Heteroconjugation of the Sulfate and Bisulfate Ions in Acetonitrile with Uncharged Hydrogen Bond Donors[1]

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Abstract: The sulfate ion in acetonitrile (AN) has a great tendency to heteroconjugate with hydrogen bond donors, denoted as HR. From $\mathrm{p}a_{\mathrm{H}}$ measurements in mixtures of tetraethylammonium bisulfate and sulfate in the presence of the hydrogen bonders *p*-bromophenol, water, and methanol, it has been concluded that only two conjugates are formed, $(\mathrm{HR})_2\mathrm{SO}_4{}^{2-}$ and $(\mathrm{HR})_4\mathrm{SO}_4{}^{2-}$. The formation constants at 25° in the order given are 2×10^7, 5×10^2, and 5×10^3 for the diconjugates and 1.3×10^{12}, 1.5×10^5, and 5.5×10^4, respectively, for the tetraconjugates. At small equilibrium concentrations of *p*-bromophenol the values of the two constants were confirmed by spectrophotometric measurements in mixtures of tetraethylammonium sulfate, 3,5-dinitrophenolate (DNP^-), and *p*-bromophenol (HR). In these mixtures formation of $(\mathrm{HR})_2\mathrm{DNP}^-$ was negligible, its formation constant, $K^{\mathrm{f}}{}_{(\mathrm{HR})_2\mathrm{DNP}^-} = [(\mathrm{HR})_2\mathrm{DNP}^-]/[\mathrm{HR}][\mathrm{HR}\cdot\mathrm{DNP}^-]$, being found to be 1.5×10^1. Sulfuric acid in AN forms a mono- and a dihydrate with formation constants 1.0×10^1 and 2.1×10^1, respectively. No indication has been obtained of hydration of the bisulfate ion in AN. On the other hand, *p*-bromophenol was found not to conjugate with sulfuric acid but to form a monoconjugate $\mathrm{HR}\cdot\mathrm{HSO}_4{}^-$ with bisulfate, with a formation constant of 2.7×10^1. Hydrogen bond donors greatly affect the potentiometric neutralization curve of tetraalkylammonium bisulfate with tetraalkylammonium hydroxide.

In a previous paper[2] it was concluded that the medium activity coefficient of the sulfate ion, with reference to that in water, is many orders of magnitude greater in acetonitrile (AN) than in water. Therefore it is expected that the sulfate ion in AN will have a great tendency to heteroconjugate with uncharged hydrogen bond donors, denoted as HR. In the present paper water, methanol, and *p*-bromophenol have been used as hydrogen bond donors in AN, and it is shown that they have a great affinity toward the sulfate ion.

The effect of these hydrogen bond donors on the $\mathrm{p}a_{\mathrm{H}}$ of mixtures of tetraethylammonium bisulfate and sulfate was measured with the glass electrode. From the change in $\mathrm{p}a_{\mathrm{H}}$ the formation constants of the conjugates were derived. The hydrogen bond donors used are such weak acids that no proton transfer with sulfate ion occurs.

A hydrogen bond donor can conjugate with both sulfate and bisulfate ions. Therefore it was necessary to determine separately the heteroconjugation constants of HR with the bisulfate ion in order to calculate the heteroconjugation constants of HR with sulfate. For this purpose the effect of HR on $\mathrm{p}a_{\mathrm{H}}$ in mixtures of sulfuric acid and bisulfate was measured. Under our experimental conditions the hydrogen bond accepting properties of *p*-bromophenol toward sulfuric acid can be neglected. This is no longer true with the much stronger bases water and methanol which can conjugate with the hydrogen bond donor, sulfuric acid, besides reacting with the solvated proton to form the hydrated or methanolated proton.[3]

The $\mathrm{p}a_{\mathrm{H}}$ of mixtures of a monobasic weak acid, HA, and its tetraalkylammonium salt in the presence of HR, which is both a hydrogen bond donor toward A^- and hydrogen bond acceptor toward HA, is given by the following relation previously derived[4]

$$f^2W^2a_{\mathrm{H}^+}{}^2C_{\mathrm{s}} - fVWK^{\mathrm{d}}{}_{\mathrm{HA}}a_{\mathrm{H}^+}[(C_{\mathrm{a}} + C_{\mathrm{s}}) + K^{\mathrm{f}}{}_{\mathrm{HA}_2{}^-}(C_{\mathrm{s}} - C_{\mathrm{a}})^2/VW] + V^2K^{\mathrm{d}}{}_{\mathrm{HA}}{}^2C_{\mathrm{a}} = 0 \quad (1)$$

