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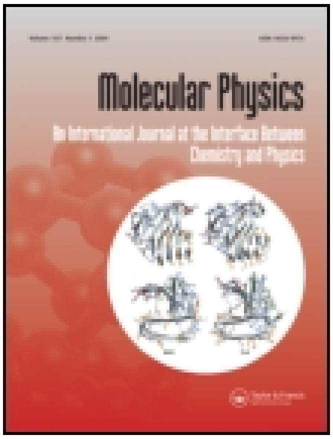

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Unstable intermediates

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Unstable intermediates
Part X. Aliphatic carbonium ions

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The preparation of solutions thought to contain simple aliphatic carbonium ions is described and their spectra recorded. Alternative explanations are considered, and the nature of the electronic transition is discussed.

1. INTRODUCTION

Reactions which occur between strong acids and simple aliphatic olefins, alcohols and related compounds have been reviewed recently [1, 2, 3]. Extensive study has centred on solutions in dilute aqueous acids and hardly at all on solutions in concentrated acids, probably because oxidation and polymerization may occur in the latter media.

It has been concluded that in concentrated sulphuric acid alkyl hydrogen sulphates are first formed and that the equilibrium

$$RHSO_4 \rightleftharpoons R^+ + HSO_4^- \qquad (1)$$

is the main cause of subsequent dis-proportionation, polymerization, etc. However, it has been stated that "there is no evidence which would lead us to suppose that the degree of ionization is large and it seems reasonable to presume that in every case the equilibrium lies well on the side of the un-ionized hydrogen sulphate" [2].

It has long been known that solutions of many alcohols and olefins in sulphuric acid become yellow on standing. Visible and ultra-violet spectra of concentrated solutions of certain tertiary alcohols were reported by Lavrushin [4], who found a shoulder in the 450 mμ region and a broad band at about 300 mμ. A similar band at 300 mμ was reported by Gonzalez-Vidal *et al.* [5], for solutions of octene-1 in sulphuric acid. They established that sulphur dioxide and certain saturated hydrocarbons were formed under these conditions and ascribed the band at 300 mμ to unspecified oxidation products.

It has been inferred from a study of monoaryl carbonium ions [6] that, provided very dilute solutions are used and care is taken to prevent interaction between carbonium ions and uncharged solute during the process of dissolution, relatively stable solutions of these ions can be obtained. Our main aim has been to discover if aliphatic carbonium ions could be formed in detectable quantities under similar conditions.

2. EXPERIMENTAL AND RESULTS

2.1. *Materials*

Solvents and solutes were highest grade commercial products, further purified when necessary by standard methods and characterized by boiling or melting points and refractive indices. Sulphuric acid (98 per cent) was either 'AnalaR' grade or further purified by distillation. Oleums were prepared as described previously [7]. 'AnalaR' grade *n*-hexane was shaken repeatedly with sulphuric acid, washed with distilled water, dried over sodium and distilled, b.p. 80–81°. *Tert.* butanol, twice distilled from anhydrous calcium sulphate, had b.p. 82° and m.p. 25·3°.

Trimethylborine was prepared by the action of methyl magnesium iodide on boron trifluoride, in a nitrogen atmosphere, according to the method of Brown [8]. The gaseous product was passed into degassed *n*-hexane, samples of which were run off periodically and their ultra-violet spectra recorded. The concentration of trimethylborine in these solutions was estimated using 1 : 2 : 5 : 8-tetrahydroxy-anthraquinone [9].

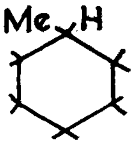
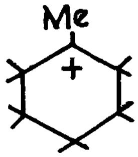
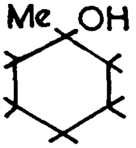
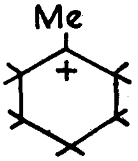
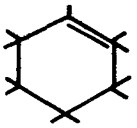
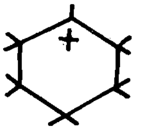
Compound	Probable ion	λ_{max} (mμ)	$\epsilon_{max} \times 10^3$	ΔH cm^{-1}†
*n*PrOH	Me_2CH^+	296	‡	5300
iso-PrOH	,,	,,	,,	,,
$Me_2C:CH_2$	Me_3C^+	291	6·0	5000
n-BuOH	,,	290	6·4	4500
iso-BuOH	,,	290	6·3	4800
sec.BuOH	,,	292	6·1	4900
tert.BuOH	,,	293	6·4	4800
Me_3CCl	,,	292	6·3	4600
Me_3CBr	,,	292	6·3	4400
Me_3COAc	,,	293	6·4	4700
$Me_2C:CHMe$	Me_2C^+Et	295	2·4	5100
$Me_2C(OH)Et$	,,	296	2·8	5200
$CH_2=C{\cdot}Et_2$	MeC^+Et_2	297	2·1	5000
		293	5·1	5100
		293	4·9	6000
Et_3COH	Et_3C^+	298	4·4	5200
		300	4·9	4400
$Me_3C.CH:CMe_2$	Me_3C^+	292	10·4	5500

Table 1. Details of the ultra-violet absorption spectra of carbonium ions in sulphuric acid.

