

252. The Spectrophotometric Determination of the Ionisation Constants of Aromatic Nitro-compounds.

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The ultra-violet absorption spectrum of aromatic nitro-compounds is modified characteristically in powerfully acid (H_2SO_4 and $\text{H}_2\text{SO}_4\text{-SO}_3$) solvents by the transfer of a proton to the nitro-group, yielding ions of the formula $\text{Ar}\cdot\text{NO}\cdot\text{OH}^+$, with alteration of the binding energies (but not the number) of the π -electrons. The ionisation constants have been evaluated from the spectra in sulphuric acid media. Simple mononitro-compounds are weak bases in anhydrous sulphuric acid, but are quantitatively ionised in concentrated oleums. Di- and tri-nitro-compounds are much less basic and are incompletely ionised in the most powerfully acid oleum media. In terms of H_0 , the acidity of the oleums falls 3 units below that of anhydrous sulphuric acid.

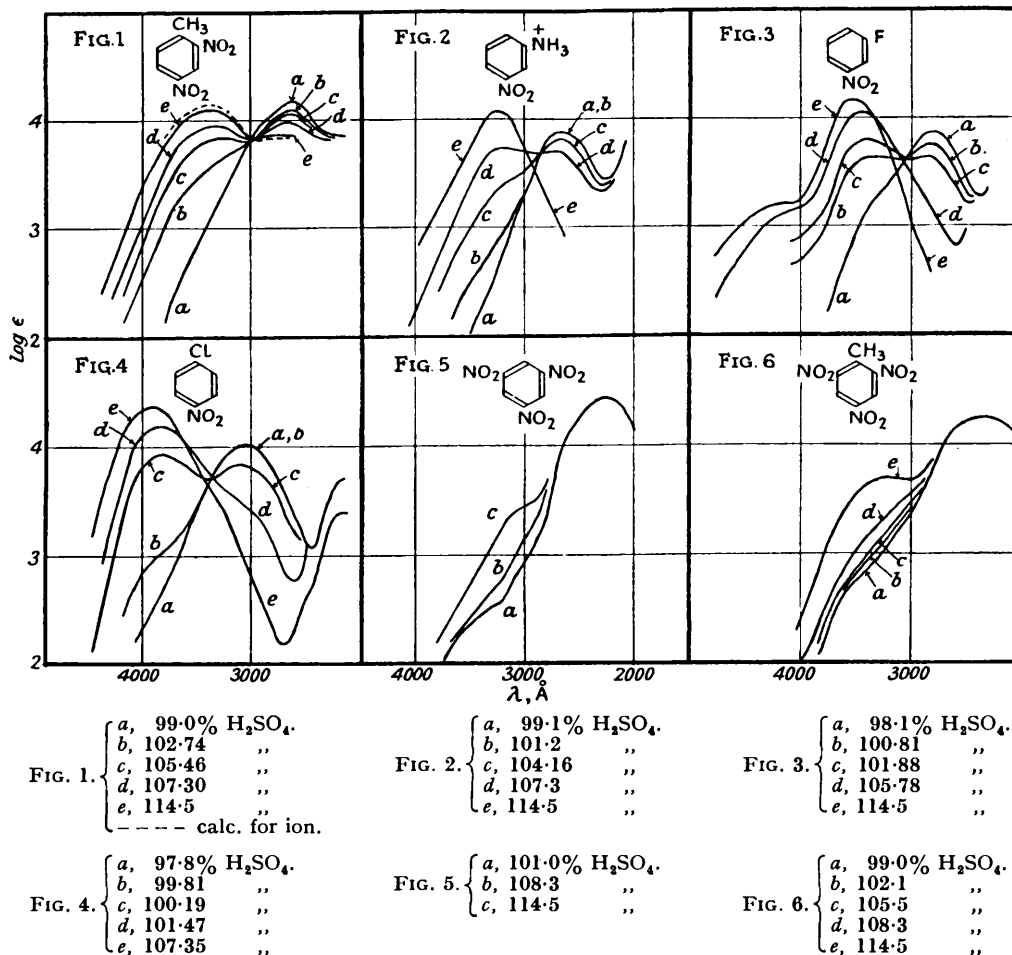
The influence of substituents on the ionisation constant is generally in semi-quantitative agreement with the electrostatic theory, but the entropy of ionisation shows that environmental factors are not inappreciable. Attention is drawn to the discrepancy between the ionisation constants reported here and those obtained by cryoscopic methods (Gillespie, *J.*, 1950, 2542), and the reasons for this are discussed.

ALL mononitro-derivatives of benzene behave as weak bases in sulphuric acid solution. The ions formed, $\text{Ar}\cdot\text{NO}\cdot\text{OH}^+$, are isoelectronic with derivatives of benzoic acid, but are more powerfully acidic owing to the formal charge on the central nitrogen atom and the large resonance energy associated with the nitro-group. As a class they are the strongest cation acids about which there is reasonably quantitative information. The basicity of the nitro-group was discovered cryoscopically by Hantzsch in 1908 (*Z. physikal. Chem.*, **65**, 41) and approximate ionisation constants were later evaluated by this method (Hammett, *J. Chem. Physics*, 1940, **8**, 644; Gillespie, *J.*, 1950, 2542). Ionisation constants may also be determined from the ultra-violet spectrum, which is modified in a regular, characteristic fashion by the transfer of the proton (Brand, *J.*, 1950, 997). No other general methods seem to be available at present.

