

832. *The Conductometric Determination of Basic Dissociation Constants of Weak Bases in Sulphuric Acid. Part I. The Basicities of Substituted Nitrobenzenes.*

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In order to take into account the reduction in solvent molarity in more concentrated solutions of weak bases, and hence also the reduction of the solvent contribution to conductance, the conductivities of solutions of weak bases have been compared with conductivities of potassium hydrogen sulphate in sulphuric acid-sulphuryl chloride mixtures having equal molarity of "free" sulphuric acid; thence the degrees of dissociation of weak bases are estimated. The basic dissociation constants of a number of substituted nitrobenzenes obtained at 10° and 25° in this way agree with recorded cryoscopic and spectrophotometric data. A plot of pK_b values against Brown's σ^+ constants gives a good straight line, as expected since the protonated nitrogen can conjugate with the *para*-substituent. The standard heats and entropies of dissociation have been calculated, and are discussed in conjunction with the corresponding data for autoprotolysis of the solvent.

THE conductometric method for the calculation of basic dissociation constants of weak bases in sulphuric acid, suggested by Gillespie and Solomons,¹ is based on the fact that, in solutions in sulphuric acid, solvent self-ions, conducting by the proton-jump mechanism, carry practically the whole of the current through the solution. Therefore solutions of bases, having equal conductivity, were supposed to have equal concentrations of HSO_4^- ions, and hence the degrees of dissociation of weak bases were calculated from a comparison with the solutions of an "average" strong base, KHSO_4 . The fact was neglected, that in solutions of weak bases the molarity of sulphuric acid, and therefore also the ionic product of the solvent, were reduced by the relatively high concentration of weak base and by its hydrogen bonding with the solvent. However, the solvent contribution to conductance is determined by its ionic product and therefore will not be the same in solutions of a strong base as in the more concentrated solutions of a weak base, both solutions having equal conductivity. A modified method is reported here, based on the fact that it is possible to vary the molarity of sulphuric acid in solutions of strong bases by adding a non-electrolyte. In this way the conditions in solutions of strong bases are made closely comparable with those in solutions of weak bases. The concentration of HSO_4^- ions in such solutions is then approximately equal to the concentration of these ions in solutions of weak bases, both solutions having equal conductivity and equal molarity of "free" sulphuric acid.

By the original conductometric method it was possible to determine basic dissociation constants only for bases no weaker than *p*-chloronitrobenzene.¹ The values for the weakest bases amongst these must, however, be in error because no allowance was made for the reduced solvent contribution. Also a decreasing trend in the values of the basic dissociation constants with increasing concentration of the base was apparent in most cases. It was hoped that, by taking adequate account of the solvent contribution to conductance, basic dissociation constants could be obtained conductometrically for all bases amenable to spectrophotometric study in the 100% sulphuric acid range, which according to Brand, Horning, and Thornley,² include bases much weaker than *p*-chloronitrobenzene. It was also hoped that the decreasing trend of the dissociation constants with concentration would be reduced or eliminated in the same way.

There are few non-electrolytes that could be chosen for the "dilution" of sulphuric acid, because some dinitro-compounds studied before¹ were expected, on the basis of spectrophotometric data,² to prove weak bases rather than non-electrolytes. Sulphuryl

¹ Gillespie and Solomons, *J.*, 1957, 1796.

² Brand, Horning, and Thornley, *J.*, 1952, 1374.

chloride and 1,3,5-trinitrobenzene were both known from cryoscopic investigations of Gillespie, Hughes, and Ingold³ to be certainly non-electrolytes; the former has been used by us as diluent, with again¹ potassium hydrogen sulphate as strong electrolyte. Substituted nitrobenzenes were chosen as weak bases to be studied, because spectrophotometric² and cryoscopic⁴ data on the basicity of a number of them in sulphuric acid are available for comparison. Since the modified conductometric method was expected to give more reliable values of the basic dissociation constants, their temperature coefficients could be meaningful. Therefore all conductivity measurements were carried out at 10° and 25°. Densities, necessary for the analysis of the results, were determined for all solutions at both temperatures.

The modified conductometric method described here is applicable also to solutions of weak acids in sulphuric acid; only data for the conductivity of a strong acid in solvent mixtures with variable molarity of sulphuric acid would be needed for comparison.

RESULTS

The measurements of the conductivity of potassium hydrogen sulphate in sulphuric acid and in mixtures of sulphuric acid and sulphuryl chloride are reported in Table 1 and the data for 25° are plotted in Fig. 1. The agreement with recent measurements by Gillespie and his co-workers⁵ on potassium hydrogen sulphate in pure sulphuric acid is reasonable. The conductivities of the solutions of sulphuryl chloride in sulphuric acid at 25° (Fig. 2) are in excellent agreement with earlier data,¹ but the concentration range covered is wider.

TABLE 1.

Specific conductivities of KHSO₄ in pure sulphuric acid and in mixtures H₂SO₄-SO₂Cl₂ at 10° and 25°.

