206. *Aromatic Sulphonation. Part I. The Ionisation Constants of* p-*Nitrotoluene, Nitrobenzene, and* p-*Chloronitrobenzene, and the Acidity Function of Oleum.*

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The ionisation constants (pK_a) of *p*-nitrotoluene ($-10{\cdot}28$), nitrobenzene ($-11{\cdot}26$), and *p*-chloronitrobenzene ($-11{\cdot}49$) have been determined spectrometrically, and the acidity-function scale of sulphuric acid has been extended into oleum containing up to 14% of sulphur trioxide.

Aromatic mononitro-compounds are weak, although not unobservably weak, bases and their ionisation can be measured in a strongly acidic medium. This basic property was first noticed by Hantzsch (*Z. physikal. Chem.*, 1908, **65**, 41) who found that *p*-nitrotoluene lowered the freezing point of sulphuric acid more than did a non-electrolyte and concluded that the *p*-nitrotoluene was partly converted into an oxonium salt. Cherbuliez (*Helv. Chim. Acta*, 1923, **6**, 281) and Masson (*J.*, 1931, 3200) showed independently that the conductivity of anhydrous sulphuric acid was enhanced by dissolved nitrobenzene and successfully prepared a crystalline addition product, regarded as the hydrogen sulphate, $[C_6H_5{\cdot}NO_2H]^+SO_4H^-$. The ionisation of nitrobenzene in sulphuric acid was confirmed cryoscopically by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1708), and Gordy and Stanford (*J. Chem. Physics*, 1940, **8**, 170) estimated the order of magnitude of the ionisation constant from a comparison of the frequency of the O–D stretching vibration of methyl deuteroalcohol in benzene and nitrobenzene solution.

In the present series of measurements, the degree of ionisation of *p*-nitrotoluene, nitrobenzene, and *p*-chloronitrobenzene was determined spectrometrically in media of successively increasing sulphuric acid concentration. If the ion and free base are assumed to absorb independently, the extinction coefficient (ε) of a solution containing both forms is $\varepsilon = \varepsilon_{BH^+}[BH^+] + \varepsilon_B[B]$, where ε_{BH^+} and ε_B, $[BH^+]$ and $[B]$, are respectively the extinction coefficients (at a particular wave-length) and the relative concentrations of the ion and free base. Because $[BH^+] + [B] = 1$ this equation can be written as $[B]/[BH^+] = (\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_B)$, which enables the indicator-ionisation ratio to be evaluated directly from the absorption measurements. The ionisation ratio is related to the ionisation constant of the base and the acidity function of the medium by the equation (Hammett, *Chem. Reviews*, 1935, **16**, 67):

$$H_0 = pK_a + \log [B]/[BH^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

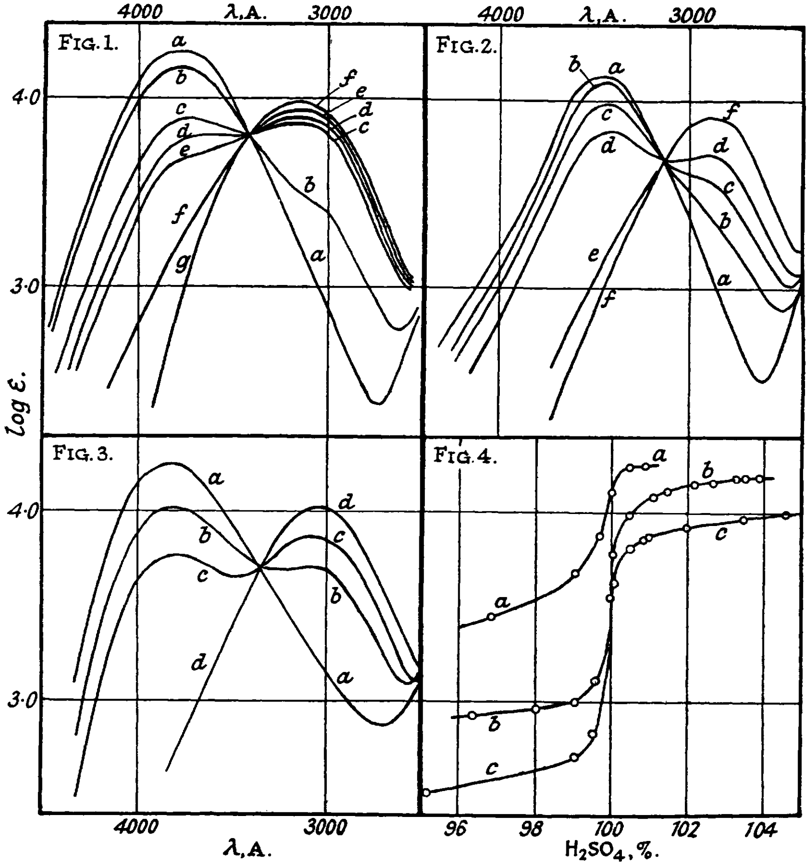
where K_a is the acidic ionisation constant of the ion BH^+ and H_0 is the acidity function of the medium with respect to an uncharged base. The acidity function of sulphuric acid up to 100% has been determined (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827), and by combining these results with a cryoscopic measurement of the degree of ionisation Hammett (*J. Chem. Physics*, 1940, **8**, 644) found pK_a −11 for nitrobenzene. An improved determination by the same method (Gillespie and Millen, *Quart. Reviews*, 1948, 292) * gave pK_a −11·0. The measurements now reported yield the following values for pK_a:

p-Nitrotoluene	−10·28	*p*-Chloronitrobenzene	−11·49
Nitrobenzene	−11·26		

Although the ionisation constants are in the expected order, the large effect of the *p*-methyl compared with that of the *p*-chloro-substituent is unusual. The result suggests that the transfer

Absorption spectra of p-*nitrotoluene, nitrobenzene and* p-*chloronitrobenzene in sulphuric acid.*

p-*Nitrotoluene.* *Nitrobenzene.*



p-*Chloronitrobenzene.*

Variation of ε *with acid composition,* λ = 3650 A.

FIG. 1.

	Acid, %.
a	(*calc.*).
b	100·00
c	99·70
d	99·36
e	99·08
f	96·86
g	85·5

FIG. 2.

	Acid, %.
a	103·2
b	100·8
c	100·24
d	100·02
e	99·0
f	95·2

FIG. 3.

	Acid, %.
a	103·54
b	100·46
c	100·06
d	99·05

FIG. 4.

a	p-*Nitrotoluene*
b	p-*Chloronitrobenzene*
c	*Nitrobenzene*

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* The authors appear to use the original acidity-function scale, which is 0·29 unit higher (less negative) than the scale adopted in this paper (Hammett and Paul, *loc. cit.*).

TABLE I.

Evaluation of ionisation constants and acidity function (temp. 21° ± 3°).