† Total band width at half height.

‡ About 500 in 100 per cent sulphuric acid, and strongly dependent on acidity.

2.2. *Preparation of solutions*

The reactants used were olefins and their corresponding alcohols and halides (see table 1). The procedure for preparing stable solutions in sulphuric acid was as described earlier [6], that involving preliminary solution in acetic acid being the most satisfactory. Concentrations were generally less than 10^{-3} M, and were estimated by direct weighing for alcohols and halides. Stock solutions of olefins in acetic acid were treated with an excess of a standardized solution of bromine in acetic acid and the decrease in optical density at 407 mμ was used to estimate the olefin concentration.

2.3. *Spectrophotometric measurements*

These were made using a Unicam S.P. 500 quartz spectrophotometer and S.P. 700 recording spectrophotometer, pure solvents being used for reference. When possible stoppered cells were used.

For most olefins, spectra were recorded with freshly prepared solutions, and showed no change over a period of days. In contrast, the 293 mμ band rapidly increased in intensity for alcohols and alkyl halides but remained constant after about three days. The results recorded in table 1 relate to solutions for which spectra were invariant.

Within experimental error, the spectra from $Me_2C:CH_2$, the four butanols, Me_3CCl, Me_3CBr and Me_3COAc were identical: in other cases the olefins and their corresponding alcohols gave the same spectra. The bands from the butanols were fully developed after a few hours. In contrast, several weeks were required before the band was developed from *sec.* butyl chloride.

Propyl compounds behaved erratically. A band at about 296 mμ developed from solutions of the alcohols at rates comparable with the butanols. The apparent extinction coefficient was strongly dependent upon acidity and was not very reproducible. Extinction coefficients as high as $2{\cdot}2 \times 10^3$ were obtained using dilute oleums. *Iso*-propyl chloride gave no band in the 296 mμ region after several weeks in sulphuric acid.

Di-*iso*-butylene was the only olefin studied whose spectrum changed with time. Initially an extinction coefficient of $5{\cdot}0 \times 10^3$ was calculated, which increased quite rapidly to $10{\cdot}4 \times 10^3$.

2.4. *Spectrum of trimethylborine*

In early work, solutions in hexane, prepared as described above, had an intense band with a maximum at 260 mμ [10]. However, it was found that in the presence of oxygen this band increased in intensity, and further study showed that, despite care taken to exclude air during preparation, this band was due to some oxidation product. Very scrupulous removal of oxygen from the solvent and exclusion of air during the preparation and spectral measurements gave solutions whose spectra showed that trimethylborine itself has no peak at 260 mμ. These spectra are characterized by intense absorption in the 200–220 mμ region and the shape of the curve suggests that there is a maximum at wavelengths just below 200 mμ. This result is in accord with unpublished results of Dr. John Murrell, who measured the spectrum of trimethylborine in the gas phase. It is also in agreement with the results of Davies *et al.* on more complex trialkylborines [11].

2.5. *Spectra of concentrated solutions*

Spectra of solutions more concentrated than about 10^{-3} M changed markedly with time, and in general, a new band in the 350 mμ region appeared. Sometimes a hydrocarbon layer separated on standing. A typical spectrum is shown in figure 3. Matsen *et al.* have shown that under these conditions sulphur dioxide is formed [5].

2.6. *Dependence on acidity*

Solutions of *tert.* butanol in sulphuric acid were stored until their ultra-violet spectra were invariant. Aliquots were diluted with aqueous sulphuric acids and the composition of the resulting solutions determined by measuring their densities and comparing with standard tables. The spectra of these solutions were measured, and the results are recorded in figure 4, as a plot of the acidity function H_0 against log Q, where Q is defined by equation 2 [12]:

$$Q=\frac{[\text{carbonium ion}]}{[\text{olefin}]}=\frac{\epsilon_{\text{exp}}}{\epsilon_{\text{max}}-\epsilon_{\text{exp}}}. \qquad (2)$$

(ϵ_{exp} is the apparent extinction coefficient at 293 mμ at a given value of H_0, and ϵ_{max} is the extinction coefficient in 98% sulphuric acid).

