193. *The Basic Character of Some Aromatic Ketones and of Their Methyl Ethers.*

By L. A. Wiles and E. C. Baughan.

Earlier work on hydrochloride formation by heterocyclic methoxy-ketones (xanthones, thioxanthones, and anthraquinones) has been extended to aromatic ketones such as benzophenone, benzoin, benzil, and their *o*- and *p*-methoxy-derivatives. All the compounds form hydrochlorides. At low temperatures *o*-methoxy-ketones, in particular, absorb large quantities of hydrogen chloride.

The solvent sulphuric acid has been used to investigate the basicity of ketones. The separate contributions of the methoxy- and keto-groups to the basicity of methoxy-ketones have been studied. Methoxyanthraquinones are monoacid bases in sulphuric acid except when methoxyl groups are *ortho* to *both* carbonyl groups, in which case they become diacid bases.

The monoketone benzophenone, and the diketones benzil and dibenzoylmethane, are monoacid bases in sulphuric acid. The change of basicity in this solvent by interposing an increasing number of methylene groups between the carbonyl groups of a series of aromatic diketones has been investigated. It has been shown that dibenzoylpropane and higher members are diacid bases.

A rough interpretation of these ionisation studies is given by the electrostatic theory well known in its application to aliphatic dicarboxylic acids.

The basic character of ketones and other oxygen-containing organic compounds has long been known. Unsubstituted saturated ketones have only very slight basic strength so that compounds with acids cannot be isolated at room temperature, but their basic nature is shown by solubility in concentrated sulphuric acid, and at low temperatures compounds stated to be polyhydrochlorides have been prepared. The increase in the basic strength of some heterocyclic ketones when a methoxy-group is substituted *ortho* to a carbonyl group was investigated by Smiles and his co-workers (*J.*, 1929, 863, 1322; 1931, 520; 1932, 1792), who studied the basic strengths of methoxythioxanthones and methoxyxanthones, and by Roberts, who extended the work to methoxyanthraquinones (*J.*, 1932, 1982). *o*-Methoxy-ketones of these series are readily soluble in cold, concentrated hydrochloric acid, and with hydrogen chloride form solid hydrochlorides at room temperature. If a methoxy-group is present in the molecule but is not *ortho* to a carbonyl group then the compound is only feebly basic, and it does not form a hydrochloride under these conditions.

The object of this work was to investigate the basic properties of a number of aromatic ketones and their *o*- and *p*-methyl ethers. The research was developed along two main lines: (1) the absorption of hydrogen chloride by the compounds, (2) the ionisation of the compounds in sulphuric acid. The work is related to the effect of salt formation on the reducibility of the keto-group in methoxyanthraquinones already reported (Wiles, *J.*, 1952, 1358).

(1) *Absorption of Hydrogen Chloride.*—The ketones selected for examination were not sufficiently basic to be soluble in concentrated hydrochloric acid or generally to form stable hydrochlorides with hydrogen chloride at room temperature, but they took up hydrogen chloride when the temperature was lowered sufficiently, and a fairly sharp onset of this process was evident from the marked deepening in colour. In order to obtain results which could be compared numerically, the ketones were surrounded by a cooling mixture of solid carbon dioxide and acetone at −78°, and the stream of hydrogen chloride was itself passed through anhydrous calcium chloride in a similarly cooled bath. The products were readily decomposed at room temperature and the starting materials were recovered.

A few *o*-hydroxy-ketones were studied in a similar manner, and some observations on methoxyanthraquinones were also made for comparison with the earlier work of Roberts (*loc. cit.*).

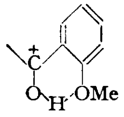
The results are summarized in the Table and the following points are evident: (i) The presence of *o*- or *p*-methoxy-groups in a ketone molecule increases its ability to absorb hydrogen chloride. The hydrochloride formed in the process is markedly bathochromic. (ii) The absorption of hydrogen chloride is usually most pronounced when a methoxy-group is *ortho* to carbonyl (Nos. 3, 7, 8, 12, 16, 17), and is generally rather less with *p*-methoxy-compounds (cf. Nos. 3 and 5; 12 and 13). (iii) The presence of two carbonyl groups in an α-diketone does not markedly increase the hydrogen chloride absorption of *o*- or *p*-methoxy-ketones (cf. Nos. 12 and 3; 13 and 5). The basicity of α-diketones is considered more fully later.