The cryoscopic and optical methods both have important limitations. Cryoscopy can be used in sulphuric acid containing a trace of water, but is not adaptable outside the limits of a narrow range of solvent composition. For the present purpose this operates rather unfavourably because the degree of ionisation of bases weaker than nitrobenzene itself is inconveniently low in such media. The optical method has a free choice of medium, but suffers from the disadvantage that it is necessary to know the spectrum of the conjugate ion of the nitro-compound. The very feebly basic trinitro-compounds, for example, are too incompletely ionised, even in the most strongly acid medium, to be treated quantitatively. In addition, quite serious difficulties arise from the physical influence of a change of medium on the spectra. These disadvantages are at least partly offset by the access to a useful range of media in which H_0 falls 3 units below that of anhydrous sulphuric acid. The ionisation constants of several nitro-compounds have now been evaluated in these mixtures.

The characteristic spectral effect of the proton is to move the principal absorption band some 6000—9000 cm^{-1} towards lower frequencies and simultaneously to increase ϵ_{max} nearly two-fold. Weaker bands on the long wave-length shoulder are also displaced, and may remain prominent or disappear, depending on other substituents present in the molecule (Figs. 1—6). The main band must represent the same transition in the ion and the uncharged molecule, which have the same π -electron configuration, and it has been suggested that it corresponds to the transition of benzene at 50 000 cm^{-1} (Doub and Vandenberg, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414; Platt, *J. Chem. Physics*, 1951, **18**, 101). This assignment meets with the following difficulty. In the spectrum of

the univalent ion of 2 : 4-dinitrotoluene (Fig. 1, broken curve) two intense bands are present, the first with the frequency and intensity characteristic of the ion of a mononitro-compound (3500 Å), and the second characteristic of an un-ionised mononitro-compound (2650 Å). The evidence from the spectrum of 2 : 4-dinitrochlorobenzene is similar, but less complete, and in either case the absorption is quite different from that of an ionised mononitro-compound (e.g., *m*-nitroaniline cation, Fig. 2, curve *e*). The simplest interpretation is that the 40 000 cm.⁻¹ transition of nitrobenzene does not involve the benzene orbitals but



is localised mainly in the nitro-group, a suggestion which has been advanced previously to account for the photochemical formation of nitrosobenzene (Matsen and Hastings, *J. Amer. Chem. Soc.*, 1948, **70**, 3514). On this view the transition becomes $2a_g \times 2b_g$ (${}^1A_1 - {}^1B_1$), allowed by the electronic selection rules with polarisation perpendicular to the symmetry axis of the molecule. "Mixed" transitions of π -electrons from the upper, filled level ($2a_g$) of the nitro-group to unfilled benzenoid levels may account for two of the weak, partially submerged transitions at longer wave-lengths where certainly two, possibly four, weak bands can be observed. The "mixed" transitions are allowed by the symmetry selection rules but are weakened by small overlap.

EXPERIMENTAL

Materials.—The preparation, storage, and analysis of the media were as described by Brand (*loc. cit.*). Measurement of the electrical conductivity was adopted for the more accurate

analysis of dilute oleum and concentrated sulphuric acid. The conductivity was determined at $25^\circ \pm 0.005^\circ$ in a U-shaped cell, bright platinum electrodes and a screened A.C. bridge (James and Knox, *Trans. Faraday Soc.*, 1950, **46**, 254) being used, and was stable and reproducible for several days. The measuring frequency was 1000—3000 cycles per second, and the cell was standardised by using Jones and Bradshaw's 0.1M-potassium chloride solution. Existing measurements of conductivity (Reinhardt, *J. Amer. Chem. Soc.*, 1950, **72**, 3359, where earlier references are given) are in very poor agreement with one another. Our results agree, within a few units %, with those of Bergius (*Z. physikal. Chem.*, 1910, **72**, 338) for fuming acids and of Lichty (*J. Amer. Chem. Soc.*, 1908, **30**, 1834) for aqueous acids; but there is no agreement with Reinhardt's figures. In view of the discrepancy between different workers, calibration curves were drawn up with the batch of oleum used for the optical measurement, the same electrodes being used; the oleum was diluted with 90% H_2SO_4 in a closed apparatus, and the resistance measured continuously.

Measurements.—The extinction coefficients, ϵ (cm. mole l^{-1}) $^{-1}$, were measured with a 'Unicam' photoelectric spectrophotometer or, at 3650 Å only, with a Hilger "Spekker" Absorptiometer. "AnalaR" Sulphuric acid (1-cm. path) was adequately transparent at wave-lengths above 2000 Å. In oleum there was absorption of the shorter wave-lengths (Fajans and Goodeve, *Trans. Faraday Soc.*, 1936, **32**, 511); the minimum solvent transmission being set at 50%, oleum containing 26% of "free" sulphur trioxide could be used above 2400 Å, and 65% oleum above about 2850 Å. Oleums were prepared in the range 0—36% and 60—65% of "free" SO_3 ; the intermediate acids crystallise too readily. Sulphur dioxide absorbed in the region 3100—2500 Å (Gold and Tye, *J.*, 1950, 2932), and was eliminated as described by Brand (*loc. cit.*).

Temperature was not controlled accurately. The mean dependence of ϵ on T (15—45°) varied considerably; the results in the tables refer to $18^\circ \pm 2^\circ$. Typical values of $(1/\epsilon)$ (de/dT) in 99.9% H_2SO_4 were: for *p*-F·C₆H₄·NO₂, +0.008; for *p*-Me·C₆H₄·NO₂, +0.0005 (3650 Å).

