THE BEHAVIOUR OF ORGANIC COMPOUNDS IN SULPHURIC ACID

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Numerous observations have been recorded which relate to whether an organic compound is dissolved, not dissolved, or decomposed by sulphuric acid: and if dissolved, whether or not it is recoverable by dilution; and whether or not the solution is coloured. Such observations have been of value in qualitative organic analysis, but for many years they remained empirical. The study of the nature of solutions of organic substances in sulphuric acid was initiated by Hantzsch,[1] who made a cryoscopic investigation of a wide range of compounds in 100% sulphuric acid. The interest which this work aroused has in recent years considerably intensified.

Before reviewing in detail the behaviour of various groups of organic compounds, we shall consider why this subject has been so extensively studied. Four important reasons may be distinguished.

(1) The wide variety of ways in which organic substances behave when treated with sulphuric acid itself provokes interest. This may be illustrated by considering the effect, at room temperature, of sulphuric acid on the following compounds: benzene, glucose, benzyl alcohol, methyl benzoate, ethanol, methyl mesitoate, and dicinnamylideneacetone. Benzene does not dissolve, glucose is charred, and benzyl alcohol instantly forms an insoluble pink resin. The remaining substances dissolve, but if the solutions are immediately diluted with ice-water, these further results are found: the methyl benzoate is precipitated unchanged, the ethanol is found to have been esterified, the methyl mesitoate hydrolysed, and the dicinnamylideneacetone sulphonated.

(2) By the use of sulphuric acid we can observe the behaviour of organic molecules in an environment of extreme acidity, since sulphuric acid is the most strongly acidic solvent yet studied. Hence, it is not surprising that many substances function as bases in sulphuric acid which from their behaviour in other solvents are not generally considered to have basic properties. These compounds, which ionise according to the equation $X + H_2SO_4 = XH^+ + HSO_4^-$, include, for example, many ketones, carboxylic acids, and even some aromatic hydrocarbons. It is possible to study the relative basicities of such extremely weak bases by accurate cryoscopic and spectrometric measurements. Certain compounds ionise in a more complex fashion, to give stable cations that are of great interest. Examples are the nitronium ion NO_2^+ from ethyl nitrate, the mesitoyl ion $(CH_3)_3C_6H_2{\cdot}CO^+$ from mesitoic acid, and the triphenylcarbonium ion Ph_3C^+

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[1] *Z. physikal. Chem.*, 1907, **61**, 257.

from triphenylmethanol. All these ions are acids in the Lewis sense, and can exist only in a strongly acidic medium where the anions that are present are only very weakly basic.

(3) Many colourless or slightly coloured substances produce intensely coloured solutions in sulphuric acid. Such observations, which are often very striking, account for much of the early interest in this subject.

(4) Sulphuric acid has certain properties which render it an excellent cryoscopic solvent.[2] The development of a relatively simple yet accurate technique for cryoscopic measurements in sulphuric acid, and the fact that for this solvent the interpretation of the results in terms of the mode of ionisation of the solute is simple and in the majority of cases unambiguous, have provided further incentives for research on sulphuric acid solutions.*

The cryoscopic method, first used by Hantzsch, has remained the most important, although it has been supplemented by spectrometric and electrical conductivity measurements. Coupled with the physical methods, the chemical examination of dilution products has been of essential importance.

We shall be concerned in this Review almost exclusively with the behaviour of compounds dissolved in 96—100% sulphuric acid at temperatures from 0° to 35°. It may perhaps seem surprising that under these conditions very many organic compounds are stable, in the sense that they undergo neither complete decomposition by oxidation or dehydration, nor extensive sulphonation. Sulphuric acid is, however, a rather weak oxidising agent at ordinary temperatures. Moreover, 100% sulphuric acid and slightly aqueous sulphuric acid contain only very small concentrations of the active sulphonating agent sulphur trioxide or HSO_3^+. Reactive compounds which might be expected to sulphonate readily often do not do so because their activating groups become protonated, and hence, deactivating.

No quantitative measurements of the solubility of organic substances in sulphuric acid have been reported, but qualitatively they fall fairly clearly into two groups : soluble and insoluble. The former group contains most of the oxygen-, sulphur-, and nitrogen-containing compounds, and some aromatic hydrocarbons, while the latter group includes the paraffins, benzene and naphthalene, and alkyl and aryl halides. Solution in sulphuric acid may be regarded as a primarily chemical process ; only those compounds containing basic groups or atoms which can be protonated or can form hydrogen bonds with the sulphuric acid dissolve appreciably.

Paraffins.—Ingold, Raisin, and Wilson [3] were the first to show that hydrogen exchange occurs between paraffins and sulphuric acid. It has recently been found that such exchange occurs readily only in the cases of hydrocarbons that contain hydrogen atoms on tertiary carbon atoms (tertiary hydrogens). The mechanism of the exchange process has been established by studies of the racemisation of optically active paraffins in

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[2] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473. [3] *J.*, 1936, 363, 1643.

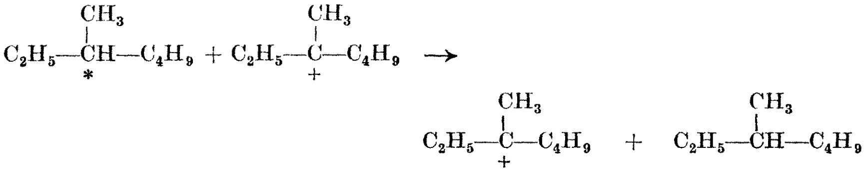
* The results of cryoscopic measurements are generally expressed in terms of the *i*-factor or the ν-factor of the solute. The former is an approximate and the latter an exact measure of the number of kinetically separate, dissolved particles that are produced by the addition to the solution of one molecule of the solute.[2]

sulphuric acid,[4] and by a detailed mass-spectrographic investigation using mono-deuterated butanes and $[^{13}C_1]$*iso*butane.[5]

The initial step is the formation of a very small concentration of tertiary carbonium ions by oxidation, $R_3CH + 2H_2SO_4 = R_3C^+ + HSO_4^- + SO_2 + 2H_2O$, followed by a chain reaction between the carbonium ions and paraffin molecules involving exchange of hydride ions between tertiary carbon atoms: $R_3C^+ + R_3CH = R_3CH + R_3C^+$. An important postulate of the mechanism is that the carbonium ion intermediate is able to undergo rapid and complete exchange of hydrogen with the sulphuric acid solvent, whereas the hydrocarbon molecules are quite unreactive in this respect. The chains are thought to be terminated by some irreversible side reactions leading to non-volatile products.

This mechanism requires that each paraffin molecule should exchange its tertiary hydrogen with another paraffin molecule and not with the solvent, but should exchange all its remaining hydrogen with the solvent. Moreover, other forms of exchange such as intramolecular exchange of tertiary with primary and secondary hydrogen atoms, should not occur. All these requirements of the mechanism have been tested. It was shown [5] that when *iso*butane is bubbled through 96% sulphuric acid at 25°, hydrogen exchange is the only significant reaction, half conversion being attained in about 3 hours whereas *n*-butane is unchanged by a similar treatment. The rate of exchange is increased by addition of small amounts of *iso*butylene: this is in agreement with the proposed mechanism since the resulting increase in carbonium concentration (see p. 43) will in turn increase the number of reaction chains. The relative lack of reactivity of hydrocarbons containing only primary and secondary hydrogens is considered to be due to primary and secondary carbonium ions' having too short a life in this medium to participate in chain-propagating steps.

The work that has been carried out on the racemisation of optically active hydrocarbons in sulphuric acid is of particular interest since these compounds are extremely resistant to racemisation, and the racemisation of a simple hydrocarbon had not been previously reported. It was found [4] that in 90% or more concentrated acid 3-methylheptane is racemised, the rate being 1/15th of the rate of hydrogen exchange with the acid. The racemisation presumably occurs during the chain-propagating step of the above mechanism, *i.e.*,



$$C_2H_5-\underset{*}{\overset{CH_3}{\overset{|}{CH}}}-C_4H_9 + C_2H_5-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-C_4H_9 \longrightarrow C_2H_5-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-C_4H_9 + C_2H_5-\overset{CH_3}{\overset{|}{CH}}-C_4H_9$$

The carbonium ion involved appears to have a sufficiently long existence to enable it to exchange approximately 15 of its 17 hydrogen atoms with the

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[4] Burwell and Gordon, *J. Amer. Chem. Soc.*, 1948, **70**, 3128.

[5] Otvos, Stevenson, Wagner, and Beeck, *ibid.*, 1951, **73**, 5741.

solvent. The rate of exchange is of the same order as that of other tertiary paraffins but more than 100 times greater than that of *n*-octane. The addition of olefins was again found to increase the rate of exchange and also of racemisation.

The use of sulphuric acid as an isomerisation catalyst has been described in several papers.[6] It appears that under rather more severe conditions than those that we have so far considered, paraffins may undergo not only exchange of hydrogen atoms but also skeletal rearrangements. Thus, when heated at 80° for ten hours with 98% sulphuric acid, 2 : 4-dimethylpentane undergoes 47% conversion into isomers, mainly 2 : 3-dimethylpentane. Here, also, it has been found that reaction occurs much more readily with paraffins which contain tertiary hydrogen : *n*-octane and 2 : 2-dimethylbutane, for example, react only extremely slowly. It seems very probable that carbonium ions are intermediates in these rearrangements also. Sulphuric acid appears to act as a specific catalyst for shifting methyl groups in a paraffin chain. No explanation for this has yet been offered.

Olefins.—The behaviour of olefins in 100% sulphuric acid, with the exception of those containing aryl substituents which are dealt with in the next section, has not been very extensively studied, although much work has been carried out in aqueous acid. But-1-ene, but-2-ene, pent-1-ene, and pent-2-ene all dissolve in 75% or more concentrated sulphuric acid, and on dilution secondary hydrogen sulphates are obtained.[7] *iso*Butylene, trimethylethylene, and 2-methylbut-1-ene dissolve readily in acid as dilute as 60%. In the latter cases dilution with water produces tertiary alcohols, but this is probably due to rapid hydrolysis of the tertiary hydrogen sulphate. It is not unreasonable to suppose, therefore, that in 100% sulphuric acid olefins in general dissolve initially to form alkyl hydrogen sulphates. In all cases except that of ethylene, which gives rise to the stable ethyl hydrogen sulphate, subsequent oxidation and polymerisation reactions occur similar to those taking place in solutions of the corresponding alcohols (see p. 47).

