr{:}CH_2 + NMe_3$$

$$\overset{-}{O}H + CH_3\cdot CH_2\cdot\overset{+}{S}Me_2 \longrightarrow OH_2 + CH_2{:}CH_2 + SMe_2$$

$$\overset{-}{O}H + CH_3\cdot CH_2\cdot SO_2\cdot Et \longrightarrow OH_2 + CH_2{:}CH_2 + \overset{-}{S}O_2Et$$

$$\overset{-}{O}Et + CH_2Ar\cdot CH_2Br \longrightarrow HOEt + CHAr{:}CH_2 + \overset{-}{B}r$$

To these examples we may first add two others, chosen because they show that conditions similar to those required for the bimolecular formation of the double bond $C{:}C$ by olefin elimination also apply to the formation of the double bonds $C{:}N$ and $N{:}N$ by corresponding elimination processes :

$$\overset{-}{O}H + Ph\cdot CH_2\cdot NMe\cdot SO_2Ar \longrightarrow OH_2 + Ph\cdot CH{:}NMe + \overset{-}{S}O_2Ar$$

$$\overset{-}{O}Et + Ac\cdot NH\cdot NH\cdot SO_2Ar \longrightarrow HOEt + Ac\cdot N{:}NH + \overset{-}{S}O_2Ar$$

The first of these equations expresses the hydrolysis of a sulphonamide, containing a suitably disposed hydrogen atom, by means of concentrated alkali, to a sulphinic acid and a Schiff's base (instead of, as might be thought normal, to a sulphonic acid and an amine). The second equation, together with the presumed decomposition $AcN_2H \longrightarrow AcH + N_2$, constitutes a representation of McFadyen and Stevens's method of converting a carboxylic acid into the corresponding aldehyde by alkaline alcoholysis of a sulphonyl derivative of the acid hydrazide. We give one more example, which is due to Sommers and Whitmore :

$$\overset{-}{O}H + SiCl_3\cdot CH_2\cdot CH_2Cl \longrightarrow HO\cdot SiCl_3 + CH_2{:}CH_2 + \overset{-}{C}l$$

It is mentioned in order to illustrate the point that other groups than hydrogen may have a sufficient affinity for a strongly nucleophilic reagent to fulfil the same function as that which hydrogen often fulfils in the general reaction. (In practice, the compound $HO\cdot SiCl_3$ is hydrolysed to silicic acid.)

The originally advanced evidence of mechanism was largely circumstantial : it had reference to the conditions and course of the reaction, especially the obvious need for a strong base. Much firmer evidence has been supplied since by the use of reaction kinetics and of the isotopic indicator method.

Eliminations which proceed by the bimolecular mechanism normally exhibit second-order kinetics. Such kinetics have been formally established in representative cases extending over the following range of variation of the electron-attracting group Y and the basic reagent Z :

$$\cdot Y = \cdot\overset{+}{N}R_3,\ \cdot\overset{+}{S}R_2,\ \cdot Cl,\ \cdot Br,\ \cdot I$$

$$Z = \overset{-}{O}H,\ \overset{-}{O}Et$$

However, just as with bimolecular nucleophilic substitution, this correspondence between mechanism and reaction order is not universal. In the investigated cases of it, a strongly basic reagent is employed, as in the following example ($Ar = C_6H_5$) :

$$\overset{-}{O}H + Ar\cdot CH_2\cdot CH_2\cdot\overset{+}{N}Me_3 \longrightarrow OH_2 + Ar\cdot CH{:}CH_2 + NMe_3 \qquad (E2;\ \text{2nd order})$$

But if the vulnerable hydrogen atom is further activated by an appropriate constitutional change, a much weaker base will suffice ; and that may be a solvent molecule. If, in the above example, a *p*-nitro-group is introduced into the 2-phenylethylammonium ion, the following reaction will take place, which is of the first order in aqueous solution ($Ar = p\text{-}C_6H_4\cdot NO_2$) :

$$OH_2 + Ar\cdot CH_2\cdot CH_2\cdot\overset{+}{N}Me_3 \longrightarrow \overset{+}{O}H_3 + Ar\cdot CH{:}CH_2 + NMe_3 \qquad (E2;\ \text{1st order})$$

In spite of its kinetic order, this reaction is undoubtedly bimolecular in mechanism, as is shown by the large increases of speed which are observed when small amounts of some stronger base than water are added initially. (Kinetic complications do not arise from the production of the base NMe_3, because this accepts a proton from the simultaneously formed $\overset{+}{O}H_3$, thus instantly losing its basic properties.)

Although the kinetic results are consistent with the bimolecular mechanism, they do not of themselves exclude a two-stage process, in which the basic reagent first extracts a proton from the alkyl compound, leaving an anionic form, which then suffers unimolecular change with loss of the electron-attracting group. This possibility has, however, been excluded by Skell and Hauser, by examination of the following reaction in " heavy " alcohol, EtOD, as solvent :

$$\bar{O}Et + Ph\cdot CH_2\cdot CH_2Br \longrightarrow HOEt + Ph\cdot CH{:}CH_2 + \bar{B}r$$

They showed that 2-phenylethyl bromide, isolated after the reaction had proceeded part way, contained no deuterium, and that therefore the anionic form $\overset{-}{C}HPh\cdot CH_2Br$ could not have been produced as an intermediate product.

Sectional Summary.—This Section surveys the evidence for, and established range of application of, the bimolecular mechanism of elimination.

References.—(a) *Ammonium salts.* (1) Hanhart and Ingold, *J.*, 1927, 997; (2) Ingold and Vass, *J.*, 1928, 3125; (3) v. Braun, Teuffert, and Weissbach, *Annalen*, 1929, **472**, 121; (4) v. Braun and Buchmann, *Ber.*, 1931, **64**, 2610; (5) v. Braun and Hamann, *Ber.*, 1932, **65**, 1580; (6) Ingold and Patel, *J.*, 1933, **68**; (7) Hughes and Ingold, *ibid.*, p. 523; (8) Hughes, Ingold, and Patel, *ibid.*, p. 526; (9) Part VII, this vol., p. 2043.

(b) *Phosphonium salts.* (10) Fenton and Ingold, *J.*, 1929, 2342; (11) Hey and Ingold, *J.*, 1933, 531.

(c) *Sulphonium salts.* (12) Green and Sutherland, *J.*, 1911, **99**, 1174; (13) Ingold, Jessop, Kuriyan, and Mandour, *J.*, 1933, 533; (14) Ingold and Kuriyan, *ibid.*, p. 991; (15) Hughes and Ingold, *ibid.*, p. 1571; (16) Gleave, Hughes, and Ingold, *J.*, 1935, 236; (17) Part VIII, this vol., p. 2049; (18—21) Parts XII—XV, this vol., p. 2072 *et seq.* Cf. also refs. 3 and 9.

(d) *Sulphones.* (22) Fenton and Ingold, *J.*, 1928, 3127; (23) *idem*, *J.*, 1929, 2338; (24) *idem*, *J.*, 1930, 705.

(e) *Halides.* (25) Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 1087, 1093; (26) Hughes, *J. Amer. Chem. Soc.*, 1935, **57**, 708; (27) Hughes and Ingold, *J.*, 1935, 244; (28) Hughes, Ingold, and Shapiro, *J.*, 1936, 225; (29) Hughes and Shapiro, *J.*, 1937, 1177; (30) *idem*, p. 1192; (31) Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899; (32—34) Parts IX—XI, this vol., p. 2055 *et seq.* Cf. also refs. 9 and 17.

(f) *Esters.* (35) W. Hückel, Tappe, and Legutke, *Annalen*, 1940, **543**, 191; (36) Hauser, Shivers, and Skell, *J. Amer. Chem. Soc.*, 1945, **67**, 409.

(g) *Sulphonamides.* (37) Holmes and Ingold, *J.*, 1926, 1305.

(h) *Sulphonhydrazides.* (38) McFadyen and Stevens, *J.*, 1936, 584.

(i) $SiCl_3$*-substituted halides.* (39) Sommers and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485; (40) Sommers, Goldberg, Dorfman, and Whitmore, *ibid.*, p. 1083.

(j) *Reaction kinetics.* Cf. refs. 7, 9, 12, 15—21, and 28—34.

(k) *Isotopic indicator.* (41) Skell and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1661.

(1.2) *Unimolecular Mechanism* (E1).—This process was signalised as a general mechanism by Hughes in 1935. It is known as yet only for the important case in which X is a hydrogen atom, and *a* and *b* are carbon atoms. Its main characteristic is that the electron-attracting group **Y** breaks away without the co-operation of the proton-extracting reagent Z, leaving a carbonium ion, which subsequently loses a proton to the solvent or some other proton acceptor. The reaction thus has two stages, of which the first, the heterolytic separation of Y, is rate-determining; so that the rate of the overall reaction is independent of any added base. The mechanism may be formulated thus,

$$\left.\begin{array}{r} H{-}CR_2{-}CR_2\overset{\curvearrowright}{-Y} \xrightarrow[\text{slow}]{} H{-}CR_2{-}\overset{+}{C}R_2 + Y \\ H{-}CR_2{-}\overset{+}{C}R_2 \xrightarrow[\text{fast}]{} \overset{+}{H} + CR_2{:}CR_2 \end{array}\right\} \quad \ldots\ldots\ldots \quad (E1)$$

where the group Y may be either formally neutral or positively charged before reaction, becoming, as the case may be, either negatively charged or neutral afterwards.

Up to the present this mechanism has been established (in one case, made probable) over the following range of electron-attracting groups :

$$\cdot Y = \cdot\overset{+}{S}R_2,\ \cdot Cl,\ \cdot Br,\ \cdot I,\ \cdot O\cdot SO_2R$$

Two illustrations may be given of eliminations for which this mechanism is prominent :

$$CH_3\cdot CMe_2Br \longrightarrow \overset{+}{H} + CH_2{:}CMe_2 + \bar{B}r$$

$$CH_3\cdot CMe_2\cdot\overset{+}{S}Me_2 \longrightarrow \overset{+}{H} + CH_2{:}CMe_2 + SMe_2$$

Our evidence of this mechanism is derived mainly from the study of the reaction kinetics, particularly with reference to its insensitiveness to bases, its relation to concurrent unimolecular substitution, and its orientation.

We may emphasise the generality of what has been pointed out in particular cases before, *viz.*, that the bi- and uni-molecular mechanisms, *E*2 and *E*1, must merge into each other. For in mechanism *E*2 the attack of Z assists the separation of Y, whereas in mechanism *E*1 the reagent Z gives no such aid; and there must be a wide range of degrees of assistance which Y might require and a suitable Z could render.

Sectional Summary.—This Section surveys the evidence for, and the established range of application of, the unimolecular mechanism of elimination.

References.—(a) *Halides.* (26) Hughes, *loc. cit.*; (42) Hughes, Ingold, and Scott, *Nature*, 1936, **138**, 120; (43) *idem*, *J.*, 1937, 1271; (44) Hughes, Ingold, and Shapiro, *J.*, 1937, 1277; (45) Cooper, Hughes, and Ingold, *J.*, 1937, 1280; (46) Hughes, Ingold, and MacNulty, *J.*, 1937, 1283. Cf. also refs. 9, 17, 21, 33, and 34.

(b) *Sulphonium salts.* (47) Part VI, this vol., p. 2038. Cf. also refs. 9, 17, 20, and 21.

(c) *Sulphonic esters.* (48) W. Hückel and Tappe, *Annalen*, 1939, **537**, 113. Cf. also ref. 35.

(d) *Reaction kinetics.* Cf. refs. 9, 17, 20, 21, 33, 42, 43, 44, and 45.

(2) EMPIRICAL ORIENTATION RULES AND THEIR GENERAL SIGNIFICANCE.

During the classical period of organic chemistry, a peculiar situation arose in relation to the rules which summarised empirical knowledge concerning the orientation of elimination. We shall sketch this situation in the present Section, since an important part of the problem with which we were confronted was that of fitting it into the mechanistic framework outlined in Section 1.

It was observed by Hofmann (*Annalen*, 1851, **78**, 253; **79**, 11) that when a quaternary ammonium hydroxide contains different primary alkyl radicals, so that various olefins might be produced by decomposition in different directions, the principal olefin to be formed in the actual decomposition of the quaternary compound is always ethylene if an ethyl group is present. Though originally given with the limitations stated, this rule has since, by an obvious generalisation, been taken to require the preferential formation, from a quaternary ammonium hydroxide containing only primary alkyl groups, of that ethylene which carries the *smallest* number of alkyl substituents.

It was pointed out by Saytzeff (*Annalen*, 1875, **179**, 296) that, of the isomeric olefins which could be formed from a secondary or tertiary alkyl halide by elimination in the different branches of the alkyl chain, the one actually produced in greatest proportion is determined by the condition that the eliminated hydrogen atom is lost preferentially from that carbon atom which bears the smallest number of hydrogen atoms. An equivalent expression of the same rule is that it requires the preferential production, from a secondary or tertiary alkyl halide, of that ethylene which carries the *largest* number of alkyl substituents.

So long as Hofmann's and Saytzeff's rules were regarded as merely expressing the observed effects of unknown causes in unrelated fields of organic chemistry, their antithetical relation to each other was hardly noticed. But after Hanhart and Ingold had given a treatment of the decompositions of quaternary ammonium compounds which placed the reactions of those substances in the same class as those of alkyl halides, then it at once became a challenge to discover why two contradictory rules, jointly summarising all that was known about the orientation of elimination, should govern different applications of the same general reaction.

From the outset of this enquiry our basic assumption has been that the co-existence of two antithetical orientation rules betrays the presence of two internal orientational processes. Each may well require a different set of systemic conditions for its most effective operation. Each will certainly be driven forward by a diffreent set of forces. It is fundamental to this general picture that the two sources of energy shall be independent each of the other, in order that the two processes may be able to work in the same system, without mutual interference, and either in conjunction or in opposition.