Evaluation of the Ionisation Ratios.—The ionisation ratios were calculated by the relation $[Base]/[Ion] = (\epsilon_{ion} - \epsilon)/(\epsilon - \epsilon_{base})$. The sources of error, apart from the experimental error of measurement of ϵ , which is relatively unimportant, are as follows.

(1) The reference spectrum of the ions was difficult to determine. In this respect the bases could be divided into (a) bases weaker than nitrobenzene, and (b) nitrobenzene and alkylnitrobenzenes. Compounds under (b) ionised quantitatively in moderately dilute oleum, but sulphonated at appreciable speed: ϵ was therefore extrapolated to the time of mixing. With bases under (a) there was no sulphonation but it could not be readily confirmed that ionisation was really complete, because a range of media of sufficient acidity did not exist. Nitrobenzene itself appeared to be quantitatively ionised in 30—36% oleum. Because 36—60% media were excluded, the closest approach to the ions of the weaker bases was in 60—65% oleum, in which H_0 was about 0.8 unit lower than in 36% oleum. Calculations with *m*- and *p*-chloro- and -fluoro-nitrobenzene were based on a reference spectrum in this medium, but the ionisation of 2:4-dinitrotoluene (and weaker bases) was still incomplete.

(2) A rising concentration of sulphur trioxide displaces the reference spectra of base and ion along the wave-length axis towards longer wave-lengths, with little alteration of the shape of the curves or the value of ϵ_{max} . (Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103). The effect can be minimised therefore by working at a wave-length of maximum absorption. However, it is doubtful if this simple medium effect holds in the strong (65%) oleum, where formation of $Ar \cdot NO_2 \cdot SO_3$ in place of, or in equilibrium with, $Ar \cdot NO \cdot OH^+$ is probable.

Measurements were usually made at the absorption maximum of the ion. This has two advantages: the change of ϵ is greater and the medium is transparent, even with the strongest oleums. In some cases readings were taken at both maxima.

Calculation of Ionisation Constants.—Ionisation ratio, acidity function, and ionisation constant are related by the equation $H_0 = pK_a + \log_{10} [Base]/[Ion]$, where $K_a = a_H + a_{base}/a_{ion}$, the activities referring to the standard state of an infinitely dilute aqueous solution (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721). The ionisation ratio of the bases was plotted as a function of the medium composition (Fig. 7), and the acidity function of the fuming sulphuric acid (Fig. 8) determined from this group of approximately parallel curves. The numerical values are based on the figure $pK_a = -10.34$ for the *p*-toluyl nitracidium ion,* obtained in slightly aqueous media. In view of the long, stepwise derivation of H_0 and pK_a the accuracy, in the absolute sense, is probably low.

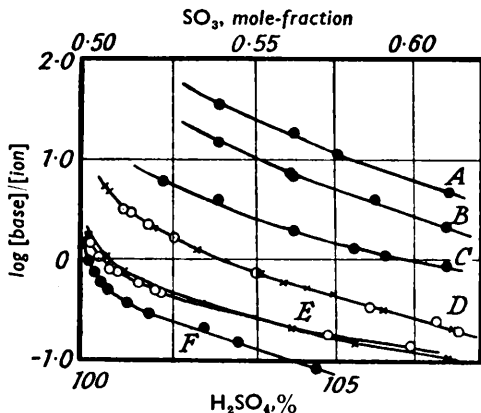
* Conjugate ions of the nitro-compounds are conveniently termed "nitracidium ions."

Some results are collected in Tables 1—3. Individual cases are referred to below.

Nitrobenzene and p-Nitrotoluene (Table 1).—The extinction coefficients at 3650 Å were reported by Brand (*loc. cit.*). In both cases the wave-length falls on a sloping part of the spectrum and the measurements have been repeated at the maximum of the nitracidium ions. In 99—100% H₂SO₄ the results are consistent with the H₀ data obtained by Hammett and Deyrup (*loc. cit.*) with the indicator 2 : 4 : 6-trinitroaniline.

m- and p-Chloro- and -Fluoro-nitrobenzene (Figs. 3 and 4).—The conclusion was formed from the values of ε at 3650 Å (Brand, *loc. cit.*) that ionisation of *p*-chloronitrobenzene was complete in 25% oleum. The new ionisation ratios are significantly different from the old, and this conclusion is now corrected. To obtain further information on the medium effect, the ionisation ratios of each of the bases were determined at the maxima of both the ion and the uncharged molecule. The ratios evaluated from the absorption of the base were then found to be about

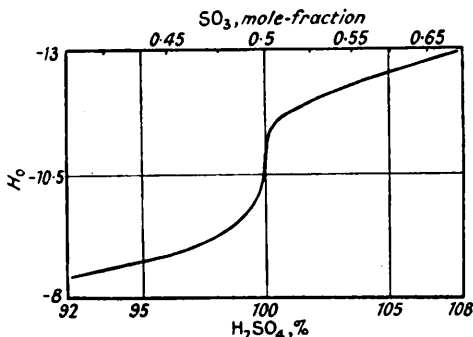
FIG. 7. Ionisation ratios in oleum media.



Key to Fig. 7:

- A. 2 : 4-Dinitrochlorobenzene.
- B. *m*-Nitroaniline cation.
- C. 2 : 4-Dinitrotoluene.
- D. { × *m*-Chloronitrobenzene.
○ *m*-Fluoronitrobenzene.
- E. { × *p*-Chloronitrobenzene.
○ *p*-Fluoronitrobenzene.
- F. Nitrobenzene.

FIG. 8. Acidity function of oleum.



