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Dissociation Constant, K_a, and Stability Constant, $K(HA_2^-)$, of the 1:1 Homoconjugate of Sulfuric and Nitric Acids in Acetonitrile at 298.1 K. Revised Values

Izaak M. Kolthoff[†] **and Miran K. Chantooni, Jr.***

Department of Chemistry, University of Minnesota, Smith and Kolthoff Halls, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0432

Previously reported values of pK_a and $K(HA_2^-)$ of sulfuric (first step) and nitric acids in acetonitrile derived from spectrophotometric indicator data have been revised. The revised values are 8.0_4, 2.7×10^3 mol^{-1} dm^3 and 10.5_9, 1.2×10^3 mol^{-1} dm^3, respectively. Both K_a and $K(HA_2^-)$ of sulfuric acid are some 1.7 times smaller than those reported from potentiometric glass electrode data. An estimate of $K_aK(HA_2^-)$ of sulfuric acid was made from simultaneous spectrophotometric nitroaniline indicator and electrolytic conductivity measurements in solutions allowed to stand for various times. The glass electrode was used in mixtures of nitric acid and tetraethylammonium nitrate, pK_a and $K(HA_2^-)$ being 10.53 and 1.15×10^3 mol^{-1} dm^3, respectively. The homoconjugation constant was verified from the increase in solubility of sodium nitrate in the presence of nitric acid. The protonation constant of aniline, $10^{10.57}$ mol^{-1} dm^3, was determined spectrophotometrically in aniline−anilinium perchlorate mixtures with *p,p′*-dimethylaminoazobenzene and found to be in excellent agreement with the literature value.

Introduction

Dissociation of several inorganic monobasic uncharged acids, HA, whose p$K_a \leq 1$ in water, into the solvated proton, A^- and HA_2^-, has been reported in dipolar aprotic solvents (DAS) by several authors. These acids, which are included in an excellent monograph by Izutsu (1990), are leveled extensively in water, but to a much lesser extent in DAS of intermediate dielectric permittivity and low donor strength, such as acetonitrile (AN), propylene carbonate, and sulfolane. In a previous study by Kolthoff et al. (1961), conductometric and/or spectrophotometric methods employing nitroaniline indicators were used in freshly prepared solutions of hydrogen chloride, hydrogen bromide, and sulfuric and nitric acids in AN. In many instances the solutions were poorly buffered. The glass electrode later was found to exhibit a practically Nernstian response to $a(H^+)$ in AN (Coetzee and Padmanabhan, 1962). It was calibrated in picric acid (HPi)−tetrabutylammonium picrate mixtures, using the redetermined value of pK_a(HPi) = 11.0 (Kolthoff and Chantooni, 1965).

In the present study the potentiometrically determined value of $K_a/K(HA_2^-)$ of sulfuric acid with the glass electrode (Kolthoff and Chantooni, 1968) has been checked spectrophotometrically in mixtures of sulfuric acid and excess tetraethylammonium bisulfate (MA) in AN, using HPi as indicator. In these solutions practically all the sulfuric acid is converted into the completely dissociated homoconjugate salt, MHA_2, MA being incompletely dissociated. The symbols K_a and $K(HA_2^-)$ in eq 1 represent the simple dissociation constant of the acid and stability constant of the 1:1 homoconjugate, respectively. Also, $C(HA)$ and $C(MA)$ denote the analytical concentrations of acid and salt, respectively, and $y^{\pm}$ the mean ionic activity coefficient. Hence

$$K_a/K(HA_2^-) = \{a(H^+)[A^-]^2y^{\pm 2}(A^-)\}/\{C(HA)\,y(HA_2^-)\} \quad (1)$$

where $[A^-] = C(MA) - C(HA) - [MA]$.

In solutions of sulfuric acid alone, or in the presence of a small amount of MA, the electrolytic conductivity in AN increases with time of standing, while $a(H^+)$ was found to decrease to the same extent, as monitored spectrophotometrically with a nitroaniline indicator. In most cases both attain a constant value after 50 h. Janz and Danyluk (1959) observed a similar increase in conductivity of hydrogen chloride and hydrogen bromide solutions in AN (“aging”). The product, $K_aK(HA_2^-)$, of sulfuric acid, therefore, was estimated in this study from simultaneous electrolytic conductivity and spectrophotometric indicator measurements in the same solution, using eq 2 and assuming $[HA_2^-] \gg [A^-]$.

$$K_aK(HA_2^-) = \{[H^+][HA_2^-]y^{\pm 2}\}/[HA]^2 = \{1 \times 10^3\kappa[IH^+](1 + K_I[I])^{1/2}y^{\pm 2}\}/\{[I]K_I\Lambda[HA]^2\} \quad (2)$$

In eq 2 κ represents the specific molar conductivity and Λ the molar conductivity of $H^+HA_2^-$ corrected for ion atmosphere effects. The nitroaniline indicator base is denoted by I, its protonated form by IH^+, and the protonation constant by K_I. Presence of the salt attenuates the aging process.