Already in 1930, when this work was begun (preceding paper), a somewhat similar position had arisen with reference to another group of organic reactions; and it was then in the process of being interpreted. The reactions were those of aromatic substitution; and we shall here recall what happened in that matter, because it provides a helpful analogy with the problem with which we have to deal concerning the orientation of eliminations. Two partly contrary orientation rules of aromatic substitution had been recognised. A large class of substituents oriented further substitution, either to the ortho- and para-, or to the meta-positions, according to the direction of the dipole associated with the link between the substituent and the aromatic ring. Another class of substituents, those connected to the ring through a negative or neutral atom having unshared electrons, directed uniformly towards the ortho- and para-positions, even when such orientation was contrary, as in most cases it was, to the effect to be expected from the direction of the link dipole.

The first step in the interpretation involved associating each of the rules of orientation with a separate form of electron displacement. The second step was to show, through a combined study of the orientation and velocity of substitution, that the two effects to a large extent enter at different stages during any individual molecular act of substitution. Putting these two points together, the conclusion was that inductive electron displacement is responsible for the orientation connected with the link dipole, and is largely a polarisation, *i.e.*, a displacement which is prominent in the initial state of the reacting system; but that electromeric electron displacement produces the orientation originating in the unshared electrons, and is mainly a polarisability effect, *i.e.*, a displacement which belongs chiefly to the transition state of the reacting system. The third step in the interpretation, *viz.*, the recognition of the fundamental reason for the mutual independence of the two effects, was not completed until **1933**, when it was shown that, whereas the forces driving the inductive effect are of the classical electrostatic type, the driving force behind the electromeric effect is basically non-classical, being of the same general nature as are the forces of exchange degeneracy in the theory of co-valency. That was the real reason why a substituent like chlorine could, in the same reaction, give rise to phenomena which suggested a simultaneous attraction and repulsion of electrons (Allen, Oxford, Robinson, and Smith, *J.*, **1926**, **401**; Ingold and Ingold, *ibid.*, p. **1310**; Ingold and Shaw, *J.*, **1927**, **2918**; Ingold, *J.*, **1933**, **1120**).

This theory of aromatic substitution provides a very close parallel to the theory which we are going to build concerning elimination. Again we start with antithetical orientation rules. And in the interpretation we shall find the same two forms of electron displacement, the same kind of distinction between the time of appearance of each in the course of a molecular act of elimination, and that same sort of independence, of ability to work in opposite directions without mutual interference, which produces the *prima facie* impression of a group behaving towards electrons (and protons) in both of two inconsistent ways.

Sectional Summary.—The Hofmann and Saytzeff rules for the orientation of elimination are so antithetical as to suggest that they signalise internal processes of electron displacement which are energised in independent ways. The analogy of aromatic substitution is cited as a guide for the construction of a theory on these general lines.

(3) ORIENTATION AND REACTION RATE. MORE DETAILED INTERPRETATION.

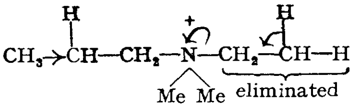
(**3.1**) *Bimolecular Elimination in 'Onium Ions : The Inductive Effect.*—The internal mechanism underlying Hofmann's rule was identified with the general inductive effect by Hanhart and Ingold. A heterolytic elimination always involves a strongly electron-attracting group, which, by inducing a positive charge on all the surrounding carbon atoms, loosens the protons, a sufficient loosening of a β-proton permitting the elimination mechanism *E*2. A group which, by releasing electrons, tends to neutralise the induced positive charge on the β-carbon atom, and thus to tighten its hold on the β-protons, will inhibit reaction. The terminal methyl radical of the *n*-propyl group acts in this way, and so determines that, in accordance with Hofmann's rule, the *n*-propyl group will show relatively little tendency to engage in an olefin-forming process if an ethyl group is available to fulfil this function (formula I, below).

Similarly, an *iso*butyl group will not participate to any great extent in elimination if a *n*-propyl group (still more, if an ethyl group) is available; and, naturally, the terminal methyl radicals in the *n*-propyl and *iso*butyl groups may be replaced by ethyl or higher homologous radicals without changing these comparisons. This is the generalised rule given in Section **2**, which actually was obtained by Hanhart and Ingold from the theory, Hofmann's original empirical rule being recognised as a special case.

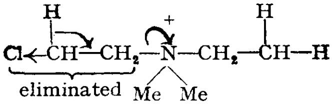
Further generalisation follows from the consideration that the protective electron displacement can be relayed to the β-carbon atom from non-adjacent atoms, but only with considerable loss of intensity. Thus the protective effect to be observed in the *n*-propyl group will be increased in the *n*-butyl group, but it will not be so great there as in the *iso*butyl group. In general the effect will increase with homology, tending to a limit but always subject to the condition that a branched-chain radical is more effective than the isomeric normal chain.

Outside the range of hydrocarbon radicals, we expect electron-attracting substituents to promote elimination, and to do so with greatest effect if they are directly attached to the β-carbon atom (formula II).

(I.)



$$CH_3 \rightarrow \overset{H}{C}H-CH_2-\overset{+}{N}(Me)_2-\underbrace{CH_2-\overset{H}{C}H}_{\text{eliminated}}-H$$



$$Cl \leftarrow \underbrace{\overset{H}{C}H-CH_2}_{\text{eliminated}}-\overset{+}{N}(Me)_2-CH_2-\overset{H}{C}H-H$$

(II.)

With various degrees of elaboration and completeness, these deductions from theory have been tested and established for a number of primary alkyl and substituted alkyl groups, not only for ammonium hydroxides and ammonium ethoxides, but also for sulphonium hydroxides and for the alkali-promoted decompositions of sulphones (Section 1.1, refs. 1, 2, 6, 13, 14, 22, and 23).

Although the bimolecular mechanism was presupposed in the theory, no control over the reaction kinetics was established at the time of these experiments, the existence of the unimolecular mechanism of elimination being then unsuspected. However, the investigations were almost entirely concerned with alkaline decompositions involving primary alkyl groups, and subsequent research has shown that in these conditions the mechanism is in fact wholly bimolecular. The actual method of experiment was orientational, the measurement relating to the proportions in which products were formed in decompositions capable of proceeding in a number of alternative directions.

One form of the method was to place two olefin-forming alkyl groups in competition with each other in the same 'onium ion (or sulphone), as illustrated in the preceding formulæ. Using this method, it has been shown, for instance, that in the decompositions of sulphonium hydroxides the first four primary alkyl groups stand in the following order with respect to the facility with which they split off as olefins :

ethyl > *n*-propyl > *n*-butyl > *iso*butyl.

Another method of comparison employed 'onium ions containing only one olefin-yielding alkyl group, and otherwise only methyl groups. The basic assumption was that changes in the olefin-forming group would not much affect the tendency of a methyl group to split off in a substitution reaction. Accordingly, the success of the elimination with different olefin-forming groups, in competition with this more or less standard process of displacement of the methyl group, was taken as a measure of the intrinsic tendency of the variable alkyl group to yield an olefin. It was also assumed that the comparison would not be upset by any large tendency among the variable alkyl groups to be displaced by substitution, and that seems to be true to a fair degree of approximation. The decompositions of ammonium hydroxides, for instance, have been studied in this way, and the following primary alkyl groups have thus been placed in order with respect to the ease with which they yield olefins in this reaction :

ethyl > *n*-propyl > *n*-butyl > *n*-amyl ~ *n*-octyl > *iso*amyl > *iso*butyl > ψ-hexyl

After duality of mechanism for eliminations generally, and the consequent need for kinetic control, had been realised, it was felt desirable not only to confirm kinetically that the reactions studied are bimolecular, as those which produce olefin from primary alkyl groups in ammonium and sulphonium ions certainly are (Section 1.1, refs. j), but also to ascertain whether the rates of bimolecular olefin formation from such ions really do vary with homology in the sense indicated by theory, and by the experiments on orientation. For the simpler primary alkyl groups this has been done, and that part of the work which relates to sulphonium ions* is now published (Part XII). The results are consistent with theory, and with the orientational data. Thus the second-order rate-constants for the reaction

$$RR'CH{\cdot}CH_2{\cdot}\overset{+}{S}Me_2 + \overset{-}{O}Et \longrightarrow HOEt + RR'C{:}CH_2 + SMe_2$$

where R, R' = H, Me, Et, in dry ethyl alcohol at 64°, with sulphonium iodide and sodium ethoxide initially at concentrations 0·05 and 0·095M, respectively, are as follows [$k(E2)$ is in sec.$^{-1}$ g.-mol.$^{-1}$ l.] :

Alk in $Alk\overset{+}{S}Me_2$	Ethyl.	*n*-Propyl.	*n*-Butyl.	*iso*Butyl.
$10^5k(E2)$	60	27	17	14

The remarkable effect on rate which was observed (Part XII) with R = Ph will be considered in Section 3.4.

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* The part which relates to ammonium ions is being developed as a study of salt effects, and is therefore not yet ready for publication.

At the outset of our work it was known that the Hofmann rule applied to primary alkyl groups in 'onium ions, and that the Saytzeff rule applied to secondary and tertiary alkyl groups in halides; but nobody knew whether the change of rule was due to the difference in the type of alkyl group, to the difference in the type of the electron-attracting group, or to a difference of mechanism. We therefore proceeded to delimit the possibilities by extending our study of the bimolecular mechanism of elimination to secondary and tertiary alkylsulphonium ions. These experiments had reference both to the orientation and the velocity of elimination, but even the orientation experiments were made under kinetically controlled conditions, a precaution which is certainly necessary when dealing with secondary and tertiary alkyl groups.

As to orientation, the answer for secondary alkyl groups is given by the following result for bimolecular elimination from the dimethyl-*sec.*-butylsulphonium ion (Part XIII) :

$$\underset{+\mathrm{OEt}^-}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH(\overset{+}{S}Me_2){\cdot}CH_3}} \xrightarrow[(E2)]{} \underset{26\%}{\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH_3}} + \underset{74\%}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH{=}CH_2}}$$

This is orientation according to the extended Hofmann rule, the principal olefinic product being the ethylene which carries the smaller number of alkyl substituents. It is theoretically explained by an assumed protection of the β-hydrogen atom in the longer branch of the *sec.*-butyl group by an electron-displacement from the terminal methyl substituent in that branch.

Reaction rates confirm this diagnosis. For the second-order rate-constants of the reaction

$$\mathrm{R{\cdot}CH_2{\cdot}CHMe{\cdot}\overset{+}{S}Me_2} + \overset{-}{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \text{Olefins} + \mathrm{SMe_2}$$

with R = H, Me, in ethyl alcohol at 64°, and with salt concentrations 0·05 and 0·095M as before, the following values [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.] were found (Part XIII) :

Alk in Alk$\overset{+}{\mathrm{S}}$Me$_2$....................		*iso*Propyl.	*sec.*-Butyl.
$10^5k(E2)$: total		1040	695
	longer branch	520	185
	shorter branch	520	510

It will be noticed that the higher homologous group gives olefin more slowly, as though the β-linked methyl substituent, which it contains, was producing a protecting effect. Further, practically the whole of the reduction of rate is due to the diminished rate of entry of the double bond into that alkyl branch which contains the β-methyl substituent, the rate of its entry into the other branch being almost unaffected. This shows that the protecting action is localised in the molecule, just as one would expect of the inductive electron displacement, which is postulated.

Even in the figures thus far quoted there is a warning that the theory of the Hofmann rule is not a complete theory of orientation and velocity in bimolecular elimination from primary and secondary alkyl-sulphonium ions. The secondary groups, *iso*propyl and *sec.*-butyl, differ from the primary groups, ethyl and *n*-propyl, respectively, in that the secondary groups possess an extra α-linked methyl substituent. According to the theory of the Hofmann rule, this extra substituent could exert some protective effect on the β-protons of the other branch of the secondary alkyl group ; but it would be a small effect, not nearly as big as if the extra substituent were in the β-position, and therefore close to the β-protons. Thus, as compared with ethyl and *n*-propyl, respectively, we should expect olefin formation in those branches of *iso*propyl and *sec.*-butyl with respect to which the extra methyl group can be regarded as an α-substituent to proceed at a slightly reduced rate. Actually it proceeds at a considerably increased rate—a rate 7—9 times larger than in the absence of the α-methyl substituent. An enormously enlarged effect in the same direction is observed when we introduce an α-phenyl substituent (Part XIII). Obviously these α-substituents are acting in some way of which our theory has yet to take account : we shall consider what it is in Section 3.2, and discuss these particular applications in Section 3.4.

As to tertiary alkyl groups, the nature of the orientation governing bimolecular elimination from sulphonium ions is shown by the following result for the reaction of the dimethyl-*tert.*-amylsulphonium ion (Part XIV) :

$$\underset{+\mathrm{OEt}^-}{\mathrm{CH_3{\cdot}CH_2{\cdot}CMe(\overset{+}{S}Me_2){\cdot}CH_3}} \xrightarrow[(E2)]{} \underset{14\%}{\mathrm{CH_3{\cdot}CH{=}CMe{\cdot}CH_3}} + \underset{86\%}{\mathrm{CH_3{\cdot}CH_2{\cdot}CMe{=}CH_2}}$$

This again is orientation according to the generalised Hofmann rule, and the explanation previously illustrated applies. The fact that the ratio in which the isomeric olefins are formed is about 6 : 1, whereas in the corresponding reaction of the dimethyl-*sec.*-butylsulphonium ion it was only about 3 : 1, is intelligible on statistical grounds alone, since the tertiary group has two shorter branches in competition with the longer branch, whilst the secondary group has only one.