Concn. (mole/kg·soln.)	10 ² κ ₁₀ (ohm ⁻¹ cm. ⁻¹)	10 ² κ ₂₅ (ohm ⁻¹ cm. ⁻¹)	Concn. (mole/kg·soln.)	10 ² κ ₁₀ (ohm ⁻¹ cm. ⁻¹)	10 ² κ ₂₅ (ohm ⁻¹ cm. ⁻¹)
Solvent: pure sulphuric acid. ($\bar{\alpha}_4^{10} = 1.8420$; $\bar{\alpha}_4^{25} = 1.8271$)			Solvent: 0.2682 mole of SO ₂ Cl ₂ per kg. of soln. ($\bar{\alpha}_4^{10} = 1.8376$; $\bar{\alpha}_4^{25} = 1.8221$)		
0.0000	0.5780	1.044	0.0000	0.5393	0.967
0.0048	0.5809	1.050	0.0113	0.5796	1.019
0.0123	0.6064	1.086	0.0265	0.6893	1.158
0.0161	0.6415	1.119	0.0336	0.7533	1.241
0.0238	0.6985	1.187	0.0587	1.016	1.598
0.0347	0.8022	1.332	0.0962	1.381	2.115
0.0513	0.9405	1.520			
0.0703	1.153	1.815	Solvent: 0.3849 mole of SO ₂ Cl ₂ per kg. of soln. ($\bar{\alpha}_4^{10} = 1.8356$; $\bar{\alpha}_4^{25} = 1.8198$)		
0.0825	1.270	1.986	0.0000	0.5244	0.937
0.1014	1.444	2.234	0.0083	0.5448	0.964
Solvent: 0.1462 mole of SO ₂ Cl ₂ per kg. of soln. ($\bar{\alpha}_4^{10} = 1.8395$; $\bar{\alpha}_4^{25} = 1.8241$)			0.0237	0.6487	1.094
0.0000	0.5579	1.003	0.0387	0.7962	1.288
0.0105	0.5789	1.032	0.0694	1.139	1.758
0.0199	0.6321	1.099	0.0816	1.229	1.887
0.0295	0.7099	1.198	0.0985	1.399	2.133
0.0586	1.014	1.608	Solvent: 0.5980 mole of SO ₂ Cl ₂ per kg. of soln. ($\bar{\alpha}_4^{10} = 1.8316$; $\bar{\alpha}_4^{25} = 1.8157$)		
0.0901	1.239	1.925	0.0000	0.4961	0.878
0.0987	1.392	2.147	0.0110	0.5352	0.929
Solvent: 0.5054 mole of SO ₂ Cl ₂ per kg. of soln. ($\bar{\alpha}_4^{10} = 1.8333$; $\bar{\alpha}_4^{25} = 1.8175$)			0.0199	0.6024	1.012
0.0000	0.5094	0.904	0.0305	0.7042	1.144
0.0102	0.5439	0.949	0.0468	0.871	1.365
0.0195	0.6078	1.029	0.1021	1.430	2.150
0.0290	0.6941	1.139			
0.0457	0.867	1.371			
0.0564	0.999	1.551			
0.0962	1.383	2.094			

³ Gillespie, Hughes, and Ingold, *J.*, 1950, 2473; see also ref. 2.

⁴ Gillespie and Robinson, *J.*, 1957, 4233.

⁵ Bass, Flowers, Gillespie, Robinson, and Solomons, *J.*, 1960, 4315.

The conductivity measurements on solutions of nitro-compounds in sulphuric acid are given in Table 2. Since some mononitro- and dinitro-compounds were studied before,¹ the measurements for only some of them were repeated at 25° (nitrobenzene, *p*-chloronitrobenzene, *o*-, *m*-, and *p*-dinitrobenzene), and new values were obtained for 10°. The agreement with earlier measurements at 25° is excellent for nitrobenzene and very good for *p*-chloronitrobenzene (the new results being 0.2% lower in the middle concentration range), but not so good for *o*- and *p*-dinitrobenzene (the new results being somewhat higher and somewhat lower, respectively)

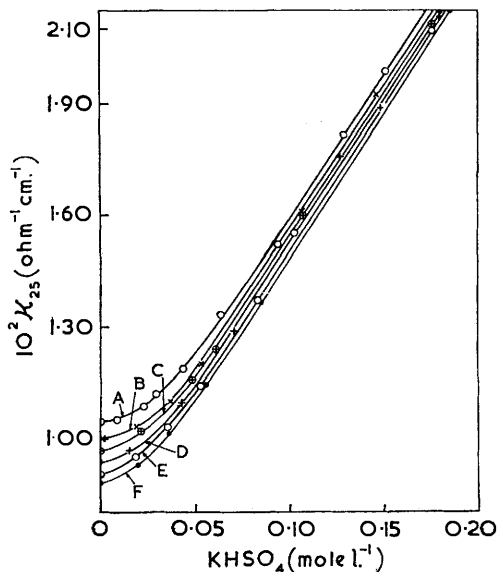
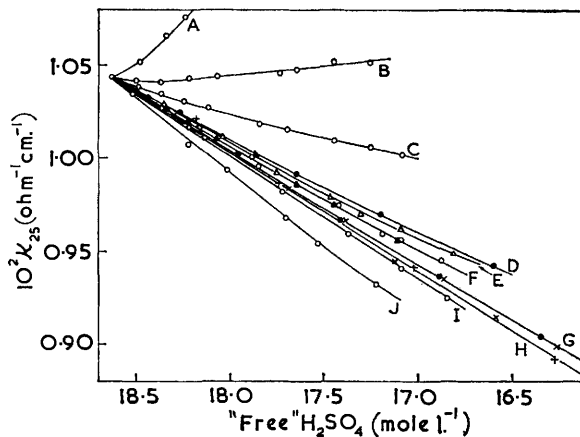


FIG. 1. Conductivities of KHSO_4 in pure sulphuric acid (A) and in H_2SO_4 - SO_2Cl_2 mixtures at 25°. The concentrations (mole per kg. of solution) of SO_2Cl_2 are (B) 0.1462, (C) 0.2682, (D) 0.3849, (E) 0.5054, and (F) 0.5980.

FIG. 2. Conductivities of non-electrolytes and very weak bases at 25° plotted against the molarity of "free" H_2SO_4 .