In general, it is found, as has been exemplified above, that olefins which form tertiary hydrogen sulphates dissolve in less concentrated acid than those which form secondary hydrogen sulphates. Moreover, in an acid of a given concentration it is found that olefins which give rise to tertiary hydrogen sulphates dissolve more rapidly than those that give secondary, which in turn dissolve more readily than those which give primary hydrogen sulphates. For example,[8] the rates of solution of ethylene, propylene, and *iso*butylene are in the ratios 1 : 300 : 54,000. It seems reasonable to suppose that the formation of an alkyl hydrogen sulphate occurs by the rate-determining addition of a proton followed by the rapid addition of a hydrogen sulphate ion : the above evidence suggests that the stabilities of primary, secondary, and tertiary carbonium ions increase in this order. This also provides a justification of Markownikoff's rule.

The polymerisation reactions that occur in solutions of olefins in sulphuric

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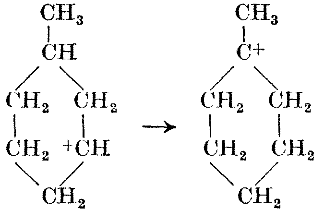
[6] (*a*) Gordon and Burwell, *J. Amer. Chem. Soc.*, 1949, **71**, 2355 ; (*b*) Komarewsky and Ruther, *ibid.*, 1950, **72**, 5501.

[7] Norris and Joubert, *ibid.*, 1927, **49**, 873.

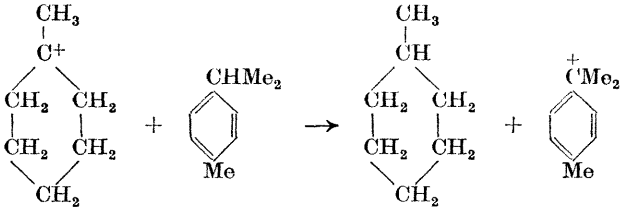
[8] Davis and Schuler, *ibid.*, 1930, **52**, 721.

acid and the alkylation of paraffins by olefins that takes place in the presence of sulphuric acid[9] strongly suggest that carbonium ions are formed by the ionisation of alkyl hydrogen sulphates in sulphuric acid: $RHSO_4 = R^+ + HSO_4^-$. There is no evidence which would lead us to suppose that the degree of ionisation is large, and it seems reasonable to presume that in every case the equilibrium lies well over on the side of the un-ionised hydrogen sulphate. Cryoscopic measurements on solutions of ethyl alcohol (see p. 47) show that ethyl hydrogen sulphate has an *i*-factor of approximately unity. The stability of solutions of ethyl hydrogen sulphate may be plausibly attributed to there being only an exceedingly small concentration of ethyl carbonium ions which causes polymerisation reactions to be very slow. The degree of ionisation of alkyl hydrogen sulphates would be expected theoretically to increase in the series primary $<$ secondary $<$ tertiary, *i.e.*, the stability of the resulting carbonium ion would be expected to increase in this order. This is consistent, for example, with the very slow rate of exchange of hydrogen with sulphuric acid shown by paraffins containing only primary and secondary hydrogens compared with that of those containing tertiary hydrogens, which has been attributed to primary and secondary carbonium ions' having too short a life in sulphuric acid to participate in chain-propagating reactions (see p. **41**).

It appears that generally when possible a primary carbonium ion will rearrange to a secondary, and a secondary to a tertiary; *e.g.*, 4-methyl*cyclo*hexene is reduced to methyl*cyclo*hexane by *p*-cymene in the presence of sulphuric acid,[10] but such reduction does not occur with *cyclo*hexene itself. These facts are explained if it is assumed that the secondary carbonium ion (I) formed initially from 4-methyl*cyclo*hexene rearranges to the tertiary ion (II). Tertiary carbonium ions can accept hydride ions from paraffins which have tertiary carbon atoms (see p. 41): *p*-cymene fulfils this condition and thus methyl*cyclo*hexane is produced:



(I) (II)



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[9] See, *e.g.*, Marschner and Carmody, *J. Amer. Chem. Soc.*, 1951, **73,** 604.
[10] Linsk, *ibid.*, 1950, **72,** 4257.

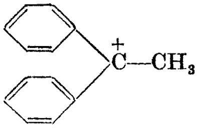
This rearrangement is confirmed by the fact that 4-methyl*cyclo*hexene and 1-methyl*cyclo*hexene both form the same alkylation products with benzene in the presence of sulphuric acid, *i.e.*, 1-methyl-1-phenyl*cyclo*hexane and *p*-di-(1-methyl*cyclo*hexyl)benzene.

Aryl-substituted Olefins.—The formation in sulphuric acid of relatively stable carbonium ions has recently been demonstrated in the case of a number of aryl-substituted olefins. Gold, Hawes, and Tye[11] found that 1 : 1-diphenylethylene gave an *i*-factor of 2·0 and that with 1-α-naphthyl-1-phenylethylene, although the freezing-point depression increased with time, probably owing to sulphonation, extrapolation to zero time showed the initial value of the *i*-factor to be approximately 2. The only reasonable interpretation of these results is that the olefin dissolves to form a carbonium ion, *e.g.*,

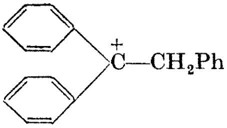
$$Ph_2C{:}CH_2 + H_2SO_4 = Ph_2\overset{+}{C}{\cdot}CH_3 + HSO_4^-$$

Gold and Tye[12] found the ultra-violet spectra of 1 : 1-diphenylethylene, 1-α-naphthyl-1-phenylethylene, and triphenylethylene in sulphuric acid solution to be greatly different from the corresponding spectra in *cyclo*hexane. By dilution of the sulphuric acid solutions, extraction with *cyclo*hexane, and re-determination of the spectra, the original substances were shown to be recovered. The spectra in sulphuric acid were therefore attributed to carbonium ions. The work was complicated by the occurrence of sulphonation, and the spectra were therefore obtained by extrapolation of successive readings to zero time. In each case the change in the spectra after a given time was consistent with the percentage recovery of the original substance on dilution.

The position of attachment of the proton and the relative basicity of these olefins were determined. The spectra in sulphuric acid of 1 : 1-diphenylethylene, triphenylethylene, and also of anthracene were found to be similar with peaks at 3050—3150 and at 4250—4350 Å. The spectrum of 1-α-naphthyl-1-phenylethylene was of similar shape but displaced to higher wave-lengths. These results are readily understood if the positions of protonation are as shown.



(III)



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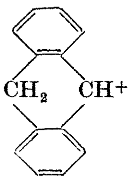

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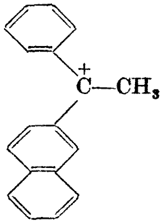

(VI)

In (III), (IV), and (V) resonance of the positive charge can occur in essentially the same conjugated system : in (VI) extended conjugation would be expected to lead to absorption of light at higher wave-lengths.

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[11] *J.*, 1952, 2167.

[12] *J.*, 1952, 2172.

The relative basicities of these compounds were determined by partition experiments between sulphuric acid–water mixtures and *cyclo*hexane, and the following sequence found:[13]

1 : 1-diphenylethylene $\sim$ 1-α-naphthyl-1-phenylethylene $\geqslant$ triphenylethylene $>$ stilbene $\sim$ tetraphenylethylene

(the last two substances are insoluble in sulphuric acid). This order was shown to be in accordance with a theoretical calculation of their basicities by the molecular-orbital method.[14] The qualitative argument will be summarised. Since the basicity of an olefin R depends on the relative stability of R and the conjugate acid RH^+, the effect of structural features on the stability of both R and RH^+ must be estimated in order to determine the relative basicity of the hydrocarbon: $R + H_2SO_4 = RH^+ + HSO_4^-$. It is reasonable to suppose that the stability of RH^+ will depend on the extent to which the positive charge can be delocalised. In the case of aryl-substituted olefins the deciding factor in delocalising the charge is the mesomeric effect of the aromatic nuclei. Thus 1 : 1-diphenylethylene is more basic than stilbene because the positive charge can be shared by resonance more widely in the former than in the latter. The low basicity of tetraphenylethylene and also of stilbene is explained by the fact that in order to form RH^+ in each case a highly conjugated system must be disrupted, with the consequent loss of resonance energy. As might be expected from these considerations, triphenylethylene is intermediate: it is more basic than stilbene but less basic than diphenylethylene.

The carbonium ions so far discussed are of the type $\text{Alkyl(Aryl)}_2\overset{+}{C}$. Newman and Deno[15] have examined a number of compounds cryoscopically to find whether stable carbonium ions containing only one aromatic nucleus are formed. In only one case, that of the mesityldimethylcarbonium ion formed from 1-mesityl-1-methylethylene, could ion formation be clearly demonstrated, and even in this case sulphonation was rapid.

The higher polyenes are known to dissolve in sulphuric acid, the colour of the solution deepening with the length of the chain.[16] Considerations already given suggest protonation as follows:

$$C_6H_5{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}[CH{:}CH]_n{\cdot}C_6H_5$$

Some evidence for this is provided by the fact that 1 : 4-diphenylbutadiene and 1 : 4-bisdiphenylenebutadiene are insoluble in sulphuric acid, whereas 1-diphenylene-4-phenylbutadiene is soluble. This is comparable to the case of stilbene, tetraphenylethylene, and triphenylethylene which has already been discussed.

The conclusion may be drawn that with aryl-substituted olefins the equilibrium $R + H_2SO_4 = RH^+ + HSO_4^-$ lies well over to the right-hand side. In many cases, however, further reactions occur. These include polymerisation and sulphonation, which are probably due to the presence of a small amount of the un-ionised olefin. Thus only those aryl-substituted

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[13] Gold and Tye, *J.*, 1952, 2181.

[14] *Idem*, *J.*, 1952, 2184.

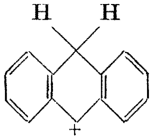
[15] *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

[16] Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 87.

olefins that are sufficiently basic to exist completely in the form of the carbonium ion give stable solutions in sulphuric acid.