Reaction rates in the tertiary series confirm control by the factors underlying the Hofmann rule. For the second-order rate-constants of the reaction

$$\mathrm{R{\cdot}CH_2{\cdot}CMe_2{\cdot}\overset{+}{S}Me_2 + \overset{-}{O}Et \longrightarrow HOEt + Olefins + SMe_2}$$

where R = H, Me, in 97% ethyl alcohol at 25°, with sodium ethoxide in large excess at concentrations about 0·25N, the following values [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.] were determined (Part XIV) :

Alk in Alk$\overset{+}{\mathrm{S}}\mathrm{Me_2}$		*tert.*-Butyl.	*tert.*-Amyl.
$10^5k(E2)$: total		80	56
	longer branch	27	8
	each shorter branch	27	24

Again the higher homologue gives olefin more slowly, and nearly the whole of the diminution of velocity arises from the reduced rate of entry of the double bond into that alkyl branch which has the extra β-methyl substituent. The factor by which the β-linked methyl substituent in the *tert.*-amyl group reduces the rate of establishment of a contiguous double bond is 0·30. From the rates already given for the secondary alkyl compounds one may see that the same factor for the *sec.*-butyl group is 0·36. And from the rates for the primary compounds it follows that the factor for the *n*-propyl group is 0·45. One may reasonably conclude that just the same type of protective effect as has been assumed to arise from β-alkyl substituents in primary alkyl groups is also at work in suitably constituted secondary and tertiary alkyl groups. We interpret this effect as due to inductive electron displacement.

As compared with the secondary groups *iso*propyl and *sec.*-butyl, the two tertiary groups *tert.*-butyl and *tert.*-amyl possess an extra α-methyl substituent. The rate figures already given do not enable the effect of this α-substituent to be assessed because the temperatures are not all the same. However, at still another temperature the primary, secondary, and tertiary series have been directly compared with respect to bimolecular elimination rates, by means of the groups ethyl, *iso*propyl, and *tert.*-butyl, which respectively possess 0, 1, and 2 α-methyl substituents. For the second-order rate-constants of the reaction

$$\mathrm{CH_3{\cdot}CRR'{\cdot}\overset{+}{S}Me_2 + \overset{-}{O}Et \longrightarrow HOEt + CH_2{:}CRR' + SMe_2}$$

where R,R′ = H, Me, in ethyl alcohol at 45°, with sulphonium iodide and sodium ethoxide initially in concentrations 0·02 and 0·095M, respectively, the following values [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.] have been determined (Part XIV) :

Alk in Alk$\overset{+}{\mathrm{S}}\mathrm{Me_2}$		Ethyl.	*iso*Propyl.	*tert.*-Butyl.
$10^5k(E2)$	total	5	114	2930
	per branch	5	57	977

If, in all three cases, we consider the rate of establishment of the double bond in a given alkyl branch, then we see that, starting with ethyl, the effect of introducing the single α-methyl substituent present in the *iso*propyl group is to increase the rate by a factor of 11, whilst the effect of the second similar substituent additionally present in the *tert.*-butyl group is a further increase of the rate by a factor of 18. There can be no doubt, therefore, that the effect of an α-alkyl substituent is to accelerate bimolecular elimination, and, as we have noticed already, that is not intelligible on the basis of the simple electrostatic theory underlying the Hofmann rule.

Sectional Summary.—We here summarise our conclusions concerning bimolecular elimination from 'onium ions. Studies of orientation and reaction rate at first with ammonium and sulphonium ions containing only primary alkyl groups, and then with secondary and tertiary alkyl groups, have shown, for each of these series, that orientation corresponds to the generalised Hofmann rule, and that rate comparisons between different compounds confirm the picture of constitutional influences which follows from that rule. These orientational and kinetic phenomena satisfy in detail the requirements of Hanhart and Ingold's original interpretation of the Hofmann rule as an application of the inductive effect; and this is the dominating constitutional effect for the stated range of phenomena. However, rate comparisons between the primary, secondary, and tertiary alkyl series reveal the simultaneous operation of a constitutional effect not covered by the explanation.

(3.2) *Bimolecular Elimination in Halides : The Electromeric Effect.*—When Baker and Nathan (*J.*, 1935, 1844) first adduced evidence for the view that the electrons of a CH-bond participate in tautomeric electron-displacements, much in the manner of unshared electrons, although in general with less freedom (compare, for instance, H—C—C═C with RO—C═C), we saw immediately that this might be the internal mechanism responsible for the elimination phenomena summarised under Saytzeff's rule. However, this idea could not at once be established formally.

For in the first place, the evidence for the special form of electron displacement which Baker and Nathan had postulated, hyperconjugation, as it was subsequently called by Mulliken, Rieke, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 41), itself required to be strengthened. That has since been done, with the result that today hyperconjugation is a well-established concept (see review * by Deasy, *Chem. Reviews*, 1945, **36**, 145).

Secondly, since the whole theory, in its application to elimination, had a much wider range of consequences than was comprised within the Saytzeff rule, these more general consequences had to be tested by new experiments. This programme has now been largely fulfilled, and the record of a considerable part of it is in the preceding papers.

In the Section **3**.1 we treated inductive electron-displacement as though it were the only internal mechanism; and, by restricting illustrations to a range of examples in which it was dominating, we were able to give an interpretation of orientation and reaction rate on the basis of the inductive effect alone, although the presence of a disturbing influence was noted. In a similar manner, we shall, in this Section, make the simplifying assumption that only tautomeric electron-displacements need be considered; and we shall confine illustration to a range of cases in which this effect is dominating. By following this plan we shall be able, in the first place, separately to explain and illustrate the two complementary parts of the theory in a relatively simple way. There will then remain the problem of the co-existence of the two effects, of the range over which either is dominating, and of what determines those ranges : this aspect of the matter will be discussed in Section **3**.4.

In elimination, tautomeric electron displacements originating in alkyl groups can arise only during the course of reaction : obviously there is no opportunity for Baker and Nathan's type of hyperconjugation in the initial state of a reaction of a saturated alkyl compound. Thus the internal process is one which we should classify as a polarisability effect, and we may therefore give it its specific name, the electromeric effect. Instead of considering the whole, detailed course of reaction, we may adopt the usual simplification of concentrating attention on the transition state. In this state, the electrons of a γ-CH-bond become hyperconjugated with the unsaturation electrons of the partly formed $C_{\beta}C_{\alpha}$-double bond. The hyperconjugation of these electrons modifies their wave-functions in such a way as to give them a larger share of configuration space, and therefore a smaller energy. This follows from the uncertainty principle, and is typical of those quantal effects, which are often summarised as resonance, and which at all levels of complexity, from the exchange degeneracy of a single bond onward, provide the forces of covalent combination. In our case, the result is a reduction of the energy of the transition state, and therefore of the activation energy, with a corresponding facilitation of the elimination process.

We have to extend this theory in one respect. According to Baker and Nathan's original principle, the resonance effect of an alkyl group attached to an unsaturated carbon atom would be a maximum when the alkyl group was methyl, but would diminish, and finally disappear, if it

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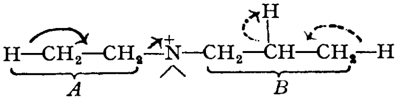
* Note by Dr. J. W. Baker.—One statement in this review requires correction. Deasy, referring to olefin-elimination from quaternary ammonium salts, states : " Hyperconjugation, which can function as indicated at *A* but cannot function at *B* because the elimination of a negative ion cannot occur, *was assumed to be the decisive factor* " (italics new).



The argument used by Baker (*J.*, 1935, 1845) was to show why hyperconjugation was *not* operative in determining into which alkyl side-chain the double bond was introduced because " it would be ineffective in retarding cationisation of the β-hydrogen atom, which will be influenced solely by the normal inductive effect of the alkyl group attached to C_{β}."

This conclusion, although reached before the recognition of the significance of hyperconjugation in determining the course of all 1 : 2-eliminations which occur by the *E*1 mechanism and in neutral secondary and tertiary halides by the *E*2 mechanism, is in agreement with the findings of Professor Ingold and his collaborators in this series of papers concerning *E*2 reactions of " 'onium " compounds.

were changed successively to ethyl, *iso*propyl, and *tert.*-butyl, owing to the progressive, and finally complete loss of suitably situated CH-bonds. However, it was suggested by Hughes, Ingold, Masterman, and MacNulty (*J.*, 1940, 899) that even in the case of the *tert.*-butyl group a residual resonance effect will be found, and that in other cases a part of the total observed effect is not dependent on CH-bonds. This is because of the expectation that, when two atoms of identical nuclear charge are linked, the electrons will concentrate in the direction of the less saturated; for to do so gives them freer motions, thereby stabilising the system in accordance with the uncertainty principle. An equivalent statement is that even the electrons of saturated CC-bonds have an appreciable mobility in respect of a hyperconjugation, $\mathrm{C{-}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{=}C}$, formally analogous to that in which the electrons of CH-bonds participate, $\mathrm{H{-}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{=}C}$; but that such mobility in saturated CC-electrons is smaller than the analogous kind of mobility in CH-electrons. This extension of Baker and Nathan's theory is naturally quite general,* though we are here concerned only with its application to the transition state in elimination. In this application we shall for convenience use the term electromeric effect to cover both Baker and Nathan's original form of hyperconjugation and the extension described.†

In the preceding Section we considered the separate operation of the electrostatic, or inductive, effect in the bimolecular mechanism of elimination, *E*2; and we derived a set of consequences, which could be verified: included amongst them was the Hofmann rule. Just in the same way, we shall now apply the concept of the resonance, or electromeric, effect to the bimolecular mechanism, *E*2. We shall obtain a very different set of consequences, amongst which will appear the Saytzeff rule.

Our primary deductions from the theory of the electromeric effect may be set out under four heads. First, on account of the electromeric effect, an alkyl radical attached to the β-carbon atom of a complete alkyl group will stabilise the transition state of elimination in that group, and will therefore facilitate its degradation to an olefin. This predicted effect, which is the opposite of the action of the inductive effect, may be applied either to the relative rates of bimolecular eliminations involving different alkyl groups each in a different molecule under the same environmental conditions, or to the reactions of different alkyl groups, or of dissimilar branches of the same alkyl group, in the same molecule. Applied to primary alkyl groups, either in different molecules or in the same molecule, it means, for example, that a *n*-propyl group should give propylene more easily than an ethyl group should give ethylene; and that an *iso*butyl group should give *iso*butylene more easily still. A similar application may be made to symmetrically branched secondary and tertiary alkyl groups. Thus an *iso*propyl group should yield propylene less easily than a 3-*n*-amyl group yields pent-2-ene, and a *tert.*-butyl group should give *iso*butylene less easily than a triethylcarbinyl group gives methyldiethylethylene. If we apply our deduction differentially to the unequal branches of an unsymmetrical secondary or tertiary alkyl group, we get Saytzeff's rule. That is illustrated for the *sec.*-butyl group in formulæ (III) and (IV). Of the two possible transition states of elimination that which has a methyl radical attached to the β-end of the αβ-unsaturated bond will possess a lower-lying energy than the other, and hence the β-hydrogen atom preferentially lost on elimination will come from the most alkylated (or least hydrogenated) β-carbon atom. An alternative statement is that the preferentially formed ethylene will carry the larger number of alkyl groups, two instead of only one.

Our second main deduction is that, since either end of the developing double bond is equally available for hyperconjugation, alkyl radicals attached to the α-carbon atom of the complete

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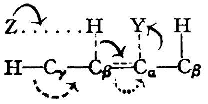
* It may be held responsible for the shortening of the central bond in 1 : 5-dienes (Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 391; 1947, *A*, **188**, 222). We suggest that, as a mechanism for securing increased overlap, the orbitals of the central bond acquire increased *p*-content from the adjacent CH-bonds, and hence change shape, shrinking longitudinally and swelling laterally in such a way as to promote overlap with the orbitals of the double bonds. One can understand thus how a bond might contract (longitudinally) without an increase of electron-content.

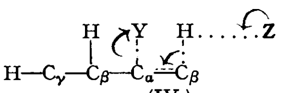
† Two extensions of Baker and Nathan's original theory have been discussed by de la Mare, Hughes, and Ingold (this vol., p. 21). They postulate hyperconjugation in the systems $\mathrm{C{=}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{-}Y}$ and $\mathrm{H{-}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{-}Y}$, where Y is an electron-attracting group. The first of these hyperconjugated systems, which had already been postulated by Baker (*J.*, 1939, 1155), could have importance for the transition states of elimination in special structures, *e.g.*, certain polyhalogen compounds. The second will be present in the initial states of all systems undergoing 1 : 2-elimination. The only reason why we are not compelled to take explicit account of it throughout is that it appears as an essentially constant factor in most of our comparisons.

alkyl group will exert an effect on elimination generally similar to that of alkyl radicals attached to a β-carbon atom. This will evidently be a primary effect, and it therefore provides another strong contrast to the consequences of the theory of the inductive effect, according to which an α-situated radical should exert only a very small influence, owing to the distance through which electrostatic induction has to travel in order to reach the β-hydrogen atom. We can accordingly feel sure that the electromeric effect of α-alkyl radicals is the effect which will dominate in all circumstances. It follows that secondary alkyl groups should suffer bimolecular elimination more readily than primary, and tertiary more readily than secondary, provided we can assume that β-radicals, if present, are exerting comparable effects in the cases compared. Thus we should observe increasing facility of bimolecular elimination along the series ethyl, *iso*propyl, *tert.*-butyl, or along the series *n*-propyl, *sec.*-butyl, *tert.*-amyl.



(III.)

(Dotted arrows below formula denote hyperconjugation stabilising the transition state of the elimination represented by the full-line arrows above formula. Thus the *sec.*-butyl group gives 1 : 2-dimethylethylene as the main olefinic product.)



(IV.)

(There is no similarly situated γ-CH group to stabilise the transition state of this elimination, represented by the curved arrows, and hence the *sec.*-butyl group gives ethylethylene as a minor product only.)