The glass electrode was used in this study to determine pK_a and $K(HA_2^-)$ of nitric acid in freshly prepared mixtures of the acid and its tetraethylammonium salt. The following relation holds (Kolthoff and Chantooni, 1965).

$$K(HA_2^-) = \{C(MA)r^2 - r[C(HA) + C(MA)] + C(HA)\}/r\{C(MA) - C(HA)\}^2 \quad (3)$$

where $r = \{a(H^+)\,y(H^+)\}/\{a(H^+)_{1/2}\,y(H^+)_{1/2}\}$, the subscript

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* Corresponding author. Fax (612) 626-7541.

[†] Deceased, March 1993.

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Table 1. Indicator Ratio, $[IH^+]/[I]$, of *o*-Nitro-*p*-chloroaniline, 3.0×10^{-5} mol dm^{-3}, and Specific Conductivity, κ, in Aging Solutions of Sulfuric Acid HA in Acetonitrile in the Presence of Tetraethylammonium Bisulfate

time of standing/h	$[IH^+]/[I]$	$[H^+]$s/(mol dm^{-3}) $\times 10^5$	κ/(S cm^{-1}) $\times 10^4$	κ due to H_2SO_4/(S cm^{-1}) $\times 10^4$	$[HA_2^-]$/(mol dm^{-3}) $\times 10^3$	$y^{\pm 2}$	$[H_2SO_4]$/(mol dm^{-3}) $\times 10^2$	pK_a − log $K(HA_2^-)$
C(HA) = 0.0609 mol dm^{-3}, $C(Et_4NHSO_4) = 6.10 \times 10^{-4}$ mol dm^{-3}								
0.58	1.50	9.46	1.34	0.48	0.927	0.811	5.97	4.66
0.83	1.31	8.27	1.44	0.58	0.992	0.810	5.83	4.67
2.50	0.81	5.11	2.13	1.28	1.47	0.772	5.85	4.72
3.33	0.72	4.54	2.49	1.65	1.71	0.757	5.69	4.69
5.83	0.58	3.66	3.44	2.61	2.38	0.725	5.55	4.63
C(HA) = 0.0560 mol dm^{-3}, $C(Et_4NHSO_4) = 1.38 \times 10^{-3}$ mol dm^{-3}								
0.25	0.81	5.11	2.38	0.51	1.72	0.756	5.12	4.55
0.83	0.61	3.85	2.67	0.83	1.91	0.745	5.08	4.61
1.50	0.51	3.22	2.91	1.06	2.09	0.736	5.04	4.65
3.01	0.37	2.33	3.48	1.77	2.61	0.670	4.94	4.71
5.00	0.28	1.77	3.97	2.21	2.93	0.660	4.88	4.78
7.33	0.23_6	1.49	4.44	2.71	3.29	0.650	4.81	4.79
8.50	0.31[a]	1.96	4.69	2.96	3.48	0.644	4.76	4.65
13.0	0.26	1.64	5.40	3.69	4.04	0.625	4.65	4.65
24.2	0.28	1.77	9.46	7.79	7.24	0.575	4.01	(4.27)[b]
26.0	0.21	1.33	9.66	8.04	7.52	0.571	3.96	(4.37)[b]
34.5	0.14	0.88	9.02	8.41	7.61	0.570	3.94	(4.53)[b]

[a] Indicator freshly added. [b] Not included in average in Table 5.

1/2 denoting the midpoint, at which $C(HA) = C(MA)$. Since [MA], as well as $[MHA_2]$, can be considered negligible, $a(H^+)_{1/2}y^{\pm}{}_{1/2} = K_a$ (Khudyakova and Rozhkova, 1980). The nitric acid−tetraethylammonium nitrate system, furthermore, was studied in the vicinity of the midpoint, using picric acid as indicator. The value of $K(HA_2^-)$ of nitric acid was also obtained from the increase in solubility of sodium nitrate in the presence of nitric acid using eq 4.

$$K(HA_2^-) = \{[Na^+]^2 y^{\pm 2} - K^{sp}\}/K^{sp}\{C(HA) - [Na^+]\} \quad (4)$$

A similar experiment with *p*-bromophenol instead of nitric acid yielded the stability constant of the 1:1 heteroconjugate.