Aromatic Hydrocarbons.—Examples of polynuclear hydrocarbons which dissolve in sulphuric acid to form coloured solutions have long been known. It has been found in the cases of perylene,[17] anthracene,[18] and 3 : 4-benzopyrene [19] that the original hydrocarbon can be recovered on dilution with water. The spectra of some of these solutions were measured by Radulescu.[20]

The recent spectroscopic work of Gold and Tye [12] has made it very probable that anthracene and 3 : 4-benzopyrene behave as simple bases forming the carbonium ions (VII) and (VIII). Although benzene is only very slightly soluble in sulphuric acid, its very small basicity is demonstrated by the exchange that occurs with deuterium in deuterosulphuric acid.[21] This reaction presumably involves an activated complex of the type (IX).



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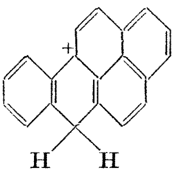

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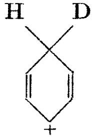


(IX)

Aliphatic Alcohols.—Of the simple alcohols, only methyl and ethyl alcohols have been shown to give stable, colourless solutions in sulphuric acid at ordinary temperatures.[22] They both give approximately 3-fold depressions of the freezing point and yield the alkyl hydrogen sulphate on dilution with water.[23] These results can be interpreted as being due to the rapid formation of the alkyl hydrogen sulphate according to the equation $ROH + 2H_2SO_4 = RHSO_4 + H_3O^+ + HSO_4^-$. A detailed examination of the results of accurate cryoscopic measurements [22] shows further that the alkyl hydrogen sulphate is probably slightly ionised as a base, $RO{\cdot}SO_3H + H_2SO_4 = RO{\cdot}SO_3H_2^+ + HSO_4^-$, or is possibly slightly ionised into a carbonium ion and a hydrogen sulphate ion : $RHSO_4 = R^+ + HSO_4^-$ (see p. 41).

n-Propyl and other straight-chain primary alcohols [22, 23, 24] give initially pale yellow solutions and an approximately 3-fold depression of the freezing point, indicating the formation of the alkyl hydrogen sulphate. The *i*-factors, however, increase markedly with time and obvious subsequent reactions occur leading to a deepening of the colour of the solutions to a dark red or brown, the evolution of sulphur dioxide, and the separation of a colourless hydrocarbon layer. It is impossible to give any interpretation of the *i*-factors for these substances after the solutions have stood for more than a very short time because of the complexity of the reactions

[17] Scholl, Seer, and Weitzenbock, *Ber.*, 1910, **43**, 2202.

[18] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2115.

[19] Berenblum, *Nature*, 1945, **156**, 601.

[20] *Ber.*, 1931, **64**, 2233.

[21] Ingold, Raisin, and Wilson, *J.*, 1936, 1637.

[22] Gillespie, *J.*, 1950, 2542, and unpublished experiments.

[23] Oddo and Scandola, *Gazzetta*, 1909, **39**(II), 1.

[24] Hantzsch, *Z. physikal. Chem.*, 1908, **65**, 41.

and the heterogeneity of the system. Some branched-chain primary alcohols and secondary alcohols give initial *i*-factors between 2 and 3 which increase rapidly with time because of similar reactions to those that occur with most of the straight-chain alcohols.[23] The initial *i*-factors indicate extensive, if not complete, formation of the alkyl hydrogen sulphate. Tertiary alcohols give initial *i*-factors of approximately 2.[23, 24, 25] Thus they appear to give initially an oxonium ion $ROH + H_2SO_4 = RO\overset{+}{H}_2 + HSO_4^-$. This ion probably reacts further to give an alkyl hydrogen sulphate but it does so only slowly and this reaction is masked by simultaneous reactions leading to evolution of sulphur dioxide, colour deepening, etc., as in the case of the secondary and the majority of primary alcohols.

The stability of methyl and ethyl hydrogen sulphate may plausibly be attributed to the fact that the carbonium ions derived from them cannot rearrange to give secondary and tertiary carbonium ions, whereas carbonium ions from other primary alcohols can do so. Secondary and tertiary carbonium ions seem to be much more reactive than primary, and this may be because they are stable enough to exist in significantly large standing concentrations (see p. 42).

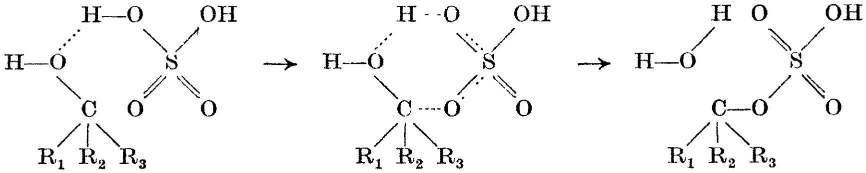
The mechanism of the sulphation process has been investigated by Burwell [25a] and by Newman and Deno [26] who showed that the rate of reaction obeyed the second-order law,

$$\text{Rate} = k_2[\text{ROH}][\text{H}_2\text{SO}_4]$$

for a wide variety of alcohols, and that secondary alcohols always reacted more slowly than primary. They also showed that the sulphation of optically active (+)-butan-2-ol in 96·5% sulphuric acid proceeded in its early stages with nearly complete retention of configuration, although an increasing amount of racemisation occurred as the reaction proceeded. They suggested that this result could be best explained by assuming a mechanism which does not involve the breaking of the alkyl–oxygen bond in the alcohol:

$$\text{RO}{-}\vdots{-}\text{H} + \text{HO}{-}\vdots{-}\text{SO}_3\text{H} \longrightarrow \text{RO}{\cdot}\text{SO}_3\text{H} + \text{H}_2\text{O}$$

and therefore proceeds with complete retention of configuration, followed by a partial racemisation of the formed alkyl hydrogen sulphate. The results could equally well be explained by assuming that sulphation proceeds largely by an internal rearrangement of a hydrogen-bonded complex of sulphuric acid and the alcohol, proceeding with complete retention of configuration followed by a partial racemisation of the formed alkyl hydrogen sulphate:



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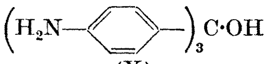
[25] Newman, Craig, and Garrett, *J. Amer. Chem. Soc.*, 1949, **71**, 869.

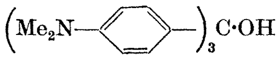
[25a] *Ibid.*, 1942, **64**, 1025; 1945, **67**, 220.

[26] *Ibid.*, 1950, **72**, 3852.

The observation that secondary alcohols are sulphated more slowly than primary alcohols is in accord with the freezing-point evidence that primary alcohols have *i*-factors of 3, secondary between 2 and 3, and tertiary of 2 or a little greater. Tertiary alcohols appear to be sulphated very slowly. No conclusive evidence for the existence of tertiary alkyl hydrogen sulphates has, in fact, been found, but this may well be because they are hydrolysed extremely rapidly during isolation.

Aryl-substituted Alcohols.—It has long been known that when triphenylmethanol is dissolved in sulphuric acid it ionises according to the equation $Ph_3C{\cdot}OH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^-$ to give a stable yellow solution. This mode of ionisation is demonstrated by the absorption spectrum of the solution,[27] which is very similar to that of the electrically conducting solution of triphenylmethyl chloride in sulphur dioxide,[28] by the molar freezing-point depression which is 4 times that of a non-electrolyte,[23, 24] and by the reaction of the sulphuric acid solution with alcohols to form ethers: $Ph_3C^+ + R{\cdot}OH \longrightarrow Ph_3C{\cdot}OR + H^+$. Recently, by means of spectroscopic and cryoscopic measurements, the tri-*o*-methyl-, tri-*p*-methyl-, tri-*p*-chloro-, and tri-*p*-nitro-derivatives of triphenylmethanol, which give stable orange-red solutions, have been shown to ionise in an exactly analogous manner to triphenylmethanol itself.[15] In all cases the methanols are recovered unchanged when their sulphuric acid solutions are poured on ice. The tri-*p*-amino-, tris-*p*-dimethylamino-, and bis-*p*-dimethylamino-derivatives of triphenylmethanol, (X), (XI), and (XII), have also been investigated cryoscopically [3] and found to have *i*-factors of 6·0, 6·0, and 5·7 respectively. These results show that only two of the three NH_2 or NMe_2 groups in (X) and (XI) are protonated, and that the second NMe_2 group of (XII) is incompletely protonated. It appears that the ions obtained from (X) and (XI) are more correctly represented by the quinonoid structure (XIII) than by the more usual carbonium ion formulation (XIV).


(X)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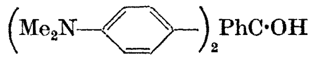
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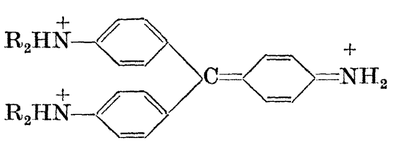
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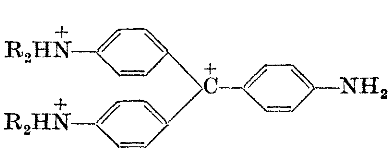
(XIV)

These results are somewhat unexpected in view of the fact that 68% of the carbonium ions from tris-*p*-dimethylaminophenylmethanol add two protons in 1% hydrochloric acid solution [29] which has an acidity measured in terms of the acidity function H_0 approximately ten H_0 units less than that of

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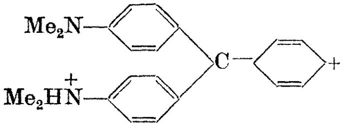
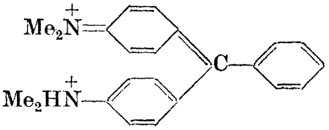
[27] Hantzsch, *Ber.*, 1921, **54**, *B*, 2573; Gold and Hawes, *J.*, 1951, 2102.

[28] Walden, *Ber.*, 1902, **35**, 2018.

[29] Adams and Rosenstein, *J. Amer. Chem. Soc.*, 1914, **36**, 1452.

100% sulphuric acid. The incomplete protonation of the second $\mathrm{NMe_2}$ group of (XII) suggests that, as well as structures such as (XV), the structure (XVI), in which the carbonium charge has been transferred to one of the $\mathrm{NMe_2}$ groups, must contribute strongly to the structure of the singly protonated ion.