The third prediction represents an extension of the first two, inasmuch as it defines the relative effects of different alkyl radicals, attached either to the β-carbon atom, or to the α-carbon atom, of the complete alkyl group. In either position, the largest effect will be exerted by the methyl radical, since it has three hydrogen atoms available for hyperconjugation. The effect will be reduced in any higher primary alkyl radical, and reduced more if a secondary alkyl radical, and still more if a tertiary alkyl radical, is substituted.

We can draw one more conclusion : for there is nothing in the theory which restricts its application to alkyl groups. We have noted how a methyl radical attached to either the β- or the α-carbon atom of the complete alkyl group, can enter into hyperconjugation with the developing double bond, thus assisting its formation. Obviously an effect of the same kind, but stronger, is to be expected if the methyl radical is replaced by an unsaturated, and therefore properly conjugated, radical such as vinyl or phenyl. The theory of the electromeric effect on elimination is, indeed, general for unsaturated and pseudo-unsaturated substituents.

Just as in the preceding Section we found the predictions of the theory of the inductive effect to be much broader than the empirical rule of Hofmann, which they included, so now we notice that the theory of the electromeric effect has a much greater range of verifiable consequences than those empirically recognised in the rule of Saytzeff. Numerous observations in the older literature of eliminations are consistently accommodated by this broader theory; but we have thought it desirable to subject its predictions to the more severe test of reaction kinetics, and it was with that object that much of the work described in the preceding papers was carried out. We shall now illustrate the above-mentioned consequences of the theory of the electromeric effect by reference to bimolecular eliminations from alkyl bromides.

The effect of β-substituents in primary alkyl groups is shown by the following second-order rate-constants [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.], applying to the reactions

$$\mathrm{R{\cdot}CH_2{\cdot}CH_2Br + \bar{O}Et \longrightarrow HOEt + R{\cdot}CH{:}CH_2 + \bar{B}r}$$

$$\mathrm{R_2CH{\cdot}CH_2Br + \bar{O}Et \longrightarrow HOEt + R_2C{:}CH_2 + \bar{B}r}$$

where R = H, Me, Et, *n*-Pr, and Ph, in ethyl alcohol, at 55°, with total salt concentrations of about 0·1M (Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*; and Part IX) :

Group	Ethyl.	*n*-Propyl.	*n*-Butyl.	*n*-Amyl.	*iso*Butyl.	2-Phenylethyl.
R or R$_2$	H	Me	Et	*n*-Pr	Me$_2$	C_6H_5
$10^5k(E2)$	1·6	5·3	4·3	3·5	8·5	561

We see that a single β-methyl substituent increases the bimolecular rate of elimination, that two β-methyl substituents increases it more, and that a single β-phenyl substituent does so very strongly; and we notice that higher alkyl β-substituents also increase the rate, but not so strongly as methyl does. These relationships are probably quite general, for we can illustrate some of them by means of rate constants [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.] applying to secondary and tertiary alkyl groups. Thus for the secondary halide reactions

$$\mathrm{R{\cdot}CH_2{\cdot}CHMeBr} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{R{\cdot}CH{:}CHMe} + \overline{\mathrm{Br}}$$

where R = H, Me, and Et, in ethyl alcohol, at 25°, with a total salt concentration of about 1·0M, we find the following second-order rate-constants (Part X) :

Group	*iso*Propyl.	*sec.*-Butyl.	2-*n*-Amyl.
R	H	Me	Et
$10^5k(E2)$	0·118	0·282	0·196

For the secondary halide reactions

$$\mathrm{R{\cdot}CH_2{\cdot}CHEtBr} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{R{\cdot}CH{:}CHEt} + \overline{\mathrm{Br}}$$

where R = H and Me, under the same conditions as before, the following second-order rate-constants have been found (Part X) :

Group	*sec.*-Butyl.	3-*n*-Amyl.
R	H	Me
$10^5k(E2)$	0·065	0·200

Finally, for the tertiary halide reactions

$$\mathrm{R{\cdot}CH_2{\cdot}CMe_2Br} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{R{\cdot}CH{:}CMe_2} + \overline{\mathrm{Br}}$$

where R = H and Me, still under the same conditions, we have the following second-order constants (Part XI) :

Group	*tert.*-Butyl.	*tert.*-Amyl.
R	H	Me
$10^5k(E2)$	1·00	4·20

The effect of α-substituents on the bimolecular elimination rates of alkyl bromides seems to be equally regular, as may be illustrated by some further rate constants [$k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.]. The following second-order constants relate to the reactions

$$\mathrm{CH_3{\cdot}CHRBr} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{CH_2{:}CHR} + \overline{\mathrm{Br}}$$

$$\mathrm{CH_3{\cdot}CR_2Br} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{CH_2{:}CR_2} + \overline{\mathrm{Br}}$$

where R = H, Me, Et, *n*-Pr, and Ph, in ethyl alcohol, at 25°, with a total salt concentration of about 1·0M (Parts X and XI; the figures for ethyl and 1-phenylethyl are estimated from measured rates under other conditions—cf. Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*) :

Group	Ethyl.	*iso*Propyl.	*sec.*-Butyl.	3-*n*-Amyl.	*tert.*-Butyl.	*tert.*-Amyl.	1-Phenylethyl.
R or R_2	H	Me	Et	*n*-Pr	Me_2	MeEt	C_6H_5
$10^5k(E2)$	0·025	0·118	0·065	0·080	1·00	0·85	0·79

We notice that a single α-methyl substituent increases the second-order rate-constant, and that two α-methyl substituents do so more strongly, as also does a single α-phenyl substituent; and again we find that, although higher alkyl substituents increase the rate, they do so less strongly than methyl does. Some of the same relationships can be illustrated for the reactions

$$\mathrm{CH_3{\cdot}CH_2{\cdot}CHRBr} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{CH_3{\cdot}CH{:}CHR} + \overline{\mathrm{Br}}$$

$$\mathrm{CH_3{\cdot}CH_2{\cdot}CR_2Br} + \overline{\mathrm{O}}\mathrm{Et} \longrightarrow \mathrm{HOEt} + \mathrm{CH_3{\cdot}CH{:}CR_2} + \overline{\mathrm{Br}}$$

in which an extra β-linked methyl substituent is present, and R = H, Me, and Et. Under the same conditions as before, the second-order rate-constants are as follows (Parts X and XI; the figure for *n*-propyl is estimated from measured rates under other conditions—cf. Part IX, and also ref. 31 of Section 1.1) :

Group	*n*-Propyl.	*sec.*-Butyl.	3-*n*-Amyl.	*tert.*-Amyl.
R or R_2	H	Me	Et	Me_2
$10^5k(E2)$	0·083	0·282	0·200	4·20

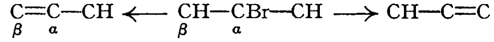
It is interesting to notice that the methyl radical exerts a larger effect from the α-position, whilst the phenyl radical acts more strongly from the β-position. This may possibly be a result of the simultaneous presence of the electrostatic effect, which becomes important in the case of β-linked substituents, and for β-methyl (inductive electron-repulsion) opposes the resonance effect, but for β-phenyl supports it (electron attraction due to the Ar–C bond dipole).

The manner in which the above-described effects on bimolecular elimination rate combine together to produce orientational effects in secondary and tertiary alkyl halides can be understood from Table I. There the second-order rate-constants for elimination under a uniform set of conditions are given in the form of the partial rates which correspond to elimination along the different branches of the alkyl groups. These partial rates are entered against the associated alkyl branches on either side of the chemical formulæ, and adjacent to each rate figure is a note of the substituents attached to the α- and β-ends of the double bond formed, the labels α- and β- denoting, as usual, those carbon atoms from which the halogen and hydrogen atoms, respectively, are lost in the formation of the double bond.

TABLE I.

Itemised Second-order Rate-constants of Elimination, arranged to show the Manner in which they determine Orientation, in the Bimolecular Eliminations of Alkyl Halides.

Reactions of alkyl bromides with *ca.* 1N-sodium ethoxide in dry ethyl alcohol at 25°. Second-order rate-constants, $k(E2)$, in sec^{-1}. g.-mol.$^{-1}$ l. Notation for showing positions of substituents :



$$\underset{\beta}{C}{=}\underset{\alpha}{C}{-}CH \longleftarrow \underset{\beta}{CH}{-}\overset{\alpha}{\underset{\alpha}{C}}Br{-}\overset{\beta}{CH} \longrightarrow CH{-}\overset{\alpha}{C}{=}\overset{\beta}{C}$$

No.	Substituents. β.	Substituents. α.	$10^5k(E2)$ per branch.	Alkyl halide.	$10^5k(E2)$ per branch.	Substituents. α.	Substituents. β.
1	—	Me	0·118	$CH_3{\cdot}CHBr{\cdot}CH_3$	0·118	Me	—
2	Me	Me	0·282	$CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$	0·065	Et	—
3	Et	Me	0·196	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$	0·080	*n*-Pr	—
4	Me	Et	0·200	$CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2{\cdot}CH_3$	0·200	Et	Me
5	—	Me_2	1·00	$CH_3{\cdot}CBr{<}^{CH_3}_{CH_3}$	1·00 1·00	Me_2 Me_2	— —
6	Me	Me_2	4·20	$CH_3{\cdot}CH_2{\cdot}CBr{<}^{CH_3}_{CH_3}$	0·85 0·85	MeEt MeEt	— —

Comparing entries 1 and 2, one sees (left-hand columns) that, in agreement with theory, the extra β-Me in example 2 accelerates the formation of but-2-ene as compared with its lower homologue, whereas (right-hand columns) the replacement of α-Me by α-Et retards, as it should, the formation of but-1-ene. Both rate changes contribute to the production of a considerable orienting effect according to Saytzeff's rule (Part X) :

$$(81\%)\ CH_3{\cdot}CH{:}CH{\cdot}CH_3 \xleftarrow[E2]{} CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3 \xrightarrow[E2]{} CH_3{\cdot}CH_2{\cdot}CH{:}CH_2\ (19\%)$$

Comparing entries 2 and 3, we find (left), again in agreement with theory, that the replacement of β-Me by β-Et retards the formation of pent-2-ene in comparison with but-2-ene, whereas (right) the replacement of α-Et by α-Pr, which in theory should have but little effect, actually slightly accelerates the formation of pent-1-ene in comparison with but-1-ene. The result is still an orientation according to the Saytzeff rule; but it is a weaker orientation in the case of the pentenes than in that of the butenes, contrary to what might naïvely have been assumed in view of the greater dissymmetry of the 2-*n*-amyl than of the 2-*n*-butyl radical (Part XI) :

$$(71\%)\ CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_3 \xleftarrow[E2]{} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3 \xrightarrow[E2]{} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2\ (29\%)$$

In such a manner does the theory accommodate a number of fine details, which are not expressed in any empirical rule.

If we compare examples 4 and 3 in Table I, we see (left) that an interchange of the substituents Me and Et between the α- and β-positions has scarcely any effect on the rate of establishment of the double bond in the left-hand alkyl branch. This is in no way surprising. The whole of the orienting effect which is introduced on passing from symmetric 3-*n*-amyl bromide to asymmetric 2-*n*-amyl bromide is due to the decreased ease of establishment of the double bond in the right-hand alkyl branch. As to this, although two groups become changed (see Table I, right), most of the effect is doubtless due to the loss of the β-Me substituent.

Examples 5 and 6 of Table I show (left) that the extra β-Me group in the left-hand branch of the *tert.*-amyl bromide molecule accelerates the formation of a double bond in that direction, as it should according to our theory. But it is also apparent (right) that the same structural change amounts to a replacement of α-Me by α-Et with respect to the establishment of the double bond in either of the right-hand branches of the molecule. Hence the alteration should have a retarding effect on those processes, as in fact it has. The orientational proportions are a resultant of these two effects, together with that of the doubled statistical weight of the terminally unsaturated, with respect to the non-terminally saturated, olefin (Part XI) :

$$(71\%)\ \mathrm{CH_3{\cdot}CH{:}C(CH_3)_2} \xleftarrow[E2]{} \mathrm{CH_3{\cdot}CH_2{\cdot}CBr(CH_3)_2} \xrightarrow[E2]{} \mathrm{CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH_2}\ (29\%)$$

Reference may be made to the orientational result represented in the following scheme (Part XV) :

$$(82\%)\ \mathrm{(CH_3)_2C{:}CH{\cdot}CH_3} \xleftarrow[E2]{} \mathrm{(CH_3)_2CH{\cdot}CHI{\cdot}CH_3} \xrightarrow[E2]{} \mathrm{(CH_3)_2CH{\cdot}CH{:}CH_2}\ (18\%)$$

No rates have been measured for this case, but we should expect the extra methyl substituent which is here present, over and above those which appear in example 2 of Table I, to increase the rate of formation of the non-terminally unsaturated olefin, and, essentially for this reason, to lead to the still more decided orientation of the observed Saytzeff type.