A, *p*-Chloronitrobenzene; B, *o*-chloronitrobenzene; C, *m*-chloronitrobenzene; D, 2,4-dinitrotoluene;¹ E, *p*-dinitrobenzene; F, *o*-dinitrobenzene (○), *m*-dinitrobenzene (▲); G, sulphuryl chloride (●), 1,3,5-trinitrobenzene (×);¹ H, 2,4,6-trinitrotoluene;¹ I, 1-chloro-2,4-dinitrobenzene; J, 2,5-dichloronitrobenzene.



and poor for *m*-dinitrobenzene (the new results being considerably lower). In view of these discrepancies the measurements were repeated, but the second, completely independent, series gave results in agreement with the first. A few other nitro-compounds were also studied, which were expected to decrease or increase the conductivity of the solvent only slightly (*o*- and *m*-chloronitrobenzene) or to behave as non-electrolytes (2,4-dichloronitrobenzene and 1-chloro-2,4-dinitrobenzene). The conductivities of all nitro-compounds which are non-electrolytes or bases weaker than *p*-chloronitrobenzene are plotted against the molarity of "free" sulphuric acid in Fig. 2. The molarity of "free" acid is the number of formula weights of H_2SO_4 per l. of solution, obtained by subtracting from the total molarity the number of moles of acid involved in hydrogen bonding with the solute. As was done by Gillespie and Solomons,¹ the solvation

number of 1 was assumed for SO_2Cl_2 , and a solvation number of 1 per nitro-group for the nitro-compounds.

Densities of solutions of sulphuryl chloride were measured by Gillespie and Wasif,⁶ whose values are higher than those given in Table 1, the more so the higher the concentration. Densities of solutions of potassium hydrogen sulphate in pure sulphuric acid as well as in mixtures with sulphuryl chloride increase linearly with ω , the concentration of solutions in mole kg^{-1} (soln.), and the slope of the straight lines is practically independent of the solvent. At

TABLE 2.
Specific conductivities of nitro-compounds in sulphuric acid at 10° and 25°.

Concn. (mole/kg. _{soln.})	$10^2\kappa_{10}$ (ohm ⁻¹ cm. ⁻¹)	$10^2\kappa_{25}$	Concn. (mole/kg. _{soln.})	$10^2\kappa_{10}$ (ohm ⁻¹ cm. ⁻¹)	$10^2\kappa_{25}$
Nitrobenzene			<i>o</i> -Dinitrobenzene		
0.0451	0.6225	1.111	0.0534	0.5623	1.017
0.0730	0.6549	1.153	0.0639	0.5602	1.016
0.0992	0.6891	1.201	0.0977	0.5533	1.001
0.1457	0.745	1.279	0.1013	0.5514	0.996
0.2010	0.809	1.368	0.1568	0.5397	0.975
0.2375	0.840	1.410	0.1598	0.5397	0.972
0.3095	0.904	1.492	0.1886	0.5338	0.960
0.3743	0.948	1.560	0.2021	0.5319	0.956
			0.2306	0.5283	0.945
<i>o</i> -Chloronitrobenzene			<i>m</i> -Dinitrobenzene		
0.0234	0.5766	1.042	0.0179	0.5710	1.036
0.0442	0.5772	1.041	0.0389	0.5662	1.026
0.0646	0.5786	1.043	0.0541	0.5623	1.019
0.0976	0.5816	1.044	0.0741	0.5572	1.010
0.1360	0.5865	1.046	0.1014	0.5539	1.002
0.1692	0.5905	1.048	0.1319	0.5451	0.986
0.2050	0.5942	1.052	0.1582	0.5403	0.975
0.2386	0.5977	1.052	0.2044	0.5308	0.956
<i>m</i> -Chloronitrobenzene			<i>p</i> -Dinitrobenzene		
0.0223	0.5742	1.039	0.0372	0.5675	1.028
0.0450	0.5714	1.034	0.0782	0.5587	1.011
0.0657	0.5697	1.030	0.1159	0.5490	0.992
0.0883	0.5681	1.026	0.1532	0.5445	0.979
0.1348	0.5661	1.018	0.1762	0.5390	0.970
0.1603	0.5650	1.015	0.2033	0.5373	0.962
0.2031	0.5640	1.009	0.2475	0.5325	0.949
0.2391	0.5631	1.005			
0.2690	0.5622	1.001	2,5-Dichloronitrobenzene		
			0.0177	0.5697	1.035
			0.0645	0.5556	1.008
			0.0968	0.5481	0.994
			0.1492	0.5345	0.968
			0.1767	0.5268	0.954
			0.2263	0.5157	0.932
<i>p</i> -Chloronitrobenzene			1-Chloro-2,4-dinitrobenzene		
0.0243	0.5826	1.052	0.0336	0.5653	1.026
0.0501	0.5929	1.066	0.0599	0.5572	1.011
0.0682	0.6008	1.076	0.1134	0.5430	0.983
0.1012	0.6176	1.098	0.1580	0.5315	0.960
0.1215	0.629	1.111	0.1922	0.5223	0.941
0.1641	0.645	1.135	0.2231	0.5158	0.927
0.2026	0.665	1.158			
0.2413	0.680	1.177			
0.3056	0.697	1.196			

25°, the mean value of $(d - d_0)/\omega$ is 0.072 ± 0.002 (in very good agreement with Gillespie and Wasif's figure⁶), and at 10° the slope is the same (0.071) in all solvents.

Densities of solutions of nitro-compounds can be expressed, for comparison, in the same manner as has been done by Gillespie and Solomons,¹ *i.e.*, as linear functions of ω in the form: $d = d_0(1 - a\omega)$, but it is more convenient to express them in terms of the slope $s = (d - d_0)/\omega$ because this value is the same at 10° and at 25° for several solutes, *e.g.*, for nitrobenzene — 0.118,

⁶ Gillespie and Wasif, *J.*, 1953, 215.

o-chloronitrobenzene —0.100, *m*-chloronitrobenzene —0.103, and *p*-dinitrobenzene —0.080. For other solutes s is higher at 25° (value in parentheses): *p*-chloronitrobenzene —0.098 (—0.100), *o*-dinitrobenzene —0.086 (—0.088), *m*-dinitrobenzene —0.075 (—0.076), 2,5-dichloronitrobenzene —0.084 (—0.085), and 1-chloro-2,4-dinitrobenzene —0.058 (—0.059). Comparing the values of the slope for *o*-, *m*-, and *p*-dinitrobenzene with the data of Gillespie and Solomons¹ shows that their values are ad_0 (not merely a), and that they are very close to the $-s$ values obtained in this work. Densities of *p*-nitrotoluene solutions were interpolated from the values given by Gillespie and Wasif,⁶ and those of *o*- and *m*-nitrotoluene solutions were estimated from the data for more concentrated solutions given by Liler and Kosanović.⁷