(XV)


(XVI)

Diphenylmethanol appears to form the diphenylcarbonium ion in sulphuric acid:[30] on dilution with methyl alcohol, diphenylmethyl methyl ether is formed; but on standing sulphonation and polymerisation occur. Several other diarylmethanols have been investigated, and the only ones that have been found to give stable solutions are di-*p*-chlorophenylmethanol[15] and diphenylmethylmethanol.[12] Both these solutes give *i*-factors of 4, indicating complete carbonium-ion formation. On being poured on ice, the former gives a good yield of bis-4 : 4′-dichlorophenylmethyl ether, and the latter 1 : 1-diphenylethylene.

Benzyl alcohol was first shown by Cannizzaro in 1854 to yield a pink insoluble polymer in sulphuric acid.[31] *p*-Chlorobenzyl alcohol similarly gives a red polymer. Heptamethylbenzyl alcohol and $\alpha : \alpha : 2 : 4 : 6$ pentamethylbenzyl alcohol give *i*-factors which vary rapidly with time but by extrapolation to zero time initial *i*-factors of approximately 4 are obtained.[15] On dilution, the sulphuric acid solution of the pentamethyl alcohol gives 2-mesitylpropylene in a yield which decreases with the time of solution. There is evidence that sulphonation occurs to give water-soluble products. It appears that *p*-nitrobenzyl alcohol,[15] which gives a constant *i*-factor of 3·2 and an uncrystallisable oil on dilution, forms a hydrogen sulphate in the same way as methyl and ethyl alcohols.

There appears to be a marked contrast between the stabilities of solutions of triphenylmethanols in sulphuric acid and those of di- and monophenylmethanols. Whereas all the triphenylmethanols that have been investigated give stable solutions, only two diphenylmethanols and one monophenylmethanol are known which give such solutions. It seems likely that the instability is due to the presence of a small amount of un-ionised methanol which is readily sulphonated or undergoes a polymerisation reaction with the carbonium ion. If this is so it must be supposed that the triarylmethanols are much more completely ionised than the mono- and di-arylmethanols. Now, it is often thought that the triphenylcarbonium ion is stabilised by resonance with structures such as (XVII) which distributes the positive charge among all three aromatic nuclei. There is, however, considerable evidence that the stability of this ion and its derivatives cannot be attributed entirely to this factor. Thus, Szwarc[32] has pointed out that,

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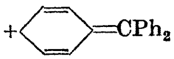
[30] Welch and Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 4748.

[31] *Annalen*, 1854, **92**, 114.

[32] *Discuss. Faraday Soc.*, 1947, **2**, 47.

because of steric hindrance between *ortho*-hydrogen atoms, the molecule cannot have the planar configuration which is necessary for maximum resonance stabilisation; and Newman and Deno[15] showed that both tri-*p*-tolyl- and tri-*o*-tolyl-methanols developed the orange-red colour characteristic of carbonium-ion formation in methyl-alcoholic solution containing only 5% sulphuric acid as compared with 50% of sulphuric acid for triphenylmethanol itself. Clearly, the tritolyl- are considerably more stable than the triphenylcarbonium ions notwithstanding the fact that, as shown by models, the benzene rings in tri-*o*-tolylmethanol must be at an angle of approximately 60° to each other. In the latter case resonance stabilisation can involve only one ring to any significant extent. On the basis of this and other evidence, Newman and Deno have suggested that in all cases resonance stabilisation of these ions involves only one or at the most two of the aromatic rings. This may well be true, and if so, the remarkable stability of the triarylcarbonium ions must be attributed mainly to factors other than resonance stabilisation. First, it seems that there must be considerable delocalisation of the positive charge among the aromatic nuclei by the inductive effect,[33] since otherwise it would be expected that the aromatic nuclei that are not involved in resonance would be rapidly sulphonated. Secondly, steric factors must be of considerable importance. It seems likely that the stability of the protonated carbinol $Ph_3C{\cdot}OH_2^+$, which is almost certainly the precursor of the carbonium ion, is considerably reduced by relatively large steric repulsions between the phenyl groups and the $\overset{+}{O}H_2$ group which are very much smaller in ions of the type $Ph_2RC{\cdot}\overset{+}{O}H_2$ and $PhR_2C{\cdot}\overset{+}{O}H_2$, where R is an alkyl group or hydrogen. There would similarly be considerable steric hindrance in triarylcarbonium ions to combination with a hydrogen sulphate ion to form the un-ionised alkyl hydrogen sulphate.


(XVII)

Ethers.—Diethyl ether dissolves in sulphuric acid to give an initial *i*-value of 2, which may be attributed to the formation of an oxonium ion,[24, 34] $Et_2O + H_2SO_4 = Et_2\overset{+}{O}H + HSO_4^-$, but on standing, the freezing-point depression slowly increases[35] owing to formation of ethyl hydrogen sulphate, $Et_2O + H_2SO_4 = EtOH + EtHSO_4$, which is followed, of course, by rapid sulphation of the alcohol: $EtOH + H_2SO_4 = EtHSO_4 + H_3O^+ + HSO_4^-$.

In the cases of ethyl, di*iso*propyl, and certain other aliphatic ethers, Oddo and Scandola[34] were able to isolate small quantities of the corresponding alkyl hydrogen sulphate after the ethers had stood for short times in solution in sulphuric acid. In the cases of the higher aliphatic ethers the formed alkyl hydrogen sulphate undoubtedly undergoes further complex reactions as discussed on p. 43. Aromatic ethers have been little investigated but they appear to be insoluble or only very sparingly soluble

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[33] Brand, Horning, and Thornley, *J.*, 1952, 1374.

[34] Oddo and Scandola, *Gazzetta*, 1910, **40**(2), 163.

[35] Gillespie, unpublished experiments.

in sulphuric acid. This may plausibly be attributed to the oxygen lone-pair electrons being less available to accept a proton than the aliphatic ethers because of their participation in resonance structures such as

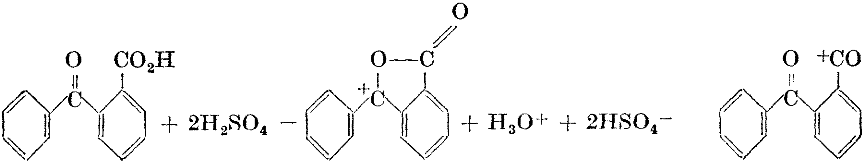
Carboxylic Acids.—A large number of aliphatic monocarboxylic acids were investigated cryoscopically by Hantzsch,[1] and by Oddo and Casalino.[36] With the exception of formic acid, which decomposes, they were all found to give stable solutions and to behave as simple bases : $R{\cdot}CO_2H + H_2SO_4 = R{\cdot}CO_2H_2^+ + HSO_4^-$. Unsubstituted carboxylic acids are in general fully ionised, but the introduction of electron-withdrawing substituents reduces the basicity and the degree of ionisation correspondingly. Thus, whereas acetic acid is fully ionised, the replacement of hydrogen by chlorine successively reduces the basicity until with trichloroacetic acid the ionisation is scarcely measurable.[1]

A number of aromatic acids, *e.g.*, benzoic acid, ionise similarly to the aliphatic acids.[1, 36] The existence of a second type of ionisation was revealed by the work of Treffers and Hammett [37] on mesitoic and certain other acids. Mesitoic acid gives a 4-fold depression of the freezing point : on dilution of the sulphuric acid solution with water, the acid is recovered, but on dilution with methanol, methyl mesitoate is obtained. Treffers and Hammett suggested that the mesitoyl ion is formed according to the equation

$$Me_3C_6H_2{\cdot}CO_2H + 2H_2SO_4 = Me_3C_6H_2{\cdot}\overset{+}{C}O + H_2O^+ + 2HSO_4^-$$

This interpretation has been confirmed by more recent work,[38] and it has been shown, for example, that both 2 : 3 : 5 : 6-tetramethyl- and pentamethyl-benzoic acid have *i*-factors of 4, and ionise similarly to mesitoic acid. 2 : 6-Dimethylbenzoic acid and 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acid, which have *i*-factors of 3·5 and 2·4, respectively, are believed to ionise partly in the above " complex " manner and partly as simple bases.

A very similar type of ionisation has been observed in certain aromatic keto-acids. For instance, Newman, Kuivila, and Garrett [39] found that *o*-benzoylbenzoic acid has an *i*-factor of 4, which was considered to indicate the following ionisation :



(XVIII)

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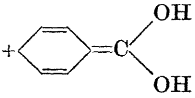
[36] *Gazzetta*, 1917, **47**(2), 200.
[37] *J. Amer. Chem. Soc.*, 1937, **59**, 1758.
[38] Newman and Deno, *ibid.*, 1951, **73**, 3651.
[39] *Ibid.*, 1945, **67**, 704.

Chemical evidence was obtained in favour of the cyclic ion, and against the alternative formulation (XVIII).

Other acids which appear to behave in a similar manner are *o*-mesitoylbenzoic, 1 : 8-naphthaldehydic, and 4 : 5-phenanthraldehydic acid, which have *i*-factors of 3·68, 3·94, and 3·66,[38] respectively. In two of these cases the complex ionisation appears to be considerable though not complete, and is probably accompanied by a certain amount of simple basic ionisation.

The factors which cause the occurrence of the complex types of ionisation in certain structures are not entirely clear. In the first group of substances it appears that two *ortho*-substituents are necessary. This suggests that steric factors are important. Thus, whereas mesitoic acid has an *i*-factor of 4, 2 : 4 : 5- and 3 : 4 : 5-trimethylbenzoic acids [37] have *i*-factors of only 2. This can be attributed to steric inhibition of resonance by the other substituents, since the conjugate acid of the carboxylic acid will be stabilised by structures such as (XIX) in which the protonated carbonyl group is in the plane of the aromatic ring. When coplanarity is prevented by other substituents, it is conceivable that the acyl ion becomes the more stable form, and for this reason complex ionisation occurs. In addition, however, it appears that a number of electron-donating groups must also be present in order to stabilise the acyl ion. For example, 2 : 6-dimethylbenzoic acid has an *i*-factor of 3·5, but 2 : 6-dibromobenzoic acid and 3-nitro-*o*-toluic acids have *i*-factors of only 2.[37] Again, whereas mesitoic acid has an *i*-factor of 4, 3 : 5-dibromomesitoic acid has an *i*-factor of only 2·4.