Medium.		Extinction coefficient,	$-\frac{1}{\varepsilon}\frac{d\varepsilon}{dt}$		Acidity function,*	Ionisation constant,
% H_2SO_4.	% SO_3.	ε.	% per min.	log [B]/[BH+].	H_0.	pK_a.
A. *Nitrobenzene*, $\varepsilon_{ion} = 9000$, $\varepsilon_{base} = 300$ *at* λ 3650 A.						
84·6	—	203	—	—	—	—
87·6	—	231	—	—	—	—
90·76	—	254	—	—	—	—
95·10	—	329	—	2·5	−8·8	−11·3
99·02	—	507	—	1·61	−9·61	−11·22
99·07	—	511	—	1·61	−9·64	−11·25
99·10	—	505	—	1·62	−9·65	−11·27
99·50	—	686	—	1·34	−9·91	−11·25
99·51	—	686	—	1·34	−9·92	−11·26
99·53	—	693	—	1·33	−9·93	−11·26
99·55	—	664	—	1·36	−9·94	−11·30
						−11·26 ± 0·02
100·05	—	4,320	—	0·08	−11·18	—
100·06	—	4,080	—	0·10	−11·16	—
100·08	—	4,230	—	0·08	−11·18	—
100·09	—	4,350	—	0·06	−11·20	—
100·46	2·04	6,530	0·01	−0·40	−11·66	—
100·51	2·26	6,580	0·02	−0·41	−11·67	—
100·87	3·86	7,250	0·03	−0·60	−11·86	—
100·94	4·18	7,460	0·02	−0·68	−11·94	—
101·00	4·45	7,540	0·02	−0·70	−11·96	—
101·91	8·48	8,350	0·04	−1·09	−12·35	
101·97	8·74	8,400	0·04	−1·13	−12·39	—
103·5	15·5	9,340	0·08	—	—	—
104·6	20·4	9,980	0·15	—	—	—
106·2	27·6	10,570	0·28	—	—	—
108·0	35·5	11,200	0·60	—	—	—
B. p-*Chloronitrobenzene*, $\varepsilon_{ion} = 15{,}900$, $\varepsilon_{base} = 810$ *at* λ 3650 A.						
94·8	—	762	—	—	—	—
96·36	—	845	—	—	—	—
98·02	—	910	—	—	—	—
99·04	—	980	—	1·94	− 9·61	−11·57
99·05	—	1,020	—	1·85	− 9·62	−11·47
99·58	—	1,280	—	1·49	− 9·97	−11·46
99·59	—	1,280	—	1·49	− 9·99	−11·48
99·99	—	3,570	—	0·65	−10·87	−11·52
100·06	—	5,970	—	0·28	−11·18	−11·46
100·07	—	6,090	—	0·27	−11·19	−11·46
100·47	—	9,570	—	−0·14	−11·66	−11·52
100·48	—	9,640	—	−0·15	−11·66	−11·51
						−11·49 ± 0·03
100·50	2·22	9,860	—	−0·18	−11·67	—
101·11	4·93	12,040	—	−0·46	−11·95	—
101·48	6·57	12,910	—	−0·61	−12·10	—
101·49	6·61	13,120	—	−0·65	−12·14	—
102·26	10·0	14,180	—	−0·89	−12·38	—
102·68	11·9	14,490	—	−0·99	−12·48	—
103·30	14·6	15,080	—	−1·24	−12·73	—
103·55	15·8	15,250	—	−1·35	−12·84	—
103·89	17·3	15,520	—	—	—	—
105·74	25·5	15,890	—	—	—	—
107·7	34·2	15,890	—	—	—	—
C. p-*Nitrotoluene*, $\varepsilon_{ion} = 18{,}000$, $\varepsilon_{base} = 1850$ *at* λ 3650 A.						
95·30	—	2,370	—	1·48	− 8·79	−10·27
98·73	—	4,280	—	0·75	− 9·50	−10·25
98·91	—	4,500	—	0·71	− 9·56	−10·27
99·07	—	4,780	—	0·65	− 9·64	−10·29
100·50	2·22	17,320	0·11	−1·36	−11·64	−10·31
100·92	4·08	17,890	0·26	—	—	—
						−10·28 ± 0·02

* Values of the acidity function of media for which % $H_2SO_4 \leqslant 100{\cdot}0$ are taken from the Tables of Hammett and others (*loc. cit.*).

of charge by conjugation or hyperconjugation between the *p*-chloro- or *p*-methyl substituent and the point of attachment of the proton is comparatively great, certainly greater than in the corresponding isoelectronic *p*-substituted benzoate ions (which, however, are anion bases). Additional evidence on this point will be considered in the following paper. Similar effects are observed in the series of *p*-substituted acetophenones (Flexser and Hammett, *J. Amer. Chem. Soc.*, 1938, **60**, 885).

EXPERIMENTAL.

Materials.—*p*-Nitrotoluene, f. p. 51·5°, was purified by several recrystallisations from alcohol and from light petroleum. *p*-Chloronitrobenzene, m. p. 83°, was obtained in white crystals by recrystallisation from light petroleum and then successively from 50% nitric acid and aqueous alcohol. Nitrobenzene, f. p. 5·72°, was prepared from purified benzene, f. p. 5·5°, according to the directions of Masson (*Nature*, 1931, **128**, 726).