Although there is considerable experimental error, the results follow a line having unit slope fairly closely. This is a necessary property of an equilibrium involving proton transfer but not of one involving hydration. The spectra of solutions in dilute aqueous sulphuric acid were transparent above 210 mμ, but reacidification with concentrated sulphuric acid resulted in an immediate and quantitative reappearance of a band at 293 mμ.

2.7. *Other solvents*

Addition of dilute oleum to solutions of *tert.* butanol in sulphuric acid did not alter their spectra. Solutions in perchloric acid (72 per cent w.w.), methanesulphonic, and trifluoroacetic acids also gave bands at 293 mμ but in the last two

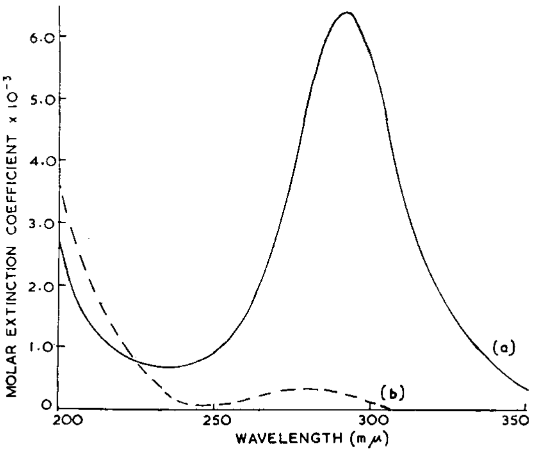


Figure 1. Absorption spectrum of (*a*) *tert.* butanol, and (*b*) sulphur dioxide in 98 per cent sulphuric acid.

solvents the rate of growth was slow and the apparent extinction coefficients were smaller than usual.

2.8. *Possibility of oxidation*

If the postulate that this band is a property of carbonium ions is wrong, then the most probable alternative is that it is due to an oxidation product. This could have been formed by direct oxidation by solvent to give sulphur dioxide, by reaction with dissolved oxygen, or by disproportionation, such as that shown in equation (3):

$$Me_3C^+ + Me_2C=CH_2 \longrightarrow Me_3CH + CH_2=C(Me)\cdot CH_2^+. \qquad (3)$$

Accordingly, we have endeavoured to develop sensitive methods for the detection of sulphur dioxide in sulphuric acid. The reaction rate for *tert.* butanol has been measured in the absence of oxygen, and the behaviour of saturated hydrocarbons in sulphuric acid has been studied. In addition, a wide range of the more simple possible oxidation products in sulphuric acid have been studied by spectrophotometry.

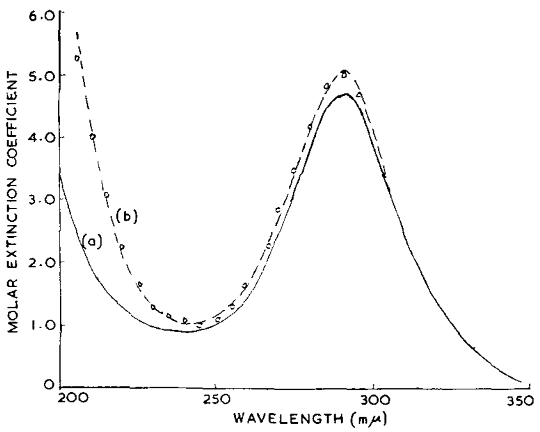


Figure 2. Absorption spectrum of (*a*) 1-methyl-*cyclo*-hexane-1-ol and (*b*) methyl-*cyclo*-hexane in 98 per cent sulphuric acid. The circles represent points calculated by the addition of curve (*b*) figure 1 to curve (*a*) figure 2.

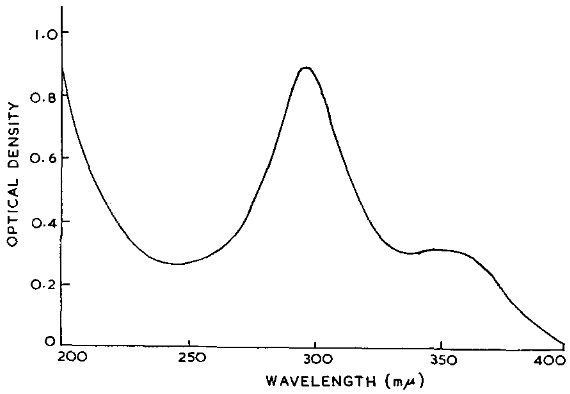


Figure 3. Absorption spectrum of *tert.* butanol (10^{-2} M) in 98 per cent sulphuric acid.