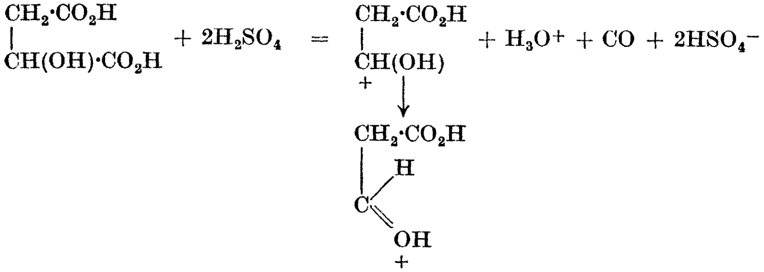
(XIX)

In the case of the second group of compounds, exemplified by *o*-benzoylbenzoic acid, steric inhibition of resonance is again probably of importance, although here only one *ortho*-group is present. The cyclic ion is stabilised by resonance, which leads to the distribution of the positive charge over two aromatic nuclei. When this is possible, it appears that other electron-donating substituents are not necessary. In agreement with this interpretation is the fact that phthaldehydic acid has an *i*-factor of only 2·2 : [38] this may be due to a very small amount of complex ionisation, but more probably to the addition of an average of 1·2 protons to the carbonyl and carboxyl groups.

A number of carboxylic acids, both aromatic and aliphatic, are unstable in sulphuric acid, and decompose to give carbon monoxide according to the general equation $R{\cdot}CO_2H + 2H_2SO_4 = R^+ + CO + H_3O^+ + 2HSO_4^-$. This decomposition appears to occur generally when R^+ is a stable ion in sulphuric acid, or can give rise to a stable ion by further decomposition. Thus it is observed with formic acid ($R^+ = H^+$) and oxalic acid

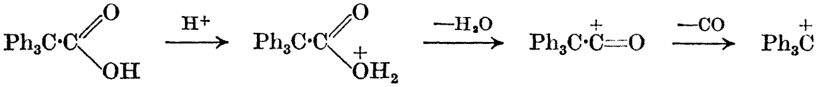
$(R^+ = \overset{+}{C}O_2H \rightarrow CO_2 + H^+)$, generally with α-keto- and α-hydroxy-carboxylic acids, *e.g.*,

$$Ph\cdot CO\cdot CO_2H + 2H_2SO_4 = Ph\cdot CO^+ + CO + H_3O^+ + 2HSO_4^-$$



$$\begin{array}{l}CH_2\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{array} + 2H_2SO_4 = \begin{array}{l}CH_2\cdot CO_2H\\ |\\ CH(OH)\\ +\end{array} + H_3O^+ + CO + 2HSO_4^-$$

and with triphenylacetic acid $(R^+ = Ph_3C^+)$. The kinetics of the decomposition have been studied in the cases of formic,[40] oxalic,[41] citric,[42] benzoylformic,[43] triphenylacetic,[44] and malic acids.[45] In each case the reaction is of first order with respect to the organic compound, and in each case the rate increases markedly with increasing sulphuric acid concentration over that part of the range 90—100% sulphuric acid that was investigated. The mechanism of the reaction has not been definitely established in any case, but it seems probable that it occurs by an initial rapid proton addition, followed by elimination of a water molecule and the breakdown of the resulting carbonium ion to yield carbon monoxide, one of the last two stages being rate-determining, *e.g.*,



No satisfactory quantitative explanation of the increase in rate with increasing sulphuric acid concentration has yet been proposed.

Carboxylic Acid Anhydrides.—Gillespie [46] investigated acetic anhydride and benzoic anhydride cryoscopically and found that both substances give four particles per molecule in sulphuric acid. He considered that these anhydrides ionise as follows :

$$(R\cdot CO)_2O + 2H_2SO_4 = R\cdot CO^+ + R\cdot CO_2H_2^+ + 2HSO_4^-$$

The only reasonable alternative is given by the equation :

$$(R\cdot CO)_2O + 3H_2SO_4 = 2R\cdot CO\cdot HSO_4 + H_3O^+ + HSO_4^-$$

The former ionisation was preferred because it is difficult to think of any mechanism for the latter that does not involve the intermediate formation of the corresponding carboxylic acid which is then converted into the acyl hydrogen sulphate, and it is known that neither acetic acid nor benzoic

[40] (*a*) Schienz, *J. Amer. Chem. Soc.*, 1923, **45**, 447 ; (*b*) De Right, *ibid.*, 1933, **55**, 4761.

[41] Lichty, *J. Phys. Chem.*, 1907, **11**, 225.

[42] Wieg, *J. Amer. Chem. Soc.*, 1930, **52**, 4729.

[43] Elliott and Hammick, *J.*, 1951, 3402.

[44] Dittmar, *J. Amer. Chem. Soc.*, 1929, **51**, 533.

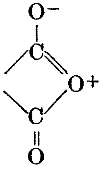
[45] Whitford, *ibid.*, 1925, **47**, 953.

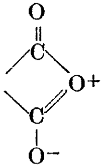
[46] *J.*, 1950, 2997.

acid is in fact converted into the corresponding acyl hydrogen sulphate in sulphuric acid (see p. 52).

However, it has recently been shown that the electrical conductivities of solutions of these anhydrides in sulphuric acid correspond much more closely to the formation of one hydrogen sulphate ion per molecule of anhydride than to the formation of two,[47] which supports the second mode of ionisation rather than the first. It must be concluded that the mode of ionisation of these anhydrides has not yet been definitely established.

A number of cyclic anhydrides have also been investigated. Hantzsch originally concluded that phthalic anhydride behaves as a non-electrolyte, but Gillespie[35] has recently shown that it has a ν-factor of 1·3. Oddo and Casalino[48] obtained an *i*-factor of 1·5 for succinic anhydride, and Newman and Deno[38] an *i*-factor of 1·8 for 1 : 8-naphthalic anhydride, which they showed to be completely recovered on dilution. Presumably these cyclic anhydrides undergo incomplete protonation. They are rather surprisingly weak bases and this may perhaps be attributed to a fairly large resonance energy in the anhydride group arising from resonance between the structures (XIX*a*) and (XX) which are of equal energy. This resonance energy is largely lost on protonation, since the group is no longer symmetrical and the canonical structures, (XXI) and (XXII), are of unequal energy.


(XIX*a*)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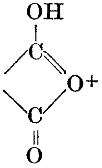
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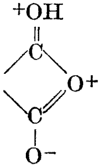
(XXII)

Esters.—The esters of carboxylic acids in general undergo solvolysis in sulphuric acid, and when the sulphuric acid solutions are poured into water the free carboxylic acids are obtained. At room temperature a number of esters such as methyl and ethyl benzoate and ethyl acetate undergo solvolysis only slowly. They give *i*-factors of 2 owing to protonation, $R{\cdot}CO_2R' + H_2SO_4 = R{\cdot}CO_2R'H^+ + HSO_4^-$, and on pouring the sulphuric acid solution into water after short storage, the esters are recovered in good yield.[1, 34, 50] The kinetics of solvolysis of methyl and ethyl benzoate and methyl *p*-toluate have been studied in sulphuric acid containing small quantities of water.[49] It was found that the rate is approximately independent of the concentration of water and is of first order with respect to the ester. Ethyl benzoate was found to react more slowly than methyl benzoate, whereas methyl *p*-toluate reacts more rapidly. A larger number of esters have been studied in a less quantitative manner by Kuhn and Corwin[50] and by Kuhn.[51] The esters were dissolved in 100% sulphuric

[47] Gillespie and Wasif, unpublished experiments.

[48] *Gazzetta*, 1917, **47**(2), 232.

[49] Graham, Ph.D. Thesis, London, 1943.

[50] Kuhn and Corwin, *J. Amer. Chem. Soc.*, 1948, **70**, 3370.

[51] Kuhn, *J. Amer. Chem. Soc.*, 1949, **71**, 1575.

acid at room temperature, the solutions were poured into water after " several minutes' " standing, and the carboxylic acids formed were isolated. The yield of acid obtained in each case is recorded in Table 1.

TABLE 1

Ester	Yield of carboxylic acid, %	Ester	Yield of carboxylic acid, %
(1) Ethyl benzoate	0	(8) 2-Ethoxyethyl 3 : 5-dichlorobenzoate	0
(2) Chloroethyl benzoate	1	(9) 2-Ethoxyethyl *p*-nitrobenzoate	0
(3) Trichlorethyl benzoate	43	(10) *iso*Propyl benzoate	36
(4) 2-Ethoxyethyl benzoate	33	(11) *tert.*-Butyl benzoate	74
(5) Ethyl *p*-anisate	18	(12) Methyl *p*-anisate	48
(6) Chloromethyl *p*-anisate	87	(13) *iso*Propyl *p*-anisate	76
(7) 2-Ethoxyethyl *p*-anisate	100		

Provided that it can be assumed that all the solutions were stored for the same time before dilution, the yield of acid gives a rough measure of the rate of solvolysis. Results 1—4 show that the rate of solvolysis of $R{\cdot}CO_2R'$ is increased by the substitution of electron-attracting atoms or groups in R′. [It is reasonable to assume that the ethereal oxygen in 2-ethoxyethyl esters is at least partly protonated in 100% sulphuric acid (see p. 51).] Result 5 shows that the rate of solvolysis is increased by the substitution of electron-donating groups in R. The combined effect of electron-attracting groups in R′ and electron-donating groups in R is shown by results 6 and 7, and the effect of electron-attracting groups in R′ opposed by electron-attracting groups in R is seen in results 8 and 9. Results 10, 11, and 13, however, appear to be inconsistent, since it would be expected in view of the preceding results that electron-donating groups in R′ would decrease the rate, whereas it appears that the substitution of ethyl by *iso*propyl and *tert.*-butyl increases the rate. Thus when R′ is an alkyl group the rate order appears to be $Me > Et < Pr^i < Bu^t$. A plausible explanation of these observations is that a change in mechanism occurs between the ethyl and the *iso*propyl esters.