provided proton transfer between the hydrogen bond donor and base, A^-, is negligible. In eq 1

$$V = 1 + K^{\mathrm{f}}{}_{\mathrm{HR}\cdot\mathrm{A}^-}[\mathrm{HR}] + K^{\mathrm{f}}{}_{(\mathrm{HR})_2\mathrm{A}^-}[\mathrm{HR}]^2 + \ldots$$

$$W = 1 + K^{\mathrm{f}}{}_{\mathrm{HR}\cdot\mathrm{HA}}[\mathrm{HR}] + K^{\mathrm{f}}{}_{2\mathrm{HR}\cdot\mathrm{HA}}[\mathrm{HR}]^2 + \ldots$$

and $K^{\mathrm{f}}{}_{\mathrm{HA}_2{}^-}$ is the homoconjugation constant of HA with A^-, while C_{a} and C_{s} denote the analytical acid and salt concentrations, respectively, and f refers to the activity coefficient of A^-.

It is easily shown[2] that in a mixture of tetraethylammonium salts of the acid anion and normal anion of a diprotic acid, $\mathrm{H_2A}$, in the presence of HR the $\mathrm{p}a_{\mathrm{H}}$ is also given by eq 1, the term involving the homoconjugation constant now becoming $K^{\mathrm{f}}{}_{\mathrm{HA}_2{}^{3-}}(C_{\mathrm{s}} - C_{\mathrm{a}})^2 \cdot f_{\mathrm{HA}^-}f_{\mathrm{A}^{2-}}/f_{\mathrm{HA}_2{}^{3-}}VW$. In eq 1 f now refers to the activity coefficient of A^{2-}.

In order to estimate the individual heteroconjugation constants of HR with A^{2-}, a plot of log C_{HR} *vs.* log V (see eq 1) was made as a first approximation. Under our experimental conditions C_{HR} becomes practically equal to the equilibrium concentration [HR] when C_{HR} is large. The slope of the plot is then equal to n, an integer, which represents the maximum number of HR molecules bound to the sulfate, while the intercept yields the value of $K^{\mathrm{f}}{}_n$ where

$$K^{\mathrm{f}}{}_n = [(\mathrm{HR})_n\mathrm{A}^{2-}]/[\mathrm{HR}][\mathrm{A}^{2-}] \quad (2)$$

With water and methanol an estimate of the average value $\bar{n}$ at various values of C_{HR} was made as a first approximation in order to find the equilibrium value [HR], $\bar{n}$ being the slope of the above plot. A set of simultaneous equations was then formulated

$$\bar{n} = \frac{K^{\mathrm{f}}{}_1[\mathrm{HR}] + 2K^{\mathrm{f}}{}_2[\mathrm{HR}]^2 + \ldots + nK^{\mathrm{f}}{}_n[\mathrm{HR}]^n}{1 + K^{\mathrm{f}}{}_1[\mathrm{HR}] + K^{\mathrm{f}}{}_2[\mathrm{HR}]^2 + \ldots + K^{\mathrm{f}}{}_n[\mathrm{HR}]^n}$$

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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.*, **90**, 5961 (1968).

[3] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **90**, 3320 (1968).

[4] I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **39**, 1080 (1967).

The calculations were then repeated using the approximate value of K^f_1, K^f_2, etc.

This method could not be used with *p*-bromophenol as HR in the sulfate–bisulfate mixture, as the decrease in pa_H was found to be very large even at small values of C_{HR}. Under these conditions a reasonable estimate of [HR] could not be made. For this reason a spectrophotometric method was developed which allowed the estimation of the equilibrium concentration of HR in mixtures containing small concentrations of sulfate and *p*-bromophenol (HR). In this method 3,5-dinitrophenolate ion (DNP^-) was used as a spectrophotometric indicator for HR. The sulfate and DNP^- ions compete for the hydrogen bonder HR. The equilibrium concentration [DNP^-] was determined spectrophotometrically without interference from any of the other constituents and [HR] calculated from the heteroconjugation constants of DNP^- with HR by using the following relation

$$[HR] = [HR \cdot DNP^-]/K^f_{HR\cdot DNP^-}[DNP^-] = \{C_{DNP^-} - [DNP^-]\}/K^f_{HR\cdot DNP^-}[DNP^-]$$