Methyl-*cyclo*-hexane (spectrograde), dissolved in sulphuric acid by the procedures developed earlier [6], reacted slowly to give a product whose spectrum was identical with that for 1-methyl-*cyclo*-hexane-1-ol except that in the 220 mμ region, the long wavelength edge of an intense band was detected (figure 2). A reconstruction of this spectrum by addition of the spectra of sulphur dioxide and 1-methyl-*cyclo*-hexane-1-ol in sulphuric acid is also shown in figure 2, from which it may be seen that about one equivalent of sulphur dioxide was formed during the reaction. If the reaction is written as

$$RH + 4H_2SO_4 \longrightarrow R^+ + 2H_3O^+ + 3HSO_4^- + SO_2 \qquad (4)$$

then there should be a one to one equivalence between the number of moles of carbonium ion and sulphur dioxide formed.

As a further check on the possibility that sulphur dioxide is formed, solutions obtained from methyl-*cyclo*-hexane and *tert.* butanol were treated with an excess of a solution formed by reaction between iodine and iodic acid in sulphuric acid. These brown solutions, thought to contain the tri-iodide positive ion [13, 14] react slowly with sulphur dioxide in sulphuric acid, with liberation of iodine. Iodine was only precipitated from solutions derived from methyl-*cyclo*-hexane, thus further establishing that sulphur dioxide is not a product of the reaction between sulphuric acid and tertiary alcohols.

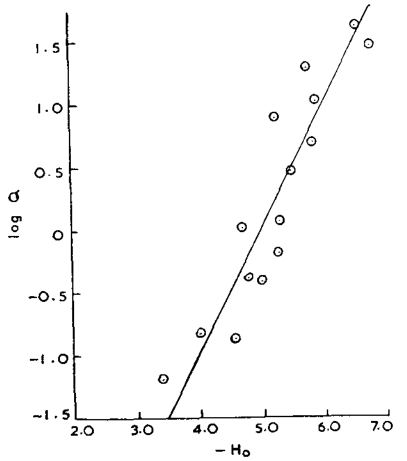


Figure 4. The concentration of trimethylcarbonium ions as a function of acidity. Q is defined in the experimental section: H_0 is the Hammett acidity function. The straight line is drawn with unit slope.

To check the possibility that oxygen was involved, solutions of *tert.* butanol were de-gassed by repeated partial freezing and warming under high vacuum. The rate of build up of the 293 mμ band was identical with that found under ordinary conditions.

Had a disproportionation occurred, such as that shown in equation (3), our results with methyl-*cyclo*-hexane establish that the *iso*-butane formed would be reoxidized by the solvent. Since sulphur dioxide would then be a product, this reaction can also be eliminated.

Solutions of a wide range of possible oxidation products in sulphuric acid have been studied spectrophotometrically in an endeavour to discover what product might have a band at 293 mμ. These included 2-methyl propane, −1, 2-diol, 2-methyl allyl alcohol; *iso*-butyric acid, 2-hydroxy-*iso*-butyric acid, acetone and acetic acid. Solutions of these compounds in sulphuric acid prepared by our procedure had spectra from which the 293 mμ band was completely absent. Some of these spectra were of considerable interest and will be the subject of a subsequent paper. The spectrum of acetone in aqueous acids is discussed by Nagakura, Minegishi and Stanfield [15], who found that in concentrated sulphuric acid condensation occurred. Dilute solutions prepared as above showed no evidence of condensation, the salient feature being a rising absorption below 230 mμ. Dilute solutions of the carboxylic acids listed above were transparent above 210 mμ, as also was acetic anhydride. (Since the latter is thought to be converted into the ion $MeCO^+$ under these conditions this result suggests that $MeCO^+$ has no absorption band in the near ultra-violet region.)

Since side reactions occur in solutions more concentrated than 10^{-3} M, it was considered impracticable to isolate reaction products after dilution with water.