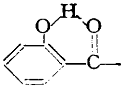
	Compound	Colour of product	Mols. of HCl absorbed at −78°
	Benzophenones		
1	Benzophenone	Dark yellow	4·1
2	2 : 2′-Dihydroxy-	Golden yellow	3·7
3	2 : 2′-Dimethoxy	Bright yellow	10·0
4	4-Methoxy-	Pale yellow	6·9
5	4 : 4′-Dimethoxy-	Bright yellow	7·7
	Benzoins		
6	Benzoin	Dark brown liquid	3·1
7	2 : 2′-Dimethoxy-	Brown liquid	9·8
8	2 : 2′-Dimethoxybenzoin methyl ether	Yellowish-brown liquid	13·0
9	4 : 4′-Dimethoxy-	Yellowish-brown liquid	13·8
	Benzils		
10	Benzil	Pale yellow	2·6
11	2 : 2′-Dihydroxy-	Pale yellow	1·5
12	2 : 2′-Dimethoxy-	Dark brown	12·0
13	4 : 4′-Dimethoxy-	Bright yellow	7·4
	Anthraquinones		
14	Anthraquinone	No visible colour change	2·4
15	1 : 8-Dihydroxy-	Reddish-yellow	2·8
16	1 : 8-Dimethoxy-	Reddish-brown	6·3
17	1 : 4 : 5 : 8-Tetramethoxy-	Dark purple	11·0

Discussion.—In view of the colour changes it seems certain that the absorption of hydrogen chloride must, in part, be attributed to compound formation. The addition of the first molecule to a simple ketone doubtless forms a hydrogen bond to the polar carbonyl group, $>\overset{+}{C}=\overset{-}{O}\cdots H-Cl$. When a methoxy-group is also present in the ketone molecule a further addition might occur in a similar manner to the oxygen of the methoxy-group, $-Me\overset{+}{O}\cdots H-Cl$. However, the evidence presented on p. 936 shows that a separate contribution by a methoxy-group to the basic strength of an aromatic ketone is unlikely.

The manner of subsequent addition of large numbers of molecules of hydrogen chloride to the ketones is not clear. That compound formation is not wholly responsible is shown by the absence of any stoicheiometric relationships. It may be that the additional numbers of molecules of hydrogen chloride measure the solubility of the gas in the highly polar medium formed by the addition of one molecule of hydrogen chloride to the carbonyl group. It is noteworthy that the most basic methoxy-ketones are not necessarily those which absorb the most gas; *e.g.*, 1 : 8-dimethoxyanthraquinone (No. 16) is readily soluble in concentrated hydrochloric acid, but only absorbs about 6 mols. of hydrogen chloride at −78°, whereas 2 : 2′-dimethoxybenzil (No. 12), although insoluble in concentrated hydrochloric acid, absorbs 12 mols. at this temperature.

This solubility hypothesis receives general support from the results. It has long been considered that *o*-methoxy-ketones form relatively stable salts by linking a proton between the carbonyl and methoxyl groups to form an ion which has a six-membered chelate ring (I). More recently Wiles (*loc. cit.*) produced additional evidence for this bond by finding that the polarographic reduction of the keto-group, when involved in salt formation, was hindered. For *p*-methoxy-ketones the electron-releasing ability of a methoxy-group will enhance the polarity of the carbonyl group, and two *p*-methoxy-groups will raise the polarity still further (Nos. 4, 5, 9, 13). Aromatic *o*-hydroxy-ketones have a six-membered chelate-ring structure (II). The hydrogen bridge would be expected to reduce the polarity of the keto-group and the absorption of hydrogen chloride is, in fact, diminished (Nos. 2 and 11). The case of 1 : 8-dihydroxyanthraquinone (No. 15; III) is of interest. The bonding of one of the carbonyl groups still leaves the other group free to exhibit its polarity, and there is no diminution in the ability to absorb hydrogen chloride.


(I)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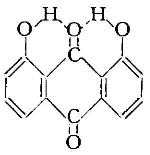
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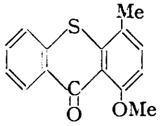

(IV)

Although in the work now described low temperatures were needed to form the hydrochlorides, instances are known where polyhydrochlorides are formed by *o*-methoxy-ketones at room temperature. Thus 1-methoxy-4-methyl-10-thioxanthone (IV) forms a trihydrochloride in correct stoicheiometric proportion (Roberts and Smiles, *J.*, 1929, 863).