Fuming sulphuric acid was prepared by distillation of sulphur trioxide from commercial oleum containing potassium persulphate into concentrated sulphuric acid in an all-glass apparatus. Sulphur dioxide was oxidised by the persulphate if the strength of the oleum did not exceed about 30% of SO_3. The storage and analysis of the acids have been described previously (Brand, *J.*, 1946, 585). At wave-lengths exceeding about 2500 A. the media were sufficiently transparent to be used in thicknesses up to 10 cm.

Measurement of Extinction Coefficients.—The extinction coefficients were determined qualitatively throughout the near ultra-violet region by use of a Hilger Spekker photometer and a medium quartz spectrograph, and were evaluated by the usual equation, $\log I_0/I = \varepsilon.c.d$, where *c* is the concentration of solute in moles per litre and *d* is the thickness, in cm., of the absorbing layer. The changes in the spectrum which accompany ionisation are shown in Figs. 1—3. More accurate values of ε (±1%) were measured at λ 3650—3663 A. with a photoelectric apparatus, and the results are collected in Tables I and II, and Fig. 4.

TABLE II.

Influence of hydrogen sulphates on the acidity function of oleum.

Medium.		Added salt.		Extinction coefficient,		Acidity function,
% H_2SO_4.	$[SO_3]$ concn., mol./kg.		concn., equiv./kg.	ε.	log $[B]/[BH^+]$.	H_0.
A. *Nitrobenzene indicator*, $\varepsilon_{ion} = 9000$, $\varepsilon_{base} = 300$ *at* λ 3650 A.						
100·46	0·26	—	—	6530 *	−0·40	−11·66
100·457	0·254	$Ba(SO_4Me)_2$	0·0830	4950	−0·06	−11·32
100·443	0·247	K_2SO_4	0·0977	4380	0·05	−11·21
100·456	0·253	K_2SO_4	0·146	3530	0·23	−11·03
100·444	0·247	$Ba(SO_4Me)_2$	0·183	2790	0·40	−10·86
100·463	0·258	K_2SO_4	0·198	2760	0·41	−10·85
100·455	0·253	K_2SO_4	0·253	1980	0·62	−10·64
100·87	0·48	—	—	7250 *	−0·60	−11·86
100·858	0·477	$Ba(SO_4Me)_2$	0·102	6180	−0·32	−11·58
100·874	0·486	K_2SO_4	0·150	5300	−0·13	−11·39
100·852	0·473	$Ba(SO_4Me)_2$	0·197	4770	−0·03	−11·29
100·844	0·469	$BaSO_4$	0·216	4820	−0·04	−11·30
100·862	0·479	K_2SO_4	0·257	3820	0·08	−11·18
100·840	0·465	K_2SO_4	0·364	2440	0·49	−10·77
100·838	0·466	K_2SO_4	0·576	1150	0·97	−10·29
B. p-*Chloronitrobenzene indicator*, $\varepsilon_{ion} = 15{,}900$, $\varepsilon_{base} = 810$ *at* λ 3650 A.						
102·68	1·49	—	—	14,490 *	−0·99	−12·48
102·57	1·43	K_2SO_4	0·0494	14,090	−0·87	−12·36
102·55	1·42	K_2SO_4	0·145	13,050	−0·63	−12·12
102·53	1·41	K_2SO_4	0·169	12,390	−0·52	−12·01
102·52	1·40	K_2SO_4	0·244	11,380	−0·37	−11·86
102·51	1·39	K_2SO_4	0·247	11,350	−0·37	−11·86
103·55	1·97	—	—	15,250 *	−1·35	−12·84
103·52	1·95	K_2SO_4	0·0988	14,560	−1·01	−12·50
103·47	1·93	K_2SO_4	0·249	13,270	−0·67	−12·16
103·39	1·89	K_2SO_4	0·488	10,460	−0·25	−11·74
103·33	1·85	K_2SO_4	0·608	8,960	−0·07	−11·56
104·44	2·47	K_2SO_4	0·246	14,440	−0·97	−12·46
104·44	2·47	K_2SO_4	0·246	14,490	−0·99	−12·48
104·35	2·42	K_2SO_4	0·479	12,510	−0·54	−12·03
104·34	2·41	K_2SO_4	0·501	11,440	−0·50	−11·99

* Table I, average.

