THE STRUCTURE OF CARBONIUM IONS

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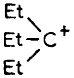
I. Introduction

Definitions, Terminology, and Nomenclature.—The term " carbonium ion " is generally applied to singly charged organic cations which cannot satisfactorily be represented by conventional formulæ in which the quadrivalency of all carbon atoms is preserved. Such species can be considered to be produced by the loss of a negatively charged atom or group (and not of an electron only) from a neutral molecule, as, for instance, the loss of a hydroxide group from an alcohol. Taking a " parent " alcohol $Et_3C{\cdot}OH$, for example, the simplest bond structure (1) of the resultant ion contains one tervalent, positively charged carbon atom. Alternatively the ion could be represented by bond structures such as (2) or (3) which involve either a bivalent hydrogen or a quinquevalent carbon atom and the formation of a ring not present in the alcohol. Formulæ of this kind, and representations involving varying degrees of participation of these extremes, have come to be discussed in recent years (although it should perhaps be pointed out that they are very improbable for the triethylcarbonium ion itself). They are often referred to as " non-classical " or bridged carbonium ions, in contrast to " classical " structures such as (1). The validity of these alternatives is discussed in Section IV. It raises some questions of nomenclature.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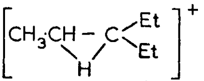
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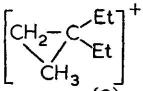
(3)

Systematic naming of structural formulæ such as (2) and (3) has not been attempted. At present the best method of naming a particular ion is by reference to the parent neutral molecule and this may be done by adaptation of the carbinol convention. On the basis of this method the ion (1), (2), or (3) would be termed the triethylcarbonium ion. In some cases it is slightly simpler to name the ion in the same way as the corresponding radical (*e.g.*, phenylcarbonium ion = benzyl cation). Neither kind of name will be used here with structural implications. The name triethylcarbonium ion may relate to (1), (2), or (3) and moreover it does not rule out the physical existence of more than one (isomeric) ionic structure.

The Review will be limited to carbonium ions related to alcohols in the above manner. It excludes acylium ions (RCO^+) which are analogously related to carboxylic acids ($RCO{\cdot}OH$).

Experimental Methods of Investigation.—Some carbonium ions (such as triarylcarbonium ions) are stable species under certain conditions, and the elucidation of their structure presents a typical problem of structural organic chemistry, although the restricted range of conditions in which the ions are stable (frequently in strongly acidic solution) imposes limitations on the methods that can be applied. The majority of carbonium ions that have been discussed in the chemical literature are, however, only transient entities. Their existence has been inferred from the study of the course of organic reactions, and their detailed structure is based on analysis of the finer details of the reaction mechanism.

Stable ions can be studied by the general methods applicable to ionic solutions, such as measurements of electrolytic conductivity and freezing-point depression in appropriate solvents. Absorption spectra of the ions may be obtained and can be applied to the spectrophotometric or colorimetric determination of ionisation constants.

For unstable ions the conclusions about structure are based on more indirect experimental evidence. Such evidence relates either to the energetics of ion formation, derived from studies of mass spectra, or to the velocities and detailed rate laws of reactions in which the carbonium ion is supposed to be an intermediate, and to the structure and composition of the products. The stereochemical relation between reactants and products, which occupies a position of key importance in this field, and rearrangements during a reaction, including their elusive forms, whose occurrence can be demonstrated by the stratagem of isotopic labelling of definite positions, come under this heading. Further, it is sometimes possible to draw inferences concerning the nature of an intermediate carbonium ion from simpler facts of product composition.

Evidence from these various lines of investigation—only in so far as it is relevant to the discussion of the *structure* of carbonium ions—will be considered in the following sections. More general reviews of the chemistry of carbonium ions, including the history of the concept and methods of formation, have already appeared in these Reviews and elsewhere.[1] Special aspects of the subject have recently been surveyed in greater detail.[2]

II. The Charge on the Carbonium Ion

Hybridisation and the Analogy between Boranes and Carbonium Ions.—Compounds of electrically neutral 4-co-ordinated carbon have the tetrahedral arrangement of valencies associated with sp^3-hybridisation of the valency electrons. Carbonium ions can be regarded as compounds of a carbon atom which has given up one of the valency electrons, *i.e.*, which are formed by ionisations of the type :

$$R_3\overset{\alpha}{C}|\text{—}X \longrightarrow R_3C^+ + X^-$$

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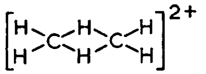
[1] (*a*) Burton and Praill, *Quart. Rev.*, 1952, **6**, 302 ; (*b*) Leffler, " The Reactive Intermediates of Organic Chemistry ", Interscience Publ. Inc., New York, 1956, Chapters V–VII.

[2] (*a*) Winstein, *Experientia*, 1955, *Suppl.* II, p. 137; (*b*) Cram in Newman's " Steric Effects in Organic Chemistry ", John Wiley and Sons, New York, 1956, Chapter V ; (*c*) Streitwieser, *Chem. Rev.*, 1956, **56**, 571 ; (*d*) Burr, " Tracer Applications for the Study of Organic Reactions ", Interscience Publ. Inc., New York, 1957, Chapter 7.

If a classical formula, such as (1), is adequate for the cation produced, the valency electrons would then be hybrids of the *sp*^{2}-type, an arrangement which is expected to lead to a planar trigonal disposition of the bonds attached to the α-carbon atom.

The same number of electrons and kind of hybridisation are met in boron and it is therefore to be expected that a carbonium ion Me_3C^+ would possess the same structure as its isoelectronic boron analogue Me_3B. The planar configuration of trimethylboron has been established by electron-diffraction.[3]

The analogy between boranes and carbonium ions cannot be pursued in every detail for various reasons, the most obvious of these being the electric charge which is associated with every carbonium-carbon atom. Thus the dimeric carbonium ion (4), which is the analogue of diborane, is not a known entity, presumably because electrostatic repulsion forces outweigh the stabilisation which might be produced by the hydrogen bridges. By contrast there would appear to be a definite possibility of the existence of entities such as (5), although they do not seem to have received serious attention so far. An ion such as (1) has no exact parallel in boron chemistry because it contains several carbon atoms only *one* of which would be described as isoelectronic with boron in a classical representation, whereas in a polynuclear borane all boron atoms are in the same valency state. On the other hand, the tendency of boranes to form hydrogen bridges seems to be related to the non-classical bonding in carbonium ions [as in formula (2)]. Both classes of molecular species may be described[4] as " electron-deficient ".



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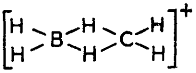

(5)

Delocalisation of the Charge.—The inherent instability of a charged molecule (and hence its tendency to nullify that charge by ionic recombination) is relieved by external and internal dissipation or delocalisation of the charge. External dissipation is achieved by interaction of the ion with the surrounding medium (solvent and oppositely charged counter-ions) (see p. 182). The term " internal dissipation " is intended to cover the various electronic effects which result in delocalisation of the charge over a larger part of the ion than a classical formula such as (1) would indicate.

Internal Charge Dissipation.—The exceedingly unstable carbonium ion CH_3^+ is stabilised if methyl groups replace the hydrogen atoms, to give Me_3C^+. Being electron-repelling substituents, the methyl groups reduce the positive charge on the centre of the ion, and thereby effectively spread that charge (or at least a large part of it) over the periphery of the ion. This stabilisation can be described in terms of an inductive effect and hyperconjugation, and accounts for the well-known sequence of increasing stability of aliphatic carbonium ions, primary < secondary < tertiary. However, it has not so far proved possible to make this theory more quantitative.

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[3] Levy and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 2085.

[4] Longuet-Higgins, *Quart. Rev.*, 1957, **11**, 121.

The occurrence of internal charge dissipation and stabilisation in simple carbonium ions is illustrated by the ionisation potentials of different alkyl radicals (collected by Stevenson and quoted in ref. 2*c*), which are tabulated below. These values relate to separated ions in the gas phase and are therefore not complicated by solvation or other effects of external charge dissipation. They illustrate the increasing charge stabilisation in the sequence Me < Et < Pr^i < Bu^t. Thus even in these simple ions at least a significant portion of the charge must be located on the outside of the ion and not just concentrated on the central carbon atom. In fact, the difference in ionisation potentials of Me· and Me_3C· (*i.e.*, the enthalpy change of the reaction $Me^+ + Me_3C\cdot \longrightarrow Me\cdot + Me_3C^+$) is of just the order to be expected on the naïve electrostatic model of the reaction as the transfer of an electronic charge from a small charged conducting body (of the size of the methyl group) to a larger one (of the size of the *tert.*-butyl group).†

Energetics of ionisation (according to Stevenson [2c])

		Saturated radicals					Conjugated radicals	
	H	Me	Et	Pr^n	Pr^i	Bu^t	$CH_2\cdots CH\cdots CH_2$	$Ph\cdot CH_2$
Ionisation potentials of radicals (kcal.)	312	230	201	183	171	159	188	178
ΔH for gas-phase reaction $RCl \longrightarrow R^+ + Cl^-$ (kcal.) *	328	220	192	177		149	158	
		223			168	150	161	152

* Values in the top row are based on heats of formation of the anion and of the corresponding alkane and the appropriate C–H dissociation energy. Values in the bottom row were obtained from appearance potential of R^+ in the mass spectrum of RCl, and the electron affinity of chlorine.

Stabilisation in Conjugated Ions.—A greater extent of stabilisation of carbonium ions occurs in conjugated systems where it is possible for the π-orbitals of groups attached to the central (or α-)carbon atom to overlap with the vacant *p*-orbital on that atom. Examples of this are, in increasing order of stability, the ions $(CH_2\cdots CH\cdots CH_2)^+$, $Ph\cdot CH_2^+$, Ph_2CH^+, and Ph_3C^+. In fact, the great stability of the triphenylcarbonium ion has long been recognised (see ref. 1). The data in the Table illustrate the qualitative difference between saturated and conjugated carbonium ions. It will be noted that the values of the ionisation potentials of the allyl and *n*-propyl radicals are very close, which is consistent with the similar size of and grouping in the ions formed. Nevertheless, the ionisation of allyl chloride is

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[5] Walsh, *Discuss. Faraday Soc.*, 1947, **2**, 18.

