process. The data in Table I clearly favor the stepwise mechanism.

It may be noted that for both sets of data it can be concluded that at high acidities the C^{13} isotope effect, expressed as $k_{12}/k_{13} - 1$, is in the order of from 0.038 to 0.045. This fact, that the C^{13} isotope effect is essentially "full" when the carbon–carbon bond rupture step is rate determining, is itself of considerable interest. From the earlier mentioned analysis of the rate equation, it was concluded that the rate coefficient for step 7, the carbon–carbon bond rupture, is in the order of 10^5 sec^{-1}. This implies that this reaction is very fast and indeed the resultant calculated free energy of activation for the step is only $\Delta F^* = 10.6$ kcal/mole which, in turn, implies a potential energy valley for the process of from 8 to 10 kcal. Recalling that C^{13} isotope effects of about 0.040 also characterize very much slower bond rupture processes, one can conclude that the magnitude of the isotope effect is independent of the depth of the potential energy valley for the process. This is the well-known prediction of isotope theory.

Complexation in Acetonitrile of Tetramethylguanidinium (BH^+) Sulfate with Bisulfate, $BHSO_4^-$, and BH^+ Ions[1]

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Abstract: From the data obtained from conductance, differential vapor pressure, and solubility measurements in acetonitrile as solvent, it has been concluded that the tetramethylguanidinium ion (BH^+) forms a host of complex salts and ions with sulfate. The normal sulfate is present in solution as a stable dimer, $\{(BH)_2SO_4\}_2$, which dissociates into $(BH)_3SO_4^+$ and $BHSO_4^-$ ions, the ionic dissociation constant, K^d, being about 7×10^{-5}, while its solubility product $K_{sp} = 3.5 \times 10^{-7}$. In mixtures with a molar ratio of B:H_2SO_4 of 1.5 the solutions contain $(BH)_2SO_4\cdot BHHSO_4$ which dissociates into $(BH)_3SO_4^+$ and HSO_4^-; $K^d \sim 4 \times 10^{-4}$. This compares with a K^d of $BHHSO_4$ of 5×10^{-3}. Part of the complex is present as the dimer, $\{(BH)_2SO_4\cdot BHHSO_4\}_2$, the dimerization constant being of the order of 1.5×10^1. In mixtures with a molar ratio of B:H_2SO_4 of 1.67 a large fraction of sulfate is present as the complex $\{(BH)_2SO_4\}_2BHHSO_4$ which dissociates into $(BH)_5(SO_4)_2^+ + HSO_4^-$ with $K^d \sim 10^{-3}$. This has been substantiated by solubility measurements of $\{(BH)_2SO_4\}_2$ in dilute sulfuric acid. In a mixture of tetraethylammonium bisulfate ($K^d \sim 3 \times 10^{-2}$) with excess of B the reaction $B + HSO_4^- \rightleftharpoons BHSO_4^-$ occurs. The bisulfate also forms with $\{(BH)_2SO_4\}_2$ the complexes $Et_4N(BH)_2SO_4\cdot HSO_4$ and $Et_4N(BH)_2SO_4\cdot BHSO_4$ which are fairly strong electrolytes. Two complexes are formed between $\{(BH)_2SO_4\}_2$ and BHPi (picrate):$(BH)_2SO_4BHPi$ and $\{(BH)_2SO_4\}_2BHPi$, the latter yielding the $(BH)_5(SO_4)_2^+$ ion. Conductometric and potentiometric titrations of sulfuric acid and of tetraethylammonium bisulfate with tetramethylguanidine in the absence and presence of the hydrogen-bond donor *p*-bromophenol are reported and interpreted.

In previous papers it was shown that the sulfate ion in acetonitrile (AN) has a great affinity toward uncharged hydrogen-bond donors[2] and forms a homoconjugate with the hydrogen-bond donor bisulfate ion[3] which is very unstable because of repulsive Coulombic forces. In the present study of the neutralization of sulfuric acid with tetramethylguanidine (B), it was found that the reaction of the acid with two molecules of B to form the normal sulfate, denoted for simplicity as $(BH)_2SO_4$, was close to complete, although on the basis of the acid strength of the bisulfate ion ($pK^d_{HSO_4^-} = 25.9$[3]) and the basic strength of B ($pK^d_{BH^+} = 23.3$[4]) the reaction should be highly incomplete. The only interpretation of the stability of $(BH)_2SO_4$ is that it is a very weak electrolyte, the sulfate ion concentration in its solutions being extremely small. In the salt the charge of the sulfate ion is neutralized by BH^+. Therefore, it is expected that the normal sulfate salt by hydrogen bonding forms stable conjugate ions with HSO_4^-, $BHSO_4^-$, and BH^+. Also, the ion $BHSO_4^-$ formed by reaction in AN of BH^+ with SO_4^{2-} is expected to be stable.

From conductometric and potentiometric titrations in AN of sulfuric acid and of tetraethylammonium bisulfate with tetramethylguanidine (TMG) and from differential vapor pressure (DVP) measurements in sulfuric acid–TMG mixtures conclusions could be drawn regarding the identity of the various hydrogen-bonded species. In order to confirm these conclusions solubility determinations were made of $(BH)_2SO_4$ in solutions containing various concentrations of sulfuric acid. To obtain an estimate of the stability of the $(BH)_2SO_4BH^+$ ion (and also the $\{(BH)_2SO_4\}_2BH^+$ ion), solubility determinations of $(BH)_2SO_4$ were made in solutions containing BH picrate. The salts formed, $(BH)_2SO_4\cdot BHPi$ and $\{(BH)_2SO_4\}_2BHPi$, are strong electrolytes in AN. Most solubility determinations involving BH picrate were made in the presence of an excess of B in order to suppress acid–base dissociation of the salt (*vide infra*).

$$\{(BH)_2SO_4\}_2 \rightleftharpoons B + (BH)_2SO_4\cdot BHHSO_4$$

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-67.

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **91**, 25 (1969).

(3) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **90**, 5961 (1968).

(4) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *ibid.*, **90**, 23 (1968).

The results indicated that $(BH)_2SO_4BH^+$ is a stable complex from which it was concluded that the ionic dissociation of the normal sulfate salt either occurs according to eq 1 or 2. Conductance measurements in

$$2(BH)_2SO_4 \rightleftharpoons (BH)_2SO_4BH^+ + BHSO_4^- \qquad (1)$$

$$\{(BH)_2SO_4\}_2 \rightleftharpoons (BH)_2SO_4BH^+ + BHSO_4^- \qquad (2)$$

$(BH)_2SO_4$ solutions indicated that the normal sulfate in AN is a uniunivalent electrolyte which dissociates according to eq 2 rather than eq 1. This was confirmed by differential vapor pressure (DVP) determinations. An excess of B was used in most of these determinations; therefore the molecular weight of dissolved B in AN was also determined at various concentrations by the same method.

When the ionic strength was greater than 0.01, activity coefficients were calculated using the partially extended Debye–Hückel expression

$$-\log f = 1.53\sqrt{\mu}/(1 + (4.8 \times 10^7)a\sqrt{\mu})$$

The following values of a were taken: sulfate[3] and bisulfate, 3.10 Å; tetraethylammonium[5] and picrate,[5] 6 Å; and $(BH)_3SO_4^+$, 10 Å.

Experimental Section

Solvent. Acetonitrile was purified and dispensed as described previously.[6] The water content of the solvent was 0.003 *M*.

Acids, Bases, and Salts. Anhydrous sulfuric acid,[6] tetramethylguanidine[4] (TMG), tetramethylguanidinium picrate,[4] tetraethylammonium bisulfate,[7] and *p*-bromophenol[7] were used previously. Tetramethylguanidinium bisulfate was prepared by adding dropwise TMG to a 1 *M* sulfuric acid solution in unpurified Eastman Kodak White Label AN in a mole ratio of 1:1 and also 1:1.3, while cooling in an ice bath to hold the temperature at 25°. The crystals which separated after a day of standing were collected and washed with ice-cold AN and dried *in vacuo* at 65°. The crystals which separated at these mole ratios were identical, mp 148°. Both products were titrated in aqueous medium with standard sodium hydroxide and assayed 99.9 and 99.5%, respectively, as $TMGHHSO_4$.

Crystals of the normal sulfate, denoted for convenience as $(BH)_2SO_4$, were prepared by adding at 25° TMG to 1 *M* sulfuric acid in AN in a mole ratio 2.0:1 TMG:H_2SO_4 while keeping the temperature at 25°. The crystals were washed with ice-cold AN and dried *in vacuo* at 65°, mp 156–158° (assay by gravimetric barium sulfate analysis in aqueous medium, 99.8%).

It was found that a stable complex was formed at a mole ratio of 1.50:1 TMG:H_2SO_4 (see Results). No crystallization occurred in solutions at this mole ratio even starting with 3 *M* sulfuric acid.

Many of the TMG–sulfuric acid mixtures in a molar ratio of 2 or >2 used in conductometric and potentiometric titrations and in differential vapor pressure (DVP) measurements were supersaturated with respect to the normal salt. No precipitation occurred from these solutions even after long periods of standing.

Solubility of $(BH)_2SO_4$ in the Presence of B, Sulfuric Acid, or BHPi. To 50–300 mg of finely ground sulfate in a 10-ml volumetric flask was added 10 ml of AN and gradually either a known volume of sulfuric acid or solutions of TMG or its picrate. The flask and contents were then shaken mechanically for 2–5 days at 25°, the saturated solutions were filtered through a fine frit, a 1–7-ml aliquot was withdrawn, and the solvent was evaporated under a heat lamp.

Sulfate Analysis of Saturated $(BH)_2SO_4$ Solutions—Benzidine Method. The residue resulting from the above procedure was dissolved in a beaker with 20 ml of water, made 0.05 *M* in hydrochloric acid, and heated to boiling. The precipitation of benzidine sulfate was carried out in boiling solution,[8] the beaker and contents were then placed in an ice bath (to minimize the solubility of benzidine sulfate), and the precipitate was filtered and washed with five 1-ml portions of ice-cold water. Finally, the precipitate was transferred into a beaker containing 200–400 ml of boiling water to dissolve the precipitate and the solution titrated at the boiling point with standard sodium hydroxide using phenol red as indicator. The indicator blank was 0.01 ml of 0.13 *M* NaOH, which has been subtracted from all titration readings.

A few experiments were carried out in which the solubility of $(BH)_2SO_4$ was determined in a medium containing tetramethylguanidinium picrate and an excess of base. Since the picrate precipitates with benzidine, the aqueous solution of the residue was made 0.1 *M* in hydrochloric acid and the picric acid removed by repeated extraction with ethyl ether. As a test of the reliability of the method of analysis, the above procedure, including ether extraction, was carried out on 4 ml of a synthetic mixture 0.0282 *M* in $(BH)_2SO_4$, 0.05 *M* in B, and 0.020 *M* in BHPi. The molarity of sulfate was found to be 0.0278 *M*.

Determination of Tetramethylguanidinium Ion in Saturated Tetramethylguanidinium Sulfate Solutions. Sodium Tetraphenylborate Method. The residue from saturated AN solutions of $(BH)_2SO_4$ containing sulfuric acid or B was dissolved in 10 ml of water and heated to boiling and $BHB(C_6H_5)_4$ precipitated by slowly adding hot 0.3 *M* aqueous sodium tetraphenylborate (Aldrich Puriss grade) solution.[9] (This solution was slightly turbid and before use filtered through a 25-mμ Millipore filter.) The silver nitrate treatment in ref 9 after precipitation of the tetraphenylborate was omitted. After cooling to room temperature and standing for at least 3 hr, the precipitate was filtered on a fine sintered-glass filter and washed with cold water until the washings gave no turbidity with potassium chloride. The $BHB(C_6H_5)_4$ was dried at 100° for 2 hr and weighed. The same procedure was used with solutions containing picrate. To prevent precipitation of sodium picrate, the picric acid was removed by employing the same extraction procedure as in the sulfate determination. A mixture 0.0282 *M* in $(BH)_2SO_4$ and 0.020 *M* in BHPi thus being 0.0764 *M* in BH^+ gave by the above procedure a molarity of BH^+ equal to 0.0760.

Conductometric,[10] potentiometric,[11] and spectrophotometric[11] techniques and equipment were those as described previously. Whenever necessary, viscosity corrections were applied in plotting the conductances measured in the conductometric titrations with TMG. The following viscosities of TMG solutions in AN were found in 0.308, 0.592, 1.10, 1.75 *M* TMG; 0.358, 0.371, 0.390 and 0.432 cP, respectively. The viscosity of pure AN is 0.345 cP at 25°. All experiments were carried out at 25.0°.

Vapor-Pressure Osmometry. A Hewlett-Packard No. 302 differential vapor pressure osmometer operated at 37° was used for all molecular weight determinations. Readings were taken 7.5 min after deposition of each drop. The average value of readings obtained from at least three different drops were reported.

The osmometer was calibrated with 0.02–0.08 *M* benzil solutions in AN. Since benzil is monomeric in many different solvents,[12] it is safe to assume that it is so in AN. The experimental *r* values in the tables refer to the osmometric concentration, *i.e.*, the sum of the molar concentrations of the undissociated species plus the sum of the concentrations of the uniunivalent cations and anions in solution.

Results

Dissociation Constants of Tetramethylguanidinium Salts. From the conductivity data in Table I, tetramethylguanidinium picrate appears to be a strong electrolyte. The experimental and theoretical Onsager slopes were found to be 348 and 410, respectively. From the value of $\Lambda_{0,BHPi}$ equal to 161 and $\lambda_{0,Pi^-} = 77$,[13] a value of $\lambda_{0,BH^+} = 84$ is found. Tetramethylguanidinium bisulfate like other amine bisulfates is incompletely dissociated in 0.1 *M* solution. A Fuoss and Kraus treatment of the conductivity data in Table I yields a dissociation constant of 5.4×10^{-3} taking

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[7] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **85**, 2195 (1963).

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[11] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **87**, 4428 (1965).

[12] Hewlett-Packard Vapor Pressure Osmometer Model 302, Operating and Service Manual, p 14.

[13] J. F. Coetzee and C. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).

Table I. Conductivity of Some Salts

Tetramethylguanidinium picrate C_{BHPi}, $M \times 10^3$	Λ	Tetramethylguanidinium bisulfate C_{BHHSO_4}, $M \times 10^3$	Λ
0.99	150.5	3.74	115
2.91	138	7.48	94
5.66	130.5	18.7	69
9.90	122	$\Lambda_0 = 184$	
14.5	111		
16.6	106.6		
20.2	99		
$\Lambda_0 = 161$			

$\Lambda_{0,BHHSO_4}$ equal to 184, from the previously reported value[3] $\lambda_{0,HSO_4^-} = 100$ and $\lambda_{0,BH^+} = 84$.

Conductivity and Differential Vapor Pressure (DVP) Measurements in Mixtures of Tetramethylguanidine and Sulfuric Acid in Mole Ratios >1.0. Information obtained from a set of data in a given table was required to interpret the data given in another table. For example, in order to calculate the ionic dissociation constants of the various species denoted by XY in Table III, it was necessary to know the state of aggregation of XY, which was found from DVP measurements in Table IV. On the other hand, in order to find the molar concentration of XY from DVP measurements, it was necessary to take into account the concentration of ions given in Table III. Also, to interpret the data obtained in mixtures of B:H_2SO_4 in a molar ratio of 1.5 (Tables III and IV) and in mixtures with a molar ratio >2 in the presence of BHPi (picrate) (Table V), solubility data of $(BH)_2SO_4$ in sulfuric acid (Table VII) and BHPi solutions (Table VIII), respectively, were necessary. In order to evaluate the contribution of XY to DVP values in solutions in which the molar ratio B:$H_2SO_4 > 2$ (Tables IV and VI), an appreciable correction for the contribution of the free base (r_{B+B_2}) had to be applied. DVP data in pure tetramethylguanidine (B) solutions are presented in Table II.

Table II. DVP Data of Tetramethylguanidine in AN

C_B, $M \times 10^2$	$r_{obsd} \times 10^2$ [a]	$\beta \times 10^{-2}$ [b]
2.83	1.88	1.1
4.80	3.00	1.2
4.80	3.10	0.9
8.0	4.78	1.0
12.8	7.70	0.7$_4$
		Av 1.0 × 10^2

[a] Observed osmometric molarity. [b] $\beta = [B_2]/[B]^2$.

From these data it is seen that B is partly dimerized in AN. Hence the analytical concentration C_B is

$$C_B = [B] + 2[B_2] \qquad (3)$$

while the observed DVP molarity r_{obsd} is

$$r_{obsd} = r_B + r_{B_2} \qquad (4)$$

Introducing eq 3 and 4 into the expression for the dimerization constant, β, eq 5 results. The dimerization constant of TMG as calculated from eq 5 is found equal to 1×10^2.

$$\beta = [B_2]/[B]^2 = (C_B - r_{obsd})/(2r_{obsd} - C_B)^2 \qquad (5)$$

Table III. Conductivity Data in Mixtures of Sulfuric Acid and Tetramethylguanidine (B)[a]

$C_{H_2SO_4}$, $M \times 10^2$	Λ	Λ_e[b]
A. Mole Ratio TMG:H_2SO_4 = 2.4–6. Main Species $\{XY\}_2 = \{(BH)_2SO_4\}_2$		
0.374	30.4	176
0.748	20.4	175
1.87	14.0	172
3.74	11.2	170
5.90	9.9$_5$	167
10.0	8.6	160
B. Mole Ratio TMG:H_2SO_4 = 1.67. XY = $\{(BH)_2SO_4\}_2$ $BHHSO_4$		
6.00	29.4	154
10.0	21.6	154
18.0	17.4	150
24.6	13.8	146
C. Mole Ratio TMG:H_2SO_4 = 1.50. XY = $(BH)_2SO_4 \cdot BHHSO_4$		
0.374	117	170
0.748	67	167
1.87	41	164
3.74	28.$_4$	162
6.00	22	160
10.0	18.$_4$	157
14.0	14.$_7$	155
22.0	12.$_2$	151

[a] $\Lambda_{0,\{XY\}_n} = 180$. [b] Sum of ionic mobilities corrected for ion atmosphere effects.

Conductivity and DVP data of mixtures of tetramethylguanidine and sulfuric acid are presented in Tables III and IV, respectively. In these tables, XY refers to the simplest undissociated complex present in the solution and $(XY)_2$ to a dimer. For example, from DVP measurements in Table IV (section A) and conductometric ion concentration measurements in Table III (section A), it is concluded that $(BH)_2SO_4$ is present as a dimer $(XY)_2$. Its stability is so large that the dimerization constant could not be determined by the methods used. From conductometric titration curves in Figure 3 it can be concluded that formation of $\{(BH)_2SO_4\}_2$ is complete when the concentration of sulfuric acid is $\geqslant 0.01$ M and the mole ratio of B:H_2SO_4 is $\geqslant 2.4$. In Table III, section A, the concentration of the dimer $\{(BH)_2SO_4\}_2$ is equal to one-half of the molarity of the sulfuric acid used in the preparation of the mixture (first column). In finding the DVP molecular concentration, $r_{\{XY\}_2}$, of undissociated $\{XY\}_2$ in Table IV, double the molar concentration of the ions was subtracted from the total experimental DVP molarity, r_{obsd}, of the mixture. In the case of $\{(BH)_2SO_4\}_2$ in section A of Table IV, $r_{\{XY\}_2} = r_{obsd} - r_{B+B_2} - 2r_{X^+}$. The dimer $\{(BH)_2SO_4\}_2$ dissociates according to eq 2, the dissociation constant $K^d{}_{\{XY\}_2}$ being found equal to 7×10^{-5}, from conductance data in Table III and using the Ostwald dilution law.

From conductometric titration curves of sulfuric acid with TMG (Figure 3) and from solubility measurements of tetramethylguanidinium sulfate in the presence of sulfuric acid (see Table VII), it appears that at 1.5 mole ratio of TMG:sulfuric acid, a slightly dissociated double salt $(BH)_2SO_4 \cdot BHHSO_4$ (XY) is formed. This salt is formed quantitatively when $C_{H_2SO_4} \geqslant 0.01$ M.

$$2H_2SO_4 + 3B \rightleftharpoons (BH)_2SO_4 \cdot BHHSO_4 \qquad (6)$$

Analysis of the conductance data in tetramethylguanidine–sulfuric acid mixtures in Table III (section

Table IV. Differential Vapor Pressure (DVP) Data in Mixtures of Sulfuric Acid and Tetramethylguanidine (B)

$C_{H_2SO_4}$, $M \times 10^2$	C_B, $M \times 10^2$	$[X^+]$, $M \times 10^3$	$[XY] + 2[\{XY\}_2]$, $M \times 10^2$	Excess base $2C_b - C_{H_2SO_4} = \{[B] + 2[B]_2\}$	$r_{obsd} \times 10^2$	DVP values $r_{B+B_2} \times 10^2$	$r_{XY+(XY)_2} \times 10^2$
A. Mole Ratio TMG:H_2SO_4 = 2.4; [XY] = 0; $\{XY\}_2 = \{(BH)_2SO_4\}_2$; $X^+ = (BH)_3SO_4^+$; $Y^- = BHSO_4^-$							
3.74	9.00	1.3_1	1.74	1.5	3.05	1.11	1.68
5.90	14.1	1.9	2.85	2.3	4.70	1.63	2.69
10.0	24.9	2.9	4.71	4.1	7.53	2.66	4.31
B. Mole Ratio TMG:H_2SO_4 = 1.67; $[\{XY\}_2] = 0$; XY = $\{(BH)_2SO_4\}_2BHHSO_4$; $X^+ = \{(BH)_5(SO)_4)_2\}^+$; $Y^- = HSO_4^-$							
6.00	10.0	4.6	1.54	0	3.23	0	2.31 2.34[a]
10.0	16.7	5.7	2.76	0	4.64	0	3.50 3.95[a]
18.0	30.0	8.7_3	5.13	0	6.70	0	4.96 6.95[a]
24.6	41.0	9.8_5	7.21	0	8.81	0	6.82 9.47[a]
C. Mole Ratio TMG:H_2SO_4 = 1.50; XY = $(BH)_2SO_4 \cdot BHHSO_4$; $X^+ = (BH)_3SO_4^+$; $Y^- = HSO_4^-$							
1.87	2.8	2.04	0.73	0	1.24	0	0.83
3.74	5.6	2.9	1.58	0	2.32	0	1.74
6.00	9.0	3.65	2.64	0	3.11	0	2.38
10.0	15.0	5.0	4.50	0	4.60	0	3.60[b]
15.0	22.5	6.2	6.88	0	6.51	0	5.27[b]
22.0	33	7.7	10.23	0	8.64	0	7.10[b]

[a] DVP value calculated assuming $(BH)_2SO_4 \cdot BHHSO_4$, $\{(BH)_2SO_4 \cdot BHHSO_4\}_2$, and $\{(BH)_2SO_4\}_2$ are present as molecular species and $\{(BH)_2SO_4\}_2BHHSO_4$ is absent. [b] Values of the dimerization constant, β, are found to be 1.2×10^1, 1.2×10^1, and 2.0×10^1 at $C_{H_2SO_4}$ = 0.10, 0.15, and 0.22 M, respectively.

C) at mole ratio 1.5 indicates that the double salt $(BH)_2SO_4 \cdot BHHSO_4$ dissociates as a uniunivalent electrolyte

$$(BH)_2SO_4 \cdot BHHSO_4 \rightleftharpoons (BH)_3SO_4^+ + HSO_4^- \tag{7}$$

with a dissociation constant of the order of 4×10^{-4}, which is more than an order of magnitude smaller than that of the simple bisulfate salt. In all instances a value of $\Lambda_{0,XY}$ was assumed to be 180; no effort has been made to measure individual ion mobilities in these complex systems. An error of 30% in $\Lambda_{0,XY}$ does not affect the conclusions drawn; however, the estimated ionic dissociation constants may be in error by 25%. In obtaining the molarity of XY in solutions of tetramethylguanidine–sulfuric acid at a mole ratio of 1.5 (Table IV, section C), the ionic DVP contribution $r_{X^+} = r_{Y^-}$ derived from the conductance data in Table III has been substracted from r_{obsd} to find the DVP molarity of the undissociated specie(s), $r_{XY+\{XY\}_2}$. The calculated equilibrium molarity of the undissociated form(s), $[XY] + 2[\{XY\}_2]$ (XY = $(BH)_2SO_4 \cdot BHHSO_4$), is equal to $C_{H_2SO_4}/2 - [X^+]$ (eq 6 and 7). Assuming that only monomer XY is present, the values of the molarity of XY in column 4 of Table IV agree with those obtained from DVP measurements (last column) when the concentration of sulfuric acid used in the mixture is of the order of 0.06 M or less. At higher concentrations of sulfuric acid, $r_{XY+\{XY\}_2} < [XY] + 2[\{XY\}_2]$ due to dimerization of $(BH)_2SO_4 \cdot BHHSO_4$. The dimerization constant β has been estimated in these solutions using eq 5 setting $C_B = C_{H_2SO_4} - [X^+] = [XY] + 2[\{XY\}_2]$ and r_{obsd} equal to $r_{XY+\{XY\}_2}$. An average value of β equal to 1.5×10^1 was found. As an example, $C_{H_2SO_4}$ = 0.15 M, $[X^+] = 6.2 \times 10^{-3}$, and r_{obsd} = 0.0651. Hence $[XY] + 2[\{XY\}_2]$ = 0.150/2 − 0.0062 = 0.0688. $r_{XY+\{XY\}_2} = r_{obsd} - r_{X^+} = 2r_{X^+}$ = 0.0651 − 2(0.0062) = 0.0627. The value of β (eq 5) is therefore $(0.0688 - 0.0527)/[(2 \times 0.0527) - 0.0688]^2 = 1.2 \times 10^1$. The formation of the dimer is also substantiated by solubility data in Table VII. The ions formed upon dissociation of the dimer must be more complex than those in eq 7 (see eq 11).

From conductivity and DVP data of mixtures of tetramethylguanidine and sulfuric acid at a mole ratio of 1.67 (section B, Tables III and IV), it is concluded that the predominant molecular species XY is the monomer $\{(BH)_2SO_4\}_2BHHSO_4$ arising from the following acid–base reaction

$$3H_2SO_4 + 5B \rightleftharpoons \{(BH)_2SO_4\}_2BHHSO_4 \tag{8}$$

which is assumed to dissociate as a uniunivalent electrolyte (see also eq 11) with a roughly estimated dissociation constant of 10^{-3}.

$$\{(BH)_2SO_4\}_2BHHSO_4 \rightleftharpoons (BH)_5(SO_4)_2^+ + HSO_4^- \tag{9}$$

Values of [XY] in the fourth column of Table IV, section B, have been calculated from the relation $[XY] = (C_{H_2SO_4}/3) - [X^+]$ (*cf.* eq 8), while the values of r_{XY} in the eighth column were calculated in the same way as before.

The DVP molarity of the molecular species was also calculated assuming that no $\{(BH)_2SO_4\}_2$ was present but that the solution was composed of a mixture of $(BH)_2SO_4 \cdot BHHSO_4$, its dimer, and $\{(BH)_2SO_4\}_2$. It is further assumed that the ionic dissociation of $\{(BH)_2SO_4\}_2$ is completely suppressed by the dissociation of $(BH)_2SO_4 \cdot BHHSO_4$ (eq 7). Under these conditions $[\{(BH)_2SO_4\}_2] = (C_{H_2SO_4}/6)$ and $[(BH)_2SO_4 \cdot BHHSO_4] + 2[\{(BH)_2SO_4 \cdot BHHSO_4\}_2] = (C_{H_2SO_4}/3) - [(BH)_3SO_4^+]$. Taking β, the dimerization constant of $(BH)_2SO_4 \cdot BHHSO_4$, as 1.5×10^1, the values of $[(BH)_2SO_4 \cdot BHHSO_4]$ and the molarity of its dimer were calculated from the value of $(C_{H_2SO_4}/3) - [(BH)_3SO_4^+]$. The calculated DVP molarity, r_{calcd}, entered in the last column in Table IV is equal to $r_{\{(BH)_2SO_4\}_2} + r_{(BH)_2SO_4 \cdot BHHSO_4} + r_{\{(BH)_2SO_4 \cdot BHHSO_4\}_2}$. The following values of the DVP molarities of the three individual species in the order given at various dilutions of the 1.67 mole ratio of TMG–sulfuric acid mixtures are ($C_{H_2SO_4}$ value in parentheses): (0.060 M) 0.010, 0.011, 0.002; (0.100 M) 0.0167, 0.0180, 0.0048; (0.180

Table V. Conductivity of an Equimolar Mixture of Sulfuric Acid and Tetramethylguanidinum Picrate in the Presence of Excess Tetramethylguanidine (B)

$C_{H_2SO_4} = C_{BHPi}$, $M \times 10^3$	C_B, $M \times 10^2$	Λ
2.01	6.16	156
3.01	2.70	143.5
4.81	2.75	131.5
6.01	2.79	126
9.03	4.17	115
12.1	4.90	106.5
20.1	4.80	91.5
	$\Lambda_0 = 185$	

Table VI. DVP Measurements in Mixtures of TMG, Sulfuric Acid, and BHPi in a Mole Ratio of 2.4 :1 :1[a]

$C_{H_2SO_4}$, $M \times 10^2$	$[Pi^-]$, $M \times 10^2$	C_B, $M \times 10^2$	Excess base, $[B] + 2[B]_2$, $M \times 10^3$	$r_{obsd} \times 10^2$	$r_{B+B_2} \times 10^2$	$r_A \times 10^2$[b]	C_A,[c] $M \times 10^2$	$r_{E.obsd}$,[d] $\times 10^2$	$r_{E.calcd}$,[e] $M \times 10^2$
1.22	0.90	0.32	4.6	2.88	0.40	1.58	1.22	2.48	3.05
2.00	1.35	0.65	8.0	4.25	0.63	2.28	2.00	3.63	5.00
2.70	1.73	0.97	11.0	5.45	0.87	2.85	2.70	4.58	6.75

[a] A denotes a mixture of A_1 and A_2. [b] r_A denotes DVP value of species A, *i.e.*, sum of contribution of undissociated A ($A_1 + A_2$) plus that of one of the two ions (see text). [c] C_A is the calculated value from $C_{H_2SO_4} = C_{BHPi}$ (see text). [d] $r_{E.obsd} = r_{obsd} - r_{B+B_2}$. [e] $r_{E,calcd}$ denotes DVP value corresponding to sum of concentrations of undissociated $\{(BH)_2SO_4\}_2$, BH^+, and picrate ions.

M) 0.030, 0.027$_8$, 0.0118; and (0.246 *M*) 0.0460, 0.0352, 0.0185.

The calculated values of $[XY] = [\{(BH)_2SO_4\}_2 \cdot BHHSO_4]$ and those of r_{XY} agree when $C_{H_2SO_4} \geqslant 0.18$ *M*, suggesting quantitative formation of $\{(BH)_2SO_4\}_2$-$BHHSO_4$, whereas the values of r_{XY} and r values calculated when $C_{H_2SO_4} = 0.06$ *M*, indicate that formation of $\{(BH)_2SO_4\}_2BHHSO_4$ is negligible in the 1.67 mole ratio mixture at this or greater dilution. Solubility data in Table VII confirm the existence of this complex.

DVP Measurements in Mixtures of Tetramethylguanidine, Sulfuric Acid, and Tetramethylguanidinium Picrate at Mole Ratio 2.4:1:1. In an effort to obtain independent information on the complexation of BH^+ with $(BH)_2SO_4$ or $\{(BH)_2SO_4\}_2$, conductance and DVP measurements were made in mixtures of $(BH)_2SO_4$, B, and BHPi. The results are presented in Tables V and VI. The complex salts $(BH)_2SO_4 \cdot BHPi$ and/or $\{(BH)_2SO_4\}_2BHPi$ are denoted in Table VI as A_1 and A_2, respectively. They appear to be extensively dissociated (Table V) with an ionic dissociation constant of 1.3×10^{-2}. It is proposed that the dissociation of A_1 and A_2 occurs in the following way.

Complex A_1

$$(BH)_2SO_4 \cdot BHPi \rightleftharpoons (BH)_3SO_4^+ + Pi^- \qquad (10)$$

Complex A_2

$$\{(BH)_2SO_4\}_2BHPi \rightleftharpoons \{(BH)_2SO_4\}_2BH^+ + Pi^- \qquad (11)$$

The picrate ion concentrations in these mixtures entered in the second column in Table VI were calculated using the ionic dissociation constant of both these complexes equal to 1.3×10^{-2}. The fifth column in Table VI gives r_{obsd}, the observed DVP value, and the seventh column gives the DVP values r_A, corresponding to the sum of the concentrations of undissociated complexes and one of their ions, *i.e.*, $r_A = r_{obsd} - r_{B+B_2} - r_{Pi^-}$. The value of r_A is the same for complex A_1 and A_2.

When no complexation occurs, *i.e.*, a mixture of $\{(BH)_2SO_4\}_2$ and BHPi is present (mixture denoted by E), DVP values of $\{(BH)_2SO_4\}_2$, BH^+, and picrate ions, $r_E = r_{obsd} - r_{B+B_2}$. These are entered in the ninth column of Table VI while the calculated values of r_{Ecalcd} are entered in the last column of Table VI. The salt BHPi is considered to be completely dissociated. Actually, the data in Table I are not sufficiently accurate to conclude that the salt is completely dissociated into ions; hence the true values in the last column may be slightly smaller than those presented. However, the difference in the values in the last two columns in Table VI is so large, while that between columns 7 and 8 is so small, that it is safe to conclude that practically all the BHPi is associated with $(BH)_2SO_4$ and/or its dimer. DVP measurements do not allow one to make a distinction between complexes A_1 and A_2, *i.e.*, either A_1 or A_2 or a mixture of both. Fortunately solubility determinations of $(BH)_2SO_4$ in BHPi (Table VIII) shows without any doubt that a mixture of A_1 and A_2 is formed.

Solubility in AN of Tetramethylguanidinium Sulfate in Dilute Solutions of Sulfuric Acid, Tetramethylguanidinium Picrate, or Tetraethylammonium Bisulfate. These determinations substantiate the conclusions drawn from Tables IV and III. The analytical sulfate concentration, $\Sigma C_{SO_4^{2-}}$, in a saturated solution of tetramethylguanidinium sulfate (containing 0.03 *M* tetramethylguanidine to repress acid–base dissociation of the salt) has been found to be 0.177 *M*, using the method of sulfate analysis described in the Experimental Section. The specific conductivity of the saturated solution was 1.11×10^{-4} ohm^{-1} cm^{-1}, corresponding to an ion concentration of 6.4×10^{-4} *M* (Table III) thus yielding a value of 3.5×10^{-7} for the solubility product

$$K_{sp} = [(BH)_3SO_4^+][BHSO_4^-]f^2$$

In a saturated solution the concentration of undissociated $\{(BH)_2SO_4\}_2$ is equal to $(C_{SO_4^{2-}}/2) - [(BH)_3SO_4^+] = (0.0177/2) - 0.00064 = 0.0082_2$ *M*.

The solubility of $(BH)_2SO_4$ in the presence of dilute sulfuric acid increases mainly as a result of formation of the slightly dissociated double salt $(BH)_2SO_4 \cdot BHHSO_4$ and its dimer

$$2H_2SO_4 + 3\{(BH)_2SO_4\}_2 \rightleftharpoons 4(BH)_2SO_4 \cdot BHHSO_4 + 2\{(BH)_2SO_4 \cdot BHHSO_4\}_2 \qquad (12)$$

In such saturated solutions the following material balance relations hold, taking into account dissociation of $(BH)_2SO_4 \cdot BHHSO_4$ into ions

$$\Sigma C_{SO_4^{2-}} = [(BH)_3SO_4^+] + [HSO_4^-] + 2[\{(BH)_2SO_4\}_2]_s + 2[(BH)_2SO_4 \cdot BHHSO_4] + 4[\{(BH)_2SO_4 \cdot BHHSO_4\}_2] \qquad (13)$$

Table VII. Solubility in AN of Tetramethylguanidinium Sulfate in Dilute Sulfuric Acid

	Total Solubility					$[(BH)_2SO_4 \cdot BHHSO_4] + 2[\{(BH)_2SO_4 \cdot BHHSO_4\}_2]$, M^c			
$C_{H_2SO_4}$, M	$\Sigma C_{SO_4^{2-}}$, M	ΣC_{BH^+}, M	L^a	$\Lambda_e{}^b$	$[(BH)_3SO_4^+]$, $M \times 10^3$	Sulfate analysis	BH^+ analysis	$\Sigma(C_{SO_4^{2-}} - 2[\{(BH)_2SO_4\}_2])/C_{H_2SO_4}$	$\Sigma(C_{BH^+} - 4[\{(BH)_2SO_4\}_2])/C_{H_2SO_4}$
0	0.0177	0.035	1.11×10^{-4}	172	0.64	0	0	...	...
0.0112	0.071	...	5.05×10^{-4}	159	3.2	0.024	...	4.72	...
0.0187	0.106	...	6.23×10^{-4}	156	4.0	0.041	...	4.76	...
0.028	0.152	0.256	8.40×10^{-4}	153	5.5	0.062	0.069	4.83	7.97
0.037	0.199	0.324	9.70×10^{-4}	150	6.5	0.085	0.091	4.92	7.86
0.056	0.275	0.446	1.17×10^{-3}	146	8.0	0.121	0.130	4.60	7.40
0.103	0.476	0.745	1.53×10^{-3}	140	10.9	0.218	0.227	4.32	6.70

[a] Specific conductivity of saturated solution (ohm^{-1} cm^{-1}). [b] Λ_0 of all species assumed to be 180. [c] Molecular complexes assumed to be $(BH)_2SO_4 \cdot BHHSO_4$ and its dimer.

$$\Sigma C_{BH^+} = 3[(BH)_3SO_4^+] + 4[\{(BH)_2SO_4\}_2]_s + 3[(BH)_2SO_4 \cdot BHHSO_4] + 6[\{(BH)_2SO_4 \cdot BHHSO_4\}_2] \quad (14)$$

the subscript s denoting saturated solution. Making the reasonable assumptions that the ionic dissociation of $\{(BH)_2SO_4\}_2$ in its saturated solutions listed in Table VII in dilute sulfuric acid is negligible, and that the complex and its dimer in eq 12 are the only complexes formed, the concentration of undissociated complexes, $[(BH)_2SO_4 \cdot BHHSO_4] + 2[\{(BH)_2SO_4 \cdot BHHSO_4\}_2]$, is found either from $\Sigma C_{SO_4^{2-}}$ (eq 13) or from ΣC_{BH^+} (eq 14) (see Experimental Section). In applying eq 13, $[(BH)_2SO_4^+]$ was taken equal to $[HSO_4^-]$. The results are presented in Table VII. The values of the sum of the concentrations of molecular $(BH)_2SO_4 \cdot BHHSO_4$ and twice that of its dimer, calculated from $\Sigma C_{SO_4^{2-}}$, are smaller than those from ΣC_{BH^+} (columns 7 and 8 in Table VII, respectively), indicating the presence of $\{(BH)_2SO_4\}_2 \cdot BHHSO_4$. Such a complex was postulated to be present in mixtures of TMG and sulfuric acid in a mole ratio of 1.67 (Table IV).

In comparing the analytical concentration of the complexes formed with that of sulfuric acid taken in the preparation of the saturated solutions, the values of $(\Sigma C_{SO_4^{2-}} - 2[\{(BH)_2SO_4\}_2]_s)/C_{H_2SO_4}$ (*cf.* eq 13) given in column 9 of Table VII should be 4 and those of $(\Sigma C_{BH^+} - 4[\{(BH)_2SO_4\}_2]_s)/C_{H_2SO_4}$ (*cf.* eq 14) in column 10 should be 6 if $(BH)_2SO_4 \cdot BHHSO_4$ and its dimer were the only complex species present. Actually the values are greater, but approach the values of 4 and 6, respectively, at the highest concentrations of sulfuric acid used. The data indicate that another complex is formed, which is richer in BH^+ and sulfate than $(BH)_2SO_4 \cdot BHHSO_4$, *i.e.*, $\{(BH)_2SO_4\}_2BHHSO_4$. The continuous decrease in the values in columns 9 and 10 with increasing sulfuric acid concentration is accounted for by increasing dimerization of $(BH)_2SO_4 \cdot BHHSO_4$.

Solubility data of tetramethylguanidinium sulfate in the presence of BHPi (picrate) and 0.05 M B are tabulated in Table VIII, where C_{BHPi} and $C_{SO_4^{2-}}$ refer to the analytical BHPi and sulfate concentrations, respectively. The solubility was found to increase markedly with increasing concentration of picrate due to formation of the complexes $(BH)_2SO_4 \cdot BHPi$ and $\{(BH)_2SO_4\}_2$ BHPi which dissociate according to eq 10 and 11.

Table VIII. Solubility of $(BH)_2SO_4$ in the Presence of BHPi and 0.05 M B

C_{BHPi}, M	$C_{SO_4^{2-}}$, M	$(C_{SO_4^{2-}} - 2[\{(BH)_2SO_4\}_2]_s)/C_{BHPi}$
0.020	0.043	1.30
0.0398	0.070	1.36
0.0607	0.102	1.41
0.0662	0.116	1.48
0.109	0.179	1.49

If the only species were $(BH)_2SO_4BHPi$ and its ions $(BH)_3SO_4^+$ and Pi^-, the value of the quantity $[C_{SO_4^{2-}} - 2[\{(BH)_2SO_4\}_2]_s]/C_{BHPi}$ should be unity, but when only $\{(BH)_2SO_4\}_2BHPi$ and its ions $(BH)_5(SO_4)_2^+$ and Pi^- were present, the ratio should be 1.50. The latter situation is fulfilled when $C_{BHPi} > 0.07$ M, while at lower concentrations of BHPi mixtures of the two complexes are present. No attempt was made to calculate the concentrations of the molecular complexes in the mixture to obtain the formation constant of $\{(BH)_2SO_4\}_2BHPi$. It is interesting to note that the DVP measurements in Table VI did not allow a distinction between the two complexes.

The solubility of $(BH)_2SO_4$ in the presence of 0.0208 and 0.053 M tetraethylammonium bisulfate was 0.0593 and 0.140 M, respectively, as found from sulfate analysis of the saturated solution, corresponding to values of the ratio $[C_{SO_4^{2-}} - 2[\{(BH)_2SO_4\}_2]_s]/2C_{Et_4NHHSO_4}$ equal to 1.01 and 1.16, respectively. A ratio of 1.0 is expected when the complex $Et_4N(BH)_2SO_4 \cdot HSO_4$ is formed.

Conductometric and Potentiometric Titration of Tetraethylammonium Bisulfate with Tetramethylguanidine. Conductometric and potentiometric titration curves of 1.0×10^{-2} M tetraethylammonium bisulfate with tetramethylguanidine are presented in Figures 1 and 2, respectively. The conductivity in Figure 1 decreases initially in linear fashion and becomes constant at a molar ratio of 0.5 TMG:HSO_4^-, indicative of formation of the ionic species $HSO_4 \cdot BHSO_4^{2-}$; upon further addition of base, $BHSO_4^-$ ion is formed. The tetraethylammonium salts of both species are highly dissociated.

The initial pa_H (16.8) in the potentiometric titration of tetraethylammonium bisulfate with TMG in Figure 2 agrees well with the value of $^1/_2(pK^d_{H_2SO_4} + pK^d_{HSO_4^-})$ equal to 16.86, taking $pK^d_{H_2SO_4}$ and $pK^d_{HSO_4^-}$ as 7.8 and 25.9,[3] respectively. There is no indication of a break at either 0.5 or 1.0 mole ratio of TMG:bisulfate. Apparently the $BHSO_4^-$ ion is quite stable and is only very slightly dissociated into BH^+ and SO_4^{2-}. When

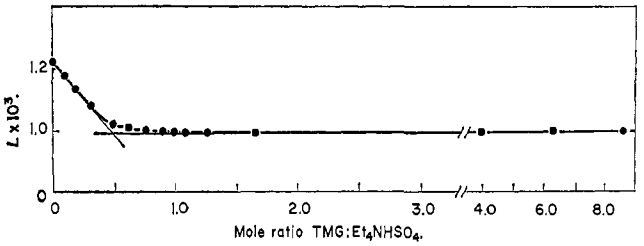

Figure 1. Conductometric titration of 1.00×10^{-2} *M* tetraethylammonium bisulfate with tetramethylguanidine.

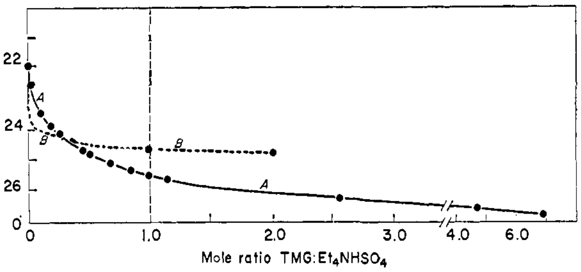

Figure 2. Potentiometric titration of 1.00×10^{-2} *M* tetraethylammonium bisulfate with tetramethylguanidine: (A) experimental curve, (B) calculated curve of 0.01 *M* bisulfate with B assuming quantitative formation of BH^+ and SO_4^{2-} ($pK^d_{BH^+} = 23.3$, $pK^d_{HSO_4^-} = 25.9$).

the excess of free base is 1×10^{-2} *M* in the titration of 1×10^{-2} *M* tetraethylammonium bisulfate (Figure 2), a pa_H of 26 is measured. Using the above value of $pK^d_{HSO_4^-}$ it follows that at this pa_H $[HSO_4^-] \cong [SO_4^{2-}]$. Since $[B] = 1 \times 10^{-2}$, we find from pa_H and $K^d_{BH^+} = 10^{-23.3}$ 4 that $[BH^+] = [SO_4^{2-}] = [HSO_4^-] =$ [illegible] $\times 10^{-5}$. This allows a rough estimate of the formation constant, $K^f_{BHSO_4^-} = [BHSO_4^-]/[B][HSO_4^-] \sim 5 \times 10^4$ and the ionic dissociation constant, $K^d_{BHSO_4^-}[BH^+][SO_4^{2-}]/[BHSO_4^-] \sim 10^{-7.4}$. The $BHSO_4^-$ ion is considered to be the anion formed in the ionic dissociation of $\{(BH)_2SO_4\}_2$ (eq 2). In the preceding section it has been shown that it forms a stable complex with $(BH)_2SO_4$. The above values of $K^f_{BHSO_4^-}$ and $K^d_{BHSO_4^-}$ are tentative.

Conductometric and Potentiometric Titration Curves of Sulfuric Acid with Tetramethylguanidine (TMG). Conductometric and potentiometric titration curves of sulfuric acid with tetramethylguanidine are presented in Figures 3 and 4, respectively. The shape of the conductometric titration curves of sulfuric acid as a monoprotic acid with TMG can be interpreted quantitatively, as has been done for similar titrations with *n*-butylamine[10] or with triethylamine.[14] In the titration of 0.2 *M* sulfuric acid with *n*-butylamine or triethylamine, a pronounced maximum in the conductance due to the formation of the homoconjugate in $H_2SO_4 \cdot HSO_4^-$ is observed at a mole ratio of $B{:}H_2SO_4$ close to 0.5.[10,14] The reason why no maximum occurs before the first equivalence point in the titration of 0.02 *M* or more dilute sulfuric acid with TMG is that $TMGHHSO_4$ has an ionic dissociation constant of 5.4×10^{-3} as compared to that of *n*-$BuNH_3HSO_4$ which is 5×10^{-4} [9] and of Et_3NHHSO_4 which is 6×10^{-4}.[14] In the titration of 3.74×10^{-2} *M* sulfuric acid with TMG, a distinct maximum is observed at a mole ratio of about 0.7 (Figure 3).

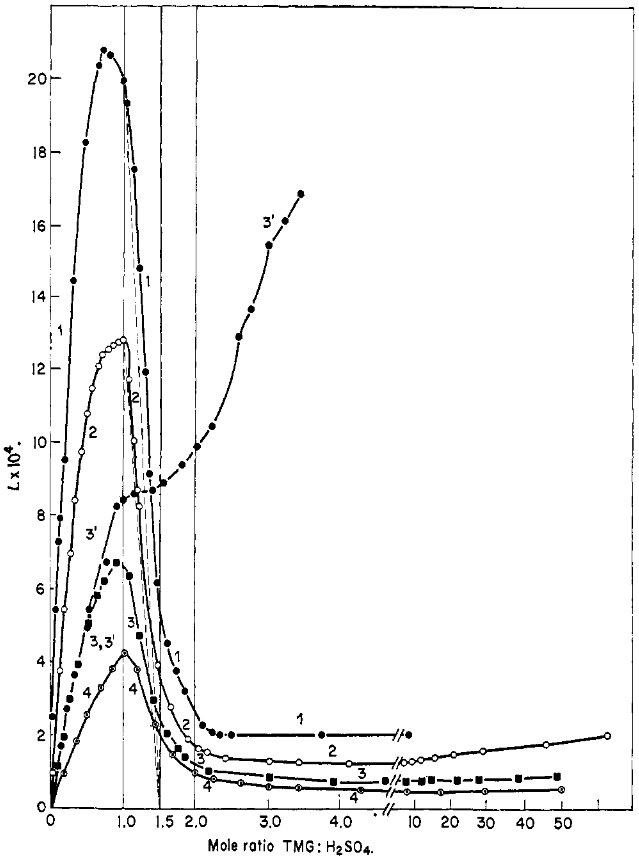

Figure 3. Conductometric titration curves of sulfuric acid with tetramethylguanidine: (1) 3.74×10^{-2}, (2) 1.87×10^{-2}, (3) 7.48×10^{-3}, and (4) 3.74×10^{-3} *M* sulfuric acid; (3′) 7.48×10^{-3} *M* sulfuric acid in the presence of 0.30 *M* *p*-bromophenol.

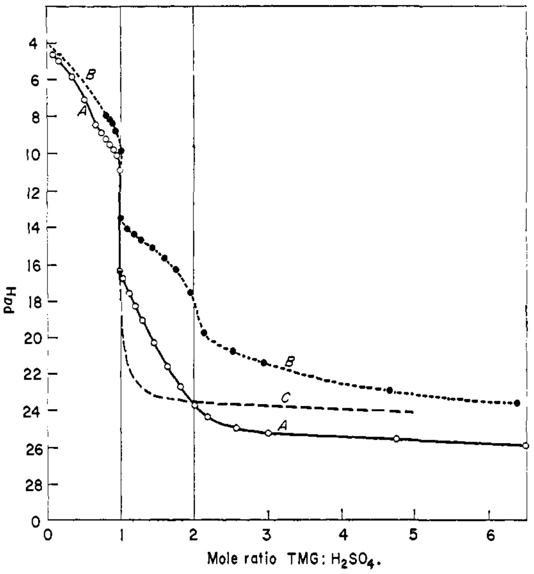

Figure 4. Potentiometric titration curves of 3.74×10^{-2} *M* sulfuric acid with tetramethylguanidine: (A) in absence of *p*-bromophenol (HR), (B) in presence of 0.303 *M* HR; (C) calculated in absence of HR assuming $(BH)_2SO_4$ is a strong electrolyte (*cf.* eq 15).

At all initial concentrations of sulfuric acid (Figure 3), a sharp decrease in conductance occurs after the first equivalence point, attributed to quantitative formation

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(14) I. M. Kolthoff and M. K. Chantooni, Jr., unpublished work.

of the slightly dissociated complex salt, $(BH)_2SO_4 \cdot BHHSO_4$, *viz.*

$$2BHHSO_4 + B \rightleftharpoons (BH)_2SO_4 . BHHSO_4 \quad (cf.\ \text{eq } 6)$$

At initial concentrations of sulfuric acid 0.02 *M*, the experimental points immediately after bisulfate formation lie on a straight line which intersects the abscissa at a mole ratio TMG:H_2SO_4 of 1.5 (dashed lines in Figure 3). Upon further addition of TMG (B) some $\{(BH)_2SO_4\}_2BHHSO_4$ and the dimer $\{(BH)_2SO_4\}_2$ are formed. There is a continued, but slight decrease in conductivity after the second equivalence point, which is attributed to gradual completion of formation of $\{(BH)_2SO_4\}_2$ with excess of base, which ionically is less dissociated than $(BH)_2SO_4 \cdot BHHSO_4$ and $\{(BH)_2SO_4\}_2BHHSO_4$. When the excess of base is sufficiently great, the conductance becomes constant, indicating quantitative formation of the dimer. This is found at mole ratios of TMG:H_2SO_4 of 2.5 in >0.04 *M* and 4 in the more dilute solutions used in Figure 3. With a very large excess of base the conductivity increases because the main species of the base is now B_2, giving rise to the various complexes derived from B_2, *e.g.*, $B_2HSO_4^-$ and $(B_2H)_3SO_4^+$. It is reasonable to expect the amines that form the B_2H^+ ion[15] will be partially dimerized in AN.

As expected, the potentiometric titration curve of sulfuric acid with TMG exhibits only one sharp break after neutralization of one proton (curve A, Figure 4), no break being observed at the second equivalence point. If the normal salt $(BH)_2SO_4$ were not dimerized and were to behave as a strong electrolyte, assuming $BHSO_4^-$ formation being negligible, the neutralization of bisulfate with B would be represented by

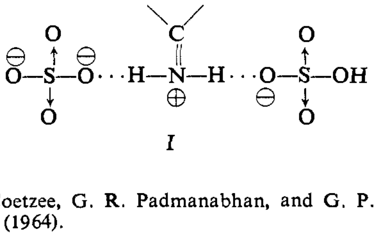
$$HSO_4^- + B \rightleftharpoons BH^+ + SO_4^{2-} \quad (15)$$

The neutralization curve of 0.01 *M* $BHHSO_4$ with B calculated on this basis, assuming the bisulfate as well as the sulfate to be strong electrolytes, is represented by curve B in Figure 4, using $pK^d_{HSO_4^-} = 25.9$ and $pK^d_{BH^+} = 23.3$.

Conductometric and potentiometric titration curves of sulfuric acid with TMG in the presence of 0.3 *M* *p*-bromophenol are also presented in Figures 3 and 4. The results are interpreted in the following section.

Discussion

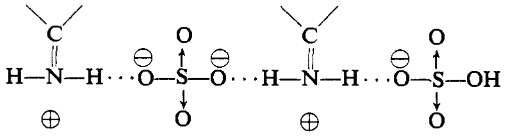
The various complexes involving sulfate, bisulfate, and BH^+ in the form of uncharged compounds and of ions postulated in the section of experimental results are summarized in the synopsis. The stability of these complexes is accounted for by hydrogen bonding of the tetramethylguanidinium ion $(R_2N)_2C{=}NH_2^+$ ($R = CH_3$) with an oxygen of the strongly basic sulfate and/or less basic bisulfate ions. Thus, the plausible structure of the complex ion $BHSO_4 \cdot HSO_4^{2-}$ (I) is



I

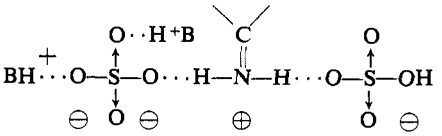
Both the hydrogens in the guanidinium ion in I are equivalent, one participating in a hydrogen bond with a sulfate oxygen, the other with an oxygen of the bisulfate ion. Owing to the greater basicity of sulfate as compared to that of bisulfate, the hydrogen bond to the former would be expected to be much stronger than to the latter. Consequently, $BHSO_4 \cdot HSO_4^{2-}$ would be expected to ionically dissociate into $BHSO_4^-$ and not into $BHHSO_4$ and SO_4^{2-}.

Addition of one BH^+ to the sulfate group of I produces the ion $(BH)_2SO_4 \cdot HSO_4^-$, for which structure II is proposed.



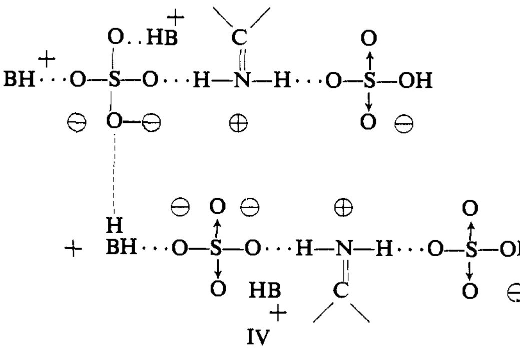
II

Addition of another BH^+ to the sulfate group of II yields the molecular complex $(BH)_2SO_4 . BHHSO_4$ (III) with the proposed structure



III

Form III is present partly as a dimer with structure IV.



IV

Form III is a weak electrolyte, which on ionic dissociation yields the ions $(BH)_3SO_4^+$ and bisulfate ion. On the other hand, the species $(BH)_2SO_4 \cdot BHPi$ is a strong electrolyte, which is dissociated into the same cation and the picrate ion.

For the dimer $\{(BH)_2SO_4\}_2$, it is simple to write either a ring or a chain structure. Lacking independent physical evidence we cannot at present distinguish between the two.

Evidence has been obtained in unpublished work in conductometric titrations of sulfuric acid in concentrations of 0.02–0.05 *M* with *n*-butylamine, secondary diethylamine, and tertiary triethylamine that the normal sulfates of these bases are also weak electrolytes. In all instances the conductances decreased considerably after the first equivalence point and usually a precipitate was formed. Apparently the sulfates of these amines are very slightly soluble (much less so than tetramethylguanidinium sulfate). Since $pK^d_{HSO_4^-} = 25.9$ and $pK^d_{BH^+}$ of the above type of amines is of the order of 18,[16] practically no proton transfer can occur according to eq 15. The very slight solubility of the

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(15) J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, **11**, 93 (1964).

(16) J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 5005 (1965).

normal sulfates and their extremely weak electrolyte character accounts for the fact that Critchfield[17] observed a slight break at the second equivalence point in the potentiometric titration of 0.1 M sulfuric acid with morpholine ($pK^d_{BH^+} = 16.6$).[16]

In a previous paper,[2] it was demonstrated that the bisulfate ion effectively becomes a much stronger acid in the presence of the hydrogen-bond donor *p*-bromophenol (HR) mainly as a result of formation of the stable conjugate $SO_4^{2-} \cdot 4HR$. For example, in the presence of 0.3 M HR the effective $pK^d_{HSO_4^-}$ is 15.9 instead of 25.9 in its absence. Thus, it is expected that *p*-bromophenol will greatly affect the conductometric and potentiometric titration curves of bisulfate. Curve 3′ in Figure 3 illustrates the conductometric titration curve of 0.75×10^{-3} M sulfuric acid with TMG in the presence of 0.3 M *p*-bromophenol. The large conductance at the first equivalence point (compare curves 3 and 3′) is due to formation of the conjugate $HSO_4 \cdot (HR)_x^-$. The BH^+ salt of this anion has a much greater K^d than $BHHSO_4$. A striking difference in conductance is observed between that at the first and second equivalence point in the presence and absence of *p*-bromophenol. In the presence of *p*-bromophenol the conductance hardly changes between the first and second equivalence points. A quantitative interpretation of the results is not possible at this time. The hydrogen-bond donor HR enhances the dissociation of $\{(BH)_2SO_4\}_2$ into two molecules of monomer. The undissociated monomer undoubtedly will combine with HR. Moreover, HR will promote the dissociation $BHSO_4^- \rightleftharpoons BH^+ + SO_4^{2-}$ because of its great affinity to SO_4^{2-}, $(BH)_2SO_4.(HR)_y$ being expected to be an intermediately strong electrolyte. Thus the main reactions may be $BH^+ + HSO_4^-(HR)_x + B + (4 - x)HR \rightleftharpoons BH^+ + BHSO_4(HR)_y^- \rightleftharpoons (BH)_2SO_4 \cdot zHR$. The claim of a relatively large dissociation constant of $(BH)_2SO_4 \cdot zHR$ is substantiated by the conductance of 0.75×10^{-3} M solution of the salt (curve 3′, Figure 3).

The large increase in conductance after the second equivalence point is due to reaction of HR with B, with formation of the stable homoconjugate HR_2^-. Blank experiments with *p*-bromophenol and B have confirmed this postulate.

Because of the large increase of the effective $K^d_{HSO_4^-}$, the potentiometric titration of sulfuric acid with B in the presence of 0.3 M *p*-bromophenol yields two breaks (Figure 4), a pronounced one at formation of HSO_4^- and a less pronounced one at the second equivalence point.

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Enthalpies of Hydrogen Bonding and Changes in $\Delta\nu_{OH}$ for a Series of Adducts with Substituted Phenols

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Abstract: The enthalpies of adduct formation for a series of substituted phenols with various Lewis bases have been calorimetrically determined. The acids studied now include C_6H_5OH, *p-t*-$C_4H_9C_6H_4OH$, *p*-ClC_6H_4OH, and *m*-$CF_3C_6H_4OH$. The frequency shifts of the phenols upon complexation, $\Delta\nu_{OH}$, have been measured, and the values for all of the phenols studied are found to lie on the same plot of $-\Delta H$ *vs.* $\Delta\nu_{O-H}$. The E and C parameters (*vide infra*) have been calculated for each of the phenols, and the measured enthalpies are nicely incorporated into this correlation. For a given donor, the enthalpy of adduct formation with this series of phenols correlates with the Hammett substituent constant of the phenol. A procedure is reported which makes it possible to predict enthalpies of adduct formation for any *meta-* or *para-*substituted phenol whose Hammett substituent constant is known with any donor that has been incorporated into the E and C correlation. The procedure is tested by application to *p*-FC_6H_4OH. The enthalpies predicted this way can be checked with those measured from the O–H frequency shift correlation, eliminating the need for a tedious calorimetric determination of the enthalpy of adduct formation. The accuracy of the predicted enthalpy is as good as the accuracy of the experimental measurement, ±0.2 kcal mole^{-1}.

We have been involved in an extensive study of the hydrogen-bonding interaction as part of our program in the area of Lewis donor–acceptor interactions.[2] Recently,[2b] a linear relationship was demonstrated between the calorimetrically determined enthalpy of adduct formation and the change in the frequency of the O–H stretching vibration of phenol upon complexation. The relationship is linear over the range of enthalpies from 4.8 to 9.0 kcal mole^{-1}. The existence of a correlation between $-\Delta H$ and $\Delta\nu_{OH}$ has been often challenged,[3-5] but it now appears[2] that poor data or improperly designed experiments have invariably been the cause of claims that such a correlation does not exist. The correlation applies to a large range of donors, including various oxygen and nitrogen

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[1] Abstracted in part from the Ph.D. thesis of T. D. Epley, University of Illinois, Urbana, Ill., 1968.

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