0.1 unit lower than those obtained from the maximum of the ion. The difference, which is not explained if ionisation is incomplete in the 65% oleum, can be understood if the medium effect of the 65% acid is less simple than in dilute oleums and produces (besides the wave-length shift) an increase in ε, and hence leads to values of ε_{ion} which are a few units % too high. The exaltation of intensity has a larger effect on the ionisation ratio calculated from the absorption of the nitracidium ion. It would not be difficult to make the results self-consistent by adopting

TABLE 1. Ionisation ratios and acidity constant of *p*-nitrotoluene.

Medium					Medium						
H ₂ SO ₄ , %	SO ₃ , %	ε _{mean} (λ 3750 Å)	log [Base]/[Ion]	-H ₀ *	-pK _a	H ₂ SO ₄ , %	SO ₃ , %	ε _{mean} (λ 3730 Å)	log [Base]/[Ion]	-H ₀	-pK _a
93.5	—	1 460	—	—	—	100.04	0.18	16 370	-0.74	11.09	10.35
96.65	—	2 245	1.33	8.97	10.30	100.09	0.40	16 670	-0.80	11.16	10.36
98.98	—	4 370	0.70	9.60	10.30	100.11	0.49	16 810	-0.83	11.19	10.36
99.27	—	5 380	0.54	9.75	10.29	100.21	0.93	17 280	-0.94	11.32	10.38
99.42	—	5 750	0.49	9.83	10.34	100.31	1.38	17 650	-1.05	11.41	10.36
99.53	—	6 400	0.41	9.93	10.34	102.16	9.6	19 050	—	—	—
99.65	—	7 360	0.30	10.04	10.34	102.43	10.8	19 090	—	—	—
99.73	—	8 200	0.21	10.14	10.35						
99.85	—	10 100	0.02	10.32	10.34						
99.95	—	13 760	-0.36	10.69	10.33						
										Mean	10.34

* Values of H₀ for media of <100% H₂SO₄ are from Hammett and Deyrup, corrected according to Hammett and Paul (*loc. cit.*).

a lower value of ϵ_{ion} at the longer wave-length, but in the absence of further evidence that this is the correct thing to do the experimental figure has been retained. In the case of the *m*-substituted derivatives, H_0 and pK_a suggest that ionisation is a few units % incomplete in the 65% medium; but comparison of results at the two wave-lengths shows that the effect of this is made up for by the exaltation of intensity which is believed to occur.

m-Nitroaniline Cation.—As judged from the curves in Fig. 2, the second-stage ionisation must be incomplete in 65% oleum. Because the NH_3^+ group is remarkable for its small influence on ultra-violet spectra, the reference value of ϵ_{ion} is assumed to be the same as that of the phenylnitracidium cation. Support for this is as follows. (1) The values of ϵ_{max} of the *m*-nitroaniline cation and (un-ionised) nitrobenzene are very nearly equal in concentrated sulphuric acid as solvent. (2) Several pairs of compounds differing by a *p*- NH_3^+ group have been compared in aqueous solution (Doub and Vandenberg, *loc. cit.*) and the values of ϵ_{max} differ by an average of 1000 units only (the cation always absorbs more strongly). A difference of this magnitude would raise the ionisation ratios by an average of <0.05 unit; moreover, in the *m*-series closer agreement is not improbable.

TABLE 2. The second ionisation constant of *m*-nitroaniline.

Medium			ϵ_{mean} (λ 3200 —3250 Å)	log [Base]/ [Ion]	$-H_0$	$-pK_a$	Medium			ϵ_{mean} (λ 3200 —3250 Å)	log [Base]/ [Ion]	$-H_0$	$-pK_a$
H_2SO_4 , %	SO_3 , %						H_2SO_4 , %	SO_3 , %					
99.0	—	600	—	—	—	105.85	26.0	3 690	0.60	12.61	13.21		
102.73	12.1	1 600	1.16	12.10	13.26	107.30	32.4	5 500	0.33	12.80	13.13		
104.16	18.5	2 470	0.86	12.37	13.23	114.5	64.5	12 050	—0.46	13.67	13.21		
104.22	18.8	2 570	0.83	12.38	13.21			16 000 = ϵ_{ion}					
												Mean	13.21

2 : 4-Dinitrotoluene (Fig. 1) and 2 : 4-Dinitrochlorobenzene.—To calculate pK_a and ϵ_{ion} , the ionisation ratio is re-written as

$$[\text{Base}]/[\text{Ion}] = (\epsilon_{\text{ion}} - \epsilon)/(\epsilon - \epsilon_{\text{base}}) = K_a/h_0; H_0 = -\log_{10} h_0$$

Rearrangement gives $\epsilon_{\text{ion}} - \epsilon = K_a \{(\epsilon - \epsilon_{\text{base}})/h_0\}$. The factor in $\{\}$ is tabulated in col. 7, Table 3; K_a , and hence ϵ_{ion} , are evaluated by the method of least squares.

TABLE 3. Ionisation constant of 2 : 4-dinitrotoluene (3300—3350 Å).