This is a convenient place in which to refer to the differential influence of alkyl structure on elimination and substitution in the second-order reactions of alkyl halides, and to the consequential effect on the proportion of olefin formed. Considering first the successive introduction of α-linked methyl substituents, we know that in the series ethyl, *iso*propyl, *tert.*-butyl, the rate of bimolecular substitution decreases (Ref. 31 of Section 1.1; Dostrovsky, Hughes, and Ingold, *J.*, 1946, 157); and we have seen above that the rate of bimolecular elimination increases: therefore the proportion of olefin, $E2/(S_N2 + E2)$, must increase strongly. The following rate-constants [$k(S_N2)$ and $k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l.], and olefin proportions, for the bimolecular reactions of the alkyl bromides with sodium ethoxide (1N or more) in ethyl alcohol at 55°, illustrate this :

	Ethyl.	*iso*Propyl.	*tert.*-Butyl.
$10^5k(S_N2)$	118	2·1	small
$10^5k(E2)$	1·2	7·6	50
Proportion of olefin, %	1·0	79	~100

With regard to successively introduced β-linked methyl radicals, we know that in the series ethyl, *n*-propyl, *iso*butyl, the rate of bimolecular substitution falls, though not so strongly as before; and we have noticed above that the rate of bimolecular elimination rises, but again less markedly than in the previous series; therefore the proportion of olefin will exhibit an increase, which, however, will be less pronounced than that produced by α-linked methyl radicals. In illustration, the following rate constants and olefin proportions may be quoted, which refer to the bimolecular reactions of the alkyl bromides with sodium ethoxide (about 0·1N) in ethyl alcohol at 55° :

	Ethyl.	*n*-Propyl.	*iso*Butyl.
$10^5k(S_N2)$	172	55	5·8
$10^5k(E2)$	1·6	5·3	8·5
Proportion of olefin, %	0·9	8·9	60

Different relations will naturally obtain for the bimolecular reactions of 'onium salts, whose eliminations are controlled largely by the inductive, rather than by the electromeric, effect. However, we have insufficient data on bimolecular substitution rates in 'onium salts for the purposes of a general discussion, the difficulty being that the presence of several different groups in most of the 'onium salts whose decompositions have been kinetically studied usually makes the substitution process composite and tedious to analyse.

Sectional Summary.—We now summarise the general results of our study of rate and orientation in the bimolecular eliminations of alkyl halides. In these reactions the general rule is that the formation of a double bond in any given position is accelerated by an alkyl radical at either end of it, the most effective alkyl radical being methyl, although phenyl is considerably more effective than any simple alkyl radical. On this basis, one can understand the variation with structure of the rates of bimolecular elimination in a large variety of primary, secondary, and tertiary alkyl halides; and also the orientational data for dissymmetrically branched secondary and tertiary alkyl halides. The orientational results all conform to the qualitative, empirical rule of Saytzeff; but they also disclose quantitative variations, which agree in detail with the more general rule stated above. All these effects of structure on reaction rate and orientation are rendered intelligible by the proposed theory of the electromeric effect, which consists in the assumption of a hyperconjugation or conjugation operating between the developing double bond and the radicals adjacent to it, in the transition state of reaction. This appears as the controlling influence; but certain detailed results, such as the dissimilar changes in the effectiveness of a methyl radical and of a phenyl radical when shifted from one end of the double bond to the other, point to the presence of a disturbance, which can plausibly be identified as the inductive effect.

Not only do alkyl groups at either end of a developing double bond increase the rate of its formation in these bimolecular reactions of alkyl halides : they also decrease the rate of the concomitant bimolecular substitutions. Therefore they increase largely the proportion in which olefins are formed in the total bimolecular decomposition.

(3.3) *Unimolecular Elimination in Halides and Sulphonium Salts : The Electromeric Effect.*—Unimolecular elimination has been observed with secondary and tertiary alkyl halides, and secondary and tertiary alkylsulphonium ions : it has not yet been realised (except in association with molecular rearrangement) for primary alkyl halides, or for 'onium ions containing only primary alkyl groups.

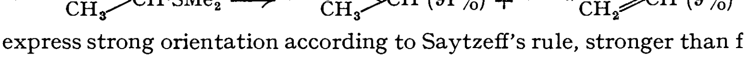
All our evidence concerning the orientation of unimolecular elimination, whether of alkyl halides or of alkylsulphonium salts, points to the conclusion that the controlling influence is the electromeric effect. In particular, orientation follows the Saytzeff rule. It is, of course, not remarkable that the unimolecular eliminations of halides and of sulphonium salts should behave similarly in this respect, even though the bimolecular eliminations of halides and of sulphonium salts behave very differently; for orientation in unimolecular elimination is a property of the carbonium ion, which is an intermediate of that mechanism, and the carbonium ion corresponding to a given alkyl group is the same, whether it comes from an alkyl halide or an alkylsulphonium ion. Qualitatively then, orientation in unimolecular elimination, either of halides or of sulphonium ions, resembles orientation in the bimolecular eliminations of alkyl halides. But we shall find that orientation in the unimolecular reactions is quantitatively more extreme than in the bimolecular reactions of halides.

Because of the two-stage nature of the unimolecular mechanism, the rate constant of elimination, $k(E1)$, is composite, and this has to be borne in mind when using it for the purpose of assessing constitutional effects. It is the product of the rate of heterolysis, and the fraction of the formed carbonium ion which completes an elimination. From some points of view this fraction, that is, the percentage of olefin formed in the unimolecular reaction, is more simply related to structure than is the rate of the separate process of elimination. Some secondary alkyl bromides are compared below with respect to the percentage of olefin which they yield in " 60% " aqueous ethyl alcohol at 80° (Part X) :

R in RBr........................	$\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right>\mathrm{CH}$	$\left.\begin{matrix}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3}\end{matrix}\right>\mathrm{CH}$	$\left.\begin{matrix}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH_2}\end{matrix}\right>\mathrm{CH}$	$\left.\begin{matrix}\mathrm{CH_3.CH_2{\cdot}CH_2}\\ \mathrm{CH_3}\end{matrix}\right>\mathrm{CH}$
Proportion of olefin, %.........	4·6	8·5	15·1	6·8
$10^5k(E1)$	0·32	0·63	0·90	0·38

The rate constants for elimination [$k(E1)$ in sec.$^{-1}$] are seen to show much the same trend as the olefin proportion. Even though data are not available which would permit the figures for the two unsymmetrical compounds to be split up into parts corresponding to reaction in the alternative branches of the alkyl group, it is clear from the results that a β-linked methyl substituent facilitates the completion of an elimination, and that a β-linked ethyl substituent does the same, but not so strongly. What we have not proved is that these effects are localised in the alkyl branch to which the substituent is attached; but it would be reasonable to assume that they are so localised : the whole picture then agrees perfectly with control by the electromeric effect.

Orientational data, such as are lacking for the unimolecular eliminations of the asymmetric secondary alkyl halides, are available for one such secondary alkylsulphonium ion (Part XV) :



$$\left.\begin{matrix}\mathrm{(CH_3)_2CH}\\ \mathrm{CH_3}\end{matrix}\right>\mathrm{CH{\cdot}\overset{+}{S}Me_2} \longrightarrow \left.\begin{matrix}\mathrm{(CH_3)_2C}\\ \mathrm{CH_3}\end{matrix}\right>\mathrm{CH}\ (91\%) + \left.\begin{matrix}\mathrm{(CH_3)_2CH}\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{CH}\ (9\%)$$

These figures express strong orientation according to Saytzeff's rule, stronger than for the already mentioned bimolecular reaction of the corresponding alkyl iodide. This again corresponds to control by the electromeric effect. The proportion of total olefin was 7%, a figure which is of the same order of magnitude as those obtained for the corresponding reactions of the secondary alkyl bromides, though precise comparison is not possible, because the solvent and temperature were not the same as for the bromides.

A comparison of the proportions in which olefins are formed in the first-order reactions of *iso*propyl and *tert.*-butyl halides or sulphonium ions, or alternatively in the first-order decompositions of *sec.*-butyl and *tert.*-amyl halides or sulphonium ions, shows that an α-linked methyl substituent in the alkyl chain is even more effective than a β-linked methyl substituent in directing the completion of the process towards elimination. Actually, the figures available to illustrate this do not apply to identical conditions of solvent and temperature; but, as the following list shows, the differences in olefin proportion are so large that there can be no doubt about the qualitative conclusion (Parts VI, VII, VIII, and X) :

*iso*Propyl bromide	in 60%	aq. EtOH at	80°	yields	4·6%	olefin
tert.-Butyl chloride	in 80%	,,	65°	,,	36·3%	,,
$\mathrm{Bu^t\overset{+}{S}Me_2}$	in 80%	,,	65°	,,	35·7%	,,
sec.-Butyl bromide	in 60%	aq. EtOH at	80°	yields	8·5%	olefin
tert.-Amyl chloride	in 80%	,,	50°	,,	40·3%	,,
$\mathrm{Am^t\overset{+}{S}Me_2}$	in 60%	,,	65°	,,	39·8%	,,
,,	in 80%	,,	65°	,,	49·4%	,,
,,	in 80%	,,	83°	,,	53·4%	,,

A detailed analysis of the manner in which the rates and proportions of unimolecular elimination along the different branches of a dissymmetric alkyl group contribute to the effect of a structural change on the overall elimination rate, the overall olefin proportion, and the orientation of elimination can be offered in the form of a comparison either of the unimolecular reactions of *tert.*-butyl and *tert.*-amyl bromides, or of those of dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium ions. We here employ the former example (Part XI), partly because it permits an instructive comparison of bimolecular and unimolecular eliminations of the same substances, all fundamentally under the control of the electromeric effect, and partly because we shall be using the latter example in another connexion presently.

The analysis is given in the upper part of Table II. These figures may be compared with those of the similar analysis which is given for the bimolecular reactions in entries 5 and 6 of Table I. The corresponding data on the left of either table show a qualitatively similar structural influence : the extra β-Me substituent in the amyl compound facilitates the establishment of the double bond in the alkyl branch to which it belongs. But the effect is larger for the unimolecular than for the bimolecular mechanism. All this is true, whether we think of the rate at which, or the proportion in which, the double bond is established in the appropriate part of the molecule. However, the figures on the right of the two tables reveal a certain difference : the replacement of α-Me_2 by α-MeEt, which in the bimolecular reaction, consistently with the theory of control by the electromeric effect, reduced the rate of introduction of the double bond into those alkyl branches with respect to which the indicated radicals are α-substituents, is now found to accelerate the same process in the unimolecular reaction. This, however, is not an anomaly : it is immediately explained by the mechanistic difference. The rate-constant $k(E1)$ contains, as a factor, the rate of ionisation of the alkyl halide, and this is greater for *tert.*-amyl than for *tert.*-butyl bromide. We avoid this irrelevant consideration if we pay attention to olefin proportions rather than to rates; and then we find that, in the completion of unimolecular elimination, the replacement of α-Me_2 by α-MeEt reduces, as it should if the control is by the electromeric effect, the extent to which the double bond is established in those alkyl branches with respect to which these radicals are α-substituents. The way in which these itemised rates and proportions combine to produce overall results is indicated in the lower part of Table II. The orientations is again of the Saytzeff type; and it is more extreme than that of the corresponding bimolecular reaction (Section 3.2).

A closely similar discussion could be given of the reaction rates, olefin proportions, and orientation of unimolecular elimination in dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium salts, the data for which are summarised in Table III (p. 2112).

Up to this point the discussion of the present Section has been concerned with the proportions in which a total unimolecular reaction, having passed through the preliminary, slow heterolysis, will pursue the various final, rapid stages open to it, thus producing a substitution product as well as one or more olefins. We have still to deal with the effect of structure on the common preliminary heterolysis, and particularly with the question of whether the inductive or the electromeric effect principally controls the rate of this process in simple alkyl compounds. We can assume that sufficiently polar substituents will give control to the inductive, and

TABLE II.

Itemised First-order Rates of Elimination and Proportions of Olefin, arranged to show the Manner in which they determine Overall Results, in Unimolecular Eliminations of Alkyl Halides.

Reactions of alkyl bromides in ethyl alcohol at 25°. First-order rate-constants, k_1 and $k(E1)$, in sec.$^{-1}$. Notation for showing the positions of substituents :

$$\underset{\beta}{C}{=}\underset{\alpha}{C}{-}CH \longleftarrow CH{-}\overset{\alpha}{C}Br{-}\overset{\beta}{C}H \longrightarrow CH{-}\overset{\alpha}{C}{=}\overset{\beta}{C}$$

Substituents.		Per branch.		Alkyl halide.	Per branch.		Substituents.	
β.	α.	% Olefin.	$10^5k(E1)$.		$10^5k(E1)$.	% Olefin.	α.	β.
—	Me_2	6·3	0·029	$CH_3\cdot CBr{<}^{CH_3}_{CH_3}$	0·029	6·3	Me_2	—
					0·029	6·3	Me_2	—
Me	Me_2	29·6	0·323	$CH_3\cdot CH_2\cdot CBr{<}^{CH_3}_{CH_3}$	0·036	3·3	MeEt	—
					0·036	3·3	MeEt	—

Overall Rates and Olefin Proportions :

	10^5k_1.	$10^5k(E1)$.	% Olefin.
tert.-Butyl	0·45	0·086	19·0
tert.-Amyl	1·09	0·395	36·3

Overall Orientation :

	$CH_3\cdot CH{:}C(CH_3)_2$.	$CH_3\cdot CH_2\cdot C(CH_3){:}CH_2$.
tert.-Amyl, %	82	18

sufficiently unsaturated substituents to the electromeric effect; but alkyl groups present a special problem since they are neither strongly polar nor strongly unsaturated. We shall neglect the steric effect, since, as has been pointed out before, it is seldom important in unimolecular reactions (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 620; Day and Ingold, *ibid.*, p. 699; Dostrovsky, Hughes, and Ingold, *J.*, 1946, 190).