2.9. *Reaction rates*

The band at 293 mμ developed at a measurable rate with alcohols and certain alkyl halides. An approximate measure of the rate of formation of the compound responsible for this band was obtained in the following way. Solutions in sulphuric acid preheated to 25° were prepared by procedures 1 (*a*) or 1 (*b*) of [6] as rapidly as possible, and transferred to a stoppered 1 cm cell contained in a cell housing thermostated at 25°. Optical densities at the peak position were measured periodically and the final, constant value ($O.D._{\infty}$) was used to obtain the first-order rate constant from a plot of $\log(O.D._{\infty} - O.D._t)$ against time t. It was established that solvent *cyclo*hexane gave no band in the 200–300 mμ region under these conditions. However, when procedure 1 (*a*) was used the solutions were cloudy and it was necessary to de-gas the solutions by partial freezing under high vacuum to remove the solvent. A typical plot is shown in figure 5, and the results summarized in table 2.

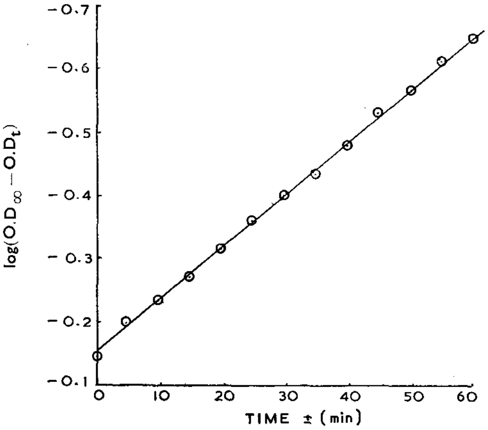


Figure 5. The rate of growth of the absorption band at 293 mμ at 25°.

3. Discussion

3.1. *Nature of the species having an absorption band at* 293 mμ

Since solutions of both methanol and ethanol in 98 per cent sulphuric acid are transparent above about 200 mμ, the 293mμ band cannot be ascribed to alkyl hydrogen sulphates, which are formed under these conditions. Also, since methyl sulphonic acid has no absorption in this region, it is unlikely that alkyl sulphonic acids are responsible. There is no apparent reason why alkyl oxonium ions, such as $Me_3COH_2^+$ should absorb in the near ultraviolet region, and since solutions of *tert.* butanol have no absorption in this region at zero time but have an extrapolated i factor of two at zero time [16], it is probable that $Me_3COH_2^+$ is formed very rapidly, and is, indeed, transparent in this region.

Other than carbonium ions, it is difficult to understand what compound could be formed in sulphuric acid which has an absorption band at 293 mμ, unless it is an oxidation product, as postulated by Matsen *et al.* [5]. This has been considered in detail (§ 2.7) and we conclude that both oxidation and disproportionation are insignificant under our conditions.

The relative rates of formation from corresponding olefins, alcohols and alkyl halides are in accord with the carbonium ion postulate and detailed comparison of the rates for butyl halides with rates for S_N1 reactions of these compounds in water seem also to support the postulate (§ 3.4). The dependence upon the H_0 acidity function rather than on the J_0 function [17] suggests that the equilibrium being followed is loss of a proton to give *iso*butene, rather than addition of water to give the alcohol. This observation is strongly supported by the rapid reformation of the 293 mμ band on re-acidification: had alcohol or polymer been formed this should have been a slow process.

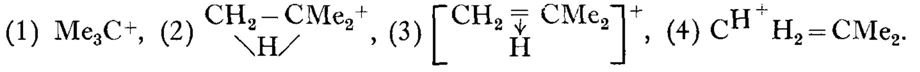
In order to utilize the results for trimethylborine, a search has been made for other compounds of similar structure, differing only in the atomic number of the central atom. A suitable series is borate, carbonate and nitrate. The first electronic absorption band for borate is well below 200 mμ, that for carbonate is at about 220 mμ and that for nitrate is in the 310 mμ region. The energy difference between the carbonate and nitrate bands is 14 000 cm^{-1} which is close to that now postulated for trimethylborine and trimethyl carbonium ions (15 800 cm^{-1}). This comparison is only valid if the transitions involved are comparable: this is discussed in § 3.3.

Since we can discover no other explanation for the spectra reported we will assume, in the following, that our postulate is correct.

3.2. *Structure and solvation of carbonium ions*

Before considering the nature of the electronic transition, it seems desirable to discuss the structure of alkyl carbonium ions, and the influence of solvent on their structure.