DISCUSSION

The Conductivity of KHSO₄ in H₂SO₄-SO₂Cl₂ Mixtures.—The conductivity of pure sulphuric acid was considered by Flowers, Gillespie, Robinson, and Solomons⁸ as being due almost entirely to the proton-jump conduction by solvent self-ions H₃SO₄⁺ and HSO₄⁻, but Wyatt⁹ recently suggested that "asymmetric dissociation" may contribute as much as 40% of the conductivity of the pure solvent. The reduction of the conductivity of the pure solvent by dissolution of non-electrolytes was interpreted by Gillespie and Solomons¹ as a result of the reduction of the concentration of the solvent self-ions, owing to the reduction of the molarity of "free" sulphuric acid (*i.e.*, after deduction from the total stoichiometric molarity of the amount of solvent involved in the solvation of the solute), because of the relation:

$$K_i = c_+c_- = K_{ap}c_0^2, \quad (1)$$

where K_i is the ionic product, K_{ap} is the autoprotolysis constant involving the molarity c_0 of "free" sulphuric acid, and c_+ and c_- are the molarities of the solvent self-ions H₃SO₄⁺ and HSO₄⁻, respectively. The mobilities of these ions were assumed to be almost constant, *i.e.*, unaltered by the presence of the non-electrolyte, and the effect of the ionic self-dehydration was neglected. The results for the conductivity of potassium hydrogen sulphate in sulphuric acid-sulphuryl chloride mixtures support this assumption, because the conductivities in solvents with increasing sulphuryl chloride concentration approach closely those in pure sulphuric acid (see Fig. 1) at concentrations of potassium hydrogen sulphate of about 0.18 mole l.⁻¹, where the autoprotolysis is largely suppressed. If the difference in the concentration of the autoprotolysis ions is taken into account, the molar conductance Λ_{KHSO_4} turns out to be smaller by only 1—2% in the solvent containing 0.598 mole kg.⁻¹ (soln.) of sulphuryl chloride than in pure sulphuric acid. This suggests that the mobilities may be primarily a function of the ratios $c_+ : c_0$ and $c_- : c_0$, which are the only quantities remaining nearly constant in the non-electrolyte solutions [see eqn. (1)]. A functional dependence of this kind would be reasonable in view of the nature of proton-jump conduction. These results are, therefore, consistent with the view that the conductivity of pure sulphuric acid, and of non-electrolyte solutions in it, is due to the solvent self-ions, whose mobilities remain largely unaffected in the relatively dilute solutions of non-electrolytes. However, a closer analysis of these results from the point of view of the "asymmetric dissociation" theory⁹ might prove them to be consistent with that theory as well. What is important for the present problem is that the solvent contribution to conductance, as described by the "asymmetric dissociation" theory, must also depend in the first place on the ionic product K_i , given by eqn. (1), and hence on the molarity of "free" sulphuric acid. Secondary effects might be present as well (*e.g.*, the effect of non-electrolytes on ion mobilities, on the dielectric constant, etc.). Therefore, when solutions of non-electrolytes, acids, or bases of equal conductivity are compared, if they also have equal c_0 (molarity of "free" sulphuric acid) it is reasonable to consider the solvent contribution to conductance, whatever its nature, as being of closely comparable magnitude.

⁷ Liler and Kosanović, in D. Hadži, ed., "Hydrogen Bonding," Symposium, Pergamon Press, London, 1959, p. 529.

⁸ Flowers, Gillespie, Robinson, and Solomons, *J.*, 1960, 4327.

⁹ Wyatt, *Trans. Faraday Soc.*, 1961, 57, 773.

Conductivities of Non-electrolytes.—How far this is true for non-electrolyte solutions can be seen from a plot (Fig. 2) of their conductivity against the molarity of "free" sulphuric acid, the latter being calculated by taking into account the amount of solvent hydrogen bonded with the solute, as explained on p. 4274. It can be seen that at 25° results for 1,3,5-trinitrobenzene,¹ 2,4,6-trinitrotoluene,¹ sulphuryl chloride, and 1-chloro-2,4-dinitrobenzene (which should practically be a non-electrolyte on the basis of spectrophotometric results²) fall close to each other, but that those for 2,5-dichloronitrobenzene are considerably lower. The results for 10° offer a similar picture. With the exception of 2,5-dichloronitrobenzene, therefore, the conductivity of non-electrolyte solutions is primarily determined by the molarity of "free" sulphuric acid. The exceptional behaviour of 2,5-dichloronitrobenzene is probably due to the large volume of the molecules owing to two chlorine substituents, so that it may exercise a bigger disruptive effect on the structure of the solvent than the smaller molecules do. From Fig. 2, sulphuryl chloride appears as an "average" non-electrolyte and it is therefore a reasonable choice as a "diluent" of sulphuric acid for the purpose of the present study.