C_{DNP^-} denoting the analytical 3,5-dinitrophenolate concentration. In a previous publication[5] $K^f_{HR\cdot DNP^-}$ was estimated. In the present work we have also investigated the formation of $(HR)_2DNP^-$ and determined its formation constant. Under our experimental conditions with sulfate, $(HR)_2DNP^-$ formation could be neglected. The analytical concentrations of HR and sulfate, denoted by C_{HR} and $C_{SO_4^{2-}}$, respectively, in the above mixture are given by

$$C_{HR} = [HR] + [HR \cdot DNP^-] + \sum_{n=1}^{n=n} n[(HR)_nSO_4^{2-}] \quad (3)$$

$$C_{SO_4^{2-}} = [SO_4^{2-}] + \sum_{n=1}^{n=n} [(HR)_nSO_4^{2-}] \quad (4)$$

By substituting eq 2 into eq 3 and 4, eq 5 results

$$\sum_{n=1}^{n=n} [HR]^n K^f_n(m - nC_{SO_4^{2-}}) + m = 0 \quad (5)$$

m being $C_{HR} - [HR] - [HR \cdot DNP^-]$.

In the derivation of eq 5 both tetraethylammonium sulfate[2] and 3,5-dinitrophenolate[4] were considered completely dissociated and $(HR)_2DNP^-$ formation negligible. Also, acid–base reaction by proton transfer involving sulfate and HR could be neglected.

An effort was made to calculate in sulfate–bisulfate mixtures the constants for $n = 1, 2, \ldots, n - 1$, using eq 5, making use of the potentiometrically found value of K^f_n. From estimated values of $K^f_1, \ldots, K^f_{n-1}$ at small concentrations of *p*-bromophenol, values of pa_H in the sulfate–bisulfate mixtures were calculated over the entire range of HR concentrations, using eq 1, and compared with the experimental ones.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[6] The following products were used previously: anhydrous sulfuric acid,[6] *p*-bromophenol,[7] methanol,[3] and tetraethylammonium salts of 3,5-dinitrophenolate,[5] sulfate,[2] and bisulfate.[6]

Instrumentation. Potentiometric pa_H measurements were performed as described previously.[8] All spectrophotometric measurements were done in 1-cm silica-stoppered cells. For absorbance measurements in sulfate–*p*-bromophenol–3,5-dinitrophenolate mixtures a Beckman DU spectrophotometer was used, while all other spectra were recorded on a Cary Model 15 spectrophotometer. All experiments were performed at 25 ± 0.5°.

Results

Potentiometric Section. Effect of *p*-Bromophenol (HR) and Water on pa_H of Sulfuric Acid–Bisulfate Mixtures. Values of the simple dissociation constant of sulfuric acid, $K^d_{H_2SO_4}$, and of bisulfate, $K^d_{HSO_4^-}$, equal to 7.8 and 25.9, respectively, have been reported previously.[2] The homoconjugation constants $K^f_{H(HSO_4^-)_2}$ and $K^f_{H(SO_4)_2^{3-}}$ were found to be 5×10^3 and 3×10^1, respectively.[2] Calculated and experimental pa_H values in sulfuric acid–tetraethylammonium bisulfate mixtures in the presence of *p*-bromophenol are entered in Table I, and those in the presence of water, in Table II. The following heteroconjugation constants yielded the best agreement between the calculated and experimental

Table I. Effect of *p*-Bromophenol (HR) on pa_H of Mixtures of Sulfuric Acid–Tetraethylammonium Bisulfate[a]

C_{HR}, *M*	[HR], *M*	$pa_{H,obsd}$	$pa_{H,calcd}$
5.60×10^{-4} *M* H_2SO_4, 5.43×10^{-3} *M* Et_4NHSO_4, $f = 0.78$			
0	0	10.10	10.00
0.020	0.018	9.77	9.67
0.069	0.066	9.23	9.12
0.153	0.149	8.70	8.64
0.388	0.384	8.18	8.05
0.610	0.605	7.82	7.73
1.12×10^{-2} *M* H_2SO_4, 0.90×10^{-3} *M* Et_4NHSO_4, $f = 0.90$			
0	0	4.98	4.98
0.084	0.084	4.96	4.96
0.270	0.270	4.87	4.93
0.560	0.560	4.63	4.88

[a] $K^f_{H(HSO_4^-)_2} = 4.7 \times 10^3$, $K^f_{HR\cdot HSO_4^-} = 2.7 \times 10^1$, $K^f_{HR\cdot H_2SO_4} = 0$.

Table II. Effect of Water on pa_H of Mixtures of Sulfuric Acid–Tetraethylammonium Bisulfate[a]

C_{H_2O}, *M*	[H_2O], *M*	$pa_{H,calcd}$	$pa_{H,obsd}$
1.05×10^{-3} *M* H_2SO_4, 5.10×10^{-3} *M* Et_4NHSO_4, $f = 0.77$			
0	0	9.60	9.60
0.033	0.033	9.63	9.61
0.11	0.10	9.65	9.62
0.22	0.21	9.66	9.66
0.385	0.38	9.70	9.70
0.55	0.55	9.75	9.77
0.77	0.77	9.81	9.87
5.10×10^{-3} *M* H_2SO_4, 5.10×10^{-3} *M* Et_4NHSO_4, $f = 0.77$			
0	0	7.74	7.70
0.033	0.028	7.90	7.81
0.077	0.072	8.04	7.98
0.143	0.138	8.19	8.10
0.22	0.21	8.36	8.30
0.385	0.375	8.58	8.59
0.55	0.54	8.80	8.80
0.72	0.71	8.97	8.97
0.88	0.87	9.12	9.11
1.11	1.10	9.29	9.27

[a] $K^f_{H(HSO_4^-)_2} = 4.7 \times 10^3$, $K^f_{H_2O\cdot H_2SO_4} = 1.0 \times 10^1$, $K^f_{2H_2O\cdot H_2SO_4} = 2.1 \times 10^1$, $K^f_{H_2O\cdot HSO_4^-} = 0$.

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(5) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Am. Chem. Soc.*, 88, 5430 (1966).

(6) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, 83, 3927 (1961).

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

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Table III. Effect of *p*-Bromophenol on pa_H of Tetraethylammonium Sulfate–Bisulfate Mixtures[a]

C_{HR}, M	[HR], M	V_{calcd}	W_{calcd}	$pa_{H.calcd}$	$pa_{H.obsd}$
2.01×10^{-3} M $(Et_4N)_2SO_4$, 3.63×10^{-4} M Et_4NHSO_4, $f = 0.77$					
0	0	1.0	1.0	26.45	26.45
0.0083	0.0029	2.6×10^2	1.08	24.07	23.97
0.011	0.0046	1.8×10^3	1.17	23.49	23.61
0.026	0.018	1.4×10^5	1.47	21.47	21.97
0.033	0.025	5.2×10^5	1.68	20.95	20.45
0.048	0.040	3.4×10^6	2.04	20.24	20.61
0.073	0.065	2.5×10^7	2.76	19.55	19.11
0.165	0.163	5.0×10^8	5.4	18.23	18.48
0.176	0.168	1.2×10^9	5.7	18.10	17.75
0.42	0.42	4.0×10^{10}	1.2×10^1	16.92	16.92
0.45	0.45	5.5×10^{10}	1.26×10^1	16.81	16.81
0.69	0.69	2.9×10^{11}	1.9×10^1	16.28	16.18
0.71	0.71	7.1×10^{11}	2.0×10^1	15.90	15.92
1.00×10^{-3} M $(Et_4N)_2SO_4$, 9.10×10^{-3} M Et_4NHSO_4, $f = 0.67$					
0	0	1.0	1.0	25.40	25.40
0.030	0.026	6.1×10^5	1.70	19.84	19.85
0.050	0.046	5.8×10^6	2.24	18.99	19.05
0.094	0.090	8.6×10^7	3.28	17.98	18.05
0.191	0.187	1.6×10^9	6.05	16.98	16.97
0.408	0.404	3.5×10^{10}	1.2×10^1	15.94	16.25
0.650	0.638	2.2×10^{11}	1.8×10^1	15.33	15.51

[a] $K^f_{(HR)_2SO_4^{2-}} = 2 \times 10^7$, $K^f_{(HR)_4SO_4^{2-}} = 1.3 \times 10^{12}$, $K^f_{HR \cdot HSO_4^-} = 2.7 \times 10^1$.

Table IV. Effect of Water on pa_H of $(Et_4N)_2SO_4$–Et_4NHSO_4 Mixtures[a]

C_{H_2O}, M	$[H_2O]$, M	V_{calcd}	$pa_{H.calcd}$	$pa_{H.obsd}$
0	0	1	26.45	26.43
0.033	0.027	1.45	26.29	26.05
0.067	0.059	4.6	25.80	25.67
0.11	0.10	2.1×10^1	25.13	25.07
0.22	0.21	3.1×10^2	23.95	24.10
0.33	0.32	1.6×10^3	23.24	23.34
0.50	0.49	8.8×10^3	22.50	22.48
0.665	0.65	2.72×10^4	22.02	21.80
0.89	0.88	8.9×10^4	21.50	21.14

[a] $K^f_{(H_2O)_2SO_4^{2-}} = 5 \times 10^2$, $K^f_{(H_2O)_4SO_4^{2-}} = 1.5 \times 10^5$, $K^f_{H_2O \cdot HSO_4^-} = 0$; 3.63×10^{-4} M Et_4NHSO_4, 2.01×10^{-3} M $(Et_4N)_2SO_4$, $f = 0.77$.

Table V. Effect of Methanol on pa_H of $(Et_4N)_2SO_4$–Et_4NHSO_4 Mixtures[a]

C_{MeOH}, M	[MeOH], M	V_{calcd}	$pa_{H.calcd}$	$pa_{H.obsd}$
0	0	1	26.45	26.61
0.049	0.041	9.55	25.39	25.55
0.123	0.115	2.47×10^1	24.62	24.78
0.197	0.189	8.74×10^1	24.09	24.25
0.34	0.33	1.19×10^3	23.39	23.55
0.58	0.57	7.30×10^3	22.63	22.79
0.765	0.75	1.97×10^4	22.13	22.29
0.95	0.94	4.28×10^4	21.79	21.95

[a] $K^f_{(MeOH)_2SO_4^{2-}} = 5.0 \times 10^3$, $K^f_{(MeOH)_4SO_4^{2-}} = 5.4 \times 10^4$, $K^f_{MeOH \cdot HSO_4^-} = 0$; 3.63×10^{-4} M Et_4NHSO_4, 2.01×10^{-3} M $(Et_4N)_2SO_4$, $f = 0.77$.

pa_H values: $K^f_{HR \cdot H_2SO_4} = 0$ (HR = *p*-bromophenol), $K^f_{H_2O \cdot H^2SO_4} = 1.0 \times 10^1$, $K^f_{2H_2O \cdot H_2SO_4} = 2.1 \times 10^1$, $K^f_{HR \cdot HSO_4^-} = 2.7 \times 10^1$, and $K^f_{H_2O \cdot HSO_4^-} = 0$. The pa_H calculations, with the aid of eq 1, were described in a previous publication.[3]

Effect of *p*-Bromophenol, Water, and Methanol on pa_H of Bisulfate–Sulfate Mixtures. From the potentiometric pa_H data in tetraethylammonium bisulfate–sulfate mixtures in the presence of *p*-bromophenol, water, or methanol entered in Tables III, IV, and V, plots of log V *vs.* log [HR] were constructed. A slope of 4 was found when [HR] ≥ 0.04, 0.10, and 0.70 M with *p*-bromophenol, water, and methanol, respectively, indicative of the presence of the heteroconjugate $(HR)_4SO_4^{2-}$. At lower equilibrium concentrations of HR the slopes of the log V *vs.* log [HR] plot varied from 2 to 4. It was found that these plots could adequately be described over the entire concentration range of HR in terms of formation of the diheteroconjugate $(HR)_2SO_4^{2-}$ in addition to $(HR)_4SO_4^{2-}$.

Spectrophotometric Section. Heteroconjugation Constants of *p*-Bromophenol with 3,5-Dinitrophenolate Ion. In a previous spectrophotometric study,[4] *p*-bromophenol (HR), up to an analytical concentration of 3.4×10^{-4} M, was found to form a 1:1 conjugate with the 3,5-dinitrophenolate ion (DNP^-), the formation constant being 1.3×10^3. In the present study, the concentration of HR was extended to 1.25 M; clear evidence of an equilibrium between $HR \cdot DNP^-$ and $(HR)_2DNP^-$ was indicated by a second isosbestic point at 360 mμ in the spectra of tetraethylammonium 3,5-dinitrophenolate in the presence of HR (Figure 1). From the spectra in Figure 1 the spectra of the $HR \cdot DNP^-$ and $(HR)_2DNP^-$ forms have been deduced, and the formation constant $K^f_{(HR)_2DNP^-} = [(HR)_2DNP^-]/[HR][HR \cdot DNP^-]$