† Since the three carbon valencies are planar both in the radical and in the carbonium ion,[5] the greater difference in stability between Me_3C^+ and $Me_3C\cdot$ than between CH_3^+ and $CH_3\cdot$ cannot be attributed to a release of steric strain.

energetically much more favourable than that of *n*-propyl chloride. The enthalpy change in the ionisation $RCl \rightarrow R^+ + Cl^-$ can be divided into three additive contributions corresponding to the hypothetical steps :

$$RCl \xrightarrow{\Delta H_1} R\cdot + Cl\cdot \xrightarrow{\Delta H_2} R^+ + Cl\cdot + e \xrightarrow{\Delta H_3} R^+ + Cl^-$$

ΔH_3, the electron affinity of the chlorine atom, is obviously independent of the nature of R. ΔH_2 represents the ionisation potential of the radical. The results quoted indicate that the difference in the ΔH values between allyl and propyl chloride, for the overall ionisation, must be attributed to differences in the first step, *i.e.*, to the values of the dissociation energy ΔH_1. Since allyl chloride is in no way abnormally unstable (as a result of steric effects, for example), the lower endothermicity of the dissociation of allyl chloride into radicals must be due to the increased stability of the allyl radical. In other words, the same degree of extra stabilisation is found in both the allyl radical and in the allyl cation—to a rough approximation, at any rate. Examination of the values quoted in the Table for the benzyl group leads to the analogous conclusion, *viz.*, that benzyl radicals and benzyl cations are additionally stabilised to about the same extent. This stabilisation is therefore not a consequence of the presence of an electric charge, but arises from quantum-mechanical delocalisation of electrons in the conjugated nuclear framework formed. The phenomenon may be described as mesomerism between the equivalent structures

$$CH_2{=}CH{-}CH_2\cdot \quad \text{and} \quad \cdot CH_2{-}CH{=}CH_2$$

in the case of the radical, or between the structures

$$CH_2{=}CH{-}CH_2^+ \quad \text{and} \quad {}^+CH_2{-}CH{=}CH_2$$

for the carbonium ion, whereas resonance structures of this type are obviously impossible for the chloride $CH_2{=}CH{-}CH_2Cl$. The same number of equivalent structures can be written for radical and ion, and this simple valency-bond description is therefore consistent with the experimental conclusion that allyl radicals and cations are stabilised by resonance to about the same extent.

Hückel's L.C.A.O. molecular-orbital approximation[6] leads to the same result. The allowed energy levels for the electrons in the allyl framework of carbon atoms are spaced out as shown on the left-hand side of Fig. 1. There are two π-electrons in the allyl cation and three in the radical. The lowest (" bonding ") level is therefore doubly occupied both in the cation and in the radical, and the middle (" non-bonding ") level is singly occupied only in the radical. The highest (" anti-bonding ") level will always be vacant. The total π-electron energy of the system is the sum of the energies of the individual electrons, *e.g.*, in the case of the radical $2(\alpha + \beta\sqrt{2}) + \alpha = 3\alpha + 2\beta\sqrt{2}$. The right-hand side of the Figure shows the spacing of the energy levels in a hypothetical allyl radical in which the double bond occupies a fixed position, as in the chloride. The difference in total energy

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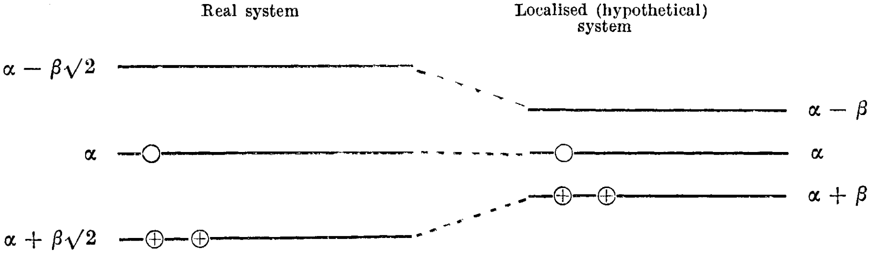
[6] Hückel, *Z. Physik*, 1931, **70**, 204.

FIG. 1

Energy levels in allyl radical and cation.



○ Electron occupying level in radical. α = Coulomb integral.
⊕ Electron occupying level in cation. β = Resonance integral.

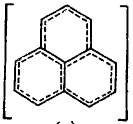
between the real and the hypothetical system is called the resonance energy. It will be seen, by comparison of the two halves of the Figure, that this resonance energy will be the same irrespective of the occupation of the middle level, *i.e.*, it will be the same in radical and cation. This treatment can be extended to all conjugated radicals and cations not possessing odd-membered rings. In every case the highest, singly occupied level in the radical is non-bonding and corresponds to the energy α, and the resonance energies of radical and cation are identical.

From the point of view of structure it is important that the theory allows the average location of the odd electron or positive charge in radical and cation to be calculated. In the valency-bond formulæ given above, the charge could be placed on either of the terminal carbon atoms, but never on the central one. It will therefore be equally divided between the two end carbon atoms. In larger conjugated cations (not possessing odd-membered rings) the charge will always be distributed between the " odd " carbon atoms, *i.e.*, carbon atoms 1, 3, 5, 7, etc., if we start numbering at a terminal carbon. Hückel's method also leads to definite values of charge densities for all odd-numbered carbon atoms, and the values are not the same at non-equivalent positions. (However, induction may relay some of the charge also to the " even " positions.)

Although this theory gives a remarkably good account of many features of conjugated carbonium ions, it is not altogether satisfactory in every detail. Thus it predicts the same value (α) for the ionisation potentials of all conjugated radicals. The Table on p. 176 shows this to be an incorrect conclusion. The basic reason for the discrepancy seems to lie in the neglect of electrostatic repulsion, which tends to drive an electric charge to the periphery of the ion but has no corresponding effect on the distribution of the odd-electron spin in the free radical. This charge repulsion can again be relieved more effectively in a larger ion than in a smaller one and, accordingly, the ionisation potentials of conjugated radicals are expected to decrease as the size of the radical (and ion) goes up. This is borne out by the last two ionisation potentials in the Table. The trend is correctly reproduced in a modified molecular-orbital theory in which this electrostatic interaction is explicitly taken into account.[7]

More extensive information about stable conjugated ions is available from studies of ionisation equilibria in solution, especially of alcohols in acidic media [8] and of chlorides.[9] These investigations have confirmed the order of stability for arylcarbonium ions (primary $<$ secondary $<$ tertiary), in semi-quantitative agreement with Hückel's molecular-orbital theory,[10] and have shown that the stability of the ions is enhanced by electron-repelling substituents in the aromatic nuclei.

Perhaps the most spectacular example of the effect of charge delocalisation is the stability of the recently discovered *cyclo*heptatrienyl (tropylium) cation [11] which was predicted [6] by Hückel in 1931. Tropylium bromide has the properties of an ionic compound. The ions are so stable that the compound can be recrystallised from ethanol, a solvent with which most carbonium ions react almost instantaneously. The resonance stabilisation of the tropylium ion is comparable with that in benzene. Another interesting case is the ion (6), the high stability of which was also deduced from molecular-orbital theory [12] before its observation.[13]



(6)

The Extent of Planarity of Conjugated Carbonium Ions.—The mesomeric stabilisation of a conjugated system is most effective when all π-bonds lie in the same plane. The interaction energy between different parts of a conjugated system which are not coplanar is expected to diminish as the first or second power of the cosine of the angle of twisting.[14]

The problem arises in connection with the structure of di- and triarylcarbonium ions. Calculations based on known bond-lengths and van der Waals radii indicate that in the planar configuration of the triphenylcarbonium ion steric interference would occur between the *ortho*-hydrogen atoms on adjacent rings. Lewis, Magel, and Lipkin [15] therefore proposed a structure in which each of the benzene rings in the ion is twisted out of the plane which contains the three bonds to the central atom. One estimate [16] puts the angle of twist required by this model as high as about 50°, with a consequent reduction of the resonance energy. Two isomeric forms of this structure should exist, in one of which all rings are twisted in the same sense, as in a propeller, whereas in the other (" distorted helical ") structure one

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[7] Hush and Pople, *Trans. Faraday Soc.*, 1955, **51,** 600.

[8] Williams and Bevan, *Chem. and Ind.*, 1955, 171 ; Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77,** 3044 ; Deno and Evans, *ibid.*, 1957, **79,** 5804.

[9] Lichtin and Bartlett, *ibid.*, 1951, **73,** 5530 ; Lichtin and Glazer, *ibid.*, p. 5537 ; Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50,** 568 ; 1955, **51,** 481.

[10] (*a*) Streitwieser, *J. Amer. Chem. Soc.*, 1952, **74,** 5288 ; (*b*) Gold, *J.*, 1956, 3944 ; (*c*) cf. Mason, *J.*, 1958, 808.

[11] Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76,** 3203.

[12] Gold and Tye, *J.*, 1952, 2184.

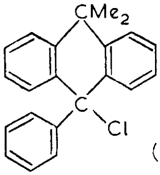
[13] Pettit, *Chem. and Ind.*, 1956, 1306.

[14] Pauling and Corey, *Proc. Nat. Acad. Sci.*, 1951, **37,** 251 ; Dewar, *J. Amer. Chem. Soc.*, 1952, **74,** 3345 ; cf. Guy, *J. Chim. phys.*, 1949, **46,** 469.

[15] G. N. Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64,** 1774.

[16] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19,** 155.

ring is twisted in the opposite sense to the other two. It has been possible to interpret the spectrum of the crystal-violet ion in terms of these two forms.[15] Simple molecular-orbital calculations of the π-electron energies of mono-, di-, and tri-arylcarbonium ions have been interpreted [10b] as implying that resonance does indeed involve all rings and that the twisting does not overwhelmingly reduce the resonance energy. This conclusion is also consistent with measurements of the ionisation of compounds such as (7), in which two of the benzene rings are constrained to approximate coplanarity.[17a] Recent studies of the infrared spectra of crystalline complex halides of the triphenylcarbonium ion have provided strong support for the propeller structure.[17b]



(7)

An alternative structure for di- and tri-arylcarbonium ions has been proposed [18, 16] in which (exactly coplanar) resonance interaction is assumed to involve only one or, at most, two of the attached aryl groups. The model was put forward in order to account for the close similarity between the electronic absorption spectra or similarly substituted di- and tri-arylcarbonium ions, and to explain in detail the effect of substituent groups on the basic strengths of the parent alcohols.[8] At least some of these phenomena may be given an alternative explanation in terms of the propeller model.[10b]

Chemical Consequences of Charge Delocalisation.—Charge stabilisation in a carbonium ion is reflected in the velocity of its formation. The transition state of an S_N1 reaction, such as the solvolysis of an alkyl chloride, requires a partial separation of the charges. The partial positive charge will be distributed over the organic portion of RCl in a similar manner to the distribution of the integral charge in the carbonium ion R^+. In consequence, structural features, such as the presence of electron-repelling substituent groups, which enhance the stability of the ion will also make the transition state more stable relatively to the starting compound and thus increase the velocity of ionisation. Thus the rates of unimolecular solvolyses of alkyl chlorides in formic acid [19] follow the expected sequence $\mathrm{MeCl} < \mathrm{EtCl} < \mathrm{Pr^{i}Cl} < \mathrm{Bu^{t}Cl}$. Of course, experimental data of this kind, determined in the main by Hughes and Ingold and their school,[20] preceded measurements of ionisation potentials of radicals and allowed correct conclusions about the stability of carbonium ions, the electronic effects of substituents, and hence also about the charge distribution to be drawn. However, the need to consider solvation forces and the possible release of steric strain during an ionisation slightly complicates the interpretation of the phenomena and has on occasions given rise to controversy.