The Modified Conductometric Method for Calculating Basic Dissociation Constants of Weak Bases.—Basic dissociation constants of weak bases, dissociating according to the equation



when calculated from conductometric data, should be defined in terms of molarities by:

$$K_b = \frac{c_{BH^+} \cdot c_{HSO_4^-}}{c_B \cdot c_{H_2SO_4}} = \frac{\alpha}{1 - \alpha} \cdot \frac{c_{HSO_4^-}}{c_{H_2SO_4}}, \quad (3)$$

i.e., they should include the total molarity of sulphuric acid. There are two reasons for this: first, the solutions are not sufficiently dilute to allow this quantity to be taken as constant and, secondly, it has been shown by Brand, Jarvie, and Horning¹⁰ that the activity-coefficient ratio in such an expression can be taken in first approximation as unity. Hence, such an expression should be a better approximation to the thermodynamic dissociation constant, than the expression

$$K_b = \frac{\alpha}{1 - \alpha} \cdot c_{HSO_4^-}.$$

To obtain α , the solution of the weak base is compared with the solution of the strong base potassium hydrogen sulphate of equal conductivity, but in a solvent where molarity of "free" sulphuric acid is equal to that in the solution of the weak base. Only when such solutions are compared, will the solvent contribution to conductance be nearly the same and the HSO_4^- concentration also nearly the same in both solutions. In such solutions c_{BH^+} may be taken as equal to c_s , the concentration of the strong base:

$$c_{BH^+} = \alpha c_w = c_s. \quad (4)$$

Here c_w is the stoichiometric molarity of the weak base. The approximate character of the method arises from the choice of the "average" electrolyte potassium hydrogen sulphate and the "average" non-electrolyte sulphuryl chloride as diluent, which means that individual variations in other solutions are certainly present. But this modified method should give a better approximation to the true degrees of dissociation than the original one, because solutions with nearly equal solvent contribution to conductance are compared. The range of molarities of "free" sulphuric acid covered by the solvent mixtures including sulphuryl chloride is wide enough for comparison with solutions of weak bases, and the number of mixtures is sufficient for interpolation of data to any molarity. The further small reduction of the molarity of sulphuric acid by the dissolution of potassium sulphate (K_2SO_4) in these mixtures was neglected in the calculations.

¹⁰ Brand, Jarvie, and Horning, *J.*, 1959, 3844.

The modified method differs from the original one also in the evaluation of c_- , since the ionic product K_1 , calculated from the reduced molarity c_0 of "free" sulphuric acid by means of eqn. (1), is used. Hence,

$$c_{\text{HSO}_4^-} = \frac{c_s}{2} + \sqrt{\left[\left(\frac{c_s}{2}\right)^2 + K_{\text{ap}}c_0^2\right]}, \quad (5)$$

where c_s is the molarity of the potassium hydrogen sulphate solution in a sulphuric acid-sulphuryl chloride mixture that has conductivity and molarity of "free" sulphuric acid equal to those of the solution of the weak base.

The values of K_{ap} used ($K_{\text{ap}}^{10} = 1.6 \times 10^{-6}$ and $K_{\text{ap}}^{25} = 2.3 \times 10^{-6}$) were calculated from the ionic product at 10° (1.7×10^{-4} mole² kg.⁻²), cryoscopically estimated by Bass, Gillespie, and Robinson,¹¹ and the ionic product at 25° (2.4×10^{-4} mole² kg.⁻²) obtained from this, again by Gillespie and his co-workers,¹² using conductometric data. The independent estimate by Kirkbride and Wyatt¹³ of the ionic product at 25° from purely thermodynamic data (3.4×10^{-4} mole² kg.⁻²) is not greatly different. An example of a complete calculation is given for *p*-chloronitrobenzene at 25° in Table 3, which can be compared with the calculation in which the original method in the paper by Gillespie and Solomons¹ was used. The comparison shows: first, that the decrease with concentration of the original basic dissociation constant, (4.9 to 3.2) $\times 10^{-3}$ mole kg.⁻¹, is considerably reduced, indeed almost eliminated, by using the modified method, which leads to smaller deviations of the constants from the mean value ($\pm 12\%$ compared with $\pm 20\%$ by the

TABLE 3.

The calculation of the basic dissociation constant for *p*-chloronitrobenzene at 25° from conductometric data.

Concn. (mole kg. ⁻¹)	c_w (mole l. ⁻¹)	$10^3\kappa_{25}$ (ohm ⁻¹ cm. ⁻¹)	$c_{\text{H}_2\text{SO}_4}$	c_0	$c_{\text{HSO}_4^-}$	α	10^4K_b
0.0243	0.0443	1.052	18.53	18.48	0.034	0.25	6.1
0.0501	0.0913	1.066	18.43	18.34	0.040	0.22	6.1
0.0682	0.1242	1.076	18.36	18.24	0.043	0.20	5.9
0.1012	0.1838	1.098	18.23	18.05	0.049	0.19	6.1
0.1215	0.2205	1.111	18.15	17.93	0.052	0.17	6.0
0.1641	0.2973	1.135	18.00	17.70	0.056	0.15	5.3
0.2026	0.3661	1.158	17.84	17.47	0.060	0.13	5.1
0.2413	0.4351	1.177	17.69	17.25	0.064	0.12	5.0

$$K_b(\text{mean}) = 5.7 \times 10^{-4} (\pm 12\%)$$

original method); and, secondly, that the absolute value of the new constant is considerably higher than the earlier estimate [the earlier mean value of 4×10^{-3} mole kg.⁻¹ should be divided by 10.2 mole kg.⁻¹ (molality of H_2SO_4) for comparison with the present K_b].

Table 4 gives mean K_b values, defined by eqn. (3), for a number of nitro-compounds (in most cases the average deviations from the mean value are not bigger than $\pm 10\%$). Since attention was concentrated here on bases weaker than nitrobenzene, earlier published conductometric data for the nitrotoluenes¹ were simply recalculated by the modified method. A comparison of the first column of the Table with the last shows that the modified conductometric method gives higher constants. The difference increases with decreasing basic strength, because the original method seriously overestimates the solvent contribution to conductance in the solutions of the weaker bases. The original method is not applicable to bases which increase only slightly, or reduce, the conductivity of the pure solvent (all bases weaker than *p*-chloronitrobenzene). Further, there is an increase in the dissociation constants with temperature, which is not negligible. The agreement with cryoscopic data for nitrobenzene is very good, but much poorer for *p*-chloronitrobenzene, probably owing to the smaller accuracy of the cryoscopic method for very weak bases. In view of the increase of the dissociation constants with temperature, the comparison of

¹¹ Bass, Gillespie, and Robinson, *J.*, 1960, 821.

