338. *Solutions in Sulphuric Acid. Part XXI.* Conductivity Measurements on Some Nitro-compounds.*

By R. J. Gillespie and C. Solomons.

The behaviour of a number of nitro-compounds in sulphuric acid has been studied by measurements of the electrical conductivities of their solutions. The mononitro-compounds studied gave solutions whose conductivities increased with increasing concentration of the nitro-compound, and it was concluded that all these substances behave as weak bases. A method for determining the dissociation constants of weak bases from conductivity measurements on their solutions is described and applied to the mononitro-compounds. No evidence was obtained for the ionisation of any of the di- or tri-nitro-compounds, all of which depressed the conductivity of sulphuric acid : it was concluded that they are all non-electrolytes. Small differences in their behaviour have been tentatively interpreted in terms of solvation. Our results are compared with, and found to be generally in good agreement with, previous studies of solutions of nitro-compounds by ultraviolet spectroscopy and by cryoscopy. Cryoscopic measurements on two nitro-compounds not previously studied by this method are also reported.

Solutions of nitro-compounds in sulphuric acid have been studied by a number of workers, mainly by the cryoscopic method, although some electrical-conductivity and ultraviolet-spectroscopic measurements have also been made. The results and conclusions of different workers have not, however, always been in agreement. Thus, although it seems clear that nitrobenzene and various methyl- and halogen-substituted nitrobenzenes are weak bases, the extent of their ionisation has not been determined with any certainty. For nitromethane Hantzsch[1] concluded that it was un-ionised, but Gillespie[2] later believed his cryoscopic measurements to show that it was a weak base. There has also been disagreement concerning various aromatic polynitro-compounds, which have generally been assumed to be non-electrolytes, although Gillespie[2] concluded from cryoscopic measurements that 2 : 4 : 6-trinitrotoluene is a weak base. It has since been shown,[3] however, that the results of cryoscopic measurements on polynitro-compounds are difficult to interpret unambiguously.

It was the purpose of the present work to obtain further information about the behaviour of nitro-compounds in sulphuric acid by electrical-conductivity measurements. The electrical conductivities of solutions in 100% sulphuric acid of a series of mono- and poly-nitro-compounds were measured at 25° and at concentrations up to approximately 0·5 mole per kg. of soln. Some new measurements were also made on solutions of sulphuryl chloride, which is believed to be a non-electrolyte,[4] for comparison. Cryoscopic measurements on *p-tert.*-butylnitrobenzene and *p*-chloronitrobenzene are also reported and discussed.

The conductivity measurements are recorded in Tables 1 and 2 and Figs. 1 and 2, and the cryoscopic measurements in Tables 4 and 5.

On the basis of the conductivity measurements, the compounds studied fall into two groups : the mononitro-compounds in Table 1, which increase the conductivity of sulphuric acid; and the polynitro-compounds and sulphuryl chloride in Table 2, which decrease the conductivity of sulphuric acid.

Mononitro-compounds.—Since each of these substances gives a solution whose conductivity increases with increasing concentration, it is concluded that they are all ionised in sulphuric acid. The magnitudes of the conductivities of their solutions make it clear

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* Part XX, *J.*, 1956, 3850.

[1] Hantzsch, *Z. phys. Chem.*, 1907, **61**, 257.

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

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

[4] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

TABLE 1. *Specific conductances of solutions of mononitro-compounds.*

Concn. (mole $kg._{soln.}^{-1}$)	κ (10^{-2} ohm^{-1} cm.$^{-1}$)	α	K_b
	Nitrobenzene		
0·0391	1·092	0·363	0·0134
0·0766	1·158	0·270	0·0105
0·0989	1·212	0·257	0·0113
0·1284	1·251	0·224	0·0101
0·1936	1·369	0·199	0·0108
0·2186	1·386	0·182	0·0099
0·2715	1·471	0·171	0·0108
0·3073	1·487	0·153	0·0095
0·3279	1·510	0·151	0·0096
0·3997	1·588	0·139	0·0096
0·4546	1·626	0·129	0·0092
	o-Nitrotoluene		
0·0121	1·071	0·875	0·1477
0·0342	1·177	0·655	0·0562
0·0977	1·562	0·549	0·0698
0·1055	1·591	0·530	0·0671
0·1806	1·938	0·450	0·0686
0·1940	1·975	0·434	0·0663
0·2457	2·153	0·395	0·0647
0·2468	2·159	0·395	0·0650
0·3245	2·358	0·341	0·0579
0·3953	2·481	0·300	0·0513
	p-Nitrotoluene		
0·0172	1·101	0·896	0·2094
0·0536	1·342	0·678	0·0874
0·0780	1·527	0·652	0·1027
0·0804	1·521	0·627	0·0944
0·1556	1·985	0·546	0·1051
0·1634	2·000	0·525	0·0974
0·2297	2·303	0·459	0·0908
0·2440	2·338	0·455	0·0938
0·3044	2·530	0·340	0·0633
0·3311	2·584	0·379	0·0773
0·3439	2·746	0·403	0·0942
0·3818	2·696	0·354	0·0746
0·4825	2·834	0·302	0·0634

Concn. (mole $kg._{soln.}^{-1}$)	κ (10^{-2} ohm^{-1} cm.$^{-1}$)	α	K_b
	p-Chloronitrobenzene		
0·0215	1·051	0·209	0·0049
0·0430	1·062	0·192	0·0047
0·0861	1·090	0·163	0·0045
0·1486	1·130	0·124	0·0038
0·2289	1·174	0·097	0·0032
	m-Nitrotoluene		
0·0118	1·067	0·826	0·0973
0·0295	1·120	0·590	0·0373
0·0564	1·205	0·442	0·0251
0·0773	1·279	0·401	0·0247
0·1218	1·404	0·339	0·0236
0·1555	1·492	0·309	0·0233
0·2199	1·627	0·266	0·0224
0·2367	1·657	0·256	0·0220
0·2902	1·735	0·229	0·0206
0·3613	1·817	0·200	0·0188
	Nitromethane		
0·0330	1·051	0·136	0·0027
0·0589	1·056	0·109	0·0023
0·0869	1·069	0·117	0·0028
0·0935	1·067	0·104	0·0024
0·1523	1·105	0·104	0·0029
0·1664	1·094	0·087	0·0022
0·2414	1·145	0·082	0·0025
0·3337	1·195	0·072	0·0024

TABLE 2. *Specific conductances of solutions of polynitro-compounds.*

Concn. (mole $kg._{soln.}^{-1}$)	κ (10^{-2} ohm^{-1} cm.$^{-1}$)
o-Dinitrobenzene	
0·0225	1·023
0·0402	1·024
0·0845	1·004
0·1005	0·996
0·1461	0·976
0·1659	0·968
0·2049	0·952
0·2300	0·941
0·2611	0·929
0·3072	0·909
0·3252	0·905
0·3674	0·900
0·3821	0·880
m-Dinitrobenzene	
0·0134	1·038
0·0398	1·027
0·0529	1·024
0·0599	1·020
0·0854	1·010
0·1178	0·999
0·1269	0·994
m-Dinitrobenzene	
0·1659	0·981
0·1717	0·977
0·2122	0·963
0·2529	0·952
p-Dinitrobenzene	
0·0210	1·035
0·0399	1·031
0·0657	1·015
0·0834	1·013
0·1107	0·998
0·1244	0·997
0·1607	0·981
0·1869	0·972
0·2054	0·965
0·2489	0·950
0·2704	0·942
0·3346	0·923
2 : 4-Dinitrotoluene	
0·0125	1·038
0·0230	1·033
2 : 4-Dinitrotoluene	
0·0429	1·025
0·0726	1·024
0·1207	0·992
0·1771	0·970
0·2518	0·942
1 : 3 : 5-Trinitrobenzene	
0·0338	1·023
0·0469	1·015
0·0966	0·984
0·1263	0·967
0·1535	0·945
0·1793	0·936
0·2077	0·915
0·2421	0·899
0·2871	0·868
0·3032	0·863
0·3576	0·826
0·3671	0·827
2 : 4 : 6-Trinitrotoluene	
0·0336	1·021
2 : 4 : 6-Trinitrotoluene	
0·0852	0·986
0·1537	0·941
0·2287	0·892
0·3024	0·844
0·3712	0·801
Sulphuryl chloride	
0·0101	1·041
0·0115	1·041
0·0317	1·034
0·0460	1·031
0·0629	1·026
0·1051	1·016
0·1370	1·006
0·1608	0·998
0·2014	0·987
0·2533	0·973
0·2899	0·964
0·3018	0·961
0·4234	0·928

that they contain either the $H_3SO_4^+$ or the HSO_4^- ion,[5] and in accord with cryoscopic and spectroscopic evidence it is assumed that they ionise as simple bases according to the equation $R{\cdot}NO_2 + H_2SO_4 = R{\cdot}NO_2H^+ + HSO_4^-$. The order of decreasing conductivity of the solutions of these substances will be the order of decreasing base strength, which is therefore *p*- > *o*- > *m*-nitrotoluene > nitrobenzene > *p*-chloronitrobenzene > nitromethane. This order of base strengths agrees well with previous cryoscopic work[2] on nitrobenzene, *p*-nitrotoluene, and nitromethane, and with spectroscopic measurements[6] on *m*- and *p*-nitrotoluene, *p*-chloronitrobenzene, and nitrobenzene.

Dissociation Constants of Weak Bases from Conductivity Measurements.—The basic dissociation constant of a weak base, $K_b = [BH^+][HSO_4^-]/[B]$ can be written

$$K_b = [HSO_4^-]\alpha/(1 - \alpha) \qquad (1)$$

where α is the degree of dissociation which can be obtained from conductivity measurements in the following manner. More than 97% of the current in a solution of any base is carried by the hydrogen sulphate ion[7] and, therefore, in so far as we can ignore the slightly different effects of different cations on the molality of the hydrogen sulphate ion,[5] the concentration of the hydrogen sulphate ion in a solution of a weak base will be the same as that in a solution of a strong electrolyte having the same conductivity. Now, in a solution of a fully ionised univalent-metal hydrogen sulphate whose stoicheiometric concentration is c_s the concentration of hydrogen sulphate ion is given to a good approximation by

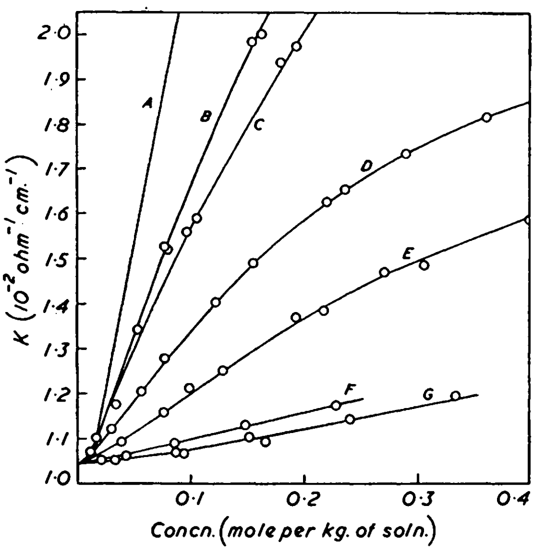

FIG. 1. *Specific conductances of solutions of mononitro-compounds.*

A, $KHSO_4$.
B, *p*-$C_6H_4Me{\cdot}NO_2$.
C, *o*-$C_6H_4Me{\cdot}NO_2$.
D, *m*-$C_6H_4Me{\cdot}NO_2$.
E, $PhNO_2$.
F, *p*-$C_6H_4Cl{\cdot}NO_2$.
G, $MeNO_2$.

$$[HSO_4^-]_s = c_s/2 + \sqrt{(c_s^2/4 + K_{ap})} \qquad (2)$$

where K_{ap} is the autoprotolysis constant.[8] For a weak electrolyte whose stoicheiometric concentration is c_w the concentration of hydrogen sulphate ion is given by

$$[HSO_4^-]_w = \alpha c_w/2 + \sqrt{(\alpha^2 c_w^2/2 + K_{ap})} \qquad (3)$$

For solutions of the same conductivity we have $[HSO_4]_s = [HSO_4^-]_w$, hence $\alpha = c_s/c_w$, and K_b may then be calculated from equation (1).

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[5] Gillespie and Wasif, *J.*, 1953, 221.
[6] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[7] Gillespie and Wasif, *J.*, 9153, 209.
[8] Gillespie, *J.*, 1950, 2516.

Dissociation Constants of Some Mononitro-compounds.—For the present calculations we have rather arbitrarily chosen potassium hydrogen sulphate as a reference strong electrolyte. This has the advantage that the conductivities of its solutions are very accurately known and that among the various fully ionised metal sulphates it exhibits an "average" behaviour.[5, 9] The values of α and K_b for the various mononitro-compounds calculated as described above, K_{ap} (25°) being taken[10] as $2{\cdot}2 \times 10^4$, are given in Table 1. The values of K_b may be seen to be reasonably constant except in some cases at the lowest concentrations, when they seem to be abnormally high. This may reasonably be attributed to inaccuracies in the concentration of hydrogen sulphate ion as calculated from equation (2) at these low concentrations. These initial high values have been ignored in calculating the mean K_b values listed in Table 3.

TABLE 3. *Dissociation constants of some nitro-compounds.*

	K_b		
	Conduct.	Cryosc.	Spectr.
p-tert.-Butylnitrobenzene	—	0·10	0·104
p-Nitrotoluene	0·095	0·17 *	0·077
o-Nitrotoluene	0·067	—	—
m-Nitrotoluene	0·023	—	0·024
Nitrobenzene	0·010	0·025 *	0·009
p-Chloronitrobenzene	0·004	0·003	0·0046
Nitromethane	0·0025	0·004 *	—

* Taken from Part VII[2] and corrected for the change in the cryoscopic constant[11] from 5·98 to 6·12.

Cryoscopic Measurements.—Freezing-point depressions produced by *p-tert.*-butylnitrobenzene were measured in sulphuric acid containing a little acetone to repress the autoprotolysis; the results are given in Table 4. Row 3 of this table gives ν', the approximate value of the number of moles of particles produced in solution by one mole of the solute, calculated by means of the equation $\Delta\theta/m_2 = 6{\cdot}12\nu'(1 - 0{\cdot}00195\theta)[1 + (4m_2 + 12m_3)/9m_1]$ where m_1, m_2, and m_3 are the molalities of sulphuric acid, *p-tert.*-butylnitrobenzene, and acetone respectively, which is an extended and slightly modified form of equation 2 of Part XIX,[11] which allows for the presence of the second electrolyte acetone ($\nu_2 = 1{\cdot}5$, $s_2 = 1$, $\nu_3 = 2$, $s_3 = 2$; cf. equation 4 of Part I[4]). Since $\alpha = \nu' - 1$, where α is the degree of dissociation, the dissociation constant K_b is given by the expression

$$K_b = [(\nu' - 1)^2 m_2 + (\nu' - 1)m_3]/(2 - \nu')$$

Values of K_b thus calculated are given in Table 4, and the mean value is given in Table 3.

Freezing-point depressions produced by *p*-chloronitrobenzene were measured in 100% sulphuric acid, and the results are given in Table 5. Column 5 of this Table gives the values of ν' calculated by means of the equation $\theta/m_2 = 6{\cdot}12\nu'(1 - 0{\cdot}00195\theta)[1 + m_2/2m_1]$ which is the appropriate form of equation 2 of Part XIX.[11] Column 6 gives values of K_b calculated by means of the expression $K_b = (\nu' - 1)[HSO_4^-]/(2 - \nu')$, and the mean value is also given in Table 3. Values of K_b that have been obtained previously[2] by the cryoscopic method for *p*-nitroluene, nitrobenzene, and nitromethane are also given in Table 3.

TABLE 4. *Cryoscopic measurements on* p-tert.*-butylnitrobenzene.*

m_2	0·0000	0·0126	0·0348	0·0629	0·0914
$\Delta\theta$	—	0·122	0·328	0·570	0·814
ν'	—	1·62	1·57	1·50	1·47
K_b	—	0·12	0·11	0·09	0·09

Molality of acetone (m_3) = 0·0632.

Comparison of Dissociation Constants obtained by Different Methods.—Brand, Horning, and Thornley[6] measured the degree of dissociation at 18° of a number of nitro-compounds in slightly aqueous sulphuric acid and in oleum by means of their ultraviolet absorption spectra. They expressed their results in terms of pK_b values which are related to the

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[9] Flowers and Gillespie, unpublished work.

[10] Gillespie and Solomons, unpublished work.

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

acidity function H_0 of the solvent by the relation $H_0 = \text{p}K_a + \log_{10}[\text{B}]/[\text{BH}^+]$ which we have converted into K_b values, for convenience of comparison, by means of the expression $\log K_b = \text{p}K_a - H_0 + \log[\text{HSO}_4^-]$. The value of H_0 and the corresponding value of the molality of the hydrogen sulphate ion $[\text{HSO}_4^-]$ were taken for 99·95% sulphuric acid. The value of $[\text{HSO}_4^-]$ was calculated from the expression $[\text{HSO}_4^-] = m/2 + \sqrt{\{(m/2)^2 + K_{ap}\}}$, where m is the molality of the water in the solvent and K_{ap} is the autoprotolysis constant,[8, 10] water being assumed to be fully ionised. The error introduced, if, as is likely, water is not quite completely ionised, is very small. These K_b values are given in the column headed " Spectr." in Table 3.

TABLE 5. *Cryoscopic measurements on* p-*chloronitrobenzene.*

m_2	F. p. (obs.)	F. p. (corr.)	θ	ν'	K_b
0·0000	10·365°	10·515°	—	—	—
0·0241	10·211	10·351	0·164°	—	—
0·0490	10·047	10·172	0·343	1·14	0·0024
0·0999	9·713	9·818	0·697	1·14	0·0029
0·1515	9·381	9·468	1·047	1·13	0·0033
0·2079	9·031°	9·102°	1·413°	1·10	0·0030
0·2634	8·673	8·734	1·781	1·09	0·0031
0·3218	8·317	8·367	2·148	1·08	0·0031
0·3739	8·003	8·050	2·465	1·07	0·0031

The values obtained from our conductivity measurements agree very well with the spectroscopic values, and the dissociation constants of the compounds listed in Table 3 may therefore be regarded as reasonably well established. It should be noted that the conductivity measurements were made at 25°, the spectroscopic measurements at approximately 18°, and the cryoscopic measurements at approximately 10°, but the effect of these relatively small temperature differences is almost certain, as pointed out by Brand, Horning, and Thornley,[6] to be negligible.

The values obtained by the cryoscopic method agree reasonably with the other values for *p-tert.*-butylnitrobenzene and *p*-chloronitrobenzene although they appear to be rather high for *p*-nitrotoluene, nitrobenzene, and nitromethane. It is noteworthy that the last three values are all earlier determinations in which water was added to repress the self-ionisation of the solvent. Brayford and Wyatt[3] recently showed that polynitro-compounds, which are non-electrolytes, give abnormally high freezing-point depressions in the presence of small amounts of water. Our results would be accounted for if mononitro-compounds exhibit the same behaviour in addition to a slight ionisation. The measurements on *p*-chloronitrobenzene were made in sulphuric acid containing no added electrolyte, and those on *p-tert.*-butylnitrobenzene in sulphuric acid containing a little acetone, and it appears from the work of Brayford and Wyatt that polynitro-compounds give normal depressions in the presence of acetone.

Effect of Substituents on the Basicity of Nitrobenzene.—It is most convenient to consider the effects of substituents in terms of the acidity constant of the conjugate acid of nitrobenzene $C_6H_5{\cdot}NO_2H^+$ which is inversely proportional to the basicity constant of nitrobenzene. The effects of some *meta*-substituents on the acidity constant have been satisfactorily accounted for by Brand, Horning, and Thornley[6] in terms of Kirkwood and Westheimer's theory[12] of the direct long-range electrostatic effect of substituent groups. Any interpretation of the effects of *ortho*- and *para*-substituents must, however, take into account the inductive and mesomeric effects. It may be noted that the conjugate acid of nitrobenzene is isoelectronic with benzoic acid, and the effects of substituents on their acid strengths might therefore be expected to be similar.

The strengths of the conjugate acids of nitrobenzene and the three nitrotoluenes are in the order H > *meta* > *ortho* > *para*, which, it is of interest, is intermediate between the order for the corresponding benzoic acids in water (*ortho* > H > *meta* > *para*) and the corresponding boronic acids in water (H > *meta* > *para* > *ortho*). Since the positive inductive effect of the methyl substituent is transmitted preferentially to the *ortho*- and

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[12] Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, 6, 506, 513.

para-positions and more strongly to the *ortho*- than the *para*-position, we would on this basis alone expect the order found in the boronic acids. The anomalous position of the *ortho*-compound in the other two cases may be attributed to a steric effect [13] which appears therefore to be greater in *o*-toluic acid than in the conjugate acid of *o*-nitrotoluene. The effect of a *p-tert.*-butyl group in decreasing the acid strength is closely similar to, and perhaps a little greater than, that of a *p*-methyl group, as is also observed for the corresponding benzoic acids in water.

The effect of a *p*-chlorine atom in increasing the acid strength may be attributed to its negative inductive effect and is quantitatively similar to its effect on the strength of benzoic acid in water.

It is of interest that, whereas acetic acid is weaker than benzoic acid, the conjugate acid of nitromethane is stronger than that of nitrobenzene. This presumably indicates that the positive mesomeric effect of the phenyl group more than counteracts its negative inductive effect in the conjugate acid of nitrobenzene, whereas it does not do so in benzoic acid. It seems plausible that the positively charged nitrogen atom of the nitro-group should enhance the mesomeric effect of the phenyl group and also, because of its low polarisibility, hinder the transmission of the inductive effect of the phenyl group through to the oxygen atoms.

Reaction between Nitromethane and Sulphuric Acid.—Aromatic nitro-compounds appear to be stable in sulphuric acid, as the conductivities of their solutions remain unchanged after several days, but the conductivity of nitromethane solutions at 25° slowly increases and the colour of the solutions changes from pale yellow to deep yellow-brown. This reaction was not noticed during previous cryoscopic measurements,[2] probably because of the lower temperature, shorter duration, and lower accuracy of the measurements. In some recent work [3] a slight drift in the freezing points of solutions of nitromethane has been reported.

The change in the conductivity, approximately 5% after one hour, was not sufficient to cause a large error in the measurements if they were made during a few hours after the first addition of nitromethane, as were all the measurements reported in Table 1. We did not study this reaction any further, except to observe that pouring a sulphuric acid solution of nitromethane into water after it had been allowed to react for some hours gave a strongly reducing solution (probably containing hydroxylamine) and a combustible gas (probably carbon monoxide). These observations are consistent with previous work on the reaction between aliphatic nitro-compounds and mineral acids.[14]

Polynitro-compounds.—All the polynitro-compounds that we investigated decrease the conductivity of sulphuric acid (Table 2; Fig. 2). We conclude that our conductivity measurements give no evidence for the ionisation of any of these solutes. The conductivity of their solutions must be attributed to the ions resulting from the self-dissociation of the solvent.

The diminution in the conductivity of sulphuric acid caused by these solutes must be due to their decreasing either the concentration of the self-dissociation ions or the mobilities of these ions, or to both these effects. The concentrations of the self-dissociation ions will be reduced because of the dilution of the solvent by the added solute, and would be further reduced if the solute is solvated. Changes in various properties of the solution, such as its dielectric constant, caused by the presence of the solute may also be contributing factors in reducing the concentrations of the self-dissociation ions. The extent to which the solute will affect the mobilities of the ions is difficult to predict, but any disruption of the structure of the liquid, which is liable to be considerable if solvation occurs, is likely to be accompanied by a decrease in the mobilities of the ions. Metal cations, which are believed to be solvated,[15] are known to reduce the mobility of the hydrogen sulphate ion [5] and they

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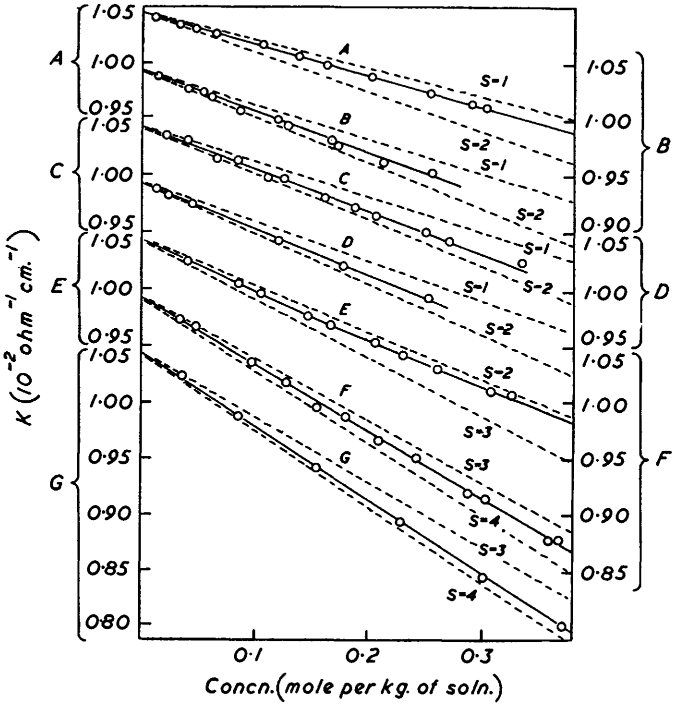
[13] See, *e.g.*, Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 743.

[14] Hass and Riley, *Chem. Rev.*, 1943, **3**, 371.

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

probably also reduce the mobility of the hydrogen ion ($H_3SO_4^+$). In the following discussion we shall consider only the ions resulting from the autoprotolysis and ignore those resulting from the self-dehydration, since the concentrations of the former are greater [8] and their mobilities are very much greater.[5] Our results can be treated quantitatively if only the dilution and solvation effects on the concentration of the autoprotolysis ions are considered, and other effects, such as those due, for example, to the changing dielectric constant of the solvent, are ignored, and if it is also assumed that the mobilities of the autoprotolysis ions remain constant. It then follows that the conductivity of the solution is proportional to the molar concentration of " free " solvent in the solution, *i.e.*, $\kappa/\kappa_0 = c_1/c_0 = (1000d - c_2M_2 - c_2sM_1)/1000d_0$, where c_1 is the molar concentration of the solvent in the solution, c_0 is the molar concentration of the solvent in the pure solvent, and M_1 is its molecular weight, c_2 is the molar concentration of the solute and M_2 is its molecular weight, s is the solvation number of the solute, d_0 is the density of the solution, κ_0 is the conductivity of the pure solvent, and κ the conductivity of the solution. It will be convenient if we convert molar concentrations (c) into units (ω) of mole per kg. of solution [17] ($c = \omega d$), then we obtain $\kappa = \kappa_0 d\omega(1 - 10^{-3}M_2 - 10^{-3}sM_1)/d_0$. The densities of the solutions were measured and they may with sufficient accuracy be expressed as linear functions of the concentration, $d = d_0(1 - a\omega)$ where a has the following values : *o*-dinitrobenzene 0·086, *m*-dinitrobenzene 0·078, *p*-dinitrobenzene 0·080, 2 : 4-dinitrotoluene 0·108, 1 : 3 : 5-trinitrobenzene 0·036, 2 : 4 : 6-trinitrotoluene 0·066. Values of κ at various concentrations were calculated for each of the solutes for various solvation numbers s. They have been plotted against concentration in Fig. 2, where they may be compared with th experimental results. The solvation numbers giving approximately the best agreement with the experimental results are listed in Table 6.

FIG. 2. *Specific conductances of solutions of polynitro-compounds.*



A, SO_2Cl_2.
B, *m*-$C_6H_4(NO_2)_2$.
C, *p*-$C_6H_4(NO_2)_2$.
D, 2 : 4-$C_6H_3Me(NO_2)_2$.
E, *o*-$C_6H_4(NO_2)_2$.
F, 1 : 3 : 5-$C_6H_3(NO_2)_3$.
G, 2 : 4 : 6-$C_6H_2Me(NO_2)_3$.

TABLE 6. *Solvation numbers of polynitro-compounds.*

	Solvation number	*s/n* *		Solvation number	*s/n* *
o-Dinitrobenzene	2·1	1·1	1 : 3 : 5-Trinitrobenzene	3·5	1·2
m-Dinitrobenzene	1·6	0·8	2 : 4 : 6-Trinitrotoluene	3·7	1·2
p-Dinitrobenzene	1·7	0·9	(Sulphuryl chloride)	1·3	—
2 : 4-Dinitrotoluene	1·7	0·9			

* *n* is the number of nitro-groups in the molecule.

In view of the fact that mononitro-compounds are partly ionised in sulphuric acid, and other evidence[16] that if it is not protonated the nitro-group tends to form hydrogen bonds with a sulphuric acid molecule, it seems reasonable to suppose that solvation occurs largely by formation of hydrogen bonds between sulphuric acid molecules and nitro-groups. It is therefore of interest that *s/n*, the ratio of the total solvation number to the number of nitro-groups, has a constant value of approximately unity (Table 6).

It should perhaps be pointed out that some of the differences in the depressions of the conductivity caused by different nitro-compounds could conceivably be due to very small but different amounts of ionisation, insufficient to increase the conductivity enough to overcome the decrease caused by solvation and other effects. If, however, we accept the cryoscopic evidence that sulphuryl chloride is a non-electrolyte,[4] it seems unlikely that the polynitro-compounds, which depress the conductivity more than does sulphuryl chloride, can be even slightly ionised.

We may conclude that our conductivity measurements show that it is unlikely that the polynitro-compounds that we have investigated are ionised at all, and that if they are the degree of their ionisation must be very small. Our conclusions are in agreement with those of Brand, Horning, and Thornley[6] from their spectroscopic measurements. It is noteworthy that these authors pointed out that Gillespie's cryoscopic results[2] on 2 : 4 : 6-trinitrotoluene, from which he concluded that it was ionised, could alternatively be accounted for if it was assigned a solvation number of four, which is close to the value that we have calculated above from our conductivity results. This agreement may, however, be fortuitous, since Gillespie's measurements were made in sulphuric acid containing a little water, and Brayford and Wyatt[3] have recently shown that polynitro-compounds give quite appreciably differing freezing-point depressions in sulphuric acid containing small amounts of various different electrolytes, including water, which cannot be satisfactorily accounted for in terms of solvation.

EXPERIMENTAL

Apparatus.—The conductivity bridge and cells, and the general procedure for making the conductivity measurements, are described elsewhere.[17] Densities of solutions were measured with a specific-gravity bottle.

Materials.—Sulphuric acid was prepared and adjusted to the composition 100% H_2SO_4 by means of its conductivity as described elsewhere.[17]

Liquid solutes were dried and redistilled and had the following b. p.s : nitromethane 100·3—100·5°; nitrobenzene 207°; *o*-nitrotoluene 218°; *m*-nitrotoluene 228°. The solid solutes were recrystallised several times, and then dried in an oven. All solutes were stored in stoppered bottles in desiccators over phosphoric oxide.

We thank the London County Council for the award of a Major County Scholarship (to C. S.), Dr. J. A. Leisten who made the cryoscopic measurements on *p-tert.*-butylnitrobenzene, Dr. J. V. Oubridge who made the cryoscopic measurements on *p*-chloronitrobenzene, and Mr. R. Flowers who made the density measurements.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.
[*Received, September 12th*, 1956.]

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[16] Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.
[17] Gillespie, Oubridge, and Solomons, following paper.