At room temperature the addition of hydrogen chloride to methoxy-ketones such as (IV) occurs in integral proportions, but at low temperatures the values of HCl/ketone are not generally integral. Stobbe and Haertel (*Annalen*, 1909, **370**, 113), who studied the formation of polyhydrochlorides by *unsaturated* aromatic ketones at low temperature, also found a divergence from whole-number ratios. An examination of the analytical figures recorded for many polyhydrohalides has revealed frequent lack of simple stoicheiometric relationship; *e.g.*, the polyhydrochloride of benzophenone, although represented as $COPh_2,7HCl$ (Maass and McIntosh, *J. Amer. Chem. Soc.*, 1911, **33**, 70), actually contained 6·6 mols. of HCl.

(2) *Ionisation in Sulphuric Acid.*—The experiments on hydrochloride formation described above, while yielding results of some general interest, did not satisfactorily advance the enquiry into the basic properties of ketones and their methyl ethers, since it was not possible clearly to distinguish chemical from physical effects. The research along this line was therefore discontinued, and the investigation turned to a study of the ionisation of ketones in sulphuric acid.

Cryoscopic studies in sulphuric acid have long been used to investigate the mode of ionisation of very weakly basic compounds in a strongly acid medium. From 1907 to 1930 Hantzsch employed Beckmann's method to determine the van't Hoff i factor for weak bases. The experimental technique was improved and the results elaborated by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) and by Newman, Kuivila, and Garrett (*ibid.*, 1945, **67**, 704). More recently, extensive work by Gillespie, Hughes, and Ingold (*J.*, 1950, 2473), confirmed by Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 5271), slightly altered the values for the freezing point and for the cryoscopic constant of sulphuric acid. The van't Hoff i factor is determined by the numbers of different kinds of particles produced in solution, and the forces they exert, and Gillespie *et al.* therefore introduced a factor, ν, to represent the number of particles only. The numerical difference between an i value and the corresponding ν value is small, and it is only possible to differentiate between them in work of a high degree of accuracy and reproducibility. Many of the compounds investigated during the present work were not entirely stable in sulphuric acid, and i values in this paper represent the approximate number of ions obtained from one molecule of solute.

The cryoscopic work now described is of two kinds. First, the ionisation of ketones containing substituted methoxy-groups was examined to determine the contribution which the carbonyl and methoxyl groups might separately make to the basic strength of methoxy-ketones, and secondly, the mode of ionisation of a series of unsubstituted aromatic diketones was studied.

In previous work of this type it has been customary to determine a series of i values by successive additions of solute to the same portion of sulphuric acid. This procedure was not followed here since instability of the compounds in sulphuric acid often rendered the results variable with time, and the data recorded are determinations made by single additions of solute to fresh portions of sulphuric acid. Where a compound was markedly unstable the lowest value of i from several experiments is recorded.

Summary of Results.—(a) *Aromatic methoxy-ketones.* Many methoxy-derivatives of benzophenone, benzil, and benzoin were examined, but they were all too unstable for reliable i values to be measured. The following figures illustrate the general nature of the results.

2 : 2′-Dimethoxybenzil. A f. p. determined within 20 min. of addition of the solid gave $i = 4{\cdot}8$. This increased to 5·4 after a further 1½ hr., and to 5·6 after 1 day.

4 : 4′-Dimethoxybenzil. This gave $i = 2{\cdot}8$ after 20 min., 3·2 after 90 min., and 5·3 after 2 days.

On pouring the solutions of these compounds into water none of the original solid was recovered.

3 : 3′-Dimethoxybenzil 3 : 3′-Dimethoxybenzoin 3 : 3′-Dimethoxybenzoin methyl ether	These compounds were attacked so rapidly by sulphuric acid that they were all irrecoverable from solution after 5 minutes' contact.

(b) *Methoxyanthraquinones.* The results for these compounds are summarized in Table 1.

TABLE 1.