¹² Gillespie, Robinson, and Solomons, *J.*, 1960, 4320.

¹³ Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, 54, 483.

TABLE 4.
Comparison of basic dissociation constants of substituted nitrobenzenes obtained by various methods.

Subst.	Conductometric K_b [eqn. (2)]		Cryoscopic ⁴ $K_b^{10}/10.2$	Spectrophotometric ³ $K_b^{18 \pm 2}$	Original conduct. ¹ $K_b^{25}/10.2$
	25°	10°			
<i>p</i> -Bu ^t			1×10^{-2}	1×10^{-2}	
<i>p</i> -Me	1.05×10^{-2}		9.2×10^{-3}	9.1×10^{-3}	9.3×10^{-3}
<i>o</i> -Me	7.3×10^{-3}		6.1×10^{-3}		6.6×10^{-3}
<i>m</i> -Me	2.8×10^{-3}		2.0×10^{-3} ^a	2.5×10^{-3}	2.3×10^{-3}
H	1.3×10^{-3}	1.0×10^{-3}	1.1×10^{-3}	9.6×10^{-4}	1.0×10^{-3}
<i>p</i> -Cl	5.7×10^{-4}	4.3×10^{-4}	3×10^{-4}	4.2×10^{-4}	4×10^{-4}
<i>o</i> -Cl	2.4×10^{-4}	1.8×10^{-4}			
<i>m</i> -Cl	1.3×10^{-4}	9.5×10^{-5}		1.1×10^{-4}	
4-Me-3-NO ₂	5.3×10^{-5}			2.9×10^{-5}	
<i>o</i> -NO ₂	2.8×10^{-5}	1.6×10^{-5} ^b			
<i>m</i> -NO ₂					
<i>p</i> -NO ₂	2.9×10^{-5}	1.7×10^{-5} ^b			
3-NO ₂ -4-Cl	Non-electrolyte			3×10^{-6} ^c	
2,5-Cl ₂	"				
3,5-(NO ₂) ₂	"				
4-Me-3,5-(NO ₂) ₂	"				

^a A strongly decreasing trend of the cryoscopic dissociation constants was observed; so this is probably not a very reliable value. ^b Probably not very reliable, because the choice of the diluent (SO₂Cl₂) introduces errors which are larger the weaker the base. ^c Corresponding to $\alpha \sim 0.002$, which is not detectable conductometrically.

conductometric values for 25° with cryoscopic values for 10° for the three nitrotoluenes probably means a very good agreement.

Comparison with Spectrophotometric Data.—Brand and his co-workers² and Gillespie and Solomons¹ found the cryoscopic to be higher than the spectrophotometric data for K_b of the nitro-compounds. In their recalculation, Gillespie and Solomons¹ assumed that the acidity function in solutions of weak bases is approximately the same as in 99.95% sulphuric acid. Although that may be a reasonable assumption for the fairly strong bases, it certainly is not for the very weak bases, which would hardly be expected to change the acidity function of the pure solvent. Therefore, in order to compare the results of the spectrophotometric study with the conductometric results for very weak bases, it was necessary to re-examine the method of comparison. From the definition of K_b , eqn. (3), and the definition of the acidity function, $H_0 = pK_a + \log [B]/[BH^+]$, one obtains directly:

$$\log K_b = pK_a - H_0 + \log [\text{HSO}_4^-]/[\text{H}_2\text{SO}_4], \quad (6)$$

where pK_a is the spectrophotometric acid dissociation constant of the conjugate acid of the base B. It was shown by Brand¹⁴ that for aqueous sulphuric acid up to 99.8% the relation $-H_0 + \log ([\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]) = 8.35$ is valid, but that deviations from it occur at still higher concentrations. In a study of weak bases in 100% acid, therefore, that relation cannot be used. For the 100% acid, $-H_0 + \log ([\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]) = 8.07$, if $H_0 = -10.89$ (this value is used here, although Paul and Long¹⁵ gave an improved value, because all spectrophotometric pK_a data for the nitro-compounds are based on it) and the molar ratio $[\text{HSO}_4^-]/[\text{H}_2\text{SO}_4] = K_{ap}^{\frac{1}{2}} = 1.5 \times 10^{-3}$. In solutions of weak bases the values of that sum should range between 8.07 (for the weakest bases) and 8.35 (for the stronger bases at higher concentrations). In order to find the value which applies to a particular solution of a base, the molar ratio $\text{HSO}_4^-/\text{H}_2\text{SO}_4$ must be known, together with H_0 as a function of that ratio. The latter can be obtained in the form of a graph from the values given by Brand,¹⁴ if the HSO_4^- concentrations in dilute solutions of water in sulphuric

¹⁴ Brand, *J.*, 1950, 997.

¹⁵ Paul and Long, *Chem. Rev.*, 1957, 57, 1.

acid are calculated by means of eqn. (5), and the molarity of sulphuric acid for the very dilute solutions is taken as constant, 18.6 mole l.⁻¹. From such a plot H_0 can now be found for any molar ratio $\text{HSO}_4^- : \text{H}_2\text{SO}_4$ in solutions of any weak base. Instead of assumptions being made about the probable value of that ratio in solutions of various weak bases, the values calculated from the conductivity data were used. For example, for *p*-chloronitrobenzene (Table 3) at $c_w = 0.1242$ mole l.⁻¹, $c_{\text{HSO}_4^-}/c_{\text{H}_2\text{SO}_4} = 2.3 \times 10^{-3}$ gives $H_0 = -10.82$ and from eqn. (6), $K_b = 4.2 \times 10^{-4}$. The choice of some other concentration c_w may result in a somewhat different value of K_b . The fourth column of Table 4 gives mean values. This method of converting spectrophotometric $\text{p}K_a$ values into K_b is thus not independent of the conductometric data, but it should be better than the earlier method¹ because it does not involve arbitrary assumptions about the value of the acidity function.