Finally, the protonation constant of aniline, $K(BH^+)$, was determined spectrophotometrically in mixtures of aniline and anilinium perchlorate, using *p,p′*-dimethylamino azobenzene (DMAAB) as indicator. Since p$K(BH^+)$ values of both aniline and DMAAB were referred to pK_a of picric acid in the literature, the present value of p$K(DMAABH^+)$ − pK(anilinium) constitutes a cross-check on the literature data.

Experimental Section

Acetonitrile was Burdick and Jackson, Reagent Grade, distilled over phosphorus pentoxide and then over calcium hydride. Specific conductivity of the purified solvent was (0.5 to 1.0) × 10^{-7} S cm^{-1}. The water content by Karl Fischer titration was typically (1 to 2) × 10^{-3} mol dm^{-3}, while basic impurities were ≤1 × 10^{-6} mol dm^{3}, as estimated from the absorbance of picric acid at 420 nm (Kolthoff et al., 1961). Anhydrous sulfuric acid was prepared by reacting 98% acid with oleum (120%), using the “fair and foggy” method (Kuntzler, 1953). Assay by alkalimetric titration in water was 100.00 ± 0.02%. Stock solutions were prepared in by introducing the acid by mass into a known volume of AN, and the concentration was checked by flooding an aliquot with 20 volumes of water and titrating alkalimetrically to the phenolphthalein end point. The two results agreed within ±0.5%. The titer slowly decreased with time as follows: initially 0.0930, after 25 h 0.0895, and after 53 h 0.0884 mol dm^{-3}; initially 0.0310, after 50 h 0.0300 mol dm^{-3}. This decrease was taken into account in calculation of $[H_2SO_4]$ of the above solutions. A constant titer was assumed in the other solutions over the entire period (<6 h). Anhydrous nitric acid was prepared by slowly dropping 100% sulfuric acid over anhydrous sodium nitrate (Merck) and distilling at 7 × 10^2 Pa, bp 257 K. It initially was very light yellow, turning lemon yellow upon storage in the dark for 3 days at 263 K. Assay by alkalimetric titration in water of both fresh and stored product was 99.5 ± 0.5%. It was used within 3 days after preparation. **CAUTION:** Care must be taken in handling the highly corrosive and fuming acid; in the distillation two liquid nitrogen traps in series are recommended. The concentration of nitric acid in AN was determined in the same way as for sulfuric acid.

Tetraethylammonium nitrate was prepared from concentrated aqueous nitric acid and Aldrich 20% tetraethylammonium hydroxide according to Pocker and Kevil (1965). Picric acid, tetrabutylammonium picrate, tetraethylammonium bisulfate, *o*-nitroaniline, *o*-nitro-*p*-chloroaniline (Kolthoff and Chantooni, 1965) and *p,p′*-dimethylaminoazobenzene (Kolthoff and Chantooni, 1966) were used previously. Aniline (Aldrich, Reagent Grade) was distilled at 9.71 × 10^4 Pa over Zn dust and used immediately. Anilinium perchlorate was precipitated in acetic acid from an equimolar mixture (∼0.5 mol dm^{-3}) of aniline and perchloric acid. Assay by potentiometric titration in AN with 1,3-diphenylguanidine was 99.8%. **CAUTION:** Anilinium perchlorate is prone to detonate.

Conductivity cells and bridge were those used previously (Kolthoff and Chantooni, 1962). Absorbances were measured on a Beckman DU spectrophotometer with 1.00, 1.75, and 1.88 cm glass-stoppered Pyrex cells. Molar absorptivities at 410 nm are 2.71 × 10^4 and 2.76 × 10^4 dm^3 mol^{-1} cm^{-1} for *o*-nitro-*p*-chloroaniline and *o*-nitroaniline, respectively, that of picrate and picric acid at 410 nm are 1.10 × 10^4 and 1.15 dm^3 mol^{-1}, respectively, while that of dimethylaminoazobenzene at 510 nm is 5.2 × 10^4 dm^3 mol^{-1} cm^{-1}. Solubility of sodium nitrate in the presence of nitric acid in AN was determined by titrating spectrophotometrically with perchloric acid in acetic acid (standardized with diphenylguanidine) using *o*-nitroaniline as indicator.