Anthraquinone	Stability of H_2SO_4 solution	Molality of H_2SO_4 solution	i
Unsubstituted	—	—	2·0—2·2 *
1-Methoxy-	Unstable; 36% increase in initial f. p. depression after 24 hr.	0·008	(2·3)
2-Methoxy-	Stable; no difference in f. p. after 24 hr.	0·007	2·2
		0·008	2·2
1 : 4-Dimethoxy-	Stable; 7% increase in initial f. p. depression after 24 hr.	0·008	3·0
		0·010	3·0
1 : 5-Dimethoxy-	Stable; no difference in f. p. after 24 hr.	0·008	2·8
		0·007	2·8
1 : 8-Dimethoxy-	Unstable; 13% increase in initial f. p. depression after 3 hr.	0·005	(2·1)
2 : 3-Dimethoxy-	Stable; no difference in f. p. after 3 hr.	0·011	2·0
		0·011	2·1
1 : 4 : 5 : 8-Tetramethoxy-	Stable; no difference in f. p. after 24 hr.	0·009	3·1
		0·011	3·1

* Determinations by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1907).

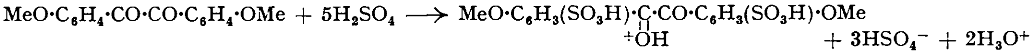
(c) *Unsubstituted aromatic diketones.* For summary, see Table 2.

TABLE 2.

Ketone (R = Ph)	Colour of H_2SO_4 solution	Stability of H_2SO_4 solution	Molality of solution	i
R·CO·R	—	—	—	1·9—2·3 *
R·CO·CO·R	Pale yellow	Stable; 8% increase in initial f. p. depression after 24 hr.	0·012	1·8
			0·005	1·8
R·CO·CH$_2$·CO·R	Pale yellow	Stable; 7% increase in initial f. p. depression after 24 hr.	0·008	2·1
			0·008	2·1
R·CO·[CH$_2$]$_2$·CO·R	Dark green initially; becomes reddish-brown on prolonged contact	Unstable; 48% increase in initial f. p. depression after 24 hr.	0·003	(3·9)
R·CO·[CH$_2$]$_3$·CO·R	Light brown; blue fluorescence	Stable; no change in f. p. after 24 hr.	0·012	3·0
R·CO·[CH$_2$]$_4$·CO·R	Pale yellow; becomes bright red after a a few hours	Unstable; 38% increase in initial f. p. depression after 3 hr.	0·016	(2·8)
R·CO·[CH$_2$]$_5$·CO·R	Reddish-brown	Stable; 8% increase in initial f. p. depression after 24 hr.	0·080	2·9
			0·011	2·9
R·CO·[CH$_2$]$_6$·CO·R	Very pale yellow	Stable; no change in f. p. after 3 days	0·015	3·0
			0·006	3·0
R·CO·[CH$_2$]$_7$·CO·R	Very pale yellow	Stable; no change in f. p. after 24 hr.	0·003	2·9
			0·004	3·0

* Determinations by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1710).

Discussion.—The experimental results show the expected difficulty of obtaining freezing-point depressions in this solvent which are not affected by sulphonation or by dehydration. The work on hydrochloride formation, described earlier in this paper, was concerned with dimethoxy-derivatives of benzophenones, benzils, and benzoins, but all of these proved too reactive in sulphuric acid for reliable i values to be obtained as, indeed, did anisole itself (cf. data on sulphonation by Schober, *Amer. Chem. J.*, 1896, **18**, 858). With the dimethoxy-compounds a limiting value of $i = 6$ would correspond with disulphonation, and values of $i > 5$ were recorded :



$$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}OMe + 5H_2SO_4 \longrightarrow MeO{\cdot}C_6H_3(SO_3H){\cdot}\underset{\overset{\Vert}{{}^{+}OH}}{C}{\cdot}CO{\cdot}C_6H_3(SO_3H){\cdot}OMe + 3HSO_4^- + 2H_3O^+$$

The effect of the methoxyl group in aromatic substitution has been examined quantitatively by de la Mare and Vernon (*J.*, 1951, 1764). They found from bromination experiments that *o*- and *p*-positions to a methoxyl group are very powerfully activated, and although the matter was not closely investigated here, it seems very probable that aromatic methoxy-ketones are rapidly sulphonated.