The calibration of the apparatus was checked by using an alkaline solution of potassium chromate (von Halban, *Z. physikal. Chem.*, 1922, **100**, 221).

Calculation of Ionisation Constants and Acidity Function.—The ionisation ratio of each base in a particular medium was calculated from the photoelectric results. Independently of the changes due to ionisation, the spectra moved gradually towards longer wave-lengths as the strength of the sulphuric acid medium was increased, and in order that this effect should not unduly affect the evaluation of the ionisation ratio, values of ε_{ion} and ε_{base} were chosen as close as possible to the steep portions of the curves in Fig. 4. To assist in this, the complete spectra were used to determine the range of composition of the medium within which ionisation took place. The ionisation constants were obtained from the values of the ionisation ratio of the indicators in concentrated sulphuric acid, by use of the established acidity scale, and the acidity function hence extended into fuming sulphuric acid containing up to 14% of free sulphur trioxide (Tables I and V). Table II contains measurements of the acidity function of fuming sulphuric acid in the presence of potassium sulphate, barium sulphate, and barium di(methyl sulphate).

The ionisation constant of *p*-nitrotoluene was also calculated at regular intervals of frequency from the extinction coefficients obtained from the spectra in Fig. 1 (Table III). The method of calculation is described by Flexser, Hammett, and Dingwall (*J. Amer. Chem. Soc.*, 1935, **57**, 2103). The spectrum of the ion of *p*-nitrotoluene, which was not measured because of sulphonation, has been calculated from the other curves.

p-Nitrotoluene and nitrobenzene reacted with fuming sulphuric acid and the transmission was extrapolated back to zero time. The rate of diminution of the intensity of absorption is recorded in Table I. *p*-Chloronitrobenzene was not attacked.

TABLE III.

Calculation of the ionisation constant of p-*nitrotoluene from the absorption spectrum,* λ 2500—4500 A.

Extinction coefficients.

Frequency, cm.$^{-1}$.	% H_2SO_4 :	85·6	95·86	99·08	99·15	99·36	99·70	100·00	ε_{ion} (calc.).	$-pK_a$.
	H_0 :	−7·9	−8·93	−9·64	−9·67	−9·80	−10·11	−10·89		
22,000		0	0	68	74	85	108	269	340	10·16
23,000		0	66	296	296	390	603	1,250	1,560	10·28
24,000		10	260	950	970	1170	1900	4,200	5,250	10·22
25,000		87	670	2250	2480	3030	4570	9,820	12,270	10·22
26,000		480	1350	4170	3890	5300	7240	14,100	17,500	10·17
27,000		1500	2360	4950	4530	6320	7820	14,100	17,300	10·13
28,000		3300	3700	5510	5380	6320	7050	10,750	12,620	10·14
29,000		5800	—	6310	6310	6460	6610	7,460	7,860	10·11
30,000		8470	—	7500	7500	7280	6920	5,180	4,350	10·10
31,000		9820	—	8510	8320	7800	7360	3,810	3,200	10·23
32,000		9890	9590	8810	8570	7850	7410	3,080	1,370	10·34
33,000		9200	8850	8130	7930	7400	6930	2,630	980	10·25
34,000		7380	7140	6700	6670	6280	5330	2,010	660	10·34
35,000		5510	5190	4980	4960	4700	3780	1,380	340	9·87
36,000		3980	—	3390	3340	3150	2510	990	260	10·45
37,000		2630	—	2190	2090	1960	1650	720	240	10·20
38,000		1800	—	1380	1310	1290	1170	600	300	9·90
39,000		1340	—	1050	1000	1010	950	650	480	9·73

Average pK_a — 10·19 ± 0·1

DISCUSSION.

The acidity function of anhydrous sulphuric acid was found by Hammett and Deyrup (*loc. cit.*) to be −10·60 units. According to the results of a revised determination of the strengths of some of the more basic indicators by Hammett and Paul (*loc. cit.*) and by Braude (*J.*, 1948, 1976) the original scale should be corrected by subtracting 0·29 unit or 0·45 unit respectively. The method of Hammett and his co-workers was modified and improved by Braude, but in this paper the value adopted provisionally is −10·89, being obtained from measurements of the same type throughout.

