XLI.—*The Salt-forming Characteristics of Doubly- and Singly-linked Elements of the Oxygen Group. Part I. The Carbonyl Group in Benzaldehyde and Acetophenone.*

By John William Baker.

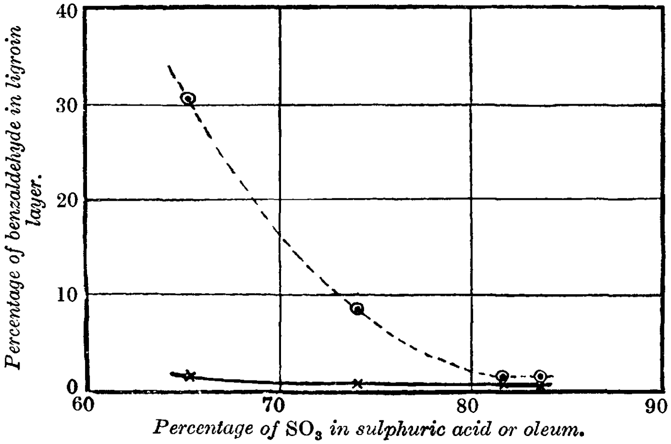
Earlier work (Baker and Ingold, J., 1930, 431) has shown that Schiff's bases of the type $\mathrm{CHPh{:}NAr}$, although readily hydrolysed by dilute acids, dissolve in concentrated or fuming sulphuric acid to form true ammonium salts of the type $\left.\overset{\oplus}{\overbrace{\mathrm{Ph{\cdot}CH{:}NHAr}}}\right\}\overset{\ominus}{\mathrm{HSO_4}}$, and the intense colour of the solutions so obtained is presumably due to the presence of the salt or its kation, since the free bases are almost colourless. The long-known fact that benzaldehyde dissolves in concentrated sulphuric acid to form a similar deep orange solution (Kauffmann and Beisswenger, *Ber.*, 1903, **36**, 561) immediately suggests that this colour is similarly due to the formation of an oxonium salt $\left.\overset{\oplus}{\overbrace{\mathrm{Ph{\cdot}CH{:}OH}}}\right\}\overset{\ominus}{\mathrm{HSO_4}}$, especially since the benzaldehyde can be recovered unchanged by dilution of the solution. It was considered of interest, therefore, to investigate the salt-forming characteristics of the carbonyl oxygen in derivatives of the type $\mathrm{Ar{\cdot}COR}$, and to extend the investigation to include singly-linked (ethereal or phenolic) oxygen, and similar groups containing sulphur and selenium.

The problem is susceptible to attack along two distinct lines, both of which it is intended to develop in subsequent papers. The first involves investigations of the condition of such groups in sulphuric acid solution by the purely physical methods of partition, colorimetry, absorption spectra, etc. Secondly, the conversion of a pseudobasic system, directly attached to a benzene nucleus, into the " onium " salt will affect the directive action of the group causing enhanced tendency towards meta-substitution, and hence the problem may be investigated along lines similar to those employed in the case of benzylidene-*m*-nitroaniline (*loc. cit.*).

The present communication describes some preliminary physical investigations relating to benzaldehyde and acetophenone. The decrease in stability of the " onium " salts in passing along the series nitrogen > oxygen > fluorine suggests that, although actual isolation of a colourless (probably pseudo-) salt of benzylidene-*m*-nitroaniline was possible (*loc. cit.*), the corresponding oxonium salts derived from benzaldehyde and acetophenone might be incapable of existence except in solution in concentrated sulphuric acid. This has actually been found to be the case, all attempts to isolate such salts proving fruitless. Nevertheless, definite evidence of their existence in solution is adduced from the observations recorded below.

FIG. 1.

Partition of benzaldehyde between ligroin and sulphuric acid.



Percentage of SO_3 *in sulphuric acid or oleum.*

× *without ammonium sulphate.*

○ *with* " "

Pure benzaldehyde was distributed, under comparable conditions, between sulphuric acid (of various concentrations) and ligroin, both with and without the addition of ammonium sulphate to the acid layer, and the proportion of benzaldehyde in the ligroin layer was determined gravimetrically as its *p*-nitrophenylhydrazone. The results are summarised in Table I, and expressed graphically in Fig. 1.

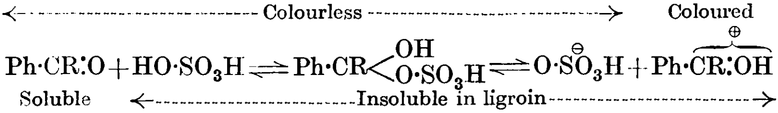
In order to interpret these results, it is necessary to consider briefly the consecutive ionic equilibria which probably exist in such solutions of benzaldehyde (or acetophenone) in sulphuric acid. First, it may be supposed that the free carbonyl compound and sulphuric acid are in equilibrium with the pseudo-(covalent) salt $CPhR(OH)(O{\cdot}SO_3H)$. The latter, in turn, will be in equilibrium

TABLE I.