It was found possible, however, for several ketones of the general series $Ph{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}Ph$, and for anthraquinone and several of its methoxy-derivatives, to obtain i values which changed but little during a day or so, and from these solutions the ketones were recoverable on pouring them into water. We therefore attribute the deviation of i from unity in these cases to ionisation.

The results obtained show that: (*a*) Benzil and dibenzoylmethane are monoacid bases ($i \simeq 2$), while αω-dibenzoyl-propane, -pentane, -hexane, and -heptane are diacid bases ($i \simeq 3$). Dibenzoylethane and dibenzoylbutane are unstable in sulphuric acid and probably give dehydration products (cf. Nowlin, *J. Amer. Chem. Soc.*, 1950, **72**, 5754; Bauer, *Compt. rend.*, 1912, **155**, 288). (*b*) Anthraquinone is a monoacid base (Hammett and Deyrup, *loc. cit.*), and so also are 1-methoxy-, 2-methoxy-, and 2 : 3-dimethoxy-anthraquinone.

The methoxy-group of itself does not therefore ionise. If there are *two* methoxy-groups in the α-positions to the *same* keto-group, the anthraquinone derivative remains a monoacid base (1 : 8-dimethoxyanthraquinone); but if there is a methoxy-group in the α-position to *each* of the keto-groups (1 : 4- and 1 : 5-dimethoxyanthraquinone) then the compounds become diacid bases ($i \simeq 3$); if each keto-group has *two* methoxy-groups in this position, the resulting compound (1 : 4 : 5 : 8-tetramethoxyanthraquinone) is still only a diacid base. These observations may be summarised in the hypotheses (i) that one keto-group ionises in anthraquinone, (ii) that the ionisation of the second keto-group is not detectable by the present technique, and (iii) that the methoxy-groups do not themselves ionise, but in the α-position increase the ionizing power of the ketone groups.

It remains to consider whether these facts and hypotheses can be simply explained. The change from mono- to di-basicity in the series $Ph{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}Ph$ somewhere between $n = 1$ and $n = 3$ could be attributed to the well-known electrostatic interaction familiar in the theory of the two dissociation constants of a dicarboxylic acid (Bjerrum, *Z. physikal. Chem.*, 1923, **106**, 219; and many later workers), and a search of the literature reveals at any rate one parallel example; *NN'*-dibenzylhydrazine gives a *mono*-hydrochloride (Curtius, *J. pr. Chem.*, 1900, **62**, 92), but bisbenzylaminomethane, $CH_2(NH{\cdot}CH_2Ph)_2$, (Kempff, *Annalen*, 1890, **256**, 226) and *NN'*-dibenzylethylenediamine, $[CH_2]_2(NH{\cdot}CH_2Ph)_2$, (Schering, *Chem. Zentr.*, 1898, ii, 743), both form *di*-hydrochlorides.

We shall therefore examine whether a simple version of the electrostatic theory will explain the present observations. In a diacid base, if the two ionisable groups are so distant as to have a negligible effect on one another, the base dissociation constant, K_1, of the first group should, for simple statistical reasons, be four times that, K_2, of the second group. If, however, a charge is established on one group, this will make an additional work term to be overcome against the coulombic force, and $\boldsymbol{R}T \ln (K_1/4K_2) = \boldsymbol{e}^2/D_{\mathrm{E}}r$ where D_{E} is a dielectric constant, $\boldsymbol{e}$ is the electronic charge, and r is the distance between the two ionisable groups. In Bjerrum's original treatment D_{E} was taken as equal to D, the dielectric constant of the solvent in bulk. This theory gives reasonable values of r for long-chain dicarboxylic acids, but values much too small for short chains (*e.g.*, oxalic or succinic acid). The theory has been refined by Kirkwood and Westheimer (*J. Chem. Physics*, 1938, **6**, 506, 513), who consider the molecule as occupying a cavity of dielectric constant, D_i, inside the bulk solvent of dielectric constant, D. Their theories give the effective dielectric constant, D_E, in terms of D and D_i (assumed equal to 2), the size and shape of the cavity, and the disposition of ionisable groups in it. This refined theory gives distances which are in good agreement with other evidence, even for the shorter chains (cf. Westheimer and Shookhoff, *J. Amer. Chem. Soc.*, 1939, **61**, 555; Westheimer, *ibid.*, p. 1977).