The rate for allyl chloride appears to be somewhat anomalous since, in

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[17] (*a*) Bartlett, *Bull. Soc. chim. France*, 1951, **18**, C 100; (*b*) Sharp and Sheppard, *J.*, 1957, 674.

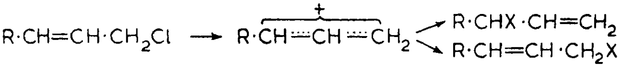
[18] Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644; Branch and Walba, *ibid.*, 1954, **76**, 1564.

[19] Bateman and Hughes, *J.*, 1940, 945.

[20] For a summary, see Ingold "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, London, 1953.

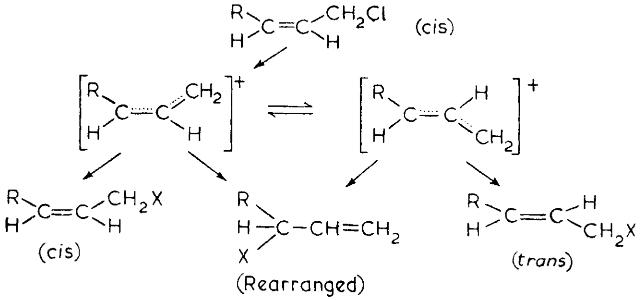
spite of the mesomeric effect, it is only about 25 times greater than that for *n*-propyl chloride.[21]

The charge delocalisation also has some more straightforward chemical consequences. Thus the distribution of the charge between positions 1 and 3 in an allyl cation implies that ionic recombination (or further reaction of the ion with another species) may involve either of these positions and, in a substituted allyl ion, may lead to a product with the original position of the double bond or to the rearranged product,[22] as shown :



$$\mathrm{R\cdot CH{=}CH\cdot CH_2Cl} \longrightarrow \mathrm{R\cdot}\overset{+}{\overbrace{\mathrm{CH{\cdots}CH{\cdots}CH_2}}} \begin{array}{l} \nearrow \mathrm{R\cdot CHX\cdot CH{=}CH_2} \\ \searrow \mathrm{R\cdot CH{=}CH\cdot CH_2X} \end{array}$$

Anionotropic rearrangements analogous to this allylic rearrangement are also possible in larger conjugated systems. It must, however, always be borne in mind that the above unimolecular (S_N1') reaction *via* carbonium ions is not the only mechanism by which rearrangement may take place.[23] It is also expected that the mesomerism in the allyl cation, which lowers the double-bond character of the initial double bond, would make the system less rigid and may permit geometrical isomerisation, *e.g.* :



This problem has not been fully studied, but there is some evidence for easy *cis*–*trans*-interconversion in conjugated carbonium ions.[24]

It also follows that a carbonium ion which is more effectively stabilised by charge delocalisation will be less reactive towards a nucleophilic entity. This phenomenon is exemplified by the inertness of the tropylium ion, mentioned above, and in the relative reactivities of different diarylcarbonium ions as alkylating agents towards anisole : the more stable diphenylcarbonium ion is less reactive than the 4 : 4′-dichlorodiphenylcarbonium ion.[25] Further, stable ions appear to be more " discriminating " : their

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[21] Vernon, *J.*, 1954, 423.

[22] *E.g.*, Catchpole and Hughes, *J.*, 1948, 4 ; for an extensive review, see DeWolfe and Young, *Chem. Rev.*, 1956, **56**, 753.

[23] de la Mare, England, Fowden, Hughes, and Ingold, *J. Chim. phys.*, 1948, **45**, 236.

[24] Oroshnik, Karmas, and Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 3807 ; Bell, E. R. H. Jones, and Whiting, *J.*, 1957, 2597.

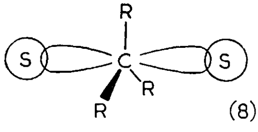
[25] Bethell and Gold, *J.*, 1958, 1905.

relative rates of reaction with a series of reagents of varying nucleophilic reactivity span a wider range than the corresponding relative rates for less stable (and more reactive) carbonium ions.[26]

Solvation.—Ions—or, more generally, electric charges—in solution are stabilised by virtue of their interaction with solvent molecules. The phenomenon is perfectly general [27] and its detailed consideration here would be out of place. The existence of solvation implies that many solvent molecules are concerned in every ionisation and, for this reason, some workers prefer to regard S_N1 reactions as multimolecular rather than as unimolecular. It is relevant to our discussion but rather a vexed problem—to which a definite answer is not available at the present time—whether some of the solvating molecules are attached in a more intimate fashion than others and whether the forces of attraction involved have directional properties. The indications are that for simple inorganic ions (like Na^+ or Br^-) solvation forces have no covalent component, *i.e.*, the attraction is purely electrostatic and therefore non-directional.* This does not, of course, imply that solvation need be equally intense around the periphery of every ion, as the nature of the charge distribution or the shape of the ion may cause the ion–solvent interaction to be stronger in some directions than in others.

Solvation numbers derived from various experimental observations are statistical averages (the method of averaging being that appropriate to the phenomenon studied) and are now generally thought not to indicate a permanent association of the ion with a particular number of solvent molecules, except in " aquated " ions such as $Cr(H_2O)_6{}^{3+}$.

One might expect these general principles to apply to carbonium ions, and hence that solvation has no *structural* significance in the usual meaning of that word. However, the opposite view has recently been taken by Doering and Zeiss [28] who consider that there is a partly or wholly covalent attachment of two solvent molecules to a carbonium ion so that the carbonium carbon atom is " pentacovalent ". This involves overlap of both lobes of the vacant *p*-orbital of the carbonium ion with orbitals of solvent molecules (S), resulting in two C–S bonds which are weaker than the other bonds of the ion (8). Grunwald, Heller, and Klein [29] have made the less specific suggestion that the molecules of the solvation sheath can be thought to occupy a definite number of sites around the ion. Both these proposals were put forward to account for the preponderance of inversion accompanying S_N1 reactions and will be further discussed in that context. The oriented interaction between ions and polar molecules which has



(8)

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[26] C. G. Swain, Scott, and Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136.
[27] Gurney, " Ionic Processes in Solution ", McGraw-Hill, New York, 1953.
[28] Doering and Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 4733.
[29] Grunwald, Heller, and Klein, *J.*, 1957, 2604.
* Some writers (cf. ref. 1*b*) use the term " solvation " to include ordinary covalent bonding between an ion and the solvent, but this is not general practice.

been postulated to exist in benzene solution[30] will be considered in connection with interionic forces in that solvent (p. 185).

A review of methods of estimating the variation of solvation energy with the structure of the carbonium ion and with the nature and properties of the solvent lies outside the scope of this article (cf. ref. 2*c*). Generally speaking, the relatively large size of most carbonium ions will cause their solvation energies to be much smaller than those of metal cations.

Interionic Forces.—Closely related to stabilisation by solvation is the external charge dissipation and stabilisation of ions by interionic attraction. In every ionic solution some stabilisation results from the ordering which is a consequence of electrostatic interaction of opposite and like charges. For dilute solutions of large ions in solvents of high dielectric constant (such as water or sulphuric acid) this phenomenon is adequately described in terms of the Debye–Hückel theory as formation of " ionic atmospheres ". At higher concentrations or, what is more relevant to the present discussion, in solvents of low dielectric constant the situation is less well understood. Electrostatic attraction or repulsion varies inversely with the dielectric constant (D) and in a solvent of lower dielectric constant the ordering effect of electrostatic forces gains in importance relatively to the disordering effect of thermal agitation. The model which can generally be invoked to give a reasonably satisfactory description of the physical behaviour (conductivities, indicator ionisation, etc.) in such systems is that of aggregation of ions into pairs, triple ions, and higher clusters.[31]

No structural significance has ever been attached to the formation of ionic atmospheres, *i.e.*, to the consequences of interionic attraction in the range of validity of the Debye–Hückel theory. On the other hand, the kinetic and stereochemical characteristics of reactions involving carbonium ions, especially in media of low dielectric constant, have been held to require that the phenomena of ion-pair and cluster formation have spatial properties, in the sense that the anion and the cation formed by ionisation of an organic compound tend to retain their relative orientations. This implies, for example, that the leaving anion tends to " shield " the carbonium ion from attack by another reagent from the same direction. We shall return to the stereochemical aspects on p. 186.

S_N1 reactions in acetic acid ($D = 6{\cdot}2$) and benzene ($D = 2{\cdot}25$) show great sensitivity to added electrolyte or polar molecules, and the phenomena observed have given rise to two further specific proposals about ion association. Winstein and his collaborators made an extensive study[32] of S_N1 acetolysis and observed, for example, that the effect of added lithium perchlorate on the reaction velocity was linear over the approximate concentration range 0·03—0·1M (called by the authors the " normal " salt

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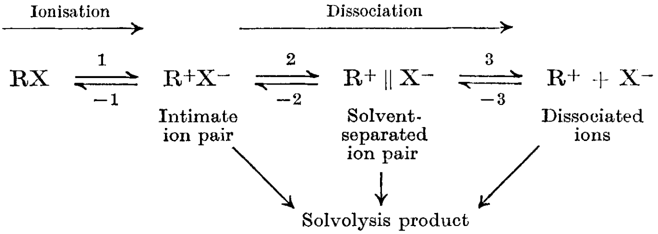
[30] (*a*) Ingold, *Proc. Chem. Soc.*, 1957, 279 ; (*b*) Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1265.

[31] Robinson and Stokes, " Electrolyte Solutions ", Butterworths, London, 1955, Chapter 14.

[32] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763, 2767, 2780 ; Fainberg, Robinson, and Winstein, *ibid.*, p. 2777 ; Winstein and Clippinger, *ibid.*, p. 2784 ; see also ref. 2*a*.

effect), but that a stronger accelerating effect (or " special " salt effect), obeying a different dependence on salt concentration, was operative below this range. These observations were interpreted in terms of the postulated existence of two distinguishable and structurally different types of ion pair. The initially formed " intimate " (or " internal ") ion pairs are thought to differ from the secondary " loose " (or " external ") ion pairs in that no solvent molecules separate the ions of the pair in the former case whereas they do so in the latter. Ionisation, dissociation, and solvolysis may thus involve the following steps :



The last form, *i.e.*, free ions, is the only one which is sensitive to a common-ion effect, and may be of negligible importance in the solvent considered. Regeneration of RX from an ion pair is not aided by the addition of the common ion X^- and has been called " internal return ". On this model, the " special " accelerating salt effect is attributed to a " scavenging " reaction between the added salt and the solvent-separated ion pair. This reaction competes effectively with the " ion-pair return " reaction (—2) and leads to a rapidly solvolysed ion pair. In their series of papers [32] Winstein *et al.* elaborate this interpretation, in particular by considering how the stability of the carbonium ion governs the nature of the salt effect. Thus " special " salt effects are considered to be absent if the reactivity of the ion is so high that it is completely destroyed by solvent attack on the " intimate " ion pair. The " normal " salt effect is considered to influence the ionisation rate (1).