There are, in principle, four mechanisms by which the solvolysis of esters in sulphuric acid might occur : they are quite analogous to the four mechanisms proposed by Day and Ingold [52] for acid-catalysed ester hydrolysis. These are uni- and bi-molecular solvolysis with acyl–oxygen fission, A_1' and A_2', respectively, and uni- and bi-molecular solvolysis with alkyl–oxygen fission A_1'' and A_2''. The overall equations representing these mechanisms for solvolysis in sulphuric acid may be written

$$A_1' \;\&\; A_2' \begin{cases} R{\cdot}CO{\cdot}OR' + 3H_2SO_4 \\ \qquad = R{\cdot}CO{\cdot}SO_4H + R'HSO_4 + H_3O^+ + HSO_4^- & i = 4 \\ R{\cdot}CO{\cdot}OR' + 3H_2SO_4 = R{\cdot}\overset{+}{C}O + R'HSO_4 + H_3O^+ + 2HSO_4^- & i = 5 \end{cases}$$

$$A_1'' \;\&\; A_2'' \quad R{\cdot}CO{\cdot}O{\cdot}R' + 2H_2SO_4 = R{\cdot}CO_2H_2^+ + R'HSO_4 + HSO_4^- \qquad i = 3$$

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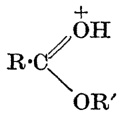
[52] *Trans. Faraday Soc.*, 1941, **37**, 686.

It should be noted that the fact that the product of solvolysis obtained in each case after dilution is a carboxylic acid gives no information about the mechanism of solvolysis, since the acyl hydrogen sulphate or acyl ion produced by acyl–oxygen fission would almost certainly be very rapidly hydrolysed by water. It is, however, possible to obtain some information about the mechanism by means of the *i*-factor measured when solvolysis is complete. Thus, as has been indicated above, acyl–oxygen fission leads to an *i*-factor of 4 or 5, whereas alkyl–oxygen fission leads to an *i*-factor of 3, provided that the carboxylic acid formed undergoes no further reaction except simple protonation.

As already mentioned, methyl benzoate gives an *i*-factor of 2 at room temperature, and this changes only very slowly on long standing. Newman, Craig, and Garrett [25] showed, however, that on heating to 45° or higher for short times (less than 1 hour), the *i*-factor increases to approximately 3. The greatest value that they obtained was 3·32 after 15 minutes' heating at 90°. When this solution was poured into water, 81% of the original ester was isolated as benzoic acid. This result suggests that under these conditions methyl benzoate undergoes complete solvolysis by alkyl–oxygen fission mechanism. The fact that an *i*-factor of somewhat greater than 3 was obtained may plausibly be attributed to a small amount of sulphonation at the high temperature employed, and this, together with the small solubility of benzoic acid in water, would account for the less than theoretical yield of benzoic acid.

By assuming that all esters undergo solvolysis in sulphuric acid by alkyl–oxygen fission, and that the change of mechanism that apparently occurs between the ethyl and the *iso*propyl esters is a change from a bimolecular to a unimolecular mechanism, all the observations may be satisfactorily accounted for. It is almost certain that esters are completely mono-protonated, presumably on the carbonyl oxygen (XXIII), and it may



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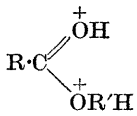

(XXIV)

be assumed that the reactive species is diprotonated (XXIV) and is formed to a different limited extent for each ester. It appears then that the function of electron-donating groups in R, which always appear to increase the rate, is to increase the basicity of the ester and thus the concentration of the diprotonated ion. Electron-attracting groups in R decrease the concentration of diprotonated ions and hence decrease the rate of solvolysis. It would be expected that electron-donating groups in R′ would increase the concentration of diprotonated ions, but they will simultaneously hinder the attack of the nucleophilic reagent (HSO_4^- or H_2SO_4) on the α-carbon atom of R′ and hence decrease the rate, and this appears to be the dominating factor. Thus, when R′ is changed from methyl to ethyl the rate of solvolysis decreases. On passing to *iso*propyl, however, it increases, and this is presumably because the mechanism has changed from bimolecular alkyl–oxygen fission to unimolecular alkyl–oxygen fission; this is in accord with the fact that secondary and tertiary carbonium ions are more stable than primary.

Methyl mesitoate gives a constant *i*-factor of 5.[37] This indicates that it undergoes rapid and complete solvolysis, which could be by acyl–oxygen fission in a manner quite analogous to the free acid:

$$C_6H_2Me_3{\cdot}CO_2Me + 2H_2SO_4 = C_6H_2Me_3{\cdot}\overset{+}{C}O + H_3O^+ + MeHSO_4 + 2HSO_4^-$$

Thus it is possible that the accumulation of electron-donating substituents in R and perhaps also the presence of *ortho*-substituents leads to another change of mechanism, in this case to acyl–oxygen fission. However, the three methyl substituents would be expected to lead to a rapid solvolysis according to the mechanism discussed above with alkyl–oxygen fission:

$$C_6H_2Me_3{\cdot}CO_2Me + H_2SO_4 = C_6H_2Me_3{\cdot}CO_2H_2^+ + MeHSO_4 + HSO_4^-$$

followed by the rapid formation of the mesitoyl ion from the protonated acid:

$$C_6H_2Me_3{\cdot}CO_2H_2^+ + H_2SO_4 = C_6H_2Me_3{\cdot}\overset{+}{C}O + H_3O^+ + HSO_4^-$$

Apparently we cannot yet distinguish between the two possible mechanisms for the solvolysis of methyl mesitoate, although the alkyl–oxygen fission mechanism is lent some support by the fact that, whereas *o*-benzoylbenzoic acid undergoes a complex ionisation like mesitoic acid (see p. 52), yet its methyl ester is solvolysed only very slowly in 100% sulphuric acid, having an *i*-factor of 2; [39] this is in accord with the presence of the deactivating benzoyl substituent in R.

It is noteworthy that esters of mesitoic acid are hydrolysed in the normal way with great difficulty, a fact which is attributed to steric hindrance. Their ionisation in sulphuric acid consequently provides a useful method of hydrolysing such esters. The reverse process, the esterification of such acids, which is also difficult by the usual methods, can also be carried out conveniently by pouring a sulphuric acid solution into the required alcohol. In this way Newman[53] prepared several esters of mesitoic acid.

Aldehydes and Ketones.—Simple aldehydes and ketones such as acetaldehyde, acetone, benzaldehyde, acetophenone, and benzophenone have been shown by cryoscopy to behave as fully ionised bases in sulphuric acid: [1, 2, 36, 37, 38]

$$RR'C{=}O + H_2SO_4 = RR'C{=}\overset{+}{O}H + HSO_4^-$$

The introduction of two *para*-chlorine atoms into benzophenone apparently does not reduce the basicity of the carbonyl group sufficiently to make its ionisation appreciably incomplete since 4 : 4′-dichlorobenzophenone has been reported as having an *i*-factor of 1·99.[38] 4 : 4′-Bisdimethylaminobenzophenone however has an *i*-factor of 3·5,[38] which indicates that both dimethylamino-groups are fully ionised, but that the carbonyl group is

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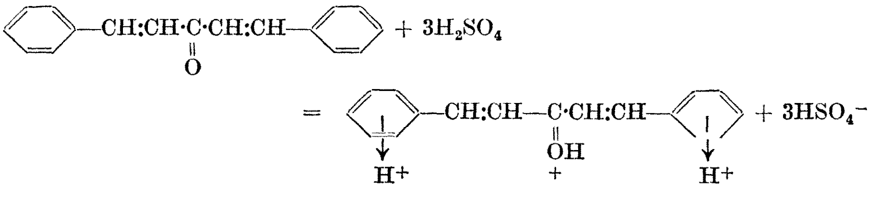
[53] *J. Amer. Chem. Soc.*, 1941, **63**, 2431.

only 50% protonated. Various aromatic ketones containing activating substituents, such as 4 : 4′-dimethoxybenzophenone, mesityl methyl ketone, and dimesityl ketone, have been found to give *i*-factors which increase fairly rapidly to high values, indicating that some reaction other than simple protonation also occurs. Since the reaction products are water-soluble, and no unchanged ketone is recovered on dilution, it is reasonable to suppose that this reaction is sulphonation.

The ionisation in sulphuric acid of unsaturated aryl ketones of the type $Ph{\cdot}[CH{:}CH]_n{\cdot}CO{\cdot}[CH{:}CH]_m{\cdot}Ph$ has provoked considerable interest, for two reasons : first, because several such ketones were found to have unusually high *i*-factors, and secondly, because the solutions are often intensely coloured. Thus, dibenzylideneacetone and cinnamylideneacetophenone were both found to have *i*-factors of 4 : the former gives an orange solution, the latter an intense red. The absorption spectra of ketones of this type have been studied by many workers.[54] The results of such investigations were ambiguous and conflicting, and so different interpretations were put upon them. Thus, Vorlander [55] believed that the colours were due to the interaction of the double bonds with the acid, Hantzsch [56] and Pfeiffer considered that only the carbonyl group was involved, while Kehrmann [54e] considered both to be necessary in order to explain the results. Hantzsch accounted for his cryoscopic results in dibenzylideneacetone by the following complex ionisation :

$$(Ph{\cdot}CH{:}CH)_2CO + 3H_2SO_4 = (Ph{\cdot}CH{:}CH)_2\overset{+}{C}{\cdot}O{\cdot}SO_3H + H_3O^+ + 2HSO_4^-$$

More recently, Dewar [57] has suggested that dibenzylideneacetone is triply protonated, one proton being attached to the carbonyl oxygen, and one to each of the aromatic rings by π-bonds



Recent work [58] has, however, shown that both these explanations of the cryoscopic results are incorrect. For example, it has been found that dicinnamylideneacetone has a constant *i*-factor of 6, a result which cannot be accommodated by either theory. Moreover, many compounds of this type are found to have *i*-factors which increase with time, in the cases of

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[54] See, *e.g.*, (*a*) Claisen and Ponndorf, *Annalen*, 1884, **223,** 142 ; (*b*) Stobbe and Haertel, *ibid.*, 1909, **370,** 99 ; (*c*) Baker, *J.*, 1907, **91,** 1491 ; (*d*) Baly, Collie, and Watson, *J.*, 1909, **95,** 144 ; (*e*) Kehrmann and Effront, *Ber.*, 1921, **54,** 417 ; (*f*) Scheibe, *Ber.*, 1925, **58,** 586.

[55] *Ber.*, 1903, **36,** 1470, 3528.

[56] *Ber.*, 1922, **55,** 953.

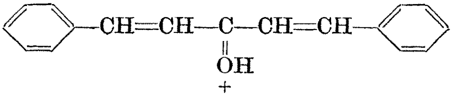
[57] " Electronic Theory of Organic Chemistry ", O.U.P., 1949, p. 170.