It is useful to refer to examples which show the effect of structure on rates of heterolysis in the aralphyl series; for the present a contrast with the corresponding reactions of simple alkyl compounds. The following relative unimolecular rates have been recorded for the heterolysis of *p*-methyl- and *p*-ethyl-benzhydryl chloride in " 80% " aqueous acetone at 0° (Hughes, Ingold, and Taher, *J.*, 1940, 949) :

$$H{-}CH_2\cdot C_6H_4\cdot CHPhCl \text{ (rate = 1)} \qquad CH_3{-}CH_2\cdot C_6H_4\cdot CHPhCl \text{ (rate = 0·75)}$$

The ethyl compound thus exhibits the lower rate (and the larger Arrhenius activation energy—*loc. cit.*), and this at once shows that the differential electromeric effect outweighs the differential inductive effect in these cases. We can conclude that the electromeric effect is important here, having, no doubt, been enhanced by the unsaturation of the p-C_6H_4 system. In the purely aliphatic series the situation is different. For the heterolysis rates of *tert.*-butyl and *tert.*-amyl bromides in ethyl alcohol at 25°, we find (Table II) the following relationship :

$$H{-}CH_2\cdot CHMe_2Br \text{ (rate = 1)} \qquad CH_3{-}CH_2\cdot CMe_2Br \text{ (rate = 2·42)}$$

Obviously the differential inductive effect now predominates : we can certainly conclude that the inductive effect is important, more so, relatively to the electromeric effect, than in the aralphyl series. On the other hand, when we replace the bromine atom in these examples by the more strongly electron-attracting sulphonium pole, then the increase of rate arising from the replacement of methyl by ethyl becomes more marked, as is shown by the following data (Table III) for the relative rates of heterolysis of dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium ions in ethyl alcohol at 50° :

$$H{-}CH_2\cdot CMe_2\cdot \overset{+}{S}Me_2 \text{(rate = 1)} \qquad CH_3{-}CH_2\cdot CMe_2\cdot \overset{+}{S}Me_2 \text{ (rate = 8·40)}$$

In these cases it seems a safe conclusion that the inductive effect is the dominating polar factor.

Sectional Summary.—We here summarise the results of our study of unimolecular elimination. For both alkyl halides and alkylsulphonium ions, the general rule has been established that the proportion in which the total unimolecular reaction is completed by a route which involves the introduction of a double bond between a given pair of carbon atoms is increased by the attachment of a methyl or ethyl substituent to either of those carbon atoms; and the increase produced by a methyl radical is greater than that produced by an ethyl radical. A considerable variety of experimental results can be referred to this rule, which includes the Saytzeff rule but is much more general: they relate to the proportions in which olefins are formed in the unimolecular reactions of secondary alkyl halides, the orientation ratio for unimolecular olefin formation from a secondary alkylsulphonium ion, and the greater proportions of olefin obtained in unimolecular reactions from tertiary than from secondary alkyl halides, and from tertiary than from secondary alkylsulphonium ions; and they include also the detailed analyses which have been made of the unimolecular rate, olefin proportions, and orientation ratios, for a pair of tertiary alkyl bromides, and again, for a pair of tertiary alkylsulphonium ions. Orientation is according to the Saytzeff rule, but is more extreme than that found for the bimolecular reactions of alkyl halides. The theoretical significance of all this is recognised to be dominating control of the final, rapid stage of unimolecular elimination by the electromeric effect.

In general, the heterolysis, which constitutes the initial slow stage of unimolecular reactions, is controlled jointly by the inductive and electromeric effects; but for simple alkyl compounds the inductive effect has a special importance, which is greater for sulphonium ions than for halides. (We may expect it to be greater still for ammonium ions, but this has not yet been verified.)

(3.4) *Co-existence of the Inductive and Tautomeric Effects.*—Originally, the Hofmann rule was applied to elimination from primary alkyl groups in ammonium ions, and the Saytzeff rule to elimination from secondary and tertiary alkyl groups in alkyl halides; and both rules were applied without reference to the kinetics of the elimination process. We have been concerned to discover what exactly bounds the separate fields of application of the two rules—whether it be the chemical nature of the original molecule ('onium salt or halide), or the type of the alkyl group (primary, secondary, or tertiary), or the mechanism of elimination (bimolecular or unimolecular). We now know that for alkyl compounds the determining circumstances are a combination of the first and third of these factors, the separate ranges being as follows: (i) bimolecular eliminations from alkyl groups in ammonium and sulphonium salts and in sulphones follow the Hofmann rule; (ii) bimolecular eliminations from alkyl halides follow the Saytzeff rule; and (iii) all unimolecular eliminations, whether of alkyl-'onium ions or alkyl halides, follow the Saytzeff rule. As we have seen, the Hofmann rule signalises control by the inductive effect, and the Saytzeff rule control by the electromeric effect.

The remarkable change which takes place in the influence of structure on the reaction rates which collectively determine orientation, when we cross the boundary between the regions of control by the two rules may be illustrated by reference to Tables III and IV. We are dealing here with identically the same structures, the dimethyl-*tert.*-butyl- and -*tert* -amyl-sulphonium ions. From Table III to Table IV we cross the boundary between the domains of the two rules merely by changing from one kinetic form of elimination to the other.

In Table III we give both the rates and olefin proportions for elimination in the various alternative directions, in order to allow comparison with Table IV. But since Table III refers to the bimolecular mechanism, it is here the rates, rather than the olefin proportions, which have the simpler relation to structure. The extra β-linked methyl substituent decreases the rate of elimination in the long branch of the *tert.*-amyl group, in accordance with the conclusion that the inductive effect is dominant. The rate of elimination in the shorter branches, which should have been substantially reduced, owing to the replacement of a methyl substituent by ethyl, if the electromeric effect had been in control, is only slightly altered; and it should be altered hardly at all by the inductive effect, because the structural change is too remote from the β-hydrogen atom to affect it appreciably by the electrostatic mechanism. The small observed rate difference could, of course, be due to a weak underlying electromeric effect: if it were present, that certainly is how it would show itself. The resultant effect of all these individual rate changes on overall rate and orientation is shown in the lower part of Table III.

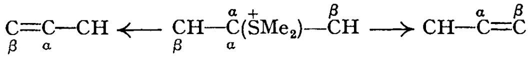
In Table IV both rates and olefin proportions are again given, but since the data refer to the unimolecular mechanism, it is now the olefin proportions, rather than the rates, which are the more simply related to structure (cf. Section 3.3). We find that the extra β-methyl substituent increases the proportion of elimination in the long branch of the *tert.*-amyl group, and reduces the proportion in the shorter branches, both in accordance with a controlling electromeric effect. In the overall results of these changes (Table IV, bottom), we find a reversal in the direction of every one of the structural effects which were found to arise in bimolecular elimination (Table III, bottom).

Another crossing of the boundary between the domains of the Hofmann and Saytzeff rules is made if we pass from the data of Table III to those in Table I, entries 5 and 6. In this case we do not change the mechanism, which is bimolecular ($E2$), but we do change the electron-

TABLE III.

Itemised Second-order Rate-constants of Elimination, arranged to show how they determine Orientation in Bimolecular Eliminations of Alkylsulphonium Salts.

Reactions of sulphonium ethoxides in " 97% " ethyl alcohol at 24°. Second-order constants k_2 and $k(E2)$ in sec.$^{-1}$ g.-mol.$^{-1}$ l. Notation for positions of substituents :



$$\underset{\beta}{C}{=}\underset{\alpha}{C}{-}CH \longleftarrow \underset{\beta}{CH}{-}\overset{\alpha}{\underset{\alpha}{C}}(\overset{+}{S}Me_2){-}\overset{\beta}{CH} \longrightarrow CH{-}\overset{\alpha}{C}{=}\overset{\beta}{C}$$

Substituents.		Per branch.		Sulphonium ion.	Per branch.		Substituents.	
β.	α.	% Olefin.	$10^5k(E2)$.		$10^5k(E2)$.	% Olefin.	α.	β.
—	Me_2	33	27	$CH_3{\cdot}C(\overset{+}{S}Me_2)<^{CH_3}_{CH_3}$	27	33	Me_2	—
					27	33	Me_2	—
Me	Me_2	14	8	$CH_3{\cdot}CH_2{\cdot}C(\overset{+}{S}Me_2)<^{CH_3}_{CH_3}$	24	41	MeEt	—
					24	41	MeEt	—

Overall Rates and Olefin Proportions :

	10^5k_2.	$10^5k(E2)$.	% Olefin.
tert.-Butyl	80	80	100
tert.-Amyl	58	56	96

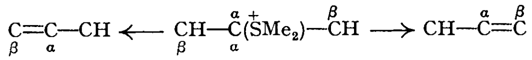
Overall Orientation :

	$CH_3{\cdot}CH{:}C(CH_3)_2$.	$CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH_2$.
tert.-Amyl, %	14	86

TABLE IV.

Itemised First-order Rates and Proportions of Elimination, arranged to show how they determine Overall Results in Unimolecular Eliminations of Alkylsulphonium Salts.

Reactions of sulphonium iodides in " 97% " ethyl alcohol at 50°. First-order constants, k_1 and $k(E1)$, in sec.$^{-1}$. Notation for positions of substituents :



$$\underset{\beta}{C}{=}\underset{\alpha}{C}{-}CH \longleftarrow \underset{\beta}{CH}{-}\overset{\alpha}{\underset{\alpha}{C}}(\overset{+}{S}Me_2){-}\overset{\beta}{CH} \longrightarrow CH{-}\overset{\alpha}{C}{=}\overset{\beta}{C}$$

Substituents.		Per branch.		Sulphonium ion.	Per branch.		Substituents.	
β.	α.	% Olefin.	$10^5k(E1)$.		$10^5k(E1)$.	% Olefin.	α.	β.
—	Me_2	17	0·30	$CH_3{\cdot}C(\overset{+}{S}Me_2)<^{CH_3}_{CH_3}$	0·30	17	Me_2	—
					0·30	17	Me_2	—
Me	Me_2	56	8·41	$CH_3{\cdot}CH_2{\cdot}C(\overset{+}{S}Me_2)<^{CH_3}_{CH_3}$	0·63	4	MeEt	—
					0·63	4	MeEt	—

Overall Rates and Olefin Proportions :

	10^5k_1.	$10^5k(E1)$.	% Olefin.
tert.-Butyl	1·8	0·9	51
tert.-Amyl	15·0	9·7	64

Overall Orientation :

	$CH_3{\cdot}CH{:}C(CH_3)_2$.	$CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH_2$.
tert.-Amyl, %	87	13

attracting group from a sulphonium pole (control by the Hofmann rule) to a halogen atom (control by the Saytzeff rule). The strong contrast of constitutional influences, which here again arises, becomes smoothed away, if we make the same change in the electron-attracting group, but now consider the unimolecular mechanism ($E1$) (control by the Saytzeff rule in both types of compound), as we may do by passing from the data of Table IV to those of Table II. The structural effects on the olefin rates shown in Table I are qualitatively similar to the effects on the olefin proportions given in Tables II and IV, as is consistent with the theory that the same type of orientational control, *viz.*, the electromeric effect, is operating on different mechanisms.

There are a number of elimination reactions which have not yet been investigated kinetically with respect to mechanism, but which have been studied in a preparative way sufficiently to disclose the predominating form of orientation. Guided by our more detailed knowledge of the reactions of ammonium and sulphonium ions, sulphones, and halides, we can use such orientational observations in order to make plausible suggestions concerning mechanism. As examples, we may consider the homogeneous dehydration of alcohols (*a*) in the presence of acids, (*b*) by the action of iodine (Hibbert's reaction). Both these reactions are known to obey Saytzeff's rule (Whitmore and Evers, *J. Amer. Chem. Soc.*, 1933, **55**, 812; Whitmore and Rothrock, *ibid.*, p. 1106; Church, Whitmore, and McGrew, *ibid.*, p. 1528; Thompson and Sherrill, *ibid.*, 1936, **58**, 745). For reaction (*b*), the further point has been established that tendency to elimination along an alkyl branch $R{\cdot}CH_2{\cdot}C_\alpha$ varies with R according to the order $H < \{Me > Et, Pr^n$, etc.$\}$. Also for reaction (*b*), it has been found that the composition of the amylenes which are produced from *tert.*-amyl alcohol is similar to that of the amylenes formed from *tert.*-amyl bromide, or from a dimethyl-*tert.*-amylsulphonium salt, when, in these cases, decomposition proceeds by the unimolecular mechanism. For both reactions (*a*) and (*b*), it has been established that tertiary alcohols can be dehydrated with ease, secondary alcohols with considerably greater difficulty, and primary alcohols scarcely at all. The catalysts suggest oxonium ion intermediates, and a comparison of all the above results with our data for sulphonium ions points decidedly to the conclusion that these intermediates are undergoing elimination by the unimolecular mechanism (*E*1). Thus we suggest the following detailed mechanisms :

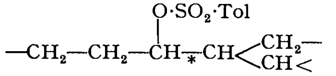
$$(a)\quad \left\{\begin{array}{lll} R{\cdot}OH + \overset{+}{O}H_3 & \underset{\text{fast}}{\rightleftharpoons} & R{\cdot}\overset{+}{O}H_2 + OH_2 \\ R{\cdot}\overset{+}{O}H_2 & \xrightarrow[\text{slow}]{} & \overset{+}{R} + OH_2 \\ \overset{+}{R} & \xrightarrow[\text{fast}]{} & \text{Olefin} + \overset{+}{H} \end{array}\right. \Bigg\}\cdots\cdots\cdots\ (E1)$$

$$(b)\quad \left\{\begin{array}{lll} R{\cdot}OH + 2I_2 & \underset{\text{fast}}{\rightleftharpoons} & R{\cdot}\overset{+}{O}HI + \overset{-}{I}_3 \\ R{\cdot}\overset{+}{O}HI & \xrightarrow[\text{slow}]{} & \overset{+}{R} + HOI \\ \overset{+}{R} & \xrightarrow[\text{fast}]{} & \text{Olefin} + \overset{+}{H} \end{array}\right. \Bigg\}\cdots\cdots\cdots\ (E1)$$

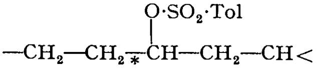
Reactions (*a*) should be paralleled, with all the consequences we have already illustrated, by the acid-catalysed formation of olefins from ethers, as we have, indeed, partly confirmed by experiments which are not yet complete enough to publish. The postulated pre-equilibrium of reactions (*b*) seems consistent with Fairbrother's ideas (*Nature*, 1947, **160**, 87), and can be supported by the special observation, details of which are reserved for inclusion in a later paper, that iodine is a moderately good electrolyte in *tert.*-butyl alcohol as solvent. We may note the implicit assumption in these explanations that bimolecular elimination (*E*2) from alkyloxonium ions would be controlled essentially by the inductive effect, with the result that orientation would follow Hofmann's rule and its various generalisations.