As an alternative and much simpler explanation it has been suggested [33] that the " normal " and the " special " salt effect may be caused by ion pairs and free ions of the added salt, respectively, and, by implication, that the assumption of two types of ion pair is unnecessary. In order to assess the adequacy of the simpler model, a detailed consideration of Winstein's results from this point of view would be welcome.

Studies of a rearrangement reaction in which a toluene-*p*-sulphonate group, labelled with ^{18}O in the alcohol-oxygen, migrates from one point of attachment in a molecule to another show incomplete equilibration of ^{18}O among the three oxygen atoms of the sulphonate group. This result has been interpreted as indicating definite structural attachment of the two halves of an ion pair,[34] but it might also arise from the existence of non-ionic intramolecular paths for the rearrangement.

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[33] Ref. 30*b*, footnote on p. 1278.

[34] Denney and Goldstein *J. Amer. Chem. Soc.*, 1957, **79**, 4948.

The importance of the state of ionic aggregation of added salts (reagent or otherwise) has been clearly pointed out in connection with a study of S_N1 reactions in benzene.[30] Here, too, electrostatic catalysis by ion pairs was observed, but the outstanding feature of the experiments was the discovery of unimolecular chloride exchange, azide replacement, and methanolysis of triphenylmethyl chloride, the velocity of the reactions being independent of the concentration, but *not* of the nature, of the substituting reagent. The interpretation of this result is based on the hypothesis that the unimolecular generation of carbonium ions is followed by an instantaneous association of the ion pair formed with an ion pair (or molecule, in the case of a non-electrolyte) of the reagent. This step is, in turn, followed by a rearrangement of the cluster to a configuration favourable to reaction, *e.g.* :

$$\mathrm{TCl} \underset{\text{Rapid}}{\overset{\text{Slow}}{\rightleftharpoons}} \underset{\substack{\text{Ion}\\\text{pair}}}{\mathrm{T^+Cl^-}} \underset{\text{Rapid}}{\overset{\substack{+\mathrm{M^+X^-}\\\text{Rapid}}}{\rightleftharpoons}} \underset{\substack{\text{Non-reacting}\\\text{cluster}}}{\mathrm{T^+Cl^-M^+X^-}} \underset{\text{Slow}}{\overset{\text{Slow}}{\rightleftharpoons}} \underset{\substack{\text{Reacting}\\\text{cluster}}}{\mathrm{T^+X^-M^+Cl^-}} \xrightarrow{\text{Rapid}} \mathrm{TX} + \mathrm{M^+Cl^-}$$

The postulated rapidity of the second step is made plausible by the magnitude of electrostatic forces in benzene. As Ingold points out,[30] two univalent counter-ions attract each other in benzene with an energy equal to the mean kinetic energy along a line, at a separation of 500 Å. The mean separation of solute neighbours in these solutions was about 50 Å and is quite likely to correspond to a distance at which electrostatic attraction between two ion pairs exceeds their kinetic energy of translation. The application of this model to unimolecular eliminations in the gas phase has also been proposed.

The structural concept introduced in this theory is the notion of what might be called " cluster isomerism ", *i.e.*, different arrangements of four ions in a quadrupole cluster can be distinguished. We are not here concerned with other kinetic repercussions of Winstein's or Ingold's proposals. If the structural ideas in either scheme have physical reality it should be possible to find support for them outside the immediate phenomena which caused their postulation. From this point of view Ingold's model appears to be more interesting. The discovery of such confirmatory evidence might open a new vista in structural chemistry.

III. The Geometry of Carbonium Ions

The Steric Course of S_N1 Reactions.—On a simple view the change in the hybridisation state of the central carbon atom from sp^3 to sp^2 during the formation of a carbonium ion involves the replacement of the tetrahedral arrangement of bonds in the original molecule by a planar configuration in the ion, and hence loss of optical activity if the central atom was the only asymmetric one in the molecule. Recent experiments have shown the need to modify this straightforward statement. Evidence which indicated carbonium-ion formation has sometimes been accompanied by other observations apparently inconsistent with a planar configuration for the ion.

The relation between reaction mechanism and the steric course of replacement reactions was pointed out in the 1930's by Hughes, Ingold, and their co-workers.[20] Briefly, their views were as follows. The unimolecular mechanism (S_N1) of reaction involves intermediate formation of a carbonium ion. If the asymmetric carbon atom in an originally optically active compound is the seat of reaction, the ionisation will yield an ion which, by virtue of its planarity, will react to give racemic products. Such behaviour has, for example, been observed in the reactions of certain diarylmethyl compounds.[35] In the single-step (bimolecular, S_N2) replacement the geometry of the transition state is such that each molecular act of substitution inverts the configuration of groups about the central (asymmetric) carbon atom.

However, in many cases of reactions known to proceed by the unimolecular mechanism, the product has been found to be optically active, indicating that some inversion of configuration had accompanied a predominant racemisation. For example, acetolysis of optically active 1-phenylethyl chloride gave a product 15% inverted and 85% racemised.[36] Degrees of inversion up to 54% have been observed [28] in methanolysis. An interesting case is the oxygen-isotope exchange of alcohols in aqueous acid: this is thought to involve carbonium ions, generated by loss of water from the protonated alcohol, but is accompanied by complete inversion.[37]

The observations can be reasonably explained in terms of the concepts of shielding and lifetime of the carbonium ion. An inherently stable ion will have a comparatively long life, surviving a number of collisions before finally reacting with a nucleophilic reagent to yield the product. During this life it will be able to free itself completely from the anion (the leaving group), and hence the " front " and the " back " of the ion will become equivalent. The reaction product will then of necessity be racemic. An inherently less stable carbonium ion, on the other hand, will tend to react very soon after its formation and may do so before it has completely freed itself from the leaving group, *e.g.*, while it is still associated with its original ionic partner in an ion pair. The leaving group will thus tend to shield one side of the carbonium ion, favouring reaction at the opposite side, with consequent partial inversion. This theory implies definite spatial orientation of the ions in a freshly formed ion pair which—in Winstein's terminology—would probably have to be described as an " intimate " ion pair.

A more quantitative elaboration of the theory has been put forward by Grunwald, Heller, and Klein.[29] They consider that in a reaction with solvent molecules (which fill the dual rôle of first solvating and then destroying the cation) the departing group will occupy the site of one of the solvating molecules, and thereby reduce in an asymmetric manner the number of sites from which attack on the cation can take place. The experimentally determined excess of inversion can then be used to calculate the number of solvation sites. Small and reasonable values are obtained.

[35] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.
[36] Steigman and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2536.
[37] Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, 604.

Doering and Zeiss's model [28, 2c] has been expressed in a different terminology. It is effectively based on the same picture, in that the leaving group is supposed to occupy a solvation site on one side of the plane of the carbonium ion. With a stable carbonium ion, the anion is replaced by a solvent molecule during the life of the ion, producing a symmetrical carbonium ion (and racemisation) ; an unstable carbonium ion is attacked by solvent before the anion has separated. The distinctive feature of the scheme is the hypothesis that only two sites (one on each side of the plane containing the carbonium valencies) are considered to be involved in the solvation of the carbonium ion. Furthermore, it is speculated that the two solvent molecules (or one solvent molecule and one leaving group) are held covalently (see formula 8). In all discussions of these phenomena it is possible to replace the concept of " life-time " of the carbonium ion by the equivalent one of rate constants for the replacement of the shielding ion by a solvent molecule and for the attack of solvent on the carbonium ion, as is done by Doering and Zeiss.

Steric Acceleration.—The formation of a planar carbonium ion from a molecule of tetrahedral configuration implies an opening-out of the remaining bonds from an initial (tetrahedral) angle of around 109° to one of 120°. Thus, any congestion existing between the groups attached to the central atom will be alleviated during ionisation. An effect of this kind is likely to be observed in the values of the equilibrium constants for the formation of triarylcarbonium ions with bulky *ortho*-substituents.[16, 18]

It is also to be expected that the solvolysis of organic halides having a congested structure would be faster than that of similarly constituted but non-congested structures, since, at the transition state of ionisation, the bonds will have opened out to somewhere between 109° and 120°. Such behaviour has been reported in solvolyses of a number of bulky tertiary alkyl compounds, *e.g.*, tri-*tert.*-butyl halides,[38] but it must be borne in mind that alternative explanations of this steric acceleration are sometimes possible, *e.g.*, hyperconjugation [39] or the formation of bridged carbonium ions.[40, 17]

Bridgehead Carbonium Ions.—Just as the steric compressions between groups attached to the central carbon atom in certain tertiary halides can be relieved during ionisation and lead to faster solvolysis, so structures which prevent the increase in bond angles which is the concomitant of ionisation should show diminished reactivity in unimolecular reactions. Such behaviour has been observed in bicyclic halides in which the halogen is attached to a bridgehead carbon atom. Thus, refluxing 1-*apo*camphanyl chloride (9) with aqueous-ethanolic potassium hydroxide or silver nitrate failed to remove the halogen.[41] The bromotriptycene (10) showed a similar lack of reactivity, despite the presence of three phenyl groups. In a favourable

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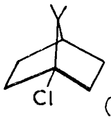
[38] *E.g.*, Bartlett and M. S. Swain, *J. Amer. Chem. Soc.*, 1955, **77**, 2801 ; H. C. Brown, *J.*, 1956, 1248.

[39] Hughes, Ingold, and Shiner, *J.*, 1953, 3827.

[40] Ingold, ref. 20, p. 417 ; cf. H. C. Brown and Kornblum, *J. Amer. Chem. Soc.*, 1954, **76**, 4510.

[41] Bartlett and Knox, *ibid.*, 1939, **61**, 3184.

orientation (but not in the forced arrangement of formula 10) the phenyl groups would stabilise the corresponding carbonium ion (cf. the triphenylcarbonium ion). Unlike the triphenylmethyl halides, this bromotriptycene dissolves in liquid sulphur dioxide to yield a colourless, non-conducting solution.[42]



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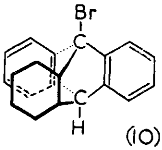


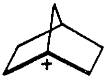
(10)

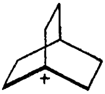
The three *o*-phenylene rings in bromotriptycene (10) are disposed symmetrically about the Br–C–C–H axis. Kekulé bonds have been omitted from the forward-protruding ring for clarity.

In both cases the rigid cyclic structure will not admit coplanarity of the bonds to the bridgehead carbon atom, thereby preventing ionisation. It has been pointed out [17] that the cyclic structure, by hindering the rearward approach of nucleophilic reagents, also prevents reaction by the S_N2 mechanism.