The quantitative application of these arguments to the present data is not simple. The bulk dielectric constant of sulphuric acid is considerably greater than that of water (a value of 110 has recently been obtained by Brand, Jones, and Rutherford, *J. Chem. Phys.*, 1952, **20**, 530), the internal dielectric constant, D_i, is not exactly known, and the effective dielectric constant, D_E, depends on the size and shape of the molecule in a manner which can be calculated only in special cases. We have calculated the *ratio* of the effective dielectric constant, D_E, in sulphuric acid and in water from Kirkwood and Westheimer's equations (9) and (10) (*loc. cit.*, p. 509; spherical cavity), and unless D_E for water is <25, this *ratio* lies between 1 and 1·3. We, therefore, *assume* that the effect, in sulphuric acid, of a charged oxygen atom in an ionised ketone is equal to that, in water, of a charge in a carboxylic acid with the same number of carbon atoms between the two ionising groups—this latter effect being taken from experiment.

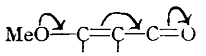
We are thus led to identify $\log_{10}(K_1/4K_2)$ for dibenzoylmethane in sulphuric acid with that (2·26) for malonic acid in water, and $\log_{10}(K_1/4K_2)$ for dibenzoylpropane in sulphuric acid with that (0·47) for glutaric acid in water. We estimate also that, in view of the scatter of experimental points and the well-known thermodynamic ambiguity of the Beckmann technique (cf., *e.g.*, Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 481, and earlier references there quoted; Bell, Baughan, and Vaughan-Jackson, *J.*, 1934, 1969), an apparently ionised group might really be up to 20% un-ionised, and *vice versa*. The Ostwald dissociation constant, K, is given by $\alpha^2c/(1-\alpha)$, where α = degree of dissociation, and c = the stoicheiometric concentration of the solute concerned (c is conventionally given in g.-mol. $l.^{-1}$). We may take as a mean value of the molality (m) of the solutions used in this work, $m =$ 0·01 g.-mol. per 1000 g. of solvent = 0·0184 g.-mol. $l.^{-1}$. If $\alpha = 0{\cdot}8$, $\alpha^2/(1-\alpha) = 3{\cdot}2$; if $\alpha = 0{\cdot}2$, $\alpha^2/(1-\alpha) = 0{\cdot}05$. Hence for a ketone "ionised" in the present sense, K is not less than $3{\cdot}2 \times 1{\cdot}84 \times 10^{-2} = 10^{-1{\cdot}2}$, and for one "un-ionised," K is not greater than $0{\cdot}05 \times 1{\cdot}84 \times 10^{-2} = 10^{-3{\cdot}0}$. Moreover, in the first ionisation of a dicarboxylic acid one expects in the limit of long chains, K_1 to equal $2K$, where K = the dissociation constant of a single carboxyl group, and equally for the second dissociation constant of a dicarboxylic acid, $K_2 = \frac{1}{2}K$ ($K_1 = 4K_2$). We can thus estimate, very roughly, what base dissociation constant, K, a single keto-group has in sulphuric acid.

(*a*) Since in a long-chain diketone both groups are ionised, $\log K_2 = (\log K - \log 2) \geqslant -1{\cdot}2$; $\log K \geqslant -0{\cdot}9$. (*b*) Since in dibenzoylmethane, the second group appears un-ionised $\log K_2 = (\log K - \log 2 - 2{\cdot}26) \leqslant -3{\cdot}0$; $\log K \leqslant -0{\cdot}5$. (*c*) Since in dibenzoylpropane the second group appears ionised, $\log K_2 = (\log K - \log 2 - 0{\cdot}47) \geqslant -1{\cdot}2$; $\log K \geqslant -0{\cdot}4$. These rough indications suggest (i) that $\log_{10}K \simeq -0{\cdot}5$, and (ii) presumably that dibenzoylpropane is only just on the limit of appearing a dibasic strong electrolyte. The latter conclusion derives support from the data on anthraquinone. The maximum distance between the oxygen atoms in dibenzoylpropane (from Fischer–Hirschfelder models) is 8·5 Å, and the free rotation distance is about 5·9 Å. The distance between the oxygen atoms in anthraquinone, which may be considered to have a rigid disc structure, is 5·3 Å (Sen, *Indian J. Phys.*, 1948, **22**, 347). One would expect, therefore, that quite a small effect would make anthraquinone appear a diacid base, and this agrees with our hypothesis that a single α-methoxy-group is sufficient to cause this.