Bethell and Gold [3] have discussed carbonium ions in terms of 'classical' and 'non-classical' bridged structures such as (1), and (2) or (3)

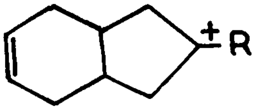


$$(1)\ Me_3C^+,\ (2)\ \underset{\diagdown H \diagup}{CH_2-CMe_2}{}^+,\ (3)\ \left[CH_2 \underset{H}{\overset{-}{\underset{\downarrow}{=}}} CMe_2\right]^+,\ (4)\ C^{H^+}H_2=CMe_2.$$

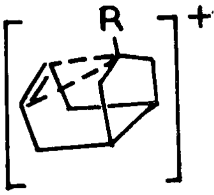
By analogy with trimethylborine, it seems most likely that (1) is the best representation [18], and that (2) or (3) are better described as transition states for the rearrangement of the ion $Me_2CHCH_2^+$ to Me_3C^+. From another viewpoint one can say that, in so far as structures such as (4) make an important contribution to the ground state of (1), the structures (2) or (3) are less probable because one only of the nine β-hydrogen atoms has been selected.

Comparison of the spectra of Me_3C^+ and Et_3C^+ shows that there is a very small shift to lower energy when methyl is replaced by ethyl. This could involve changes in either ground or excited states or both, and is too small to warrant discussion. The marked decrease in intensity when methyl is replaced by ethyl is discussed in § 3.3.

Recently, the spectrum of an ion thought to have the structure (V, R = Me) has been reported [19]:



(V)



(VI)

The ultra-violet spectrum was characterized by an intense band at 295 mμ having an extinction coefficient of $7{\cdot}5 \times 10^3$, in 60 per cent sulphuric acid. The authors infer that this is the spectrum of a bridged carbonium ion (VI, R = Me). Their spectrum, however, is closely similar to that assigned to the tri-methyl carbonium ions, which suggests that, if the double band does interact with the positive carbon, ground and excited states are equally stabilized. In view of the conclusion drawn in the next section, that the transition involves movement of electrons from methyl towards the central carbon, this coincidence would appear to be unlikely. Leal and Pettit's conclusion regarding the bridged structure is based largely on an analogy with the corresponding ion in which methyl is replaced by phenyl (V, R = Ph). The *cis* isomer gave, in 60 per cent sulphuric acid, a spectrum closely similar to that for phenyl dimethyl carbonium ions [6], the intense band at 390 mμ assigned to the latter ions being split into a doublet at 390 and 405 mμ. In this instance, the *trans* isomer was also studied, but in 60 per cent sulphuric acid, no band could be detected in the 400 mμ region. In view of the results for simple monoaryl carbonium ions [6], we conclude that the difference in behaviour of the *cis*- and *trans*-compounds is to be understood not so much in terms of delocalization of electrons and consequent spectral modification implied in the 'non-classical' structure (VI, R = Ph), but in the different reactivities expected for the two compounds. Thus, the *cis*-ion, for steric and electrostatic reasons, will not be readily protonated on the double bond, and hence dimerization or other reactions which may occur when the *trans*-compound is dissolved in 60 per cent sulphuric acid are avoided. Indeed, it is conceivable that carbonium ion formation from the *cis*-alcohol proceeds *via* initial protonation of the double bond followed by the formation of an internal ether.

Our results with secondary alcohols are not clear cut. Secondary butanol almost certainly rearranges to give trimethyl carbonium ions but the band at

297 mμ obtained from *iso*propanol (and from *n*-propanol after an induction period), is either due to a tertiary carbonium ion derived from a rearranged dimer or polymer, or to dimethyl carbonium ions. The marked sensitivity of the apparent extinction coefficient to change in acidity in 90–100 per cent sulphuric acid in contrast with the behaviour of trimethyl carbonium ions, is in accord with the expected increase in reactivity for secondary carbonium ions. However the proximity of the band to that found for tertiary carbonium ions is unexpected.

3.3. *Nature of the electronic transition*

Since neither methyl nor ethyl carbonium ions could be detected, even in 65 per cent oleum, electron release from alkyl groups must play an important role in stabilizing these ions. The conclusive proof that, in similar free-radicals, hyperconjugation is of considerable importance [20, 21] strongly suggests that it is also the main source of stability in these ions [22]. We have postulated that the electronic transition involves β–C–H bonding electrons, already delocalized by hyperconjugation, and that the transition consists of charge transfer from methyl towards the central carbon atom [10].

The shift of 15 800 cm^{-1} to higher energies when carbon is replaced by boron is in accord with this description of the transition. Indeed, the energy gap is close to that between the first bands for nitrate and carbonate (see above). The transition for these ions is thought to involve transfer of electrons in non-bonding orbitals on oxygen to a π-type level largely on the central atom [23], and is thus very similar to that proposed for the carbonium ions.