[58] Gillespie and Leisten, *J.*, 1954, 1, 7.

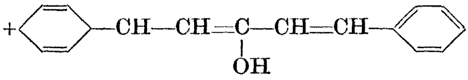
the higher members up to very high values. It was shown that *i*-factors of greater than 2 are due in all cases to sulphonation. Each sulphonation process increases the *i*-factor by approximately 2 :

$$X{-}H + H_2SO_4 = X{-}SO_3H + H_2O$$
$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

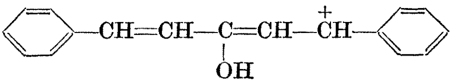
Thus, sodium salts of a monosulphonic acid of dibenzylideneacetone, a monosulphonic acid of cinnamylideneacetophenone, and a disulphonic acid of dicinnamylideneacetone were isolated from solutions of the ketones in sulphuric acid after they had been stored for appropriate times : the *i*-factors of these substances were thus quantitatively related to the occurrence of monoprotonation, and sulphonation. Moreover, 4 : 4′-dibromodibenzylideneacetone, in which the aromatic nuclei are deactivated, was found to give an *i*-factor of 2, and an orange solution. It appears, therefore, that there is nothing unusual in the ionisation of these unsaturated aryl ketones in sulphuric acid ; they undergo protonation at the carbonyl oxygen like other ketones. The intense colours of many of these ketones in sulphuric acid must be attributed to the ion, *e.g.*, (XXV), in which there is the possibility of resonance with many structures such as (XXVI) and (XXVII) in which the charge is situated in the conjugated chain. The most remarkable feature of the behaviour of these ketones in sulphuric acid is their very rapid sulphonation ; *e.g.*, dicinnamylideneacetone is completely disulphonated in 15 minutes or less at room temperature. This point is discussed again later (p. 66). The conflicting spectroscopic results already noted were clearly due to failure to recognise the occurrence of sulphonation.



(XXV)



(XXVI)



(XXVII)

Nitro-compounds.—It has been established by both cryoscopic [22] and spectroscopic measurements [58a] that mononitro-compounds in general behave as weak bases. Cryoscopic measurements show that, in a 0·1 molal solution in 100% sulphuric acid, nitromethane is approximately 20% ionised and nitrobenzene is approximately 40% ionised. The substitution of electron-donating groups, *e.g.*, alkyl groups, in nitrobenzene increases the basicity,

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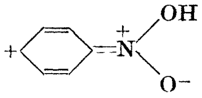
[58a] Brand, Horning, and Thornley, *J.*, 1952, 1374.

whereas electron-withdrawing groups, *e.g.*, Cl, NH_3^+, decrease it. It is noteworthy that nitrobenzene is a stronger base than nitromethane in sulphuric acid whereas aniline is a weaker base than methylamine in water. This difference is satisfactorily accounted for on the theory that the mesomeric effect in aromatic compounds displaces the electron distribution towards the nitro-group in nitrobenzene but away from the amino-group in aniline.

It is of interest that the pale yellow colour of nitrobenzene and of *p*-nitrotoluene is considerably intensified on dissolution in sulphuric acid, whereas solutions of nitromethane in sulphuric acid, and the pure substance itself, are colourless. The enhanced colour of the aromatic compounds is presumably to be associated with the increased importance, in their ions, of structures with a positive charge situated in the aromatic nucleus, *e.g.*, (XXVIII).



(XXVIII)

Amines, Amides, and related Compounds.—A number of amines including *n*-propylamine, *cyclo*hexylamine, aniline, and 2 : 4 : 6-tribromoaniline, and also the heterocyclic bases, pyridine, quinoline, and acridine, have been shown [59] to behave as fully ionised simple bases in sulphuric acid, *e.g.*,

The introduction of three nitro-groups at the *ortho-* and *para*-positions of aniline reduces the basicity by a very large factor, and 2 : 4 : 6-trinitroaniline is only approximately 95% ionised in 100% sulphuric acid.[60] The protonation of polyamino-compounds is considered later (p. 63).

Cryoscopic measurements have shown that *iso*butyramide [59] and benzamide [59] behave as fully ionised single bases, but the behaviour of anilides is more complicated. Newman and Deno [38] have investigated anilides of the type R·CO·NHPh, where R is pentamethylphenyl, mesityl, and *o*-tolyl. In the case of pentamethylbenzanilide it was found that, if the sulphuric acid solution was diluted after 90 minutes at 25°, an amount of pentamethylbenzoic acid was obtained corresponding to complete hydrolysis. The *i*-factor was found to be 2·4 initially, increasing to 5·8 on standing. The formation of the final products was represented by the equation

$$\mathrm{Me_5C_6{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + 4H_2SO_4 = Me_5C_6{\cdot}\overset{+}{C}O + \overset{+}{N}H_3{\cdot}C_6H_4{\cdot}SO_3H + H_3O^+ + 3HSO_4^-}$$

This interesting case merits further study because aniline itself is not sulphonated under these conditions.

Sulphides, Sulphoxides, Sulphones, and Sulphonic Acids.—A number of aromatic compounds of these types have been investigated by the cryoscopic method.[61, 62] Diphenyl sulphide, dibenzyl sulphide, and di-*p*-nitrobenzyl sulphide all give unstable solutions in sulphuric acid and undergo oxidation, and probably also sulphonation. Di-*p*-nitrophenyl sulphide,

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[59] Oddo and Scandola, *Gazzetta*, 1909, **39**(1), 569.

[60] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

[61] Szmant and Brost, *ibid.*, 1951, **73**, 4175.

[62] Gillespie and Passerini, unpublished experiments.

however, appears to give a stable red solution and an i-factor of 2·3. This may be attributed to the formation of a sulphonium salt

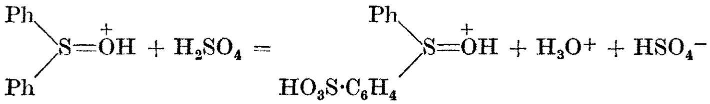
$$(NO_2\cdot C_6H_4)_2S + H_2SO_4 = (NO_2\cdot C_6H_4)_2\overset{+}{S}H + HSO_4^-$$

together with a partial protonation of the nitro-groups.

Diphenyl sulphoxide was first investigated by Szmant and Brost,[61] who found that it gave a stable solution and an i-factor of 4·8 which they interpreted as being due to the formation of a new ionic species, *viz.*, the diphenylsulphidonium ion Ph_2S^{++}:

$$Ph_2SO + 3H_2SO_4 = Ph_2S^{++} + H_3O^+ + 3HSO_4^-$$

This has, however, been disproved by subsequent work.[62] A careful examination of the freezing-point depression produced by diphenyl sulphoxide has shown that it corresponds initially to an i-factor of somewhat greater than 2 but increases rapidly with time to a fairly constant value of somewhat less than 4. When the i-factor has reached its approximately constant limiting value, none of the diphenyl sulphoxide can be recovered by pouring the sulphuric acid solution into water. The absence of any appreciable evolution of sulphur dioxide indicates that oxidation does not occur. The cryoscopic results are best interpreted if it is assumed that the sulphoxide dissolves to form initially an oxonium ion, $Ph_2SO + H_2SO_4 = Ph_2S{:}\overset{+}{O}H + HSO_4^-$, which then sulphonates fairly rapidly:

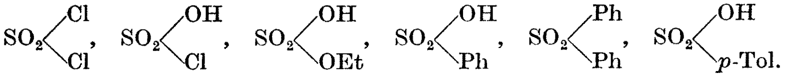


The introduction of nitro-groups into the aromatic nuclei deactivates the molecule towards sulphonation and di-*p*-nitrophenyl sulphoxide gives a stable red solution and a ν-factor of 2·0. It is not possible, however, from the cryoscopic evidence to estimate the extent of protonation of the nitro- and sulphoxide groups separately. Benzyl sulphoxide undergoes oxidation.

The sulphones seem generally to give more stable solutions than the sulphoxides and sulphides. Thus diphenyl sulphone and *p*-nitrophenyl phenyl sulphone both give colourless stable solutions and constant ν-factors of 1·20 and 1·36, respectively. Presumably in the latter case the nitro-group is partially protonated. It is noteworthy that the sulphones are considerably less basic than the sulphoxides and that the introduction of a nitro-group into one of the aromatic nuclei does not appear to decrease the basicity of the sulphonyl group appreciably.

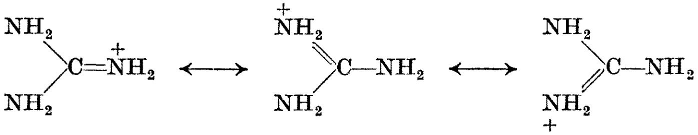
Benzenesulphonic acid and toluene-*p*-sulphonic acid have been investigated cryoscopically in the form of their sodium salts. Both give ν-factors that are appreciably greater than the value of 3·0 expected for complete solvolysis, *e.g.*, $Ph\cdot SO_3Na + H_2SO_4 = Ph\cdot SO_3H + Na^+ + HSO_4^-$. It was concluded that both acids ionise to some extent as bases, *e.g.*, $Ph\cdot SO_3H + H_2SO_4 = Ph\cdot SO_3H_2^+ + HSO_4^-$, and from the cryoscopic results it was calculated that benzenesulphonic acid would be approximately 30% ionised in a 0·1 molal solution and toluene-*p*-sulphonic acid approximately 40% ionised in a 0·1 molal solution in 100% sulphuric acid.

The results obtained with sulphones and sulphuric acids, taken together with the facts that sulphuryl chloride is un-ionised [2] and chlorosulphonic acid only very slightly ionised,[2] indicate that the basicity of the —SO_2— group increases in the series



Polybasic Compounds.—The preceding discussion has been mainly restricted to monobasic compounds. As a result of recent work it is now possible to give some account of the factors determining the position and extent of protonation in polybasic compounds. In addition to the intrinsic basicity of each group in the molecule there are two important factors upon which the basicity of such a molecule depends, *viz.*, the spatial separation of the basic groups, and mesomeric interaction between them.