One further example may be given, *viz.*, the formation of olefins from sulphonic esters, either by the action of an alkali, such as sodium ethoxide, or in the course of solvolysis in a neutral or acid alcoholic solution. The conditions in which sulphonic esters enter into bi- and uni-molecular reactions have been made the subject of an investigation by Dr. C. A. Bunton, which will be published later. He has shown that the total reaction, substitution plus elimination, of *iso*propyl toluene-*p*-sulphonate with 0·3N-sodium methoxide in methyl alcohol is kinetically of the second order, and is, accordingly, bimolecular in mechanism. He has also shown that the total solvolysis of the same ester in 50% aqueous methyl alcohol is a reaction of the first order; and that since it is not detectably accelerated by added sodium hydroxide and methoxide up to an alkali concentration of 0·05N, it is certainly unimolecular in mechanism. We may conclude that the toluene-*p*-sulphonate of most secondary alcohols will readily enter into bimolecular reactions with alkoxide ions in alcohols, but will tend to undergo unimolecular decompositions on alcoholysis or hydrolysis in the absence of alkali. Now W. Hückel, Tappe, and Legutke (Refs. 35 and 48 of Sections 1.1 and 1.2), without actually applying any form of kinetic control to their reactions, analysed the mixtures of isomeric olefins which were formed from the toluene-*p*-sulphonates of a number of secondary alcohols, not only by the action of ethoxide ions, but also under conditions of solvolysis in the absence of alkali. The alcohols they employed were cyclic, and, for such compounds, a stereochemical condition requires to be fulfilled, as we shall discuss in the next Section; but for the present we shall avoid going into this matter by restricting illustration to cases in which the condition is satisfied. Hückel, Tappe, and Legutke found that, in neutral solvolysis by ethyl alcohol, *cis*-1-decalyl I-toluene-*p*-sulphonate gave mainly 1 : 9-octalene, whilst *trans*-2-decalyl I- or II-toluene-*p*-sulphonate yielded chiefly 2 : 3-octalene; *i.e.*, the double bonds entered principally into the positions marked by asterisks in the following formulæ :

(V.)



$$-CH_2-CH_2-\overset{O\cdot SO_2\cdot Tol}{\overset{|}{C}H}\underset{*}{-}CH<\begin{matrix}CH_2-\\CH<\end{matrix}$$



$$-CH_2-CH_2\underset{*}{-}\overset{O\cdot SO_2\cdot Tol}{\overset{|}{C}H}-CH_2-CH<$$

(VI.)

Formula (V) corresponds to Saytzeff's rule, and formula (VI) to a theoretically deduced extension of Saytzeff's rule given in the preceding Section (p. 2104). Thus, the general picture is one of control by the electromeric effect, as we should expect from our assumption that elimination in solvolysis follows the unimolecular mechanism (*E*1). What is more interesting, however, is that Hückel, Tappe, and Legutke found these esters to display qualitatively the same orientations in the eliminations which they undergo in the presence of considerable concentrations of alcoholic sodium ethoxide. From this we must conclude that the bimolecular eliminations (*E*2) of alkyl toluene-*p*-sulphonates, like those of alkyl halides, are controlled by the electromeric effect.

From a consideration of all the eliminations thus far discussed, it would appear that the circumstances in which either the inductive effect or the electromeric effect may exert a dominating influence over the velocity and orientation of elimination by different mechanisms from different kinds of alkyl compound may be defined as follows : (i) When the electron-attracting atom attached to the alkyl group carries a positive ionic charge, bimolecular elimination will be controlled by the inductive effect. (ii) When this atom does not carry a positive charge, bimolecular elimination will be controlled by the electromeric effect. (iii) Independently of the nature of the electron-attracting atom, unimolecular elimination will be governed by the electromeric effect. The discussed examples may be classified as indicated in the following scheme :

(i) Inductive control of *E*2 . . . $Y = \overset{+}{N}R_3, \overset{+}{P}R_3, \overset{+}{S}R_2, \overset{+-}{SO_2}R$

(ii) Electromeric control of *E*2 . . $Y = Cl, Br, I, O{\cdot}SO_2R$

(iii) Electromeric control of *E*1 . . $Y = \overset{+}{S}R_2, \overset{+}{O}R_2, Cl, Br, I, O{\cdot}SO_2R$

The type of alkyl group, whether primary, secondary, or tertiary, has no concern with the matter. It should be emphasized that the above statements apply to heterolytic 1 : 2-eliminations in solution : we do not consider elimination by reactions, such as the oxidation of hydrazones and the pyrolysis of xanthates, which are probably homolytic; and, of course, we are excluding gas and surface reactions from our discussion.

The type of alkyl group has, of course, a vital concern with the replacement of bimolecular mechanisms by unimolecular mechanisms of substitution and elimination. Under given conditions as to reagent and solvent, and for a given electron-attracting group Y, the tendency to such replacement follows the order primary-to-tertiary of alkyl groups, as one may understand on the grounds that increasingly powerful polar effects of alkyl will favour the separate heterolysis of the bond $C_\alpha Y$. For given conditions as to reagent and solvent, and for a given alkyl group, the tendency to replacement of bimolecular elimination by unimolecular substitution and elimination varies with the electron-attracting group Y. Apparently the variation here follows the inverse order of the inductive effect, as one may partly rationalise on the basis that an increasing inductive effect must increase the vulnerability of the β-hydrogen atom towards basic reagents. Schematically, we have the following general relations :

$$\left.\begin{matrix}\text{Constitutional promotion}\\ \text{of change } E2\rightarrow E1\end{matrix}\right\}\left\{\begin{matrix}\text{Alk}\ldots.\text{Primary}<\text{Secondary}<\text{Tertiary}\\ Y\ldots.\overset{+}{N}R_3<\overset{+}{S}R_2<\text{Hal}<O{\cdot}SO_2R\end{matrix}\right.$$

The environmental factors which favour the change *E*2→*E*1 have already been considered in Part V (*J.*, 1940, 899) : the most important are the basicity and concentration of the reagent, and the ionising power of the solvent.

It can scarcely be doubted that the existence of separate fields of control by the inductive and electromeric effects on the velocity and orientation of the elimination reactions of alkyl derivatives is to be taken to mean that, in principle, both effects are always present, but that, owing to circumstances still to be considered, either one or the other dominates. Several apparent indications of a modifying influence of a minor effect on a broad result determined by a major one have been already noticed in this discussion. We may instance the accelerating effect of α-alkyl substituents in bimolecular elimination from sulphonium ions (pp. 2100 and 2101), and the considerably greater accelerations produced by a β-phenyl than by an α-phenyl substituent in bimolecular eliminations from alkyl halides (p. 2105). However, in order to obtain decisive effects, let us go outside the field of alkyl groups, and examine, on the one hand, more polar groups, and, on the other, more unsaturated groups; for then we shall find that inductive or electromeric effects, as the case may be, which would have been masked in the corresponding alkyl compounds, can be made quite clearly to dominate.

Consider, for example, the second-order eliminations of alkyl halides: they obey the Saytzeff rule, and are controlled essentially by the electromeric effect: the influence of the inductive effect is only of minor importance. However, if we introduce into the alkyl group a strongly electron-attracting β-halogen substituent, then the inductive effect of this polar substituent so loosens the β-proton that the elimination reaction is very greatly accelerated. We can show that this is not essentially an electromeric effect, due to a conjugation of the unshared electrons of the β-halogen atom with the developing double bond, though such an effect also would produce an acceleration. For the electromeric effect should work just as well from the α-position, and therefore, if we take the corresponding α-halogenoalkyl halide, instead of the unsubstituted alkyl halide, as the standard of comparison, we shall isolate the inductive effect, which is primarily a property of β-linked substituents. Such a comparison was made by Olivier and Weber (Ref. 25 of Section 1.1), when they measured the second-order rate-constants for the conversion of ethylene bromide, and of ethylidene bromide, into vinyl bromide by means of hydroxide ions in " 33% " aqueous acetone at 30°. The relative bimolecular rates were as follows:

$$(\mathrm{Br})\mathrm{CH_2{\cdot}CH_2Br}\ (\text{rate} = 205) \qquad \mathrm{CH_3{\cdot}CH(Br){\cdot}Br}\ (\text{rate} = 1)$$

The much larger rate associated with the presence of the β-bromo-substituent shows that, owing essentially to the polarity of the substituent, the inductive effect is in control—as it would not have been if the β-substituent had been an alkyl radical. Olivier himself assumed a controlling electrostatic effect, pointing out that it correctly interpreted numerous orientational results relating to the elimination reactions which polyhalogeno-paraffins undergo in the presence of alkalis. The following examples are instructive:

$$\mathrm{CHCl_2{\cdot}CH_2Cl} \xrightarrow[E2]{} \mathrm{CCl_2{:}CH_2}$$

$$\mathrm{CH_3{\cdot}CBr_2{\cdot}CHBr{\cdot}CH_3} \xrightarrow[E2]{} \mathrm{CH_3{\cdot}CBr{:}CBr{\cdot}CH_3}$$

In the first case the lost halogen atom is the single one, whilst in the second case it is one of the pair. This shows that the attachment of a second halogen atom to the carbon atom from which a halogen atom is lost (the carbon atom we label α) is not a governing orientational factor. It is the attachment of halogen to the carbon atom from which hydrogen is lost (the carbon atom we label β) which is the governing circumstance—as we should expect, if it is the inductive effect, rather than the electromeric effect, which is in control. The rule is always that, of the various hydrogen atoms which could be eliminated in association with any of the halogen atoms, the one actually eliminated, along with an appropriate halogen atom, is that which is attached to the most halogenated, and therefore most positive, carbon atom. This points decidedly to a controlling inductive effect.

Similar evidence convinced Olivier that the carboxyl substituent directs the course of eliminations by means of its inductive effect. This substituent also has the property of unsaturation, as well as a strong polarity; and thus, in principle, it is capable of exerting an electromeric, as well as an inductive, effect. However, it actually operates mainly by virtue of its inductive effect, as we could show, for example, by reference to the much greater rates of formation of olefinic acids from β-halogeno- than from α-halogeno-acids or their derivatives.

We obtain evidence of a complementary kind when we turn to the bimolecular eliminations of 'onium salts (where, for ordinary alkyl groups, the inductive effect controls orientation), and for this series of reactions consider the behaviour of substituents of low polarity and high unsaturation. Phenyl and vinyl are amongst the chief examples, and it was with the aid of the former that the first case of breakdown of the Hofmann rule was realised (Ref. 1 of Section 1.1). Notwithstanding, the distinct polarity of phenyl in attachment to a saturated side-chain, the phenyl substituent in 2-phenylethyl-ammonium, -phosphonium, and -sulphonium ions, and in 2-phenylethyl sulphones, accelerates elimination to so great an extent that we must ascribe a considerable part of the effect to the capacity of the substituent for conjugation. The total effect may be illustrated, in its application to sulphonium ethoxides, by reference to the following relative rates of bimolecular eliminations from ethyl- and 2-phenylethyl-sulphonium ions in ethyl alcohol at 64° (Part XII) :

$\mathrm{CH_3{\cdot}CH_2{\cdot}\overset{+}{S}Me_2}$ (rate = 1) $\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2}$ (rate = 430) $\mathrm{CH_3{\cdot}CHPh{\cdot}\overset{+}{S}Me_2}$ (rate = 96)

The relative rate for the corresponding 1-phenylethylsulphonium ion under the same conditions (Part XIII) is noted for comparison. For the acceleration produced by the α-phenyl substituent must represent an essentially pure electromeric effect, and its considerable magnitude confirms our assignment of a large part of the acceleration produced by the β-phenyl substituent to the unsaturation, rather than to the polarity, of this radical.

The above facts show that the inductive and electromeric effects jointly influence elimination, their relative importance depending on the polarity and unsaturation of the influencing group. But, when both the polarity and the unsaturation are small, as with alkyl groups, the relative importance of the two effects can be seen to depend also, indeed primarily now, on the system which is being influenced. Let us consider this factor.

We know that when, in the bimolecular mechanism (*E*2), the influenced system is of the form $\mathrm{HC_\beta{\cdot}C_\alpha{\cdot}\overset{+}{Y}}$ (where $\overset{+}{\mathrm{Y}} = \overset{+}{\mathrm{N}}, \overset{+}{\mathrm{P}}$, or $\overset{+}{\mathrm{S}}$), the inductive effect dominates; that when it is of the type $\mathrm{HC_\beta{\cdot}C_\alpha{\cdot}Y}$ (where Y = Cl, Br, I, or OAc), the electromeric effect takes charge; and that when, in the unimolecular mechanism (*E*1), it is $\mathrm{HC_\beta{\cdot}\overset{+}{C}_\alpha}$(sextet), once more the electromeric effect is in control. We know also from the quantitative results that the predominance of the electromeric effect is greater in this last case : we find larger effects on reaction rate, and more extreme orientation of the Saytzeff type, in unimolecular elimination with either 'onium salts or halides, than in bimolecular elimination with halides. Empirically then, the electromeric effect increases in relative importance as the influenced system takes the successive forms

(i) $\mathrm{HC_\beta{\cdot}C_\alpha{\cdot}\overset{+}{Y}}$, (ii) $\mathrm{HC_\beta{\cdot}C_\alpha{\cdot}Y}$, (iii) $\mathrm{HC_\beta{\cdot}\overset{+}{C}_\alpha}$ (sextet);

and there is a large, qualitatively important, difference of behaviour between systems (i) and (ii), and a relatively much smaller, but quantitatively appreciable, difference between systems (ii) and (iii).