The acidity function of 87—100% sulphuric acid may be calculated from the molecular composition, apart from a constant term. The ionisation ratio of an uncharged basic indicator is governed by the equilibrium

$$B + H_2SO_4 \overset{K}{\rightleftharpoons} BH^+ + SO_4H^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

and, therefore, $(B)/(BH^+) = (SO_4H^-)/K(H_2SO_4)$, where parentheses refer to activities. This equation may be combined with equation (1) to give equation (3) :

$$H_0 = pK_a + pK + \log [SO_4H^-]/[H_2SO_4] + \log\{f_{BH^+} \cdot f_{SO_4H^-}/f_B \cdot f_{H_2SO_4}\} \quad . \; . \; . \quad (3)$$

To quite a good approximation, water and molecular sulphuric acid react quantitatively to give oxonium and bisulphate ions. In mixtures in which sulphuric acid is present in molecular excess over water, the molar ratio SO_4H^-/H_2SO_4 can, therefore, be calculated directly from the composition of the medium, and in Table IV the acidity function is evaluated in this way from the semi-theoretical equation (4) :

$$H_0 = -8{\cdot}35 + \log\,[SO_4H^-]/[H_2SO_4] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

the constant term being obtained empirically. The agreement is poor at the top of Table IV owing to self-ionisation of the sulphuric acid, and the calculation cannot be extended to more aqueous acid because it is then certainly incorrect to assume that water is converted quantitatively into oxonium ions. The results for media between 87% and 99·8% sulphuric acid are satisfactory, however, in spite of the fact that the activity coefficients do not enter symmetrically into the final term in equation (3) which was disregarded in writing equation (4). The constancy of this term would imply that the ion-activity coefficients are practically constant throughout the range of medium composition under discussion, and this conclusion is difficult to justify, although the deviations would be on a reduced scale in a solvent of high dielectric constant. It is possible that the effect of neglecting the activity-coefficient term is fortuitously compensated by a small reversibility of the reaction between water and molecular sulphuric acid (cf. Ingold and others, *Nature*, 1946, **158**, 480), because the assumption that these components of the system react together *quantitatively* exaggerates the acidity of sulphuric acid and should, of itself, yield results more negative than those observed experimentally. Since the ionic activity coefficients would (initially) decrease from unity, the logarithm of their product would be negative and the approximation involved in writing equations (3) and (4) partly cancel one another. Nevertheless, the diminishing concentration of bisulphate ions in acids containing a small proportion of water (0·5—0·0% of H_2O) obviously accounts for the sharp rise of the acidity function in this region (cf. Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1144).

TABLE IV.

Comparison of calculated and observed values of the acidity function (87·5—100% H_2SO_4).

Medium.		Molar ratio,	Acidity function.	
% H_2SO_4.	% H_2O.	SO_4H^-/H_2SO_4.	Calc.	Obs.*
99·9	0·1	0·0055	−10·61	−10·49
99·8	0·2	0·0110	−10·31	−10·24
99·5	0·5	0·0282	− 9·90	− 9·91
99·0	1·0	0·0581	− 9·59	− 9·61
98·0	2·0	0·125	− 9·25	− 9·26
96·0	4·0	0·293	− 8·88	− 8·89
95·0	5·0	0·402	(− 8·75)	(−8·75)
94·0	6·0	0·532	− 8·62	− 8·63
92·0	8·0	0·897	− 8·40	− 8·40
90·0	10·0	1·53	− 8·18	− 8·19
87·5	12·5	3·48	− 7·81	− 7·91

* Hammett and others (*loc. cit.*) : the calculation uses the experimental value for the acidity function of 95% sulphuric acid.

The Acidity Function of Oleum.—Values of the acidity function of fuming sulphuric acid containing between 0% and 14% of free sulphur trioxide (*i.e.*, sulphur trioxide in excess of the composition H_2SO_4) are collected in Table V.

TABLE V.

Acidity function of fuming sulphuric acid.