It can be seen from Table 4 that spectrophotometric results for nitrobenzene and *p*-nitrotoluene are lower even than the cryoscopic values, which refer to a lower temperature. This may well be due to the difficulties encountered in the spectrophotometric measurements with these compounds, owing to an appreciable rate of sulphonation in moderately dilute oleum. The agreement between the spectrophotometric and the conductometric K_b values for *m*-nitrotoluene and for *p*- and *m*-chloronitrobenzene is excellent and it is good for 2,4-dinitrotoluene.

In view of the overall good agreement between the three methods, it may be claimed that the modified conductometric method for the evaluation of basic dissociation constants of weak bases in sulphuric acid is at least as reliable as the spectrophotometric and the cryoscopic method. The values obtained justify an examination of the substituent effects on the basicity of nitrobenzene, and evaluation of thermodynamic functions from the temperature-dependence of the basic dissociation constants.

Substituent Effects on the Basicity of Nitrobenzene.—Brand *et al.*² discussed substituent effects on the basicity of nitrobenzene, but their attempt to plot the spectrophotometric $\text{p}K_a$ values against the σ constants gave a rather poor approximation to a straight line. Good straight lines were obtained by Stewart and Yates¹⁶ in plots of $\text{p}K_{\text{BH}^+}$ values for substituted acetophenones, benzaldehydes, and benzoic acids against Brown's σ^+ constants.¹⁷ The deviations observed in a preliminary plot of $\text{p}K_b$ ²⁵ values for substituted nitrobenzenes against σ constants suggested that these values should also be plotted against σ^+ constants. $\text{p}K_b$ values in a decreasing order were plotted here, rather than the corresponding $\text{p}K_a$ values, because a recalculation to $\text{p}K_a$ by means of eqn. (6) involves assumptions about H_0 , and in any case it is irrelevant which of the two constants is used in the plot against σ^+ . In order to plot data for *m*- and *p*-dinitrobenzene, their K_b values were divided by the statistical factor of two, to allow for two identical basic centres available for the first protonation. The plot is given in Fig. 3 and it shows very good linearity for all *meta*- and *para*-substituted nitrobenzenes, which is not surprising since resonance interaction between the *para*-substituent and the protonated nitro-group is certainly possible. This good linear relation also means that environmental effects in pure sulphuric acid are no bigger than in the more dilute sulphuric acid-water mixtures, contrary to the conclusion of Brand, Horning, and Thornley.²

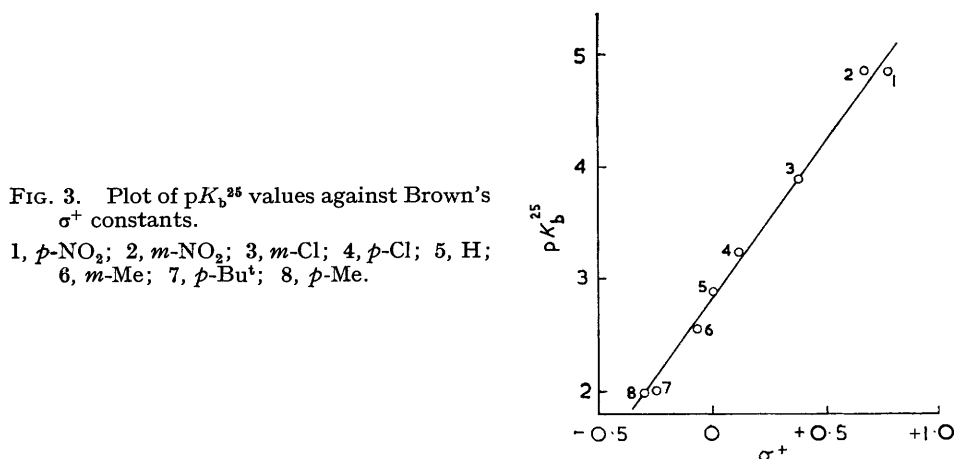
The ρ value found by the method of least squares for substituted nitrobenzenes is +2.77; it is higher than the values for either of the three groups of compounds mentioned.¹⁶ The ρ values for the four series in an increasing order are: benzoic acid 1.09, benzaldehyde 1.85, acetophenone 2.17, and nitrobenzene 2.77. If the much lower ρ for benzoic acid reveals the greater importance of resonance within the protonated carboxyl group,¹⁶ then the very high value for nitrobenzene reflects a loss of resonance within the nitro-group on protonation.

¹⁶ Stewart and Yates, *J. Amer. Chem. Soc.*, 1958, **80**, 6355; 1960, **82**, 4059; *Canad. J. Chem.*, 1959, **37**, 664.

¹⁷ Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

The absence of the *ortho*-effect in the protonation of *ortho*-substituted nitrobenzenes (see Table 4) has already been noticed by Gillespie and Solomons.¹ Both the primary and the secondary steric effects should act here in the same direction,^{18a} that is, should reduce the basic strength of the *ortho*-substituted compound. However, neither is present and this is probably due to the smaller size of the nitro-group than of the carboxyl group.^{18b}

Standard Heats and Entropies of Basic Dissociation.—These thermodynamic functions



were first calculated for the reaction (2) for nitrobenzene and values $\Delta H^\circ_{298.1} = 2.66$ kcal. mole⁻¹ and $\Delta S^\circ_{298.1} = -4.29$ cal. mole⁻¹ deg.⁻¹ were obtained. The nitrobenzene system was then chosen as standard, and results for substituted nitrobenzenes are given relative to it in Table 5. The pK_b values are for reaction (2), but the thermodynamic functions are given for the reaction:



where X is the substituent. Although the absolute values of K_b may be in error by $\pm 10\%$, it is likely that the deviations will be about the same and due to the same causes at both temperatures, so that it is justifiable to consider the relative values as more accurate.