Results

Dissociation Constant of Salts. Values of K_A in mol^{-1} dm^3 of simple salts in AN are tetraethylammonium bisul-

Table 2. Potentiometric Glass Electrode p*a*H Data in Mixtures of Nitric Acid (HA) and Tetraethylammonium Nitrate in Acetonitrile

C(HA)/(mol dm^{-3}) × 10^3	C(Et$_4$NA)/(mol dm^{-3}) × 10^3	p*a*H[a]	y(H$^+$)	K(HA$_2^-$)/(dm^3 mol^{-1}) × 10^3
0.508	2.00	11.51	0.87	1.3
1.02	1.99	11.07	0.87	1.4
1.52	1.98	10.80	0.87	
2.52	1.98	10.29	0.87	
4.98	1.96	9.54	0.87	
9.30	1.93	8.92	0.87	1.15
0.508	6.00	12.32	0.80	1.4
1.02	5.98	11.88	0.80	1.1
2.04	5.95	11.46	0.80	1.0
3.50	5.90	10.91	0.80	
4.98	5.88	10.54	0.80	
6.91	5.84	10.08	0.80	
9.77	5.77	9.58	0.80	1.26
14.4	5.66	9.24	0.81	0.7
23.1	5.45	8.51	0.81	1.1
42.4	5.00	7.82	0.82	1.2

[a] p*a*H at half-neutralization: 10.40 when C(Et$_4$NA) = (5.00 to 6.00) × 10^{-3} mol dm^{-3} and 10.50 when C(Et$_4$NA) = 1.93 to 2.00) × 10^{-3} mol dm^{-3}.

fate, 3.3 × 10^1 (Kolthoff and Chantooni, 1968), nitrate, 4.7 × 10^1 (Pocker and Kevill 1965); sodium nitrate, 1.1$_2$ × 10^3 (this work). With the exception of tetraethylammonium bisulfate in the sulfuric acid−bisulfate (excess) mixtures with picric acid as indicator, all homo- and heteroconjugate salts and simple tetraethylammonium salts have been considered as completely dissociated under the experimental conditions.

Activity Coefficients. The partially extended Debye−Hückel expression

$$-\log y^{\pm} = 1.644\mu^{1/2}/(1 + 0.4857a_0\mu^{1/2}) \qquad (5)$$

was used to calculate $y^{\pm}$, at ionic strength μ, taking a_0 = 0.30 nm for NO$_3^-$, Cl$^-$, Br$^-$; 0.40 nm for Na$^+$, HSO$_4^-$; 0.60 nm for tetraethylammonium, H(NO$_3$)$_2^-$, H(HSO$_4$)$_2^-$, *p*-bromophenol·NO$_3^-$, HBr$_2^-$, HCl$_2^-$; 0.70 nm for Na$^+$, picrate; and 0.90 nm for H$^+$.

Spectrophotometric Determination of K_a and $K(HA_2^-)$ with Picric Acid as Indicator. In this study mixtures of nitric acid (2.5 × 10^{-4} to 8 × 10^{-3} mol dm^{-3}) and tetraethylammonium nitrate (2 × 10^{-3} or 5.7 × 10^{-3} mol dm^{-3}) with picric acid and tetrabutylammonium picrate (5.2 × 10^{-5} and 2.8 × 10^{-5} mol dm^{-3}, respectively) were taken. The value of pK_a of nitric acid from the p*a*H at the midpoint agrees well with that found potentiometrically with the glass electrode (Table 5). The standard deviation in K(HA$_2^-$) divided by K(HA$_2^-$), 0.28, is about twice that from potentiometric p*a*H of solubility data, owing to the limited range of the ratio of acid to salt concentration in the vicinity of the midpoint. The spectrophotometrically determined ratio of picrate to picric acid in mixtures of sulfuric acid (1.8 × 10^{-4} to 0.011 mol dm^{-3}) and tetraethylammonium bisulfate (1.0 × 10^{-2} to 8.9 × 10^{-2} mol dm^{-3}) was determined in this study. Total picric acid concentrations were 3.9 × 10^{-5} and 5.5 × 10^{-5} mol dm^{-3}. The value of log(K_a/K(HA$_2^-$)) derived from these data is in Table 5, method A. Agreement with the potentiometric value of 11.5 is excellent.