Partition of benzaldehyde between sulphuric acid and ligroin at the ordinary temperature.

		Proportion of Ph·CHO in ligroin layer (%).	
$\frac{100\,[H_2SO_4]}{[H_2SO_4] + [H_2O]}$.	$\frac{100\,[SO_3]}{[SO_3] + [H_2SO_4]}$.	A. Without addition of $(NH_4)_2SO_4$.	B. With addition of $(NH_4)_2SO_4$.
(7·3% free SO_3)	83	0·5	1·4
100	81·6	0·81	1·03
90	73·5	0·83	8·7
80	65·3	1·77	30·8

with the ions of the true oxonium salt, the whole system being represented by the scheme



$$\mathrm{Ph{\cdot}CR{:}O + HO{\cdot}SO_3H \rightleftharpoons Ph{\cdot}CR}\!<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O{\cdot}SO_3H}\end{smallmatrix} \rightleftharpoons \overset{\ominus}{\mathrm{O}}\mathrm{{\cdot}SO_3H} + \mathrm{Ph{\cdot}}\overset{\oplus}{\overbrace{\mathrm{CR{:}OH}}}$$

The ψ-salt is assumed to be colourless because benzylidene esters are colourless, and to be insoluble in ligroin because it is a sulphuric acid. The ion, however, would be coloured because it is, in part, a carbonium ion (compare the colours of cotarnine salts and of the salts of Schiff's bases in ionising media).

The partition experiments provide information concerning the amount of free benzaldehyde (which is miscible in all proportions with ligroin) present in the solution, and show that, in the absence of ammonium sulphate, these equilibria are displaced largely towards the right, the benzaldehyde being retained almost completely in the acid layer, even in 80% sulphuric acid. Addition of ammonium sulphate, however, causes a repression of the ionic dissociation (common-ion effect) which is followed, in turn, by a further decomposition of the pseudo-salt into free benzaldehyde and sulphuric acid with the result that, under these conditions, a larger proportion of the benzaldehyde is found in the ligroin layer. The magnitude of this effect is greater the more dilute is the acid solution employed.* These results are similar to those obtained with benzylidene-*m*-nitroaniline, which has already been proved to exist almost entirely as its salt in sulphuric acid solution.

Evidence relating mainly to the second of the above equilibria has been obtained from colorimetric investigations. The colour of

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* In such dilute sulphuric acid solutions, further complications will obviously be introduced owing to the hydrolysis of one or more of the entities present, but for simplicity such equilibria have been omitted from the scheme given above.

the sulphuric acid solutions is presumably due to the presence of the carbonium–oxonium ion, and indeed, may be regarded as a direct measure of the concentration of the latter in the solution.

In this connexion two factors were considered, *viz.*, (1) the effect of varying the concentration of the carbonyl compound in the solution in sulphuric acid of a constant concentration (100%), *i.e.*, that of varying the molecular ratio $\mathrm{CPhR{:}O/H_2SO_4}$, and (2) the effect of varying the dilution of the sulphuric acid when the above molecular ratio is kept constant. The partition experiments already described indicate that in 100% sulphuric acid hardly any free benzaldehyde is present, and hence decreasing the concentration of the carbonyl compound in such a solution may be expected to result mainly in an increased ionisation of the (colourless) pseudo-salt form into the (coloured) oxonium ion, in accordance with ordinary dilution laws. Hence, solutions of benzaldehyde and acetophenone in 100% sulphuric acid should not obey Beer's law. The colour values of such solutions with decreasing concentration of the carbonyl compound are summarised in Table II.

TABLE II.

Colour values of $\mathrm{CPhR{:}O}$ *in 100% sulphuric acid at the ordinary temperature.*

$\mathrm{CPhR{:}O}$, equiv./l. (c).	Relative lengths of columns for equal colour intensity (l).	Observed "specific" colour value (s).	"Molecular equivalent" colour value (1000 s/c).	cl.
		R = H.		
0·1808	[1]	[1]	[5544]	0·1808
0·0904	1·83	0·55	6053	0·1655
0·0452	3·33	0·30	6653	0·1505
0·0226	6·15	0·16	7230	0·1390
		R = Me.		
0·1582	[1]	[1]	[6320]	0·1582
0·0791	1·71	0·59	7440	0·1353
0·0395	3·07	0·33	8350	0·1213
0·0198	5·58	0·18	9090	0·1105