It appears, therefore, that the electrostatic influence of already ionised groups is sufficient to explain the present observations provided that (*a*) for a ketonic oxygen in sulphuric acid, $K \simeq 10^{-0{\cdot}5}$, and (*b*) for an aromatic-linked methoxyl oxygen in sulphuric acid, $K < 10^{-3}$.

We consider the latter supposition first. It is known that aliphatic ethers are ionised in sulphuric acid, also that the mutual effects of the benzene ring and the amino-group are sufficient to make K for aniline about 10^6 times less than that of an aliphatic primary amine. As this would also be expected in an oxygen ether base with the oxygen directly linked to the benzene ring, one would not expect such an aromatic ether to appear ionised in sulphuric acid unless the dissociation constant of an *aliphatic* ether in sulphuric acid were greater than 10^{+3}, and this is improbably high from analogy with our estimate of $K \simeq 10^{-0\cdot5}$ for a ketone. Whether, however, this value of K for a ketone is reasonable is a more difficult question, since there is little information about base dissociation constants in sulphuric acid except that almost all the bases studied appear to be strong electrolytes. The rough estimate given, however, might be checked by partition-coefficient data. In qualitative support of our general view that the dissociation constants of ketones in sulphuric acid are such that significant proportions of them must remain un-ionised we quote Baker's data (*J.*, 1931, 307) for the partition coefficient of acetophenone (and of benzaldehyde) between sulphuric acid and the non-ionising solvent ligroin.

The experimental data in the present paper can, therefore, be understood in terms of known principles. Moreover, the absence of basic properties in the aromatic methoxyl group in sulphuric acid makes it improbable that the addition of hydrogen chloride to such compounds can be considered as due to the formation of oxonium salts by the oxygen of the methoxy-group.



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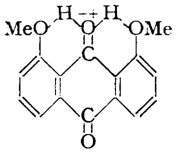

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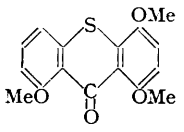
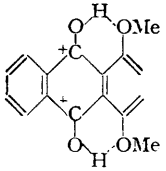
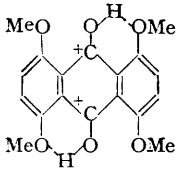


(VII)



(VIII)



(IX)

The Structure of the Ions of Methoxyanthraquinones.—The evidence above suggests that the spatial separation of the keto-groups in anthraquinone is not quite sufficient for the compound to be a diacid base, but the experiments show that the influence of methoxy-groups in the α-positions to both keto-groups is sufficient to make it so. There are two distinct ways in which a methoxy-group could enhance the basic property of a keto-group : (i) by a mesomeric effect in which the electron-donating effect of the methoxy-group increases the negative charge on the carbonyl oxygen atom, as in (V) ; (ii) by the formation in the ion of a six-membered hydrogen-bonded structure between the keto- and methoxy-groups (I). Two independent objections have been raised to (i). Flett (*J.*, 1948, 1441), from the infra-red absorption spectrum of 1 : 4-dimethoxyanthraquinone, showed that the *o*-quinonoid resonance form (V) is unlikely, and a similar view was expressed by Wiles (*loc. cit.*) from a polarographic study of the reduction of methoxyanthraquinones. The i values for methoxyanthraquinones can well be explained by (I). Thus 1-methoxyanthraquinone is a monoacid base. When two methoxy-groups are *ortho* to the same carbonyl group there is a possibility of the compound's functioning as a diacid base, *e.g.*, 1 : 8-dimethoxyanthraquinone (VI). The i value of (VI) is, however, 2 and not 3, so the linkage of two methoxyl groups by hydrogen bonds to a single carbonyl group is not realised, and this is to be expected on electrostatic grounds. In this connection it may be noted that the structure postulated by Roberts, Wiles, and Kent (*J.*, 1932, 1792) to explain the formation of a diperchlorate of 1 : 4 : 8-trimethoxy-10-thioxanthone (VII) must now be considered doubtful.

When the anthraquinone has two methoxy-groups *ortho* to *separate* keto-groups as in

1 : 4- or 1 : 5-dimethoxyanthraquinone, two hydrogen-bonded structures can be formed (*e.g.*, VIII) and $i = 3$. Similarly 1 : 4 : 5 : 8-tetramethoxyanthraquinone (IX) could only be a diacid base.