Medium		ϵ_{mean}	$\epsilon - \epsilon_{\text{base}}$	$-H_0$	$h_0 \times 10^{-11}$	$\left\{ \frac{(\epsilon - \epsilon_{\text{base}})}{h_0} \right\} \times 10^{11}$	$-pK_a$
H_2SO_4 , %	SO_3 , %						
99.0	—	1 700	—	—	—	—	—
101.64	7.3	3 400	1 700	11.86	7.2	236	—
102.74	12.2	4 170	2 470	12.10	12.6	196	—
104.23	18.8	5 870	4 170	12.38	24.0	174	—
105.46	24.3	7 060	5 360	12.56	36.3	152	12.6 _a
106.07	27.0	7 790	6 090	12.68	47.9	130	—
107.30	32.4	9 220	7 520	12.80	63.1	119	—
114.5	64.5	12 550	10 850	13.67	470	23.1	—
		$\epsilon_{\text{ion}} = 13 900$					

s-Trinitrobenzene and 2 : 4 : 6-Trinitrotoluene.—Some ionisation was apparent in 36% oleum and appreciably more, probably 10—15 and 20—30% respectively, in 65% oleum (Figs. 5 and 6). The conversion was too small for quantitative conclusions to be drawn. Trinitrotoluene is evidently a stronger base than trinitrobenzene.

DISCUSSION

The influence of substituents on the basicity of the nitro-group is shown in Table 4, where the results are expressed in terms of the acidity constant, pK_a , of the arylnitracidium cation. The pK_a 's refer to aqueous rather than sulphuric acid solutions for the following reason. In the determination of the H_0 function it is assumed that the ratios $f_{\text{base}}/f_{\text{ion}}$ (where the f 's are activity coefficients relatively to the standard state of a dilute aqueous solution) have the same value in a particular medium, excluding media of low dielectric constant, for all bases. Granting this, it follows that the K_a 's are thermodynamic dissociation constants, defined by $K_a = a_{\text{H}^+} a_{\text{B}}/a_{\text{HB}^+}$, the activities referring to the standard state in water. Theoretically, therefore, although the experiments are made in sulphuric

acid media, the activity coefficients allow automatically for the change of solvent and the acidity constants refer to the idealised but unrealisable standard of an ideally dilute solution in water. The assumption involved is supported by the demonstration, in occasional cases, that the acidity constant is independent within experimental error of the solvent used for the determination (Hammett and Deyrup, *loc. cit.*; Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, 56, 827); but it should be remarked that this test has not been applied to H₂SO₄-H₂O mixtures more concentrated than 70%.

The absolute value of the pK_a's in Table 4 is of little significance owing to the uncertainty in the H₀ scale. Essentially, the measurements yield relative acidity constants (col. 3) and the accuracy here, limited by the irregular physical effects of the medium, is probably better than 0.1 unit.

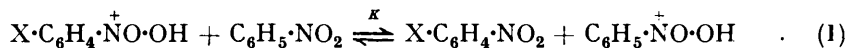
Acidity Function Scale.—The new measurements furnish values of H₀ which, in oleum, are higher (less negative) than those published by Brand (*loc. cit.*). The difference between the scales is fairly small in dilute oleum but increases with rising oleum strength, and is due entirely to the difficulty of taking the medium effects properly into account. These effects influence particularly the results in the middle range of oleum composition, where H₀ changes slowly with concentration.

TABLE 4. Influence of substituents on the acidity constant of nitrobenzene.

Substituent	Acidity constant, -pK _a	ΔpK = pK _a ^o - pK _a		Substituent	Acidity constant, -pK _a	ΔpK = pK _a ^o - pK _a	
		obs.	calc.			obs.	calc.
<i>p</i> -Bu ^t	10.2	-1.1	-0.27	<i>m</i> -Cl	12.15	0.89	0.83
<i>p</i> -Me	10.34	-0.92	-0.13	<i>m</i> -NO ₂ , <i>p</i> -Me	12.6 ₆	1.4	1.4
<i>m</i> -Me	10.84	-0.42	-0.21	<i>m</i> -NO ₂	—	—	1.5
H	11.26	0.0	0.0	<i>m</i> -NH ₃ ⁺	13.2 ₁	1.9 ₅	1.8
<i>p</i> -F	11.50	0.24	0.58	<i>m</i> -NO ₂ , <i>p</i> -Cl	13.6	2.3	2.0
<i>p</i> -Cl	11.56	0.30	0.50	3 : 5-di-NO ₂ , 4-Me and 3 : 5-di-NO ₂ :	Too weak to be measured.		
<i>m</i> -F	12.15	0.89	0.87				

The variation of H₀ with medium composition is shown in Fig. 8. In this system, disulphuric acid is a weak acid and water a strong base, and the analogy with the pH change on neutralisation in aqueous solution will be obvious; the "neutral" point is at the composition H₂SO₄.

Calculation of Acidity Constants relatively to Nitrobenzene by the Electrostatic Theory.—The method of calculation of the influence of a dipolar substituent on the acidity constant, due to Kirkwood and Westheimer (*J. Chem. Physics*, 1938, 6, 503, 513; 1939, 7, 437; *Trans. Faraday Soc.*, 1947, 43, 77), is a development of the earlier ideas of Bjerrum (*Z. physikal. Chem.*, 1923, 106, 219) and Eucken (*Z. angew. Chem.*, 1932, 45, 203). The organic molecule or ion is treated as a uniform cavity of low dielectric constant, surrounded by an isotropic medium with the dielectric constant characteristic of the pure solvent. This expresses the fact that the electrostatic field of the dipole operates both through the body of the acid molecule and through the solvent, but all other forms of interaction with the solvent are neglected. The cavities are idealised, and benzenoid molecules are approximated by an oblate spheroid, generated by rotation of an ellipse about its minor axis, the acid group and the substituent dipole lying on the focal circle (Sarmousakis, *J. Chem. Physics.*, 1944, 12, 277). The acidity constant relatively to nitrobenzene, *i.e.*, the equilibrium constant of equation (1), where log K = ΔpK (Table 4), is given by equation (2).



$$-2.3kT \cdot \Delta pK = e\mu_r \cos(\mu_r, r)/r\epsilon_r^2 + e\mu_\phi \cos(\mu_\phi, r)/r\epsilon_\phi^2 \quad (2)$$

In (2), μ_r and μ_φ are respectively the components of the substituent dipole, μ, along the radius and tangent of the focal circle, and ε_r and ε_φ are the corresponding "effective" dielectric constants; r is the length of the line joining the dipole and the acid group, forming the angles (μ_r, r) and (μ_φ, r) with μ_r and μ_φ respectively. The standard free-energy change in (1) is assumed to be equal to the net electrostatic work done.