TABLE 5.
Thermodynamic functions for the basic dissociation of substituted nitrobenzenes relative to the nitrobenzene system.

Subst.	pK_b^{25}	pK_b^{10}	ΔpK_b^{25}	ΔpK_b^{10}	$\Delta G^\circ_{298.1}$ (kcal. mole ⁻¹)	$\Delta H^\circ_{298.1}$ (kcal. mole ⁻¹)	$\Delta S^\circ_{298.1}$ (cal. deg. ⁻¹ mole ⁻¹)
<i>p</i> -Me	1.98	2.04	-0.91	-0.95	-1.24	-1.21	+0.1
<i>o</i> -Me	2.14	2.22	-0.75	-0.77	-1.02	-0.65	+1.2
H	2.89	2.99	0	0	0	0	0
<i>p</i> -Cl	3.24	3.37	0.35	0.38	0.48	0.45	-0.1
<i>o</i> -Cl	3.62	3.74	0.73	0.75	1.00	0.51	-1.6
<i>m</i> -Cl	3.89	4.02	1.00	1.03	1.49	0.80	-2.3

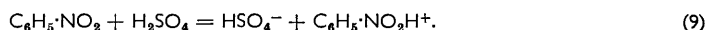
Therefore, the ΔH° values are probably accurate to ± 0.3 kcal. mole⁻¹ and the entropies to ± 1 cal. mole⁻¹ deg.⁻¹. In view of the uncertain values of K_b^{10} for *m*-nitrotoluene (cryoscopic) and for *m*- and *p*-dinitrobenzene (conductometric), the thermodynamic functions calculated for these bases were strikingly different from the rest and are not therefore included in Table 5. It can be seen from the Table, that the expectation of an entropy change close to zero for reaction (7) is best borne out by the *para*-substituted derivatives. For the *ortho*-derivatives the change is bigger, but difficult to interpret.

¹⁸ Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, (a) p. 743, (b) p. 144.

It is interesting to compare the entropy change for the standard nitrobenzene system, $\Delta S^\circ_{298-1} = -4.3$ cal. mole⁻¹ deg.⁻¹, with the value for the autoprotolysis of the solvent, $\Delta S^\circ_{298-1} = -13.7$ cal. mole⁻¹ deg.⁻¹, which was estimated by Gillespie, Robinson, and Solomons,¹² or $\Delta S^\circ_{298-1} = -9.0$ cal. mole⁻¹ deg.⁻¹, which is the estimate of Kirkbride and Wyatt.¹³ The comparison shows that the entropy decrease in the reaction



is 2—3 times as big as that in the reaction



It was suggested by Gillespie and his co-workers¹² that the autoprotolysis ions have more negative entropies in hydrogen-bonded solvents than have other ions, which was ascribed to their ability to fit into the solvent structure and to strengthen the hydrogen bonds in the surrounding solvent. The standard entropy change for the ionisation of nitrobenzene seems to support this suggestion; for it is unreasonable to assume the large nitracidium cation to be strongly solvated, since the smaller NH_4^+ has a solvation number of only 1, as estimated by Gillespie and his co-workers⁸ and by Bonner.¹⁹ The absence of extensive solvation of the protonated nitro-group follows also from the absence of *ortho*-effect. Therefore, the whole of the entropy decrease in reaction (9) could, as a first approximation, be ascribed to the solvation of the HSO_4^- ion alone. Subtracting this from the entropy decrease for the autoprotolysis reaction, an equal value, or one up to twice as big, is obtained for the H_3SO_4^+ ion. This ion may hence be more extensively solvated than the HSO_4^- ion, and this conclusion would be consistent with its higher proton-jump mobility.

EXPERIMENTAL

Sulphuric acid was prepared by mixing "AnalaR" 98% acid with oleum and adjusting the composition to obtain the minimum of conductance, $\kappa_{25} = 1.044 \times 10^{-2}$ ohm⁻¹ cm.⁻¹.

Sulphuryl chloride (B.D.H. laboratory reagent) was distilled and the fraction boiling at 68.8—69.1°/753 mm. was collected.

"AnalaR" potassium sulphate (K_2SO_4) was dried at 105°.

The nitro-compounds, all B.D.H. laboratory reagents, were purified by fractional crystallisation (nitrobenzene and *o*-chloronitrobenzene) or by two-fold recrystallisation from absolute alcohol.

Solutions of sulphuryl chloride were prepared in glass-stoppered flasks by weight and poured into the conductivity cells by a siphon arrangement, solutions not being exposed to the atmosphere for more than a few seconds. The most concentrated solutions of potassium sulphate in these mixtures were prepared by adding a weighed amount of the salt to a weighed amount of solvent. The more dilute solutions were prepared by mixing the most concentrated solutions with variable amounts of solvent or by directly weighing the salt and the solvent in a series of glass-stoppered flasks. The most concentrated solutions of the nitro-compounds were prepared by weight and further diluted also by weight. The conductance measurements were carried out always within 2 days of the preparation of solutions, which were meanwhile kept in a desiccator over P_2O_5 . The transfer of solutions from the flasks into the conductivity cells was carried out very quickly, within a few seconds only.

Conductance was measured in cells of the Jones and Bollinger type. Cell constants ranging from 20 to 70 cm.⁻¹ were determined by using 0.1demal-potassium chloride as standard. A conductance bridge of a somewhat modified Shedlovsky design was used at a frequency of 1000 cycles/sec., with head-phones as detectors of the balance point. The temperatures were kept constant within $\pm 0.05^\circ$ by using water thermostat-baths. The thermometers were calibrated against N.P.L. calibrated standards. The accuracy of the conductivity measurements is within $\pm 0.1\%$ at both temperatures.

The density measurements were carried out with a 10 c.c. specific gravity bottle at both temperatures and are not accurate to more than 1 part in 10⁵.

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¹⁹ Bonner, J., 1960, 3493.