From a theoretical point of view, one may say that the differences must arise from different states of balance between the magnitude of the positive charge induced on C_β (which controls the intensity of the inductive effect of attached alkyl substitutents, Alk → C_β), and the degree of unsaturation developed in the transition state (which governs the strength of the electromeric effect due to hyperconjugation, *e.g.*, $\mathrm{H}\overset{\curvearrowright}{—}\mathrm{C}—\mathrm{C}_\beta\overset{\curvearrowright}{\overset{---}{—}}\mathrm{C}_\alpha$). We can immediately see that the inductive effect will be greater in system (i) than in system (ii), because of the stronger electrostatic effect of a positive pole than of any electrically uncharged atom. Further, we may expect the electromeric effect to be greater in system (ii) than in system (i), because solvation assists the heterolysis of the C—Y bond, but not of the $\mathrm{C—\overset{+}{Y}}$ bond; wherefore the transition state of system (ii) tends to involve a relatively large electron-transfer (and hence a large development of unsaturation) in order to form the charges needed to produce the solvation energy. As to system (iii), it is clear that the electromeric effect will be much greater in this than in either of systems (i) or (ii), because of the intense unsaturation created by the pre-formed sextet; however, it is also clear that the inductive effect will be much greater in system (iii) than in the other systems, because of the proximity of the carbonium ionic centre to C_β. Collecting these points together, we see that theory can unequivocally account for the large difference of behaviour, to which co-operating factors contribute, between the systems (i) and (ii), but is ambiguous, because of the co-existence of counteracting factors, with respect to the much smaller difference between systems (ii) and (iii).

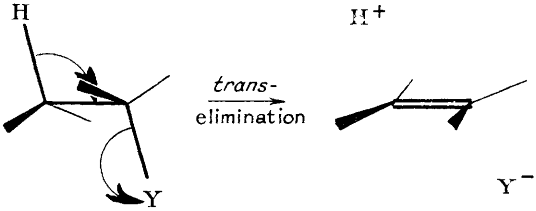
Sectional Summary.—In this Section we define the limits of structure and mechanism within which different kinds of constitutional factors exert a governing influence on the elimination reactions of alkyl compounds. Over the range cases studied, control by the inductive effect, leading to orientation according to Hofmann's rule and its generalisations, arises in bimolecular eliminations when the electron-attracting group carries a positive charge; and control by the electromeric effect, leading to orientation as given by Saytzeff's rule and its generalisations, occurs in bimolecular eliminations when the electron-attracting group is uncharged, and in all unimolecular eliminations. We have illustrated the effects on rate and orientation of crossing the boundary between these separate domains of control; and we have shown that some less fully investigated eliminations can be fitted into the general scheme.

By extending our survey beyond the range of alkyl compounds, we perceive that a substituent of sufficient polarity will exert a dominating inductive effect on an elimination in any system; and that a sufficiently unsaturated substituent will exert a dominating electromeric effect in any system. Only when both the intrinsic polarity, and the intrinsic unsaturation, of the substituent are small, as with alkyl substituents, will the system itself play a controlling role. And this it will do by calling out the latent polarity or unsaturation in the substituent by means of its own polarity or unsaturation, either as these characters exist permanently, or as they are developed in the transition state of reaction. The inductive effect, which arises from the electrostatic polarity of substituents, is exerted from the commencement of reaction. The electromeric effect, which derives from a quantal resonance of electrons having properties of unsaturation, is developed only during reaction, and thus becomes of main importance in the transition state. On these lines we can form a consistent picture of general constitutional influences on eliminations, and of the special complications that apply to alkyl compounds.

(3.5) *Stereochemical Factors in Elimination.*—As Hückel, Tappe, and Legutke have already appreciated (Ref. 35, Section 1.1), the rules which govern the stereochemical course of substitution at an aliphatic carbon atom (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, **1937**, 1252) are likely to have a close parallel in relation to elimination. In collaboration with Dr. R. Pasternak and Dr. Dorothy Usher, the task of establishing this by kinetic methods has recently been undertaken; and, though the work is not yet complete enough for report, we shall here anticipate its record for the purpose of discussing the stereochemical aspects of the orientation of elimination. For many of the statements which we have made above concerning the orientation of elimination apply only to systems which either are already in, or are easily capable of assuming, appropriate configurations; and these statements, therefore, require some qualification, especially in their application to certain olefinic and cyclic compounds, which it is necessary now to define.

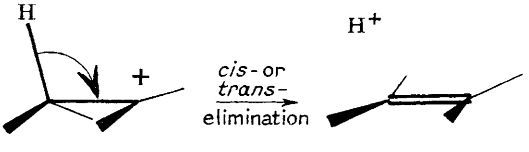
The principal stereochemical restriction is that, in bimolecular eliminations (*E*2) of the system $\overset{\curvearrowright}{\mathrm{H{-}C}_\beta}\mathrm{{-}}\overset{\curvearrowright}{\mathrm{C}_\alpha\mathrm{{-}Y}}$, where Y may be either neutral or charged, the β-CH electrons must if possible enter the octet of C_α on the side remote from Y; for this is the way in which the exchange integrals of electrons of different pairs, and therefore the total energy, of the transition state can be kept as small as is possible (cf. Cowdrey, Hughes, Ingold, Masterman, and Scott, *loc. cit.*): the result is exclusive *trans*-elimination (VII). Cristol has recently shown (*J. Amer. Chem. Soc.*, **1947**, **69**, 338) that, whilst *trans*-elimination from hexachloro*cyclo*hexanes, where permitted by the structure, takes place with ease in bimolecular reactions with alkali, *cis*-elimination can scarcely be realised under the same conditions when *trans*-elimination is excluded by the structure. In unimolecular elimination (*E*1), on the other hand, the C_β-carbonium ion tends to the same planar form, from whichever side of the plane the electron-attracting group Y has separated. Therefore, both *cis*- and *trans*-elimination are normally possible (VIII) by the unimolecular mechanism, though if the carbonium ion is very short-lived, *trans*-elimination may be favoured, and in the presence of special substituents *cis*-elimination may predominate (cf. Cowdrey *et al.*, *loc. cit.*).

(VII.)



(*E*2)

(VIII.)

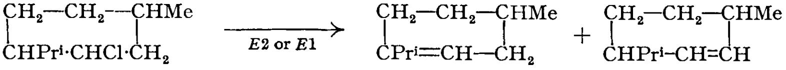


(*E*1)

Another steric effect, which would likewise apply to bimolecular eliminations only, might arise from screening of the β-hydrogen atoms from attack by the nucleophilic reagent. This ordinary sort of steric hindrance seems to be definitely less important for eliminations than for bimolecular substitutions, probably because of the relatively more exposed situation of the hydrogen atoms than of the carbon atoms in all the simpler alkyl groups. This effect, moreover, though it is appreciable in special structures, is considerably less important than that of the stereochemical course of elimination, and therefore we shall not attempt to isolate the former in the approximation to which, at present, we are discussing steric effects.

Even when the system $>CH·CRY·CH_2—$ forms part of a ring, an elimination of HY towards the methylene group is always stereochemically possible, because one or other of the methylene hydrogen atoms either is in, or can be brought into, an appropriate configuration, when the mechanism makes this necessary. But, in rings of seven atoms or less, an elimination towards the methine group may be precluded, however much polar factors might favour such a process; and it will be so precluded if the mechanism is bimolecular (*E*2), and if, in addition, the methine hydrogen atom is firmly oriented in a *cis*-position with respect to the electron-attracting group Y. (We restrict this statement to rings of seven atoms or less, because, in rings of eight atoms or more, *cis*-related bonds of neighbouring carbon atoms can be brought into an approximately antiparallel orientation by strainless rotations about the ring bonds.)

On account of polar factors, in particular the electromeric effect, alkyl halides, if free from stereochemical restrictions, undergo eliminations oriented according to Saytzeff's rule, both when the mechanism is bimolecular and when it is unimolecular. Thus the unrestricted system $>CH·CRHal·CH_2—$ should eliminate HHal by either mechanism in predominating amount towards the methine group. The inclusion of the system in, say, a six-membered ring should offer no interference to the operation of this rule, unless the mechanism is bimolecular (*E*2), and unless, in addition, the atoms which chiefly should be eliminated according to the rule are in *cis*-relation to each other. But, where both these circumstances arise, the Saytzeff rule will become abrogated, as may be illustrated by the following examples, which are due to Hückel, Tappe, and Legutke (*loc. cit.*) :



$$\begin{array}{l} CH_2—CH_2—CHMe \\ | \qquad\qquad\quad | \\ CHPr^i·CHCl·CH_2 \end{array} \xrightarrow[E2\text{ or }E1]{} \begin{array}{l} CH_2—CH_2—CHMe \\ | \qquad\qquad\quad | \\ CPr^i{=}CH—CH_2 \end{array} + \begin{array}{l} CH_2—CH_2—CHMe \\ | \qquad\qquad\quad | \\ CHPr^i—CH{=}CH \end{array}$$

(+)-*neo*Menthyl chloride + $\bar{O}Et \xrightarrow[E2]{}$ 3-Menthene (~75%) + 2-Menthene (~25%)

(−)-Menthyl chloride + $\bar{O}Et \xrightarrow[E2]{}$,, (0%) + ,, (100%)

(−)-Menthyl chloride (Solvolysis) $\xrightarrow[E1]{}$,, (~70%) + ,, (~30%)

In *neo*menthyl chloride the groups Pr^i and Cl are on the same side of the *cyclo*hexane ring, whereas in menthyl chloride they are on opposite sides. Hence *neo*menthyl chloride is not sterically precluded from undergoing bimolecular elimination in that direction which should predominate according to the Saytzeff rule, and which does, in fact, predominate in this case. But, because of its configuration, menthyl chloride cannot undergo bimolecular elimination in that direction, not even in minor amount. No such restriction applied to unimolecular elimination, and accordingly, menthyl chloride can, and does in fact, undergo this form of elimination to a predominating extent in agreement with Saytzeff's rule.

On account of polar factors, in particular the inductive effect, alkylammonium ions, if free from stereochemical restrictions, undergo eliminations which are oriented according to Hofmann's rule and its generalisations, provided that the mechanism is bimolecular (*E*2). Thus the unrestricted system $>CH·CR(\overset{+}{N}Me_3)·CH_2—$ should undergo bimolecular elimination oriented in predominating amount towards the methylene group. If the system is included in, say, a six-membered ring, one of the two methylene hydrogen atoms will invariably be situated in such a position as to allow elimination in this direction. Even so, one can recognise the modifying effect on orientation of a *cis*-relation between the methine hydrogen atom and the ammonium group; for such a relation converts what would have been merely a predominating orientation into an exclusive one, as may be seen by the following examples (*idem, ibid.*) :

(+)-*neo*Menthyl-$\overset{+}{N}Me_3$ + $\bar{O}H \xrightarrow[E2]{}$ 3-Menthene (~20%) + 2-Menthene (~80%)

(−)-Menthyl-$\overset{+}{N}Me_3$ + $\bar{O}H \xrightarrow[E2]{}$,, (0%) + ,, (100%)

This result shows that *trans*-elimination in the bimolecular reactions of alkyl halides is not due to the direction of an anionic reagent by the electrostatic field of the C–Hal dipole, any more than the Walden inversion in bimolecular substitution is due to this cause. For in the $C-\overset{+}{N}$ link, the dipole and the related electrostatic field are reversed, and yet, in bimolecular reactions with anionic reagents, we still find *trans*-elimination, just as in substitutions we still observe the Walden inversion (cf. Cowdrey, Hughes, Ingold, Masterman, and Scott, *loc. cit.*). The cause in all cases is the same, *viz.*, the need to economise energy in the transition state by the minimisation of bond-overlap : the quantal forces here involved are of much greater importance than dipole forces.

Some of the above points could also have been illustrated by the production of isomeric octalenes from stereoisomeric 1-decalyl compounds (Hückel, Tappe, and Legutke, *loc. cit.*). Certain examples, likewise belonging to the *cyclo*hexane series (but lacking evidence of mechanism), have been recorded, in which polar effects due to phenyl and carbethoxyl substituents on the direction of elimination have become inverted by stereochemical causes (Price and Karabinos, *J. Amer. Chem. Soc.*, 1940, **62**, 1159; Price and Schwarcz, *ibid.*, p. 2891). As an illustration representing the ethylene series, reference may be made to work of Chevanne (*Bull. Soc. chim. Belg.*, 1912, **26**, 287), showing that *cis*-1 : 2-dichloroethylene is converted into chloroacetylene by treatment with ethyl-alcoholic potassium hydroxide (the probable mechanism therefore being *E*2) much more easily than is the *trans*-isomeride.

Sectional Summary.—The previously discussed polar effects on the velocity and orientation of eliminations apply without qualification only to systems which either are already in, or can easily be brought into, an appropriate stereochemical configuration. The chief stereochemical restriction is that the β-CH electrons of $HC_{\beta}\cdot C_{\alpha}\cdot Y$ must if possible enter the octet of C_{α} on the side remote from Y : this applies only to bimolecular elimination; but it then applies no matter whether Y is a formally neutral group, or whether it carries a positive ionic charge. The requirement arises from the need to minimise bond-overlap in the transition state. Examples of cyclic systems are given in which the orientation of elimination is changed by this factor from what it would have been under control by the inductive and electromeric effects only.

In Part V (*J.*, 1940, 899) environmental influences on the bimolecular and unimolecular mechanisms of elimination were considered : certain sections of this subject have been more extensively treated in Parts VII and VIII (this vol., pp. 2043, 2049). These three papers, together with the present paper on constitutional influences, are intended collectively to constitute a balanced statement of the present position of the theory of heterolytic 1 : 2-eliminations. Investigations on other forms of elimination have been instituted, but have not yet reached a condition suitable for report.

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Sir William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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