The parameter r is chosen to be the distance from the substituent dipole to the projection, on the symmetry axis, of the oxygen atoms of the nitro-group. The physical basis is that in this way we calculate the sum of the electrostatic energies required to interchange with the unsubstituted system the ionisable proton *and* the $-\text{NO}_2$ dipole, the latter represented by (I) (Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 202). This is different from the case of the carboxylic acids, where the dipole of the $-\text{CO}_2\text{H}$ group is included by measuring r to the ionisable proton. Actually, the ΔpK 's differ considerably in the benzoic acid (Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3115) and the nitrobenzene system, and it is noteworthy that a physically intelligible change of r , other parameters being kept constant, will express the results in both series.

The other parameters in equation (2) conform to the known structure of the molecules. The substituent dipole was approximated by a point dipole placed at the mid-point of the bond to the aromatic nucleus, except for $-\text{NO}_2$ where it was located on the nitrogen atom. The partial distribution of the dipoles over the aromatic nucleus has to be neglected, a weakness when the theory is applied to fully conjugated systems. The quantities r and c (the radius of the focal circle) were calculated from the molecular geometry. The size of the cavity, V , is about $1\frac{1}{2}$ times the volume of the solute molecule as estimated from Traube's rule or from the van der Waals radii, and includes an empty shell between the solute and surrounding solvent molecules. The effective dielectric constants, ϵ_r and ϵ_ϕ , are determined by the dielectric constants of the cavity ($\epsilon_1 = 2.0$; Kirkwood and Westheimer, *loc. cit.*) and the solvent ($\epsilon_{20^\circ} = 80$, it being remembered that the K_a 's refer to a standard state in water), and the ratio V/c^3 which defines the location of the point dipole and the nitro-group relatively to the boundary of the cavity. The cavity volumes, bond lengths, and dipoles are as follows:

Substituent, X	F	Cl	CH_3	Bu ^t	NO_2	NH_3^+
μ, D	1.57	1.72	0.4	0.7	4.21	—
Bond length, X-Ar (Å)	1.31	1.69	1.50	(1.50)	1.46	(1.46)
Cavity volume, V (Å ³)	260	260	260	310	290	260

For *m*-derivatives the results of the calculation are satisfactory. In other cases the electrostatic theory is, by itself, insufficient. Thus, the poor agreement for *p*-fluoro- and *p*-chloro-nitrobenzene is due to resonance interaction between the substituents; this is already well known from the exaltation of the dipole moment (Groves and Sugden, *J.*, 1937, 1782; Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 2212). The ΔpK values indicate, in agreement with other evidence, that the resonance energy is greater for *p*-F than for *p*-Cl.

Environmental Factors; Entropy of Ionisation.—The anomalous behaviour of the *p*-alkyl substituents is clearly not due to hyperconjugation alone and is unlikely to have an "electronic" explanation at all. It probably arises from solvent-solute interaction which has been neglected (*i.e.*, assumed constant) hitherto. Variations here, although small, may be of the same order as the electrostatic energy differences. This can be decided from the entropies of ionisation. Using Bjerrum's formula, we have (Hammett, *J. Chem. Physics*, 1936, **4**, 613; Gurney, *ibid.*, 1938, **6**, 499)

$$\Delta S^\circ = \Delta G^\circ d(\ln \epsilon)/dT$$

where ΔS° and ΔG° refer to equilibrium (1). On Sarmousakis's model, only *p*-derivatives being considered, ϵ is replaced by ϵ_r . On either model, ΔS° and ΔG° must be of opposite sign if the theory is sufficient; otherwise $d(\ln \epsilon)/dT$ is positive, which implies a dielectric constant increasing with temperature. Because the variation of $T\Delta pK$ with T is small, only rough values of $\Delta S^\circ = 2.3Rd(\ln T\Delta pK)/dT$ are available, and to evaluate these it has been necessary to assume that the spectra themselves are independent of temperature (15–45°).

Free energy and entropy of ionisation [Equilibrium (1), 99.8% H_2SO_4].

Substituent	ΔG°_{291}	ΔS°_{291}	$d(\ln \epsilon)/dT$
<i>p</i> - CH_3	+1220	+2.1	+0.0017
<i>p</i> -F	-320	+0.64	-0.002

The result for *p*-nitrotoluene shows that ΔS° , which should be small and negative, is about 3 or 4 cal. deg.⁻¹ mole⁻¹ different from the expected value. This must be due to entropy of solvation, and it is then no longer justified to equate ΔG° with the net electrostatic work. In water the values of $d(\ln \epsilon)/dT$ and $d(\ln \epsilon_t)/dT = (\epsilon_t/\epsilon)(d \ln \epsilon/dT)$ are -0.005 and -0.0003 , respectively. The result for *p*-fluornitrobenzene is quite reasonable; ΔS_{soln} must be small, if not zero. However, effects of this kind are responsible for the fact that a plot of pK_a against the σ -constant gives a rather poor approximation to a straight line.