Spectrophotometric Determination of K_a and $K(HA_2^-)$ with Nitroaniline Indicators. In a previous publication (Kolthoff et al., 1961) K_I of *o*-nitroaniline and *o*-nitro-*p*-chloroaniline indicators was estimated by adding perchloric acid (0.485 mol dm^{-3}) in acetic acid (made anhydrous with acetic anhydride) to the indicator base in AN. It was subsequently found that acetic acid (AcOH) is protonated in AN, K(AcOH$_2^+$) being 1.2 × 10^1 (Kolthoff and Chantooni, 1973a). Correcting for the presence of AcOH$_2^+$, K_I of the two nitroanilines equals 0.85 × 10^5 and 1.59 × 10^4 mol^{-1} dm^3, respectively. In Table 5, method B, are listed spectrophotometric values of pK_a − log K(HA$_2^-$) of HBr, HCl, and H$_2$SO$_4$ in fresh solution of the acid and indicator base, recalculated using the corrected K_I values. The value of pK_a − log K(HA$_2^-$) of sulfuric acid from freshly prepared mixtures of acid (in excess) and tetraethylammonium bisulfate with *o*-nitroaniline is also listed in Table 5, method C. Experimental data of the above systems have been published (Kolthoff et al. 1961).

Determination of pK_a − log $K(HA_2^-)$ in Solutions of Sulfuric Acid in the Absence or in the Presence of Tetraethylammonium Bisulfate in Aging Solutions. Reaction with Nitroanilines Combined with Conductance Data. The conductivity and spectrophotometrically determined ratio [IH$^+$]/[I] of *o*-nitro-*p*-chloroaniline, 3.0 × 10^{-5} to 6 × 10^{-5} mol dm^{-3}, was measured separately within 0.03 h of each other in several solutions of sulfuric acid, 9.7 × 10^{-3} to 9.3 × 10^{-2} mol dm^{-3} upon standing for 0.05 to 22.5 h. In most cases, the indicator was left standing in the sulfuric acid solution. Acting as a base, it tends to retard the aging slightly, resulting in [H$^+$] being slightly larger than when the indicator is freshly added. This effect amounts to about

Table 3. Homo- or Heteroconjunction of Nitrate from Solubility of Sodium Nitrate in the Presence of Nitric Acid or *p*-Bromophenol (HR)

C(HNO$_3$) or C(HR)/(mol dm^{-3}) × 10^2	total solubility S_t)/(mol dm^{-3}) × 10^3	[Na$^+$] {S_{t-}{NaNO$_3$]}/ (mol dm^{-3}) × 10^3	cond. of satd soln[c]/(S cm^{-1}) × 10^4	$y^{\pm 2}$	K(HNO$_3$·NO$_3^-$) or K(HR·NO$_3^-$)/mol^{-1} dm^3)
		In the Presence of HNO$_3$			
0	1.89	1.02[a]	1.75	0.795	
1.01	4.26	3.39	3.84	0.680	1.26 × 10^3
2.54	6.31	5.44		0.623	1.07 × 10^3
4.06	8.56	7.69	7.76	0.578	1.23 × 10^3
6.60	11.7	10.8	11.4	0.533	1.34 × 10^3
		In the Presence of *p*-Bromophenol (HR)			
0		1.08[b]	1.85	0.79	
6.59		2.08	2.43	0.772	4.09 × 10^1
13.6		2.76	3.16	0.703	3.59 × 10^1
22.8		3.68	4.11	0.670	3.92 × 10^1
29.3		4.10	4.53	0.657	3.78 × 10^1
38.5		4.86	5.29	0.637	4.01 × 10^1
48.4		5.75	6.13	0.616	4.39 × 10^1

[a] K^{sp} = 8.2$_7$ × 10^{-7}. [b] K^{sp} = 9.26 × 10^{-7}. [c] λ_0(Na$^+$) = 76.9, Springer et al. (1969); λ_0(NO$_3^-$) = 106.4, Spiro (1973); λ_0(HA$_2^-$), λ_0(HRA$^-$) assumed to be 55 S cm^2.

Table 4. Reaction Between Anilinium Perchlorate ($BHClO_4$) and Dimethylaminoazobenzene (I) in Acetronitrile Solutions Containing Aniline

