850. *Solutions in Sulphuric Acid. Part XXIII.* Cryoscopic Measurements on Nitrobenzene and the Nitrotoluenes.*

By R. J. GILLESPIE and E. A. ROBINSON.

Cryoscopic measurements on nitrobenzene and the nitrotoluenes in 100% sulphuric acid give more accurate values of the basic dissociation constants of these compounds than those obtained earlier with slightly aqueous sulphuric acid as solvent. It is suggested that nitro-compounds in general give abnormally high freezing points in slightly aqueous sulphuric acid and a possible explanation is given.

A NUMBER of aromatic mononitro-compounds have been shown to behave as weak bases in sulphuric acid by means of cryoscopy,[1,2] conductimetry,[2] and spectroscopy.[3] The results of these different methods are in good quantitative agreement, except for some early measurements [1] carried out in slightly aqueous sulphuric acid, which gave higher values of the basic ionisation constants than the other methods. Brayford and Wyatt [4] found that polynitro-compounds, which are non-electrolytes, give abnormally high freezing-point depressions in slightly aqueous sulphuric acid. These results were attributed to salting-out of the nitro-compound by the electrolyte hydroxonium hydrogen sulphate. Gillespie and Solomons [2] suggested that, in the case of mononitro-compounds, the un-ionised portion might show the same behaviour, thus giving abnormally high overall freezing-point depressions and hence high basic dissociation constants. New cryoscopic measurements have therefore been made in 100% sulphuric acid to test this suggestion.

EXPERIMENTAL

Apparatus.—The apparatus and general procedure for making the cryoscopic and conductimetric measurements have been described.[5,6] Freezing points were measured with a solid-stem mercury-in-glass thermometer which was periodically calibrated against a platinum resistance thermometer.

Materials.—Sulphuric acid, prepared as previously described,[7] was adjusted to maximum freezing point before each experiment. Liquid solutes were dried and redistilled: nitrobenzene, b. p. 209°, n_D^{25} 1·550; *o*-nitrotoluene, b. p. 218°, n_D^{25} 1·543; *m*-nitrotoluene, b. p. 228°, n_D^{25} 1·544. *p*-Nitrotoluene, recrystallised from alcohol, had m. p. 54°.

Calculations.—The freezing-point depression θ is related to the molality of the solute m_2 by eqn. (2) of Part XIX,[8] *i.e.*,

$$\theta/m_2 = 6{\cdot}12\nu'(1 - 0{\cdot}00195\theta)[1 + (2s_2 - \nu')m_2/2m_1]$$

where ν' is approximately equal to ν, the number of moles of ions and molecules which are formed by one molecule of the solute, and the other symbols have the meanings given previously.[7] For a weak base, $B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-$, we have $\alpha = \nu - 1$, where α is the degree of ionisation and the basic dissociation constant $K_b = [BH^+][HSO_4^-]/[B] = (\nu - 1)[HSO_4^-]/(2 - \nu)$, where $[HSO_4^-]$ is the *total* concentration of hydrogen sulphate ion, including that remaining from the incompletely repressed autoprotolysis of the solvent ($K_{ap} = 1{\cdot}56 \times 10^{-4}$ mole^2 kg.$^{-2}$).

Results.—For convenience the freezing points for two experiments on each solute, in each of

---

* Part XXII, *J.*, 1957, 1804.

[1] Gillespie, *J.*, 1950, 2542.

[2] Gillespie and Solomons, *J.*, 1957, 1796.

[3] Brand, Horning, and Thornley, *J.*, 1952, 1374.

[4] Brayford and Wyatt, *J.*, 1955, 3453.

[5] Gillespie, *J.*, 1950, 2473.

[6] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.

[7] Gillespie and Oubridge, *J.*, 1956, 80.

[8] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

which an average of six separate additions of solute were made, were plotted on a large scale, and freezing points of the solutions at round concentrations interpolated. These interpolated freezing points (column 2, Table 1), after correction for the depression produced by the ions remaining from the incompletely repressed autoprotolysis of the solvent, are given in column 3 of Table 1. Values of the freezing-point depression θ, calculated from the corrected freezing points, are given in column 4 of Table 1, which also includes values of ν' and K_b.

TABLE 1. *Results of the cryoscopic measurements.*

Nitrobenzene

m_2	F. p. obs.	F. p. corr.	θ	ν'	10^2K_b	
0·000	10·365°	10·515°	—	—		
0·050	10·026	10·108	0·407°	1·33	1·1	1·1
0·100	9·682	9·742	0·773	1·26	1·1	
0·150	9·344	9·392	1·123	1·22	1·0	
0·200	9·003	9·045	1·470	1·20	1·0	
0·250	8·668	8·706	1·809	1·18	1·1	
0·300	8·320	8·355	2·160	1·17	1·1	

m-*Nitrotoluene*

m_2	F. p. obs.	F. p. corr.	θ	ν'	10^2K_b	
0·000	10·365°	10·515°	—	—		
0·050	9·976	10·033	0·482°	1·57	(3·8)	
0·100	9·628	9·679	0·854	1·39	2·5	2·0
0·150	9·284	9·322	1·193	1·30	2·1	
0·200	8·936	8·967	1·548	1·27	2·0	
0·250	8·588	8·616	1·899	1·24	1·9	
0·300	8·242	8·268	2·247	1·21	1·6	

o-*Nitrotoluene*

m_2	F. p. obs.	F. p. corr.	θ	ν'	10^2K_b	
0·000	10·365	10·515	—	—		
0·050	9·954	10·000	0·515	1·68	(8·0)	
0·100	9·552	9·584	0·931	1·52	5·9	6·2
0·150	9·152	9·177	1·338	1·45	5·7	
0·200	8·752	8·773	1·742	1·42	6·1	
0·250	8·356	8·375	2·140	1·40	6·7	
0·300	7·984	8·001	2·514	1·37	6·6	

p-*Nitrotoluene*

m_2	F. p. obs.	F. p. corr.	θ	ν'	10^2K_b	
0·000	10·365	10·515	—	—		
0·050	9·940	9·982	0·533	1·74	(11·5)	
0·100	9·520	9·547	0·973	1·60	9·3	9·4
0·150	9·096	9·118	1·397	1·52	9·0	
0·200	8·674	8·693	1·822	1·49	9·5	
0·250	8·252	8·269	2·246	1·46	9·8	

DISCUSSION

The mean values of the basic dissociation constants K_b given in Table 1 are compared in Table 2 with earlier values [1] obtained in slightly aqueous sulphuric acid. The new values are appreciably lower than earlier ones and are in good agreement with values obtained by other methods. Thus the present results substantiate Gillespie and Solomons's suggestion [2] that mononitro-compounds, like polynitro-compounds, give abnormally large freezing-point depressions in slightly aqueous sulphuric acid. A probable explanation is that the un-ionised part of the nitro-compound is salted out [4] by the electrolyte H_3O^+,HSO_4^-. Our results show that accurate values of the basic dissociation constants of mononitro-compounds can be obtained cryoscopically in 100% sulphuric acid but not in slightly aqueous sulphuric acid.

TABLE 2. *Dissociation constants of some nitro-compounds.*

	Cryoscopic			
	100% H_2SO_4	Slightly aqueous H_2SO_4	Conduct.	Spectr.
Nitrobenzene	0·011	0·025	0·010	0·009
o-Nitrotoluene	0·062	—	0·067	—
m-Nitrotoluene	0·020	—	0·023	0·024
p-Nitrotoluene	0·094	0·17	0·095	0·077
p-Chloronitrobenzene	0·003[3]	—	0·004	0·0046

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[*Received, June* 19*th*, 1957.]