A further check on the reasonableness of the assignment may be obtained by computing the energy of a cycle in which an electron is withdrawn from methyl and placed on the central carbon. This can be effected, albeit crudely, by subtracting the ionization potential for *tert.* butyl or *iso*propyl radicals from that for methane. This gives 5·57 and 5·1 ev respectively for the transition, which may be compared with the experimental value of 4·23 ev.

Muller and Mulliken have used a procedure based on the LCAO MO approximation to calculate hyperconjugation energies in alkyl radicals and carbonium ions, the very large stabilization energies found for carbonium ions being attributed to the combined effects of hyperconjugation and charge redistribution [22]. Using their model, it would seem that we are concerned with transitions involving electrons in quasi-π group orbitals having nodes in the plane of the carbon atoms. For the trimethyl carbonium ion, six π-electrons are assigned to three such orbitals, and will be largely localized on the three methyl groups, whilst the excited level will be largely localized on the central carbon, being similar to the half-filled orbital in the corresponding radical. Of the three occupied levels, one is symmetrical, and the transition would be forbidden: the other two form a degenerate pair, and it is this level that is thought to be involved in the observed transition.

Using the results of Muller and Mulliken for trimethyl carbonium ions and the corresponding radicals, we estimate a transition energy of about 3·87 ev. Again, our approach is very approximate, but the result does suggest that our assignment is reasonable.

The extinction coefficient for triethyl carbonium ions is about two-thirds that of trimethyl carbonium ions. This may be linked to the conformational requirements for suitable overlap between orbitals involved in the transition.

The small value for dimethyl ethyl carbonium ions, which has been confirmed in numerous experiments, is then anomalous, but may possibly be linked to the suggestion that the orbital involved for trimethyl carbonium ions is doubly degenerate. A change in symmetry might lift this degeneracy, but the decrease, also observed for diethylmethyl carbonium ions (table 1), is not found for methyl-*cyclo*hexyl carbonium ions.

3.4. *Reaction rates*

Our original aim in measuring the rates of growth of the band at 293 mμ was to shed further light on the postulate that this band is due to carbonium ions, rather than to compare rates within the context of this postulate. For this reason a detailed presentation and discussion of reaction rates is deferred to a future report.

The observations that, from *iso*butene the band is developed within less than a minute of the time of mixing, grows according to a first-order rate law over a period of several hours from *tert.* butyl chloride and only appears at all after 24 hours for solutions of *sec.* butyl chloride, are all in qualitative accord with the carbonium ion postulate. Detailed comparison with rates reported for reactions thought to proceed by rate determining ionization of alkyl halides (S_N1 mechanism) is not possible since S_N1 reaction rates are markedly dependent upon the solvent polarity. However, some relevant data are listed in table 2, and it may be noted that the rate of hydrolysis of *tert.* butyl chloride in water is very close to the rate of growth of the band at 293 mμ in sulphuric acid. Since both water and sulphuric acid have very high dielectric constants and since the rate of growth of the band is insensitive to addition of water within the region 80–100 per cent sulphuric acid, we conclude that this close agreement is further evidence for the validity of our postulate.

Compound	Medium	Rate × 10^4 sec^{-1}	Induction period	S_N1 rate × 10^4 sec^{-1}
n-BuOH	98 per cent H_2SO_4	3·1	5–10 min	
iso-BuOH	,,	7·0	,,	
*sec.*BuOH	,,	3·8	Very small	
	80 per cent H_2SO_4	3·5	,,	
*tert.*BuOH	98 per cent H_2SO_4	3·5	Nil	
	80 per cent H_2SO_4	3·3	,,	
*tert.*BuCl	98 per cent H_2SO_4	8·0	,,	13‡
*sec.*BuCl	,,	*ca.* 10^{-3}–10^{-4}†		*ca.* 10^{-4}‡

Table 2. Rate constants for the formation of carbonium ions in sulphuric acid and relevant data for solvolyses.

† An approximate value based on readings taken over a period of days.

‡ The rate for *tert.* butyl chloride refers to 60 per cent aqueous ethanol (Ingold, *Structure and Mechanism in Organic Chemistry*, Bell and Sons Ltd., London, 1953, p. 349), and the rate for *sec.*butyl chloride has been estimated approximately from the rate data for the corresponding bromides in formic acid (*ibid.*, p. 321).