SO_3, %	0·0	2·0	4·0	6·0	8·0	10·0	12·0	14·0
H_2SO_4, %	100·0	100·45	100·90	101·35	101·80	102·25	102·70	103·15
$-H_0$	10·89	11·65	11·89	12·06	12·22	12·37	12·53	12·68

Equations (5) and (6) represent alternative possibilities for the equilibrium between the indicator and the medium, the former being analogous to the equilibrium (2) :

$$ArNO_2 + H_2S_2O_7 \rightleftharpoons ArNO_2H^+ + S_2O_7H^- \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$ArNO_2 + SO_3 \rightleftharpoons ArNO_2{\cdot}SO_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

The ultra-violet spectra do not distinguish between the equilibria (5) and (6), but the question can be decided from the influence of bisulphate ions, added initially to the medium, on the position of the indicator equilibrium. The addition of bisulphate ions establishes a further equilibrium, the position of which lies essentially on the right hand side of equation (7):

$$SO_4H^- + H_2S_2O_7 \rightleftharpoons H_2SO_4 + S_2O_7H^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

Bisulphate ions, therefore, displace the indicator equilibrium (5) or (6) towards the left by the removal of pyrosulphuric acid (or " free " sulphur trioxide) by the reaction (7). If the indicator is engaged in the equilibrium (5) its ionisation will also be reduced by the mass-action effect of the $S_2O_7H^-$ ions produced in (7), but, on the other hand, if the equilibrium (6) is established, the indicator ionisation ratio will be comparatively insensitive to the presence of $S_2O_7H^-$ ions. The point can be tested by comparing the effects produced on the ionisation ratio of a suitable base by the addition of an equal molal concentration of water and of bisulphate ions. Water reacts quantitatively according to the equation $H_2O + H_2S_2O_7 = 2H_2SO_4$; bisulphate ions also remove pyrosulphuric acid, forming $S_2O_7H^-$ ions according to equation (7). If the indicator is involved in the equilibrium (6), the influences of water and of bisulphate ions on the indicator ionisation ratio should be similar, but if (5) is correct the effect of the bisulphate ions should exceed that of water.

The necessary comparison can be made from the results in Tables I and II, and the figures below show that the influence of potassium bisulphate on the ionisation ratio of *p*-chloronitrobenzene so far exceeds that of water as to leave no doubt that the mass-action effect of the $S_2O_7H^-$ ions on the indicator equilibrium is real. The equilibrium (5) is, therefore, established in the media under discussion, although the possibility remains that (6) may operate in very strong oleum.

Influence of water and potassium hydrogen sulphate on the ionisation ratio of p-*chloronitrobenzene* (medium: 103·55% H_2SO_4).

Added substance.			Added substance.		
	Concn., mol./kg.	log [B]/[BH⁺].		Concn., mol./kg.	log [B]/[BH⁺].
$KHSO_4$	0·00	−1·35	H_2O	0·00	−1·25
,, ...	0·10	−1·01	,, ...	0·10	−1·26
,, ...	0·25	−0·67	,, ...	0·25	−1·14
,, ...	0·49	−0·25	,, ...	0·49	−0·93
,, ...	0·61	−0·07	,, ...	0·61	−0·88

Some measurements of the degree of ionisation of 4 : 5-dibromo-2 : 7-dinitrofluorescein in weak oleum have been reported by Lewis and Bigeleisen (*loc. cit.*), but this compound is a cation base in such media and the related acidity function is H_+ and not H_0. These authors assumed that the equilibrium (6) was established between the indicator and the medium in all fuming acids, and calculated the acidity function of oleum from the partial vapour pressure of sulphur trioxide by the equation: H = a constant + $\log p_{SO_3}$. The results (cf. Deane, *J. Amer. Chem. Soc.*, 1945, **67**, 329) are quite different from those reported in this paper. It has been claimed (Deane, *loc. cit.*) that the values obtained by Lewis and Bigeleisen are consistent with measurements of the rate of cyclisation of *o*-benzoylbenzoic acid, but the test is inconclusive because the acid does not ionise as a simple base in sulphuric acid solution (Newman, Kuivila, and Garrett, *J. Amer. Chem. Soc.*, 1945, **67**, 704).

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