Note on the Kinetics of Nitration of 2 : 4-Dinitrotoluene in Oleum.—The velocity of nitration of 2 : 4-dinitrotoluene in oleum (Bennett *et al.*, *J.*, 1947, 474) falls with rising concentration of sulphur trioxide. The explanation originally offered has been shown to be incorrect (Melander, *Arkiv Kemi*, 1950, 2, 211; Ingold, Hughes, and Reed, *J.*, 1950, 2400), and it is now clear that part, at least, of the decline in velocity must be due to protonation of the dinitrotoluene, the ions produced being almost totally unreactive (Brand and Paton, *J.*, 1952, 281). It is not yet possible to allow quantitatively for the influence of the equilibrium on the kinetics, because the ionisation data refer to 18° and the rate measurements to 90°; but as they stand the changes are almost equal and opposite. The real dependence of nitration velocity on medium composition in oleum must be quite small.

The Second Ionisation Constant of m-Nitroaniline.—The pK_a value in Table 4 was evaluated by using the H_0 scale, a step which is equivalent to assuming that the dipolar positive ion $m\text{-H}_3\text{N}^+\text{-C}_6\text{H}_4\text{-NO}\cdot\text{OH}$ behaves in the same way as a univalent electrolyte. In aqueous solution this is permissible at high ionic strengths (Bjerrum, *Z. physikal. Chem.*, 1923, 104, 147; Güntelberg and Schöidt, *ibid.*, 1938, 135, 393; cf. Fuoss and Edelson, *J. Amer. Chem. Soc.*, 1951, 73, 269; Fuoss and Chu, *ibid.*, p. 949), but whether it applies in oleum media is hypothetical. However, it is possible to estimate $H_0 - H_+$, where H_+ relates to a bivalent cation with spherical symmetry of charge, and thus to decide whether in a real case it will be serious if this quantity is neglected. The method of calculation was suggested to us by Dr. V. Gold. From the definition of the acidity function

$$H = -\log (f_B \cdot a_{\text{H}^+} / f_{\text{HB}^+}); \quad H_+ = -\log (f_B \cdot a_{\text{H}^+} / f_{\text{HB}^{++}})$$

we have

$$H_0 - H_+ = \log (f_B \cdot f_{\text{HB}^+} / f_{\text{HB}^{++}} \cdot f_B) \quad \dots \quad (3)$$

Referred to the standard state in water (dielectric constant ϵ_0), and it being assumed that the free energy of transfer of an ion is equal to the electrostatic potential energy difference, the ionic activity coefficient f_i , in pure, anhydrous sulphuric acid (dielectric constant ϵ) is given by equation (4) (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, 1943, Chap. 3),

$$\ln f_i = (z_i e)^2 \left\{ \frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right\} / 2kT r \quad \dots \quad (4)$$

where z_i is the valency and r the radius of the ion, the charge distribution being supposed spherical. By using equation (4) to calculate f_B , f_{HB^+} , and $f_{\text{HB}^{++}}$ [only ratios of the f 's occur in equation (4), which helps to take non-electrostatic factors into account], and assuming that the radii of B, HB^+ , B^+ , and HB^{++} are all equal, we obtain from (3) ($f_i \rightarrow 1$ as $\epsilon \rightarrow \epsilon_0$)

$$H_0 - H_+ = -e^2 \left\{ \frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right\} / 2 \cdot 3kT r$$

(It may be noted that, with the same conventions, $H_+ + H_- = 2H_0$.) Introducing the values $\epsilon_0 = 80$, $\epsilon \sim 125$ (unpublished measurements, with Drs. James and Rutherford) and $r = 4 \text{ \AA}$ we have from this equation

$$H_+ = H_0 - 0.28 = -11.2 \text{ (100.0\% H}_2\text{SO}_4\text{)}$$

This result agrees in sign with Michaelis and Granick's observation (*J. Amer. Chem. Soc.*, 1942, 64, 1861) that an acidity scale established partly with multipolar bases in aqueous sulphuric acid is a few tenths of a unit more negative than Hammett's H_0 , but it is doubtful

if the difference really exceeds the experimental error. The increment of 0.28 unit would be an appreciable, but small, correction to the ΔpK of *m*-nitroaniline. However, bearing in mind that it refers to an ideal, spherically symmetrical cation and exaggerates the difference for ions of lower symmetry, we conclude that the correction can be dropped without serious error.

The value of ΔpK in Table 4, col. 8, is calculated from the equation (Sarmousakis, *loc. cit.*)

$$2.3 kT \cdot \Delta pK = e^2/r\epsilon_B$$

in which the symbols have the same meaning as in equation (2), and the parameters r and ϵ_B are evaluated by similar conventions.

Comparison with Cryoscopic Results.—These measurements (Gillespie, *loc. cit.*) are expressed as basic dissociation constants, $K_b = [\text{Ar}\cdot\text{NO}\cdot\text{OH}][\text{SO}_4\text{H}^-]/[\text{Ar}\cdot\text{NO}_2]$, brackets referring to concentrations. The equality being granted of the former ratios f_B/f_{NB^+} (here the f 's are relative to the standard state in water) in a single medium, $\log(K_b^\circ/K_b)$ has the same thermodynamic significance as ΔpK in Table 4. As shown below, the basicities are in the same order but the quantitative agreement is poor; nor is this due to the temperature differences, the effect of which is trivial.