The intrinsic basicity of an amino-group is such that, generally, in a polyamine, the amino-groups are all protonated, regardless of their positions in the molecule. Thus *o*-phenylenediamine produces a 3-fold depression of the freezing point,[62a] indicating diprotonation, and Gillespie and Wasif have shown by means of conductivity measurements that in hexamethylenetetramine all four nitrogen atoms are protonated.[63] It is thus all the more remarkable that guanidine, which is a strong base in water, should be found to add only 1·3 protons.[64] This incompleteness in the second stage of ionisation illustrates the importance of resonance interaction between the basic groups. The monoprotonated ion is considerably stabilised by resonance between three degenerate structures and the addition of a second proton would result in the loss of a large amount of resonance energy.



Measurements of the basicities of aromatic ketones and carboxylic acids by means of their ultra-violet absorption spectra in sulphuric acid–water mixtures [65] has shown that they are weaker bases than aniline by a factor of approximately 10^{-10}. This difference is reflected in the behaviour, in sulphuric acid, of polyamines, and of diketones, dicarboxylic acids, and ketocarboxylic acids. Thus, when the two basic groups are sufficiently

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[62a] Gillespie and Leisten, unpublished experiments.

[63] *J.*, 1953, 221.

[64] Gwyn Williams and Hardy, *J.*, 1953, 2560.

[65] (*a*) Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103; (*b*) Flexser and Hammett, *ibid.*, 1938, **60**, 885; (*c*) Zucker and Hammett, *ibid.*, 1939, **61**, 2785.

close together these latter compounds are only monoprotonated in sulphuric acid, but in a series of related compounds in which the distance between the two basic groups is progressively increased, the degree of protonation increases. This is shown by the *i*-factors obtained from cryoscopic measurements given in Table 2. The failure of the dicarboxylic acids to attain a maximum *i*-factor of 3 is not readily understood.

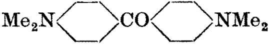
TABLE 2

		i	Ref
Benzil	$Ph{\cdot}CO{\cdot}CO{\cdot}Ph$	1·8	66
Dibenzoylmethane	$Ph{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}Ph$	2·1	,,
Dibenzoylpropane	$Ph{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO{\cdot}Ph$	3·0	,,
Dibenzoylpentane	$Ph{\cdot}CO{\cdot}[CH_2]_5{\cdot}CO{\cdot}Ph$	2·9	,,
Dibenzoylhexane	$Ph{\cdot}CO{\cdot}[CH_2]_6{\cdot}CO{\cdot}Ph$	3·0	,,
Dibenzoylheptane	$Ph{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO{\cdot}Ph$	3·0	,,
Anthraquinone		2·0—2·2	60
Oxalic acid	$HO_2C{\cdot}CO_2H$	1·3*	67
Malonic acid	$HO_2C{\cdot}CH_2{\cdot}CO_2H$	2·0	,,
Succinic acid	$HO_2C{\cdot}[CH_2]_2{\cdot}CO_2H$	2·5	,,
Glutaric acid	$HO_2C{\cdot}[CH_2]_3{\cdot}CO_2H$	2·6	,,
Suberic acid	$HO_2C{\cdot}[CH_2]_6{\cdot}CO_2H$	2·6	,,
Sebacic acid	$HO_2C{\cdot}[CH_2]_8{\cdot}CO_2H$	2·6	,,
m-Benzoylbenzoic acid		2·5	38
p-Benzoylbenzoic acid		2·5	,,

* Increases with time (see p. 53).

In the case of amino-acids and amino-ketones it might be expected from the above conclusions that the amino-groups would be fully protonated and would decrease the basicity of the carbonyl or carboxyl to an extent which would decrease with increasing separation of the groups. That this is the case is shown by the *i*-factors in Table 3.

TABLE 3

		i	Ref.
Glycine	$HO_2C{\cdot}CH_2{\cdot}NH_2$	2·2	68
β-Alanine	$HO_2C{\cdot}[CH_2]_2{\cdot}NH_2$	2·7	,,
γ-Amino-*n*-butyric acid	$HO_2C{\cdot}[CH_2]_3{\cdot}NH_2$	2·9	,,
5-Amino-*n*-pentanoic acid	$HO_2C{\cdot}[CH_2]_4{\cdot}NH_2$	3·0	,,
pp'-Dimethylaminobenzophenone		3·5	38

A number of compounds containing one or more methoxyl groups in addition to another type of basic group have been investigated. The in-

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[66] Wiles and Baughan, *J.*, 1953, 933.

[67] Wiles, *J.*, 1953, 996.

[68] O'Brien and Neimann, *J. Amer. Chem. Soc.*, 1951, **73**, 4264.

trinsic basicity of alkoxyl groups is presumably fairly large, since aliphatic ethers are completely ionised in sulphuric acid (see p. 51), although aromatic ethers appear to be very weakly basic. It seems that the basicity of the methoxy-group is very easily reduced by conjugation with an aromatic system, particularly if it contains other basic groups, and there is no evidence of the protonation of methoxy-groups in any aromatic compound in sulphuric acid. For example, 1-methoxy-, 2-methoxy-, and 1 : 2-dimethoxyanthraquinone are all monoprotonated in sulphuric acid, as is anthraquinone itself.[67] Newman and Deno [38] found an *i*-factor of 2·6 for *pp'*-dimethoxybenzophenone after 30 minutes. This value increases rapidly with time, however, because of sulphonation, and it does not seem unreasonable to assume that the initial *i*-factor would be little if any greater than 2. The investigation of methoxy-aromatic compounds is generally rendered difficult by the large activation effect of the methoxy-group which causes them to be rapidly sulphonated.

The ethylene group C=C undoubtedly has the lowest intrinsic basicity of the groups we are considering, although it is capable of being very greatly enhanced by conjugation (see pp. 43—47). However, the conjugated ethylene groups in the ketones $\text{Ph}\cdot[\text{CH:CH}]_m\cdot\text{CO}\cdot[\text{CH:CH}]_n\cdot\text{Ph}$ are less basic than the carbonyl group, since it is the latter and not the former that is protonated (see p. 59).

On the basis of the above general considerations it would be expected that the protonation of amino-groups would occur much more readily than carbonium-ion formation. The extraordinary stability and ease of formation of triarylcarbonium ions has already been commented upon (see p. 49). The *i*-factors obtained for bis(dimethylaminophenyl)phenylcarbinol and trisdimethylaminophenylcarbinol indicate that, although carbonium-ion formation is complete, the protonation of the amino-groups is not. Thus it appears that a carbonium-ion charge is able to reduce the basicity of an amino-group by resonance by such a large factor that it is incompletely protonated in 100% sulphuric acid.

Aromatic Sulphonation.—Cryoscopic and dilution experiments have indicated that certain compounds, *e.g.*, dicinnamylideneacetone, anisic acid, and dimesityl ketone, are rapidly sulphonated in sulphuric acid at room temperature. This fact is at first sight somewhat surprising in view of the drastic conditions usually employed in preparative procedures, *i.e.*, long periods of heating at high temperatures with sulphonating mixtures of high sulphur trioxide content. In order to sulphonate aniline it is recommended [69] to heat it with 98% sulphuric acid for 5 hours at 180°, for phenol [70] to heat it with 100% sulphuric acid for 6 hours at 40°, and for benzaldehyde [71] to heat it with 40% oleum for several hours at 110°. The existence of this background of fact has probably been responsible for a failure on several occasions in the past to consider the possibility that the results of

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[69] Gattermann–Wieland, "Laboratory Methods of Organic Chemistry", Macmillan, 1934, p. 185.

[70] Obermiller, *Ber.*, 1907, **40**, 3623.

[71] Moore and Thomas, *J. Amer. Chem. Soc.*, 1922, **44**, 367.

cryoscopic experiments could be explained in terms of rapid sulphonation of the solute and erroneous conclusions have thereby been reached.

It is possible, however, to understand the necessity for drastic conditions in the usual methods of preparation of sulphonic acids, while at the same time showing that it is not unreasonable to expect that certain compounds will be sulphonated rapidly under the apparently mild conditions of excess of 100% sulphuric acid at room temperature or lower, as used in cryoscopic measurement. It is unnecessary for our purpose to consider the nature of the sulphonating agent, which recent kinetic studies [72] have shown to be either sulphur trioxide and its polymers such as S_2O_6 or the ion HSO_3^+. There is no doubt that, whatever its exact nature, it increases rapidly in concentration on passing from aqueous sulphuric acid to oleum and the rate of sulphonation increases accordingly. Organic substances, with few exceptions, are either insoluble in sulphuric acid, or they dissolve to form positive ions which are strongly deactivated towards the sulphonating agent. It is generally undesirable in preparative sulphonation to use an excess of acid because of the greater difficulty of isolating the products. Hence the water formed during the reaction considerably dilutes the acid, correspondingly reduces the concentration of sulphonating agent, and strongly reduces the rate of sulphonation ; long times are therefore necessary for completion of the reaction. It is understandable, however, that if the aromatic compound is present only in low concentration, as in cryoscopic measurements, the dilution effect will be negligible and the reaction will go to completion much more rapidly. Moreover, if the compound contains non-basic or very weakly basic activating groups in addition to a protonated group, or if the protonated basic group is sufficiently separated from the aromatic nuclei, the compound will ionise and dissolve, yet the aromatic nuclei will be sufficiently activated to allow rapid sulphonation. Thus benzoic acid is quite stable under the conditions of cryoscopic measurements, but *m*-methoxybenzoic acid is sulphonated completely in about 1 hour and *o*- and *p*-methoxybenzoic acids are completely sulphonated in 4—5 hours.[38] Again, benzophenone is quite stable in 100% sulphuric acid at room temperature but 4 : 4′-dimethoxybenzophenone is completely monosulphonated in less than 2 hours and appears to undergo a second slow sulphonation.[38] The ethylenic group has a strongly activating effect, as is shown by the fact that dibenzylideneacetone is completely monosulphonated in about 2 hours under cryoscopic conditions.[58] Increasing the extent of conjugation in a molecule of this type markedly increases its reactivity : dicinnamylideneacetone is completely disulphonated in 15 minutes or less.[58] The methyl group is considerably less activating than the methoxy-group, and accordingly, *p*-methylacetophenone is stable in sulphuric acid at room temperature : mesityl methyl ketone and dimesityl ketone are rapidly sulphonated under the same conditions.[37, 38]

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[72] Brand and Horning, *J.*, 1952, 3922.