Direct evidence of the difficulty of forming bridgehead carbonium ions has been provided by electron-impact studies.[43] The appearance potentials of the ions (11) and (12) were found to be appreciably greater than that of an analogous planar ion, the trimethylcarbonium ion. Significantly, the ion (12) has a lower appearance potential than its analogue (11), in keeping with its more flexible structure which will permit a closer approach to coplanarity of the three bonds to the carbonium-carbon atom. Further, a qualitative parallelism exists between the appearance potentials of the ions and the reactivities of the corresponding bromides in unimolecular solvolyses.[44]

(11)





(12)

IV. Bridged Carbonium Ions

Origin of the Concept.—In recent years evidence has accumulated that the structures of certain carbonium ions cannot adequately be represented by the normal (or " classical ") valency formulæ considered in Sections II and III. Ions which have to be described in terms of the more recent and unconventional formulæ have come to be known as " non-classical " ions. Some of the structural notions have been outlined in the Introduction.

The idea of bridged non-classical ions arises from an explanation offered by I. Roberts and Kimball twenty years ago [45] to account for the observation that polar addition of bromine to a double bond gives exclusively the " *trans* "-product. They suggested that the ion (13) is an intermediate in

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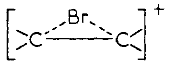
[42] Bartlett and E. S. Lewis, *J. Amer. Chem. Soc.*, 1950, **72**, 1005.

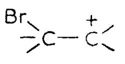
[43] Franklin and Field, *J. Chem. Phys.*, 1953, **21**, 550.

[44] Doering, Levitz, Sayigh, Sprecher, and Whelan, *J. Amer. Chem. Soc.*, 1953, **75**, 1008.

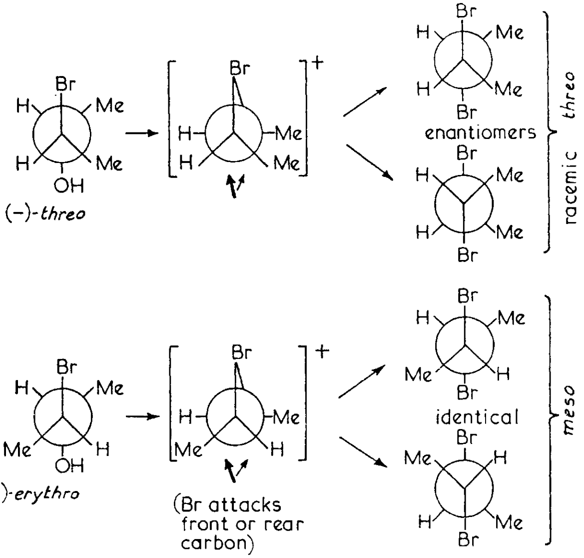
[45] I. Roberts and Kimball, *ibid.*, 1937, **59**, 947.

the reaction, the vacant p-orbital of the carbonium-carbon atom (in the classical ion) overlapping with a lone pair orbital of the bromine, thus

(13) 

 (14)

creating a bridged structure. Rotation about the carbon–carbon bond (which could occur in the classical ion 14) would thereby be prevented, and subsequent attack by bromide ion would be from the direction opposite to the bromine bridge. Evidence for similar bridged " bromonium " ions has also come from studies of substitution.[46] The configuration of the dibromides formed by reaction of hydrogen bromide with *threo*- and *erythro*-bromohydrins is consistent with the hypothesis that the first bromine serves to " hold " the configuration of the central bond in the ionic intermediate. A summary of the substitutions studied is contained in the reaction scheme below in which stereochemical formulæ have been drawn according to Newman's convention.[47] (The molecule is drawn as a substituted ethane, viewed end-on. The bonds in front of the circle represent bonds to groups attached to the ethane-carbon atom nearer the reader, and the bonds emerging from behind the circle are those of the ethane-carbon further away.) The bonding of the first bromine to both carbons in the intermediate ion is essential to the explanation of the products formed. The formation of the three-membered ring in the first step occurs with a Walden inversion at the rear carbon atom (from which OH is lost), and so does the attachment of



(Br attacks front or rear carbon)

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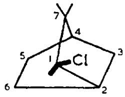
[46] Winstein and Lucas, *J. Amer. Chem. Soc.*, 1939, **61**, 1576, 1581, 2845.
[47] Newman, *J. Chem. Educ.*, 1955, **32**, 344.

bromide and breaking of the ring in the second step. The reactions have been given in detail, since their underlying stereochemical principles also form the basis of Cram's elegant demonstration of bridging by phenyl groups, which will be mentioned below, although the general consideration of organic cations containing elements other than carbon and hydrogen falls outside the scope of this Review.

Nevell, de Salas, and Wilson [48] extended the concept of bridged structures to ions containing only carbon and hydrogen. They suggested that the cationic intermediate in the acid-catalysed rearrangement of camphene hydrochloride (15) to *iso*bornyl chloride (17) had the structure (16). In classical formulæ of this ion, either $C_{(1)}$ or $C_{(2)}$ would be written as tervalent and carrying the positive charge (corresponding respectively to the initial and the final structure in the rearrangement). In the non-classical formula the carbonium character is divided between these carbon atoms, both of which are now joined to $C_{(6)}$, which thus forms a bridge between these atoms.*



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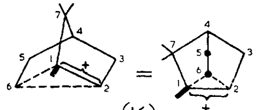

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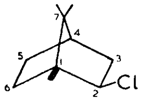


(17)

The last few years have brought to light many instances of chemica behaviour that seems to require this type of structure. The evidence has come in the main from kinetic, stereochemical, and tracer investigations of $S_{\rm N}1$ solvolyses. There does not appear to be any evidence for bridged structures in stable carbonium ions.

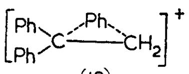
Kinetic Effects of Neighbouring-group Participation.—Unimolecular solvolyses ($S_{\rm N}1$ and $E1$) have as common rate-determining first step the generation of a carbonium ion through heterolysis of the starting species. In some reactions of this type the overall change is attended by a skeletal rearrangement (Wagner–Meerwein change), and it has been found that these particular solvolyses are often (but not always) unexpectedly fast. Simple examples are *neo*pentyl chloride ($Me_3C{\cdot}CH_2Cl$) and 2 : 2 : 2-triphenylethyl chloride ($Ph_3C{\cdot}CH_2Cl$), both of which react with wet formic acid at 95°, by a unimolecular mechanism, to give rearranged products (*tert.*-amyl compounds and triphenylethylene respectively). The reaction velocity for the first compound has a value of the order expected for the ionisation of a primary halide of this type, but the velocity for the second compound is 60,000 times greater,[49] too large to be accounted for in terms of the relative inductive effects of the methyl and the phenyl groups. The accelerated unimolecular reaction of the triphenylethyl chloride must be a manifestation of an additional effect facilitating ionisation. This can be explained as

[48] Nevell, de Salas, and Wilson, *J.*, 1939, 1188.

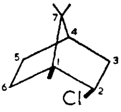
[49] F. Brown, Hughes, Ingold, and Smith, *Nature*, 1951, **168**, 65.

* Ingold has coined the word " synartesis " to describe this kind of phenomenon The name is intended to suggest that " a split single bond ' fastens together ' the locations of a split ionic charge ".[20]

participation by a neighbouring phenyl group in the ionisation, with formation of a non-classical ion (18) in which there is bridging by the phenyl group.*

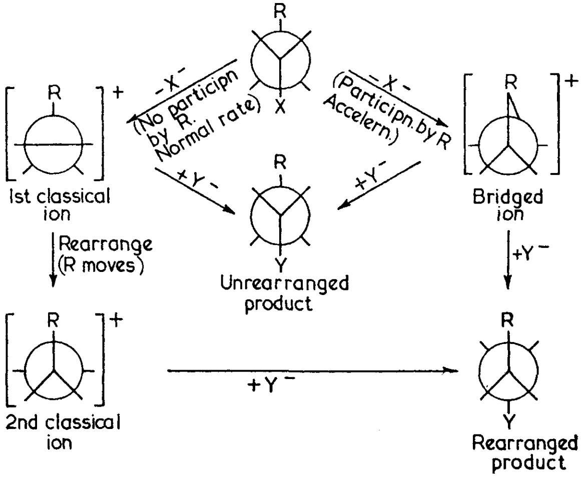


(18)



(19)

The various possibilities for ionisation, rearrangement, and product formation in systems of this general type are summarised in the attached scheme, which also indicates the assumed stereochemical course. In the two classical ions, rotation about the bond along which we are looking would be possible. The formation of the bridged ion may be likened to [51a] an S_N2 displacement on the nearer carbon atom, and its rupture to an S_N2 displacement on either the rear or the front atom, depending on whether or not a rearranged product is formed.



The generation of the bridged ion in preference to the classical ion in any particular reaction is intelligible if the non-classical ion is the more stable. In such a case the transition state for the formation of the bridged ion would also be stabilised in a corresponding manner by the incipient formation of the bridge, *i.e.*, by neighbouring-group participation. The rate would accordingly be increased and the primary step of the reaction would be the production of the bridged ion.

The occurrence of rearrangement is not itself evidence about the structure

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[50] Winstein, Lindegren, Marshall, and Ingraham, *J. Amer. Chem. Soc.*, 1953, **75**, 147.

[51] Ingold, ref. 20, pp. (*a*) 511, (*b*) 523.

* Winstein has proposed the adjective "anchimeric" to describe the effect of neighbouring-group participation as a result of which a rate-determining ionisation may be accelerated. The term applies to neighbouring carbon, hydrogen, and also functional groups.[50]

of the ion. Even when the classical ion is more stable than the bridged one, rearrangement may take place. It then involves the activated transformation of one classical ion into the other. The transition state of this rearrangement resembles the stable bridged ions in the disposition of the groups, but differs from them in being more (and not less) energised than the classical structures. The case of the *neo*pentyl cation cited above could be an instance of such a rearrangement.*

Abnormally high ionisation rates are important evidence for the formation of bridged ions, but this interpretation is not always the only possible one. In particular, they may be caused by steric acceleration, *i.e.*, a non-bonding effect of neighbouring groups which causes the ionisation to be attended by a release of steric strain. In many cases this possibility can be excluded. For example, the S_N1 ethanolysis of *iso*bornyl chloride (17) is 10^5 times faster [49, 53] than that of bornyl chloride (19). Since the departing chlorine is less crowded in the *iso*bornyl compound than in the bornyl compound, the rate difference cannot arise from steric acceleration, but it is thought to indicate the formation of the ion (16) as a reaction intermediate. In *iso*bornyl chloride the conformational dispositions of neighbouring-group and departing chlorine are favourable to the formation of the collinear transition state of the internal displacement reaction, whereas they are unfavourable to this formation of the bridged ion from bornyl chloride.