EXPERIMENTAL

(1) *Absorption of Hydrogen Chloride.—Materials.* Many of the compounds were available commercially. 2 : 2′-Dihydroxybenzophenone was most easily prepared by fusing xanthone with potassium hydroxide (Richter, *J. pr. Chem.*, 1883, **28**, 285). 2 : 2′-Dimethoxybenzoin and its methyl ether were made by Irvine's method (*J.*, 1901, **79**, 670). The benzil methyl ethers were obtained by oxidising the corresponding benzoins with Fehling's solution. 2 : 2′-Dihydroxybenzil was made by demethylating the dimethoxy-compound with pyridine hydrochloride (Gee and Harley-Mason, *J.*, 1947, 251).

Recorded m. p.s (corr.) for the following compounds are inconsistent (lit. values in parentheses). Benzophenones : 4-methoxy-, 61° (61—62°, 61—62·5°, 62°, 62—63°, 63—64°, 67—68°); 4 : 4′-dihydroxy-, 215° (205—207°, 205·5—206·5°, 210°, 212—213°, 213—214°); 4 : 4′-dimethoxy-, 146° (141°, 142—143°, 143—144°, 144°, 146°). Benzoin : 4 : 4′-dimethoxy-, 110° (109—110°, 113°). Benzil : 2 : 2′-dimethoxy-, 128° (127°, 128—129°, 130°).

Experimental Method.—A U-tube containing a weighed quantity (*ca.* ½ g.) of the dried ketone was immersed in acetone in a vacuum flask, and a steady stream of dry hydrogen chloride passed through. The temperature of the bath was kept by acetone–CO_2 at −78°. The gas was similarly cooled. After passing over the ketone, the excess of hydrogen chloride was bubbled through sulphuric acid. By comparing the rates at which bubbles entered and left the U-tube the progress of the absorption was followed, and the passage of gas was continued until absorption appeared to be complete. The product was then analysed. A slow stream of air was passed through the U-tube, the temperature allowed to rise slowly, and the hydrogen chloride liberated absorbed in standard sodium carbonate solution. The starting materials were recovered.

(2) *Ionisation in Sulphuric Acid.—Materials.* Diketones. The ketones, when not available commercially, were prepared by Friedel–Crafts reaction of benzene on the carboxylic acid dichlorides, made, in satisfactory yields, by the action of thionyl chloride.

The following diketones had m. p.s (corr.) which differed from previously recorded values (lit. values in parentheses) : dibenzoylpentane 62—63° (68°); dibenzoylhexane 91° (83—85°, 85°) (Found : C, 81·2; H, 7·5. Calc. for $C_{20}H_{22}O_2$: C, 81·6; H, 7·5%).

M. p.s (corr.) for the following diketones are also recorded, as literature values are conflicting : dibenzoylpropane 65° (62—63°, 67·5°); dibenzoylbutane 107° (102°, 104—105°, 105—106°, 107°, 106—108°, 112°); dibenzoylheptane 55—56° (44°, 56—57°).

Anthraquinones. The methoxyanthraquinones have been described by Wiles (*J.*, 1952, 1358).

Experimental Method.—The apparatus used was similar to that designed by Newman, Kuivila, and Garrett (*loc. cit.*) except that the stirrer was hand-operated. The sulphuric acid was made by adding 98% sulphuric acid to fuming sulphuric acid (both of A.R. grade) so that the concentration of the acid was 100% as determined by Brand's method (*J.*, 1946, 585). A small quantity of water was added so that the f. p. of the acid was then between 9·8° and 10·2°. The procedure in determing f. p.s was similar in most respects to that used by previous workers. The cooling bath was regulated at 8·5° ± 0·1°. Crystallization of the acid was started by touching the side of the acid container with solid carbon dioxide. By this means the supercooling was usually of the order of 0·2—0·5° and no supercooling correction was necessary. The i values were calculated from the relation $i = \theta/m \times 5{\cdot}98$, where θ = the depression of the f. p., m = the molality of the solute, and 5·98 is the cryoscopic constant of sulphuric acid.

The authors are indebted to the Referees of this paper for a number of valuable suggestions.

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[*Received, November 3rd*, 1952.]