Base	<i>p</i> -C ₇ H ₇ ·NO ₂	C ₆ H ₅ ·NO ₂	<i>m</i> -H ₃ N ⁺ ·C ₆ H ₄ ·NO ₂	C ₇ H ₅ (NO ₂) ₃
$\log(K_b^\circ/K_b)$, 9°	−0.84	(0.0)	0.31	0.63
ΔpK , 18°	−0.92	(0.0)	1.9 ₅	~3

An alternative method of comparison is to convert the spectrometric results into ν -factors (Table 5). It is then apparent that the cryoscopic figures are higher than ours (the concentration differences would have the opposite influence), and possible reasons for this are discussed below. For the calculation of K_b , the part of the ν -factor which matters is $\nu - 1$, or $\nu - 2$ in the case of *m*-nitroaniline, and it is noticeable that the best agreement is with *p*-nitrotoluene, where $\nu - 1$ is comparatively large.

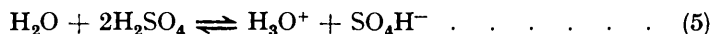
It is interesting to examine the cases of trinitrotoluene and the *m*-nitroaniline cation more closely. In neither case is there any spectral evidence of ionisation at the nitro-

TABLE 5. Number of ions produced per mole of solute (ν -factor): comparison of cryoscopic and spectrometric evidence.

Solute	Medium		$-H_0$	ν -Factor from:	
	H ₂ O, molality	H ₂ SO ₄ , %		f. p. (0.1M)	Spectrum (10 ⁻³ —10 ⁻⁴ M)
<i>p</i> -Me·C ₆ H ₄ ·NO ₂	0.061	99.89	10.4 ₅	1.63 *	1.56
C ₆ H ₅ ·NO ₂	0.059	99.89	10.4 ₅	1.26	1.13
<i>m</i> -H ₃ N ⁺ ·C ₆ H ₄ ·NO ₂	0.052	99.91	10.6	2.10	2.0 ₀
C ₇ H ₅ (NO ₂) ₃	0.074	99.87	10.4	1.09	1.0 ₀

* Small variation with concentration.

group in anhydrous sulphuric acid, the limit of detection being about 0.5 g.-ion %. The degree of ionisation of these bases is much less than the analysis of the cryoscopic data indicates, and part of the difficulty appears to be that the calculation of ν -factors from the freezing-points involves assumptions of considerable weight. First, the solutions are assumed to be ideal. Secondly, all solutes are assumed to be solvated; therefore, in spite of (1), the activity or osmotic coefficients may differ from unity unless the molalities are calculated with respect to the "free" solvent. Thirdly, solutions of electrolytes (*e.g.*, *m*-H₃N⁺·C₆H₄·NO₂·SO₄H⁻) are assumed to require a correction for the influence of the SO₄H⁻ ions on the dissociation of water (equilibrium 5) and the autoprotolysis of the solvent (equilibrium 6). Three parameters are introduced in this way, and the effect of certain adjustments of these is now shown in Table 6. For example, in the case of the



m-nitroaniline cation, if the correction for the effect of the SO_4H^- ions on (5) and (6) is dropped, the ν -factor falls from 2.10 to 2.00 (col. 11 and 12); the direct question of whether this compound is basic or non-basic, apart from the calculation of K_b , which is a question of degree, depends entirely upon a correction to the freezing point. In fact it is basic, but the basicity is only apparent at much higher acidities.

TABLE 6. *Freezing points of trinitrotoluene and m-nitroaniline in H₂SO₄ (Gillespie, loc. cit.).**

Molality of			ν -Factor				Molality of			ν -Factor	
H ₂ O	T.N.T.	F. p.	Solvation no. of				H ₂ O	<i>m</i> -Nitro- aniline	F. p.	corr.	uncorr.
0.074	—	9.691°	0 †	1	3	4	0.052	—	9.959°	—	—
..	0.0222	9.544	1.12	1.09	1.06	1.04	..	0.01045	9.834	2.08	1.98
..	0.0385	9.437	1.12	1.09	1.05	1.03	..	0.02536	9.654	2.11	1.99
..	0.0537	9.337	1.12	1.09	1.04	1.02	..	0.03191	9.569	2.10	2.02
..	0.0721	9.215	1.12	1.09	1.04	1.02	..	0.03712	9.509	2.10	2.02
..	0.0963	9.064	1.11	1.07	1.02	1.00					

$$k_f = 5.98 \text{ (deg. mole}^{-1} \text{ kg.)}$$

* The reaction of sulphuric acid with water is written as $\text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{O}^+, \text{H}_2\text{SO}_4 + \text{SO}_4\text{H}^-$, except in the column marked † where solvation of the H_3O^+ ion is omitted. The terms "corrected" and "uncorrected" refer to the supposed mass-action effect of the SO_4H^- ions upon the equilibria (5) and (6).

Although the suggestion that trinitrotoluene ionises to *ca.* 10% in anhydrous sulphuric acid is mistaken, there are nevertheless real differences between the cryoscopy of trinitrotoluene and sulphuryl chloride (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473). The convention being retained that sulphuryl chloride is a perfect non-electrolyte, the experimental result is that the osmotic coefficient of a dilute solution of trinitrotoluene is about 1.12, solvation being disregarded. If we wish at all costs to preserve the assumption that the solutions are ideal, $g - 1$ must represent the solvation correction, and this is achieved if the solvation number is 4 or 5 (Table 6). Since there are three nitro-groups this is not impossible. However, from thermodynamics alone we can determine g or i or f , but not ν ; and until the nature of the solutions is better understood small differences of ν from an integer must be interpreted with reserve.

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