In agreement with the theoretical deductions given above, the product cl is not constant as required by Beer's law, the intensity of the colour decreasing with increasing dilution more slowly than this law requires. In other words, the "molecular equivalent colour value" increases with increasing dilution in an analogous manner to the similar increase in the equivalent conductivity in solutions of electrolytes.*

* The approximate nature of colorimetric measurements and the uncertainty of the colour value at infinite dilution, together with possible complications arising from any disturbance of the first of the postulated consecutive equilibria, render valueless any attempt to apply Ostwald's dilution law to the data obtained. Correlation between colour and ion-formation is clearly

The effect of the dilution of the sulphuric acid was investigated by determination of the relative colour intensities of solutions of benzaldehyde in 100, 90, 80, and 70% sulphuric acid, respectively, in which the molecular ratio (benzaldehyde)/(absolute sulphuric acid) was kept constant, suitable correction being made for the difference in total volume of the solutions. The results are summarised in Table III.

TABLE III.

Effect of the dilution of the sulphuric acid on the colour intensity of solutions of benzaldehyde in sulphuric acid.

Mol. ratio Ph·CHO/H_2SO_4 = 1/89 (constant).

$\frac{100\,[H_2SO_4]}{[H_2SO_4] + [H_2O]}$.	Relative colour values.	
	(a) Obs.	(b) Corr. for vol. of solution.
100	[100]	[100]
90	75	85
80	34	45
70	13	21

If, as has been assumed, the intensity of the colour is a measure of the amount of the salt form present, then the figures in the last column of the table show that, of the amount of oxonium salt present in 100% sulphuric acid, 15, 55, and 79%, respectively, suffers hydrolysis in the presence of the same molecular quantity of sulphuric acid, but in 90, 80, and 70% dilution, respectively. Further dilution subsequently causes complete hydrolysis with the regeneration of benzaldehyde as observed by Kauffmann and Beisswenger (*loc. cit.*). A similar experiment with acetophenone shows that hydrolysis of the oxonium salt occurs even more readily, the diminution in colour as the strength of the acid is diminished being too rapid to admit of accurate colorimetric comparison. The approximate (corrected) colour values for the same molecular ratio, Ph·COMe/H_2SO_4 = 1/89, in 100, 90, and 80% sulphuric acid are, respectively, 100, < 10, and < 7.

EXPERIMENTAL.

Materials.—The benzaldehyde used was freshly prepared from the purified bisulphite compound and was free from benzoic acid. The acetophenone had b. p. 201°, m. p. 21°.

Partition Experiments.—A weighed amount (about 3 g.) of

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indicated by the observation that the conductivity of 100% sulphuric acid is increased by addition of benzaldehyde. The proportion (about 80—90%) of the total conductivity of such a solution due to the solvent is, however, too great to permit of accurate determination of the conductivity of the solute itself.

benzaldehyde was dissolved in ligroin, b. p. 100—120°, which had been freed from benzenoid hydrocarbons as previously described (Baker and Ingold, *loc. cit.*), and the solution made up to 50 c.c. Two equal portions (20 c.c.) of this solution were shaken for 1—2 mins. at the ordinary temperature (25°) with 5 c.c. of the appropriate sulphuric acid solution, in one case with the previous addition of 2 g. of ammonium sulphate. After standing until separation of the two layers was complete, 10 c.c. of each ligroin layer were pipetted into 25 c.c. of 12% acetic acid in a flask from which air had been displaced by carbon dioxide, the mixture was diluted with 50 c.c. of water, and 30 c.c. of a filtered solution of *p*-nitrophenylhydrazine (0·6—0·7 g.) in 30% acetic acid were added. After 5 hours the precipitated *p*-nitrophenylhydrazone was collected on a Gooch crucible, washed with 10% acetic acid, dried, and weighed in the usual manner. The results are summarised in Table IV.

TABLE IV.

Partition of benzaldehyde between sulphuric acid and ligroin at 25°.

		Data relating to ligroin layer.					
$\frac{100\,[H_2SO_4]}{[H_2SO_4] + [H_2O]}$.	Wt. of Ph·CHO taken (g.).	Wt. of *p*-nitrophenylhydrazone in 10 c.c. (g.), (*a*) without Am_2SO_4.	(*b*) with Am_2SO_4.	Wt. of Ph·CHO in 20 c.c. (g.). (*a*).	(*b*).	% of Ph·CHO. (*a*).	(*b*).
(7·3% free SO_3)	1·1745	0·0069	—	0·0030	—	0·5	—
,,	1·2004	—	0·0195	—	0·0172	—	1·4
100	1·2432	0·0117	0·0145	0·0103	0·0128	0·81	1·03
90	1·2051	0·0114	0·1190	0·0100	0·1047	0·83	8·7
80	1·2596	0·0319	0·4406	0·0281	0·3878	1·77	30·8

Colorimetric Measurements.—All colorimetric determinations were carried out at the ordinary temperature with a Klett top-reading colorimeter, a daylight lamp reflecting from ground-glass mirrors being used as a source of illumination. The colour intensities were matched against the deepest coloured solution as a standard by adjustment of the length of the column. All recorded readings are the means of at least four independent, concordant adjustments approached from either side. The adjustment of the instrument was checked for various lengths of column by comparison of the same solution placed in both tubes, the following readings being obtained:

R.-H. column (standard)	50	45	40	30 mm.
L.-H. column, mean reading	50·2	45·1	40·1	30 mm.