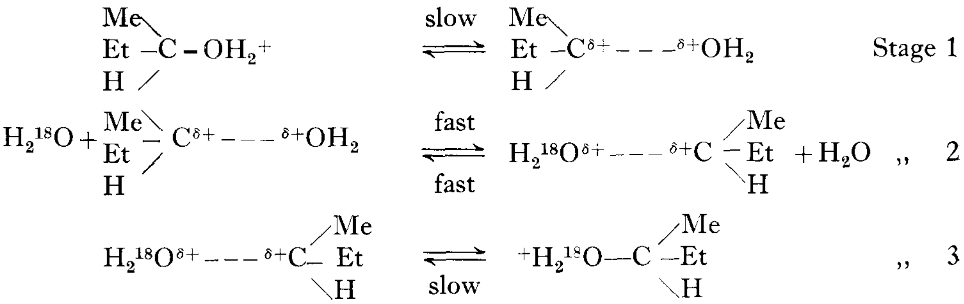
The rates of growth of the 293 mμ band from solutions of the butanols are less readily interpreted. Dostrovsky and Klein measured the rate of oxygen exchange for *tert.* butanol in dilute aqueous sulphuric acid [24], and from their data one can obtain an approximate value for the first-order rate constant assigned to reaction (5):

$$ROH_2^+ \longrightarrow R^+ + H_2O. \qquad (5)$$

The value obtained is at least one-hundred fold greater than the rate constant derived from our data. To obtain this result we have used a value of $-3{\cdot}0$ for the pK of *tert.* butanol [25]: this value is extrapolated from data for primary and secondary alcohols but it is very unlikely to be in error by as much as two pK units. The rate of growth of the band at 293 mμ is almost independent of the concentration of sulphuric acid in the 80–100 per cent region but falls off rapidly at lower acidities. This result is in accord with a pK of about $-3{\cdot}0$ for *tert.* butanol since protonation would then be effectively complete in 80 per cent sulphuric acid. If these assignments are correct it would seem that the pK value for *tert.* butanol and *iso*butene are quite similar.

The first order rate constant for *sec.* butanol is remarkably close to that for *tert.* butanol (table 2). In contrast, the rate of oxygen exchange and racemization in aqueous perchloric acid reported by Bunton *et al.* [26] is very slow compared with that of oxygen exchange for *tert.* butanol [24], though the rate still appears to be somewhat faster than we would predict from our results. It is conceivable that *sec.* butanol is converted into *sec.* butyl hydrogen sulphate by a direct displacement process prior to carbonium ion formation: this is, however, rather improbable because formation of alkyl hydrogen sulphates involves attack by the free alcohol on sulphuric acid. Under our conditions the alcohol is largely converted into its conjugate acid, ROH_2^+, which would probably not react.

It is noteworthy that Bunton *et al.* found that each step involving oxygen exchange was accompanied by an inversion of configuration. Nevertheless, they describe the reaction as of the S_N1 type: their formulation, modified in order to comply with symmetry requirements, being



The S_N1 assignment is based largely on the observation that the rate follows Hammett's acidity function, H_0, rather than the acid concentration. This is commonly thought to establish that a molecule of water does not enter into the kinetic expression for the rate-determining step [17], and hence they rejected the alternative that stage 2 of their mechanism was rate-determining. There are so many exceptions to this generalization that, taken alone, such evidence is not compelling [27]. If our results are correct, then it seems probable that, for protonated alcohols, but not halides, these displacements are not S_N1 in type, and that stage 2 of the above mechanism is rate-determining. However, results over a far wider range of conditions are required before this can be verified.

3.5. *Polymerization and rearrangements*

The results with *di-iso* butylene give good evidence that polymerization is not an important reaction under our conditions. The ' instantaneous ' build up of a band in the 293 mμ region, followed by a further relatively slow growth until the apparent extinction coefficient had grown from about 5×10^{-3} to $10{\cdot}4 \times 10^3$ is most readily explained by the postulate that depolymerization occurred to give, finally, two moles of *tert.* butyl carbonium ions per mole of di-*iso* butylene :

$$Me_3CCH{=}CMe_2 + 2H^+ \rightleftharpoons 2Me_3C^+. \qquad (6)$$

Finally, the results with *normal*, *iso*, and *sec.* butanols are best understood in terms of the postulate that, in each case, rearrangement to trimethyl carbonium ions occurs. For the two primary alcohols there is an induction period during which no absorption in the near ultra-violet can be detected: it is hoped that detailed kinetic studies will shed some light on these rearrangements.

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