In certain instances quite small rate increases (10-fold or less) have been attributed to neighbouring-group participation. Such explanations must be regarded with caution unless they are supported by other evidence. A small acceleration may well be a consequence of the ordinary inductive effect of the neighbouring group. Also, it is perhaps sometimes assumed too readily that the solvolyses studied follow the S_N1 mechanism.

Stabilisation of Bridged Structures.—The cause of the peculiar stability ascribed to some bridged carbonium ions is by no means fully understood. In general terms, one may seek to classify the stabilising factors under the headings of mesomerism, inductive charge spreading, and steric (including conformational) effects. Only the first of these appears to be capable of providing extra stabilisation of the required order of magnitude. Mesomerism is, of course, implied in formulæ such as (16) with the aid of partial bonds. This procedure is equivalent to writing a number of resonance structures :

as is sometimes done. It is not clear why this resonance should be so

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[52] Winstein and Marshall, *J. Amer. Chem. Soc.*, 1952, **74,** 1120.

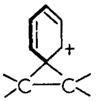
[53] Winstein, Morse, Grunwald, H. W. Jones, Corse, Trifan, and Marshall, *ibid.*, p. 1127.

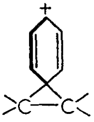
* Detailed consideration of the reaction velocities for *neo*pentyl compounds has led to the suggestion that, even in this case, there is neighbouring-group assistance through methyl bridging.[52]

important here when in other cases the delocalisation of C–C σ-bonds (or C–C hyperconjugation) is energetically rather trivial. In broad qualitative terms the effect may be ascribed to the electron-deficiency (electronic sextet) of the carbonium-carbon atom. As in the case of boron this somehow causes unusual electronic effects to come into play, so that the vacant levels may achieve at least partial occupation.[51b]

In bridging by a phenyl group this resonance stabilisation looks perhaps more convincing than in the case of alkyl groups. Resonance in these ions —which Cram calls " phenonium " ions—can now be considered to involve structures such as (20) and (21), in addition to those written above for bridging by an alkyl group, although against this we must set the loss of the normal benzene resonance within the bridging phenyl group. Simonetta and Winstein [54] have calculated the π-electron energy of such a system on the basis of a simple molecular-orbital procedure and have come to the conclusion that phenyl bridging causes a considerable increase in resonance energy. It is a less satisfactory feature of the quantitative aspect of this interpretation that several solvolyses exist for which stereochemical evidence indicates phenyl-group participation but which are not accelerated (see p. 194). It is worth noting that the predicted disposition of the bonds at the bridging carbon atom of the phenyl group is the same as the tetrahedral arrangement proposed for the intermediate in certain aromatic substitution reactions.[55]

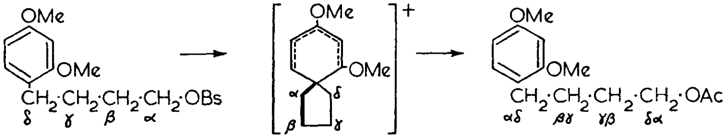
(20)





(21)

In extension of the idea of participation of phenyl groups at a neighbouring atom, the possibility of aryl participation at atoms further along an aliphatic chain has been considered.[55b, 56] On the basis of detailed comparisons of reaction velocities, Heck and Winstein [56] consider that there is evidence for the following carbonium-ion formation during acetolysis (OBs = p-bromobenzenesulphonate) :



(22)

They could find no evidence for participation at positions other than δ along a side chain, or by unsubstituted phenyl groups.

Stereochemical Evidence.—An example of the importance of other types

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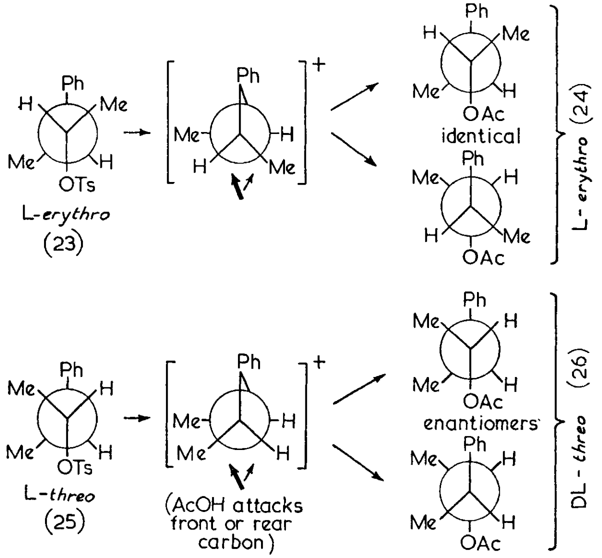
[54] Simonetta and Winstein, *J. Amer. Chem. Soc.*, 1954, **76**, 18.

[55] (*a*) Melander, *Acta Chem. Scand.*, 1949, **3**, 95 ; (*b*) Corey and Sauers, *J. Amer. Chem. Soc.*, 1957, **79**, 248.

[56] Heck and Winstein, *ibid.*, p. 3105.

of evidence for bridging is provided by the acetolysis of the toluene-*p*-sulphonates of the isomeric 3-phenylbutan-2-ols.[57] In this case there is little or no acceleration but the stereochemical results are sufficient to establish neighbouring-group participation. 3-Phenylbutan-2-ol exists in *threo-* and *erythro*-forms, each of which is an enantiomeric pair. Acetolysis of the optically active *erythro*-toluene-*p*-sulphonate (23) gave the *erythro*-acetate (24) of about 94% optical purity, whereas the *threo*-sulphonate (25) gave racemic *threo*-acetate (26). Thus both reactions proceed with retention of configuration, but only in the *erythro-* case is optical activity preserved. These results were interpreted in terms of intermediate formation of "phenonium" ions, as illustrated. The *threo*-sulphonate yields a phenonium ion possessing a plane of symmetry (in the plane of the paper), and reaction at either of the central carbon atoms then gives the *threo*-acetate, but with loss of optical activity. No such plane of symmetry exists in the case of the *erythro*-ion, so attack at either carbon atom yields the same optical enantiomer.



It has been suggested [58] that the stable form of the phenonium ion may be represented as a dynamic equilibrium between (27) and (28) (the *threo*-case being illustrated here). The symmetrical form, essential to the explanation of the stereochemical course, is the transition state for this interconversion. It is to be noted that *some* configuration-holding interaction

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[57] Cram, *J. Amer. Chem. Soc.*, 1949, **71,** 3863.

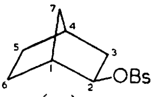
[58] Winstein, Brown, Schreiber, and Schlesinger, *ibid.*, 1952, **74,** 1140; Winstein and Schreiber, *ibid.*, p. 2165.

between the central carbon atoms and the neighbouring groups must occur throughout the reaction; otherwise both carbonium ions would assume the most favourable conformation by rotation of the central bond, and interconversion of *threo-* and *erythro*-forms would occur. Alternatively, it must be assumed that the destruction of the carbonium ion is rapid compared with the speed of rotation about a single bond (see also p. 198).

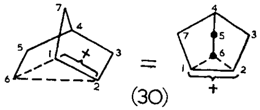
A large number of related systems have been examined by Cram and his co-workers, with the general conclusion that both open (classical) and phenyl-bridged cations can be intermediates, and that the successive formation of both these types may also be met.[59, 2b] The simultaneous possibility of migration of (and bridging by) different groups in the same molecule also brings in another " non-classical " type of isomerism.

Redistribution of an Isotopic Label.—As has already been indicated under the preceding heading, the non-classical structures for carbonium ions may have different symmetry from that of the corresponding classical structures. As a consequence, positions which are non-equivalent in the starting molecule or in the classical ion may become equivalent in the non-classical ion, so that isotopic labelling of one such position should result in random distribution of the isotope amongst all positions which become equivalent in the ion. In the hands of J. D. Roberts, and of other workers, this technique has proved one of the most searching tools in the determination of carbonium-ion structure. It has suggested the inadequacy of classical structures in certain cases, confirmed their adequacy in others, and revealed unsuspected complexities that may require modification of the simplest views of bridging in carbonium ions.

An interesting example is the S_N1 acetolysis of *exo*-norbornyl *p*-bromobenzenesulphonate (29) which, because of its high velocity, was considered to proceed by formation of a non-classical ion to which the structure (30) was assigned.[60] As the projection formula shows, this structure implies equivalence of positions 1 and 2 and of positions 3 and 7. Labelling the molecule (29) with $^{14}\mathrm{C}$ equally at positions 2 and 3 should thus result in equal distribution of the isotope over positions 1, 2, 3, and 7 in the product. The isotope was in fact found in all these positions but, in addition, 15% of the total radioactivity appeared at positions 5 and 6, a result [61] which is not immediately explained by the structure considered. The observations are consistent with the hypothesis that the ion (30) rearranges, by a hydrogen shift from position 2 to position 6, to the extent of about 45%. Hence positions 1, 2, and 6 become shuffled to a certain extent and there also is the same amount of interchange among positions 3, 5, and 7. It may now be



(29)



(30)

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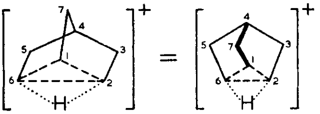
[59] Cram and Allinger, *J. Amer. Chem. Soc.*, 1957, **79**, 2859.

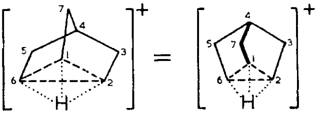
[60] Winstein and Trifan, *ibid.*, 1952, **74**, 1154.

[61] Roberts, Lee, and Saunders, *ibid.*, 1954, **76**, 4501.

asked whether this hydrogen shift indicates some extent of hydrogen participation in the ionisation step, *i.e.*, whether some of the ions formed have a structure involving both carbon and hydrogen bridging (31) or (32). It has been pointed out [2a] that the extent of additional carbon shuffling (involving the 5- and the 6-position) depends on the nucleophilic activity of the solvent, and is zero for very reactive solvents in which the life of the carbonium ion is short. This would indicate that the hydrogen transfer competes with the solvent attack and is, therefore, subsequent to the formation of the carbonium ion.



(31)



(32)

There is also other evidence for hydrogen shifts across cyclic carbonium ions. The deamination (with nitrous acid) of *cyclo*decylamine, isotopically labelled at the 1-position, yields products with the isotopic label, not only in the 1-, but also in the 5- and the 6-position. The reaction is believed to involve carbonium ions, and the result can therefore be interpreted as a transannular hydrogen shift in the *cyclo*decyl cation.[62]

Roberts and Yancey [63a] have also looked for evidence of hydrogen bridging in the ethyl cation, by examining the distribution of ^{14}C in ethanol formed by deamination of $CH_3{\cdot}^{14}CH_2{\cdot}NH_2$. The isotopic label stays almost completely in the original position. The two ends of the molecule do not, therefore, become equivalent at any stage during the reaction and, if the reaction proceeds by way of carbonium ions, the ions cannot have a symmetrical structure such as the bridged formula (33).

Corresponding studies with labelled 2-arylethylamines [63b] (to detect aryl-bridging) and with *n*-propylamine [63c] (to detect methyl-bridging) showed the occurrence of some rearrangement, but in no case was the isotope found to be equally distributed between the 1- and the 2-position. The reactions cannot, therefore, proceed *entirely* by formation of bridged ions. They *may* do so in part; but alternatively the isotope shuffling could be caused by rearrangement of classical ions.

Another interesting case is presented by the *cyclo*propylcarbonium ion. The rapid S_N1 solvolysis of *cyclo*propylmethyl derivatives (34) suggests a non-classical structure for the ion.[64, 65] Acetolysis of *cyclo*propylmethyl chloride and of *cyclo*butyl toluene-*p*-sulphonate, and deamination of *cyclo*propylmethylamine, yield mixtures of products containing, amongst others, similar proportions of *cyclo*propylmethyl and *cyclo*butyl derivatives. These

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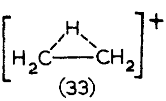
[62] Prelog, Urech, Bothner-By, and Würsch, *Helv. Chim. Acta*, 1955, **38**, 1095; see also Prelog and Küng, *ibid.*, 1956, **39**, 1394; Urech and Prelog, *ibid.*, 1957, **40**, 477; Prelog, *Experientia*, 1957, *Suppl.* VII, p. 261.

[63] (*a*) Roberts and Yancey, *J. Amer. Chem. Soc.*, 1952, **74**, 5943; (*b*) Roberts and Regan, *ibid.*, 1953, **75**, 2069; (*c*) Roberts and Halmann, *ibid.*, p. 5759.

[64] Roberts and Mazur, *ibid.*, 1951, **73**, 2509.

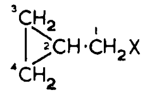
[65] Bergstrom and Siegel, *ibid.*, 1952, **74**, 145.

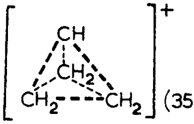
results have been explained in terms of rapid interconversion of *cyclo*propylmethyl and *cyclo*butyl cations. As a result of such interconversions each of the original carbon atoms 1, 3, and 4 may appear in the side-chain of a *cyclo*propylmethyl compound in the product. If position 1 is isotopically labelled with ^{14}C, the radioactivity should become equally distributed among carbon atoms 1, 3, and 4. Such shuffling of carbon is, in fact, observed, although the amounts of radioactivity in the three positions are not quite equal. In view of the fact that there is rate enhancement for the formation of the ion, an attractive (though not the only possible) interpretation of the results is the suggestion that there is intermediate formation of some carbonium ions of the structure (35), which has a three-fold axis of symmetry.



(33)

(34)



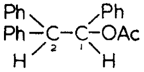


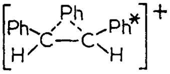
(35)

The structure of the *spiro*carbonium ion (22), mentioned earlier, implies that the α- and the δ-position of the starting compound become equivalent (and similarly the β- and the γ-position). It should therefore be possible to test the correctness of structure (22) by isotopic labelling at any one of these positions and examination of its distribution in the product.

Isotope-labelling experiments have also amplified our knowledge of reactions for which phenonium-ion formation is a possibility. Experiments have been carried out on the S_N1 solvolyses of 1 : 2 : 2-triphenylethyl compounds, such as the acetate (36), labelled on $C_{(1)}$, in the 1-phenyl group, or in the leaving acetate group.[66] The rates at which the chain and the ring label became distributed over the two halves of the molecule (to appear on oxidation in either the benzoic acid or the benzophenone formed) are a measure of the rate of phenyl migration from position 2 to position 1. Rearrangement by formation of a phenonium ion (37) by an internal S_N2 reaction would, in view of the symmetry of this structure, lead to equal distribution of the phenyl label between the two sides. In fact, the phenyl label is in some cases distributed randomly among all three phenyl groups. Since the acetate-labelling experiments indicate that the rearrangement is not accompanied by recombination ("internal return") of the ion pair

(36)





(37)

formed, the result is most easily rationalised in terms of open-chain ("classical") carbonium ions, which can undergo equilibration by phenyl migration as follows :

$$\mathrm{Ph_2CH{-}^{+}CHPh^{*}} \rightleftharpoons \mathrm{^{+}CHPh{\cdot}CHPhPh^{*}}$$

In view of the great stability of phenyl- and diphenyl-carbonium ions, classical structures may be particularly favourable in this system, and these

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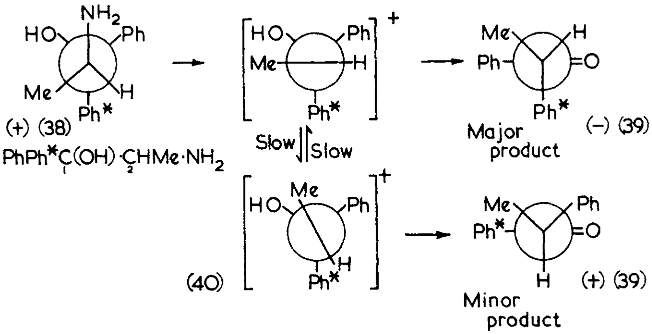
[66] Collins and Bonner, *J. Amer. Chem. Soc.*, 1955, **77**, 92, 99.

results are not irreconcilable with Cram's interpretation of his stereochemical observations (see p. 194). The importance of open carbonium ions in some rearrangements is in fact well recognised by Cram.[59, 2b]

In an important continuation [67] of this series of investigations, Collins and his co-workers examined the deamination by nitrous acid of 1 : 1-diphenyl-2-aminopropan-1-ol (38), *stereospecifically* labelled in one of the phenyl groups, to form α-phenylpropiophenone (39). In this reaction stereochemically different end products (*i.e.*, configurations at the migration terminus) were obtained according to whether the labelled or the unlabelled phenyl group migrates, as shown below. (The two phenyl groups are not equivalent because the stereospecific labelling produces asymmetry at $C_{(1)}$.) The result implies that bridge-formation between $C_{(1)}$ and $C_{(2)}$ by the migrating phenyl group cannot occur synchronously with the rupture of the C–N bond (which results in the formation of the carbonium ion), since in one case the phenyl group must attack $C_{(2)}$ from the *same* side as that occupied by the amino-group and, to be able to do so, the C–N bond must have been severed *before* this attack. This observation therefore also seems to require a classical structure for the carbonium ion (40), and this in a system considered favourable to the formation of bridged ions. To explain the precise product composition it is, however, still necessary to assume that rotation about the bond between $C_{(1)}$ and $C_{(2)}$ in the ion (40) [to interconvert the enantiomeric conformations] is not very fast compared with the product-forming phenyl migration. This conclusion amounts to the postulation of a rotation-hindering force in carbonium ions *other* than through the bridge bonding which characterises the " non-classical " structures considered up till now. This postulate could perhaps be rationalised in terms of a novel kind of hyperconjugation between the vacant *p*-orbital on the carbonium-carbon atom and the three splayed σ-bonds on the adjacent carbon atom(s). Unless there is an alternative explanation of Collins's observations, drastic reconsideration of the significance of the stereochemical evidence for bridged ions, going right back to Roberts and Kimball's hypothesis (p. 188), may be required.



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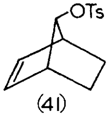
[67] Benjamin, Schaeffer, and Collins, *J. Amer. Chem. Soc.*, 1957, **79**, 6160.

V. Homoallylic and *cyclo*Propenyl Cations

The Effect of Neighbouring Double Bonds.—The acetolysis of *anti*-norborn-7-enyl toluene-*p*-sulphonate (41) is 10^{11} times more rapid than that of the 7-norbornyl analogue [68] (42). The magnitude of the acceleration indicates that this is not an inductive effect of the double bond. The phenomenon is attributed to stabilisation of the incipient positive charge on $C_{(7)}$ by the π-orbital of the double bond and formation of the ion (43). The bonding in this ion has been likened to that in the *cyclo*propenyl cation.* Simple molecular-orbital calculations,[71] analogous to those applied to phenonium ions,[54] support the increased stability of such a structure. For *syn*-norborn-7-enyl ester (44) the rate is 10^7 times slower than that for the *anti*-compound, since the leaving group now prevents the interaction between the double bond and $C_{(7)}$. The fact that the solvolysis of ester (44) is still 10^4 times faster than that for (42) has been attributed to formation of the intermediate (45) by methylene participation. Hydrolysis of the acetolysis product gives the alcohol (46), in accordance with this scheme.



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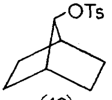

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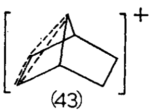

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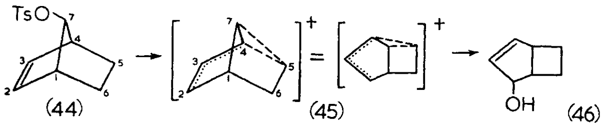
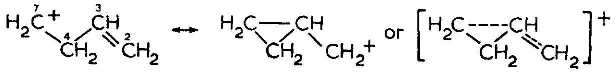


(44) (45) (46)

The interaction involved in ion (43) can also be expressed in terms of the resonance structures for the " homoallylic " representation of the carbonium ion :



and stabilisation is found in other molecules containing this arrangement of bonds. This interaction of an α-carbon and a $\gamma\delta$-double bond was, in fact, recognised by Shoppee [72] in 1946 for cholesteryl chloride (47). In agreement with this suggestion, a rate-enhancement has been observed for the solvolysis of the toluene-*p*-sulphonate.[73] The reaction of the chloride (47)

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[68] Winstein, Shatavsky, Norton, and Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183 ; Winstein and Stafford, *ibid.*, 1957, **79**, 505.

[69] Roberts, Streitwieser, and Regan, *ibid.*, 1952, **74**, 4579.

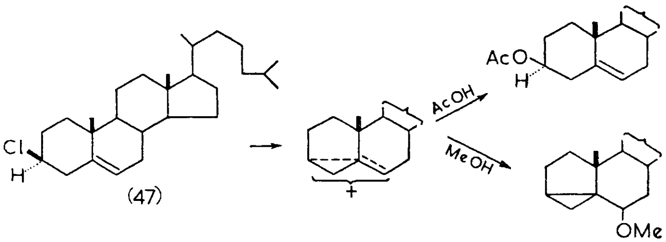
[70] Breslow, *ibid.*, 1957, **79**, 5318.

[71] Woods, Carboni, and Roberts, *ibid.*, 1956, **78**, 5653.

[72] Shoppee, *J.*, 1946, 1147.

[73] Winstein and Adams, *J. Amer. Chem. Soc.*, 1948, **70**, 838.

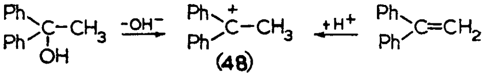
* Considerable stabilisation has been predicted [69] for the (symmetrical) *cyclo*propenyl cation and has been confirmed by the isolation of a salt of the stable 1 : 2 : 3-triphenyl-*cyclo*propenyl cation.[70]


(47)

is formulated as shown. Like allylic resonance, this type of interaction does not affect the spatial disposition of the bonds in the ion, though it will affect bond lengths.

VI. Protonated Unsaturated Systems

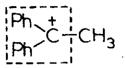
Stable Carbonium Ions formed from Olefins and Acids.—Cationic species of the same empirical formulæ can be generated either by loss of an anionic group from a neutral molecule or by addition of a proton to a related unsaturated compound. A simple example is the stable methyldiphenylcarbonium ion (48), the two modes of formation of which are easily realised



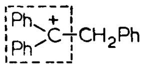
$$Ph_2C(OH)-CH_3 \xrightarrow{-OH^-} Ph_2\overset{+}{C}-CH_3 \xleftarrow{+H^+} Ph_2C{=}CH_2$$

(48)

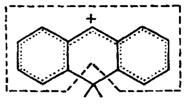
by dissolution of the alcohol or the olefin in sulphuric acid, the same species being formed in both processes.[74] These stable carbonium ions are better represented by classical formulæ[74] rather than by structures ("π-complexes") in which the proton occupies a bridging position or is loosely attached to the π-electron cloud, in a less localised fashion.[75] This view is based on the similarity of the ultraviolet absorption spectra[74] of the different species obtained by dissolving 1 : 1-diphenylethylene, triphenylethylene, or anthracene in sulphuric acid. This similarity is easily understood if the species obtained in the three cases are protonated at those positions (cf. formulæ) which simple molecular-orbital calculations[12] predict would yield the most



$Ph_2\overset{+}{C}-CH_3$



$Ph_2\overset{+}{C}-CH_2Ph$



stable classical ion. In these ions the system of electrons extends over the nuclear frame enclosed within the broken lines and is, in each case, a diphenylcarbonium system. The ions should thus have very similar electronic spectra. On the other hand, the close similarity experimentally observed would be out of place on other views of the structure of these ions. Support

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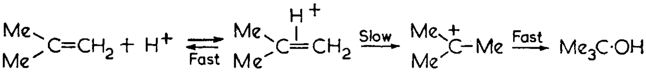
[74] Gold and Tye, *J.*, 1952, 2172.

[75] Dewar, "The Electronic Theory of Organic Chemistry", Oxford Univ. Press, London, 1949.

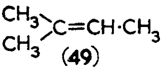
for this kind of structure in ions derived from polycyclic aromatic hydrocarbons has been obtained from the study of hydrocarbon basicities.[76]

Ionic Reaction Intermediates formed from Unsaturated Compounds in Acidic Media.—The study of the kinetics of reactions initiated by a proton transfer to an unsaturated or conjugated molecule has suggested that another structure of the carbonium ion is also possible. Taft measured the rate of hydration of *iso*butene in aqueous acid as a function of acidity and found the reaction velocity to be proportional to Hammett's acidity function h_0 ($H_0 = -\log h_0$) rather than to the concentration of hydrogen ion.[77] On the basis of the Zucker–Hammett hypothesis [78] this result was interpreted as implying that the slow step of the reaction involved only a protonated olefin species, formed in a rapid proton-transfer pre-equilibrium from olefin and acid. The specific picture proposed by Taft is the slow isomerisation of a "π-complex" to the classical carbonium ion followed by completion of



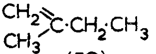
$$\mathrm{Me_2C{=}CH_2 + H^+ \underset{Fast}{\rightleftharpoons} Me_2C\overset{\overset{H^+}{|}}{=}CH_2 \xrightarrow{Slow} Me_2\overset{+}{C}{-}Me \xrightarrow{Fast} Me_3C{\cdot}OH}$$

the reaction through attachment of OH in a sequence of rapid steps which do not affect the kinetics. It is fairly clear that, if the first phase of the reaction is a rapid protonation equilibrium, the protonated species formed cannot be a classical carbonium ion, since the hydration of the isomeric 2-methylbutenes (49) and (50) yields the same product, but is not accompanied by isomerisation of unchanged olefin. The classical ion formed from each isomer would have the same structure (51) and, on loss of a proton, would obviously regenerate the same olefin mixture.[79] Several other, less direct lines of evidence [80] support the conclusion outlined but, with all this evidence in mind, Long and Paul [81] recently concluded that it "does not seem easy to exclude the possibility that olefin hydration involves a *slow* proton transfer as the rate-determining step" and, by implication, that the experiments on olefin hydration have no bearing on the structure of the intermediate carbonium ion.



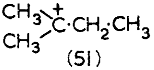
$\mathrm{(CH_3)_2C{=}CH{\cdot}CH_3}$

(49)



$\mathrm{CH_2{=}C(CH_3){\cdot}CH_2{\cdot}CH_3}$

(50)



$\mathrm{(CH_3)_2\overset{+}{C}{\cdot}CH_2{\cdot}CH_3}$

(51)

In connection with this problem Cannell and Taft [82] examined the deamination of *iso*butylamine $\mathrm{(CH_3)_2CH{\cdot}CH_2{\cdot}NH_2}$ by nitrous acid. This reaction produces trimethylcarbonium ions,[83] and involves at some stage during or after the formation of the carbonium ion the transfer of hydrogen

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[76] Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

[77] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372.

[78] Zucker and Hammett, *ibid.*, 1939, **61**, 2791.

[79] Levy, Taft, and Hammett, *ibid.*, 1953, **75**, 1253.

[80] Taft, Purlee, Riesz, and DeFazio, *ibid.*, 1955, **77**, 1584 ; Purlee and Taft, *ibid.*, 1956, **78**, 5807.

[81] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[82] Cannell and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5812.

[83] *Idem*, Abs. Papers, 129th Amer. Chem. Soc. Meeting, April, 1956, 46N.

from position 2 to position 1. If this intermediate is identical with the protonated olefin formed in the hydration of *iso*butene then the migrating hydrogen should be easily exchanged with protons from the solvent. However, it is found that when the deamination is carried out in deuterium oxide solution, the *tert.*-butyl alcohol formed contains no C–D bonds. This indicates that the migrating hydrogen is at all times firmly held, and the intermediate is different from that postulated for the olefin hydration. Cannell and Taft accordingly propose a new type of isomerism between two kinds of non-classical ions, the forms being (1) π-complex ions, formed in olefin hydration, in which the proton is weakly embedded in the π-orbital of the double bond above the plane of the other olefin valencies, and (2) bridged " protonium " ions, formed in the deamination, in which bonding by σ-electrons is involved throughout the reaction.

Some of these suggestions are closely related to conclusions drawn concerning the interaction of acids with aromatic rings. The rate of hydrogen-isotope exchange (deuterium loss) in acidic solvents has been found to follow Hammett's acidity function over a wide range of acidities, and application of the Zucker–Hammett hypothesis [78] again leads to the conclusion that the first step in the reaction is the formation, in low concentration, of a protonated species which is in rapid proton-transfer equilibrium with the solvent.[84] This species cannot have the structure (52), in which protium and deuterium occupy equivalent positions, since such a structure would break down to yield either the deuterio- or the protio-compound and, therefore, the initial rate of protonation could not be very fast compared with the exchange velocity. It has been suggested that the slow step is a rearrangement of the first carbonium ion formed. To avoid the structural implications of other names, Gold and Satchell refer to the first ion formed as an " outer complex " and to the ion (52) as an " inner complex ". Since hydrogen-exchange reactions appear to be subject to steric hindrance [85] in the *ortho*-position, one must conclude that these " outer complexes " do not readily rearrange over the whole system of conjugation, but that the initial site of protonation—if there is to be exchange—must be sufficiently close to the seat of reaction for steric hindrance by *ortho*-substituents to be perceptible. All these conclusions are again subject to the limitations of the Zucker–Hammett hypothesis and, as for Taft's mechanism, Long and Paul [81] have speculated about alternative hypotheses which would destroy the structural significance of the proposals made.

(52)

The equilibria observed in solutions of aromatic hydrocarbons in strong acids have frequently been interpreted in terms of two kinds of interaction, one looser and one more intimate, termed respectively π- and σ-complexes. The former are generally pictured as involving attachment of the proton to the electron cloud, and the second as being like structure (52). Valuable though these studies are, perhaps most of the results relating to such equilibria are not really relevant as evidence of *structure*.

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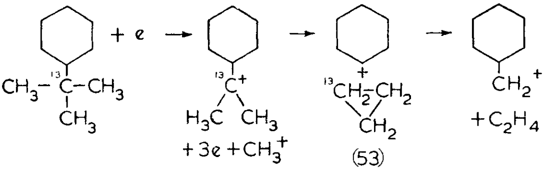
[84] Gold and Satchell, *Nature*, 1955, **176**, 602; *J.*, 1955, 3609, 3619.
[85] Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 4165.

VII. Non-classical Ions in the Gas Phase

Cationated cyclo*Propane Rings.*—An indication of other structural possibilities which have not so far received prominence in chemical speculation is provided by some mass-spectral studies.[86] *tert.*-Butylbenzene, in which the α-carbon of the side-chain had been labelled with ^{13}C yielded, on electron impact, benzyl cations, two out of three of which contained no ^{13}C. The reactions involved are formulated as shown. In the cationated *cyclo*propane ring (53) the three side-chain carbon atoms become equivalent, thus leading to the statistical distribution of ^{13}C in the benzyl cations finally produced. Evidence also exists for structures similar to (53) in which methyl cations or protons replace the phenyl cation. However, it may be that the occurrence of rapid rearrangements is characteristic of high-energy carbonium ions formed on electron impact, and that the results need not imply non-classical structures. Thus, " benzyl " cations, $C_7H_7^+$, formed from labelled alkylbenzenes by electron impact, have been found to decompose in such a manner that all seven positions contribute equally to the break-down products.[87] Taken in conjunction with values of the appearance potentials, the result has been interpreted as indicating the tropylium structure (in which all seven positions are equivalent) for the ion $C_7H_7^+$.



Conclusion

It will be apparent from the selection of material presented in this Review that the structure of carbonium ions is a lively field of chemical research and speculation. It is unlikely that all the notions now current will stand the test of time. It may even be that the variety of " non-classical " phenomena observed indicates a serious weakness of the underlying structural concepts.

The Reviewers would like to state that they have made no attempt to assess questions of priority of ideas. The presentation of suitable illustrative material was the only guiding principle in the selection of particular pieces of research. They thank Drs. P. B. D. de la Mare and C. W. Rees for comments, and Mr. J. S. Coe, M.Sc., for checking references.

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[86] Rylander and Meyerson, *J. Amer. Chem. Soc.*, 1956, **78**, 5799.

[87] Rylander, Meyerson, and Grubb, *ibid.*, 1957, **79**, 842.