Effect of varying the Mol. Ratio Ph·COR/H_2SO_4 *on the Colour Value. Deviation from Beer's Law.*—The results are given in Table V, from which the data summarised in Table II are taken.

Effect of varying the Dilution of the Sulphuric Acid on the Colour Value when the Mol. Ratio Ph·COR/H_2SO_4 *is kept constant.*—A constant weight of the carbonyl compound was weighed into a series of stoppered flasks. To each flask was added a weighed amount of 100, 90, 80, and 70% sulphuric acid respectively (made by accurate dilution of an oleum solution of known concentration), each equivalent in actual sulphuric acid content to the weight of 100% sulphuric acid taken in the first case. The colour values of these solutions were compared in pairs, that of the solution in 100% acid being taken as the standard. Since the concentration of the carbonyl compound was small, the densities of the solutions were assumed to be the same as that of the sulphuric acid employed, and

TABLE V.

Colour values of solution of Ph·COR *in* 100·4% *sulphuric acid at the ordinary temperature.*

	R = H.				R = Me.			
Weight of Ph·COR in 100 c.c. of soltn. (g.)	1·9344	0·9672	0·4836	0·2418	1·8992	0·9496	0·4748	0·2374
Lengths of columns for colour matching (mm.)	27·3	50	—	—	31·9	54	—	—
	24·6	45	—	—	28·9	50	—	—
	16·9	—	57	—	16·9	—	55	—
	—	27·3	50	—	—	30·8	55	—
	—	24·3	45	—	—	25·4	45	—
	—	17·2	—	58	—	17·6	—	55
	—	—	29·8	55	—	—	31·7	55
	—	—	27·1	50	—	—	28·1	50
Relative lengths of columns	1	1·83	3·25	6·14	1	1·73	3·26	5·35
		1·83	3·39	6·14		1·70	3·05	5·33
			3·37	6·17			2·91	5·47
Mean	1	1·83	3·33	6·15	1	1·71	3·07	5·38
Beer's law requires	1	2	4	8	1	2	4	8

TABLE VI.

Effect of the dilution of the acid on the colour values of solutions of Ph·COR *in sulphuric acid when the mol. ratio* Ph·COR/H_2SO_4 *is* 1/89 (*constant*).

	R = H.				R = Me.*		
Conc. of H_2SO_4 (%)	100	90	80	70	100	90	80
Wt. of Ph·COR (g.)	0·300	0·300	0·300	0·300	0·340	0·340	0·340
Wt. of H_2SO_4 (g.)	24·700	27·444	30·866	35·286	24·700	27·444	30·866
Mean values of lengths of columns for equal colour intensity	36·9	50	—	—	<5	55	—
	34·1	45	—	—	—	30	50
	20·8	—	55	—	—	25	40
	—	24·9	55	—	—	—	—
	—	22·4	50	—	—	—	—
	—	—	20·6	55	—	—	—
	—	—	19·4	50	—	—	—
Relative lengths of column	1	1·36	(2·64)	7·94	1	>11	>18·4
		1·32	2·96	7·66			>17·6
			2·99				
Mean relative lengths of column	[1]	1·34	2·97	7·80	1	>11	>18
Observed relative colour values	[100]	74·8	33·65	12·83	[100]	<9	<5·6
Density of solution	1·859	1·820	1·733	1·615	1·859	1·820	1·733
Total vol. of solution (c.c.)	13·45	15·25	18·0	22·0	13·45	15·25	18·0
Actual colour values (corr.)	[100]	84·8	45·0	21·0	[100]	<10	<7

* Matching in this case was only very approximate owing to the large differences in colour intensity.

hence the total volumes of the solutions were calculated in each case. The observed colour values were corrected for these small differences in total volume on the basis of Beer's law. The results are given in Table VI.

Benzylidene-m-*nitroaniline*.—An attempt to repeat a similar comparison in the case of this Schiff's base failed owing to the rapid diminution in colour intensity which occurs as the concentration of the sulphuric acid is diminished. In 100 and 90% sulphuric acid, in which the mol. ratio (base)/(actual sulphuric acid) had the constant value 1/20, the relative corrected colour values were approximately 100 and 25 respectively.

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