$C(B)$/(mol dm^{-3}) $\times 10^3$	$[IH^+]$/$[IH^+]$	$K(BH^+)$/(mol^{-1} dm^{-3}) $\times 10^{10}$	$C(B)$/(mol cm^{-3}) $\times 10^3$	$[IH^+]$/$[IH^+]$	$K(BH^+)$/(mol^{-1} dm^{-3}) $\times 10^{-10}$
$C(BHClO_4) = 5.43 \times 10^{-3}$ mol dm^{-3}, $C(I) = 2.3 \times 10^{-6}$ mol dm^{-3}					
0.219	13.1	2.12	2.19	0.83	3.35
0.438	4.8	2.89	3.28	0.55	3.38
0.876	2.12	3.28	5.46	0.34	3.28
1.53	1.21	3.29	8.75	0.22	3.17
$C(BHClO_4) = 4.63 \times 10^{-3}$ mol dm^{-3}, $C(I) = 4.6 \times 10^{-6}$ mol dm^{-3}					
0.219	5.54	4.28	2.19	0.60	3.95
0.438	3.12	3.80	3.28	0.39	4.06
0.876	1.48	4.01	5.46	0.23	4.14
1.53	0.85	3.99	8.75	0.14	4.24
$C(BHClO_4) = 9.26 \times 10^{-3}$ mol dm^{-3}, $C(I) = 4.6 \times 10^{-6}$ mol dm^{-3}					
0.219	9.70	4.89	3.28	0.80	3.96
0.438	5.10	4.65	5.46	0.49	3.88
1.09	2.34	4.07	8.75	0.30	3.96
1.53	1.65	4.12	17.5	0.16	3.71

0.11 pK unit. In the calculation of $[HA_2^-]$ from conductivity data, $\lambda_0(H^+) = 101$ S cm^2 was taken, which is the average of 109.3 (Fujinaga and Sakamoto, 1977) and 94 S cm^2 (Coetzee and McGuire, 1963), while $\lambda_0(H(HSO_4^-)_2 = 65$ S cm^2 (Kolthoff and Chantooni, 1962). The difference in values of $\lambda_0(H^+)$ introduces an uncertainty of 0.04 unit in $pK_a - \log K(HA_2^-)$. Onsager ion atmosphere corrections were applied. Production of HA_2^- by aging of the acid enhances buffering of the system. Values of $pK_a - \log K(HA_2^-)$ are constant to within 0.1 unit over the time interval, being independent of acid concentration.

Results from similar experiments in aging sulfuric acid−bisulfate mixtures are summarized in Table 1. Subtracting the conductance of the tetraethylammonium salt from the observed conductivity in these solutions leads to an uncertainty of 0.02 to 0.08 pK unit.

Taking an average value of 4.61 for $pK_a - \log K(HA_2^-)$ of sulfuric acid from nitroaniline indicator data (methods C, D, and E in Table 5) and 11.46 for $pK_a + \log K(HA_2^-)$ using picric acid as indicator (method A in Table 5), $\log K(HA_2^-) = 3.43$ and $pK_a = 8.04$, as compared to the potentiometric glass electrode values of 3.6 and 7.8, respectively (Kolthoff and Chantooni, 1968). It is reasonable to conclude that indicator and conductivity measurements in tandem can yield a reliable value of $pK_a - \log K(HA_2^-)$ in aged solutions provided insoluble adducts, such as nitrilium salts, are not formed. It is suspected that the large value of $pK_a - \log K(HA_2^-)$, 5.3 (Table 5), obtained in "fresh" solutions of sulfuric acid alone with nitroanilines as indicator is due to aging.

Potentiometric Determination of K_a and $K(HA_2^-)$ with the Glass Electrode. Potentiometric glass electrode paH data in solutions of nitric acid, 5.1×10^{-4} to 4.2×10^{-2} mol dm^{-3}, and tetraethylammonium nitrate, 2.0×10^{-3} to 6.0×10^{-3} mol dm^{-3}, are entered in Table 2. Resulting values of pK_a and $K(HA_2^-)$ calculated according to eq 3 are listed in Table 5, method F. There is no indication of $(HA)_2A^-$ formation.

Homoconjugation and Heteroconjugation Constants From Solubility Data. Values of $K(HNO_3{\cdot}NO_3^-)$ and of K(p-bromophenol$\cdot NO_3^-$) were derived from the increase in solubility of sodium nitrate in the presence of nitric acid or p-bromophenol, respectively, using eq 4. Experimental data are in Table 3. The homoconjugation constant obtained in this way agrees well with the potentiometric value (Table 5), while K(p-bromophenol$\cdot NO_3^-$) = (39.6 ± 2.5) mol^{-1} dm^3.

Protonation of Aniline. From the spectrophotometrically determined ratio of the acid to base forms of dimethylaminoazobenzene, (2.3×10^{-6} to 4.6×10^{-6}) mol dm^{-3} in solutions of aniline, (2×10^{-4} to 1.5×10^{-3}) mol dm^{-3} and anilinium perchlorate (4.6×10^{-3} to 9.3×10^{-3}) mol dm^{-3} in Table 4 a protonation constant of $(3.76 \pm 0.35) \times 10^{10}$ mol^{-1} dm^3 was derived. This is in excellent agreement with that obtained with the glass electrode by Coetzee and Padmanabhan (1965), 3.63×10^{10} mol^{-1} dm^3. Dissociation and homoconjugation constants of the mineral acids in AN are summarized in Table 5.

Discussion

Order of Acid Strength in Acetonitrile. The following order of decreasing acid strength is observed in AN (pK_a values in parentheses): $HClO_4$ (1.57) > CF_3SO_3H (2.60) > FSO_3H (3.38) > HBr (5.81) > H_2SO_4 (7.9), p-toluenesulfonic (8.0) > HCl (10.4), Cl_3CCOOH (10.57), HNO_3 (10.6), HPi (11.0) > CF_3CCOOH (12.65) > $Cl_2CHCOOH$ (13.2) > $ClCH_2COOH$ (15.34). Values of perchloric acid and sulfonic acids are from Fujinaga and Sakamoto (1977), those of substituted acetic acids from Jasinski et al. (1978), and HBr, HCl, H_2SO_4, and HNO_3 from Table 5. This order closely resembles that in the DAS nitromethane, propylene carbonate, n-butyronitrile, N,N-dimethylformamide (DMF), and dimethylacetamide (Fujinaga and Sakamoto, 1977). In

Table 5. Acid Dissociation Constant, (pK_a), and Homoconjugation Constant, $K(HA_2^-)$, of Acids, HA, in Acetonitrile

acid	method[a]	pK_a	$K(HA_2^-)$/(mol^{-1} dm^3) $\times 10^3$	$pK_a - \log K(HA_2^-)$	$pK_a + \log K(HA_2^-)$	ref
H_2SO_4	A				11.46 ± 0.12	this work
H_2SO_4	B			5.3[b]		
H_2SO_4	C			4.54[b]		
H_2SO_4	D			4.68 ± 0.10		this work
H_2SO_4	E			4.62 ± 0.13		this work
H_2SO_4	F	7.8	4.73 ± 0.53	4.2	11.5	Kolthoff and Chantooni (1968)
HBr	B			2.95[b]		
HBr	F	5.81	1.4	2.66	8.96	Kolthoff and Chantooni (1979)
HCl	B			6.99[b]		
HCl	F	10.43	4.38 ± 0.59	6.77	14.07	Kolthoff and Chantooni (1979)
HNO_3	A	10.65	0.67 ± 0.19	7.8		this work
HNO_3	F	10.53	1.15 ± 0.19	7.47	13.60	this work
HNO_3	G		1.22 ± 0.10			this work

[a] (A) Fresh HA-Et_4NA mixtures, spectrophotometrically with picric acid as indicator. (B) Fresh solutions of HA alone, spectrophotometrically with nitroanilines as indicator. (C) Same as B, but buffered mixtures of HA−Et_4NA taken. (D) HA alone at various times with nitroanilines spectrophotometrically, combined with conductance measurements. (E) Same as D, but HA−Et_4NA mixtures taken. (F) fresh HA−Et_4NA mixtures, potentiometrically with a glass electrode. (G) From solubility of NaA in the presence of HA. [b] Original data from Kolthoff et al. (1961) have been recalculated using revised values of K_I of the nitroanilines, see text.

Table 6. Difference in Gibbs Free Energy of Transfer of Bisulfate, Methanesulfonate, or Nitrate and Their Corresponding Acids from Acetonitrile (AN) to Solvent S

acid(HA)	S	$(\mathrm{p}K_a)_S$	$\Delta G_{tr}{}^0(H^+)_{AN\to S}$[d]/ kJ mol^{-1}	$\{\Delta G_{tr}{}^0(A^-) - \Delta G_{tr}{}^0(HA)\}_{AN\to S}$/ kJ mol^{-1}
CH_3SO_3H	DMF	2.98[a]	−60.3	20.5[e]
CH_3SO_3H	DMSO	1.56[a]	−64.9	16.9[e]
H_2SO_4	DMF	3.0_5[b]	−60.3	31.9
H_2SO_4	DMSO	1.44[c]	−64.9	27.3
HNO_3	DMSO	1.42[c]	−64.9	12.7

[a] Fujinaga and Sakamoto (1977). [b] Kolthoff et al. (1970). [c] McCallum and Pethybridge (1975). [d] Marcus et al (1988), extrathermodynamic assumption, $\Delta G_{tr}{}^0$(tetraphenylarsonium) = $\Delta G_{tr}{}^0$ (tetraphenylborate) used. [e] $\mathrm{p}K_a$ (CH_3SO_3H) in AN taken as 10.0 (Kolthoff and Chantooni, 1965).

the latter solvent (donor number, DN, 27.8) the difference in $\mathrm{p}K_a$ of *p*-toluenesulfonic acid and CF_3SO_3H is 1.94 − 0.68 = 1.26, while in AN (DN = 14.1) it is 5.4 units. This is attributed to the leveling effect.

Gibbs Free Energy of Transfer of Acids and Their Anions. Values of the free energy of transfer of HCl and of HBr from AN to methanol (MeOH), −11.9 and −27.3 kJ mol^{-1}, respectively, have been reported previously (Kolthoff and Chantooni, 1979). That of HNO_3, −2.4 kJ mol^{-1}, was estimated by introducing $\mathrm{p}K_a$ = 10.6 in AN (present work), 3.2 in MeOH (Charlot and Tremillon 1969), $\Delta G^0{}_{tr}(NO_3{}^-)_{AN\to MeOH} = -8.5$ kJ mol^{-1} and $\Delta G^0{}_{tr}(H^+)_{AN\to MeOH} = -36$ kJ mol^{-1} (Marcus et al., 1988) into eq 6

$$(\mathrm{p}K_a)_S - (\mathrm{p}K_a)_{AN} = \Delta G^0{}_{tr}(H^+)_{AN\to S} + \Delta G^0{}_{tr}(A^-)_{AN\to S} - \Delta G^0{}_{tr}(HA)_{AN\to S} \qquad (6)$$

where S denotes solvent. It appears that nitric acid and especially the hydrogen halides are more solvated in MeOH than in AN.

Since values of the free energies of transfer of HA or of A^- going from AN to DMF or to DMSO are not available for CH_3SO_3H, H_2SO_4, or HNO_3, the *difference* $\{\Delta G^0{}_{tr}(A^-) - \Delta G^0{}_{tr}(HA)\}_{AN\to S}$ has been evaluated from eq 6 and is listed in Table 6. This difference is positive in every case, particularly for H_2SO_4. Most likely, this is attributed to strong hydrogen bonding of H_2SO_4 to DMF and DMSO. From comparison of the β solvatochromic parameter, DMSO is a stronger hydrogen bond acceptor than DMF (Kamlet et al., 1983). The more positive values of $\{\Delta G^0{}_{tr}(A^-) - \Delta G^0{}_{tr}(HA)\}_{AN\to DMF}$ as compared to those from AN to DMSO for H_2SO_4 and CH_3SO_3H in Table 6 suggest weaker solvation of bisulfate and methanesulfonate in DMSO than in DMF.

Standard Potential of Ag in AN. Recalculation of the potentiometric data of the hydrogen electrode vs $AgNO_3$ (0.010 mol dm^{-3}) in sulfuric acid−tetraethylammonium bisulfate mixtures from Kolthoff and Thomas (1965) using the present spectrophotometric value of $\mathrm{p}K_a - \log K(HA_{2-})$ of sulfuric acid, 4.61, results in $E°$ (Ag) = 0.072 V as compared to 0.096 V reported by Kolthoff and Thomas (1965). Combining the former with the accepted value of 0.7994 V in water yields $\{\Delta G^0{}_{tr}(Ag^+) - \Delta G^0{}_{tr}(H^+)\}_{AN\to water} = 70.0$ kJ mol^{-1}. A value of 67.7 kJ mol^{-1} was reported by Kolthoff and Chantooni (1972) from the solubility product of silver picrate, solubility of picric acid, and K_a(HPi) in the two solvents. Uncertainties in the hydrogen electrode potential, liquid junction potential, and extrapolation to zero ionic strength can amount to 1.5 kJ mol^{-1}.

Heteroconjugation. The hydrogen bond donor, *p*-bromophenol (HR), serves as a useful indicator of hydrogen bond accepting capacity of many simple anions in DAS. The formation constants of $HR{\cdot}NO_3{}^-$, 4.0 × 10^1 (this work), $HR{\cdot}CH_3SO_3{}^-$, 3.4 × 10^1 (Kolthoff and Chantooni, 1973b), and $HR{\cdot}HSO_4{}^-$, 2.7 × 10^1 (Kolthoff and Chantooni, 1969) in AN are small, as a consequence of extensive charge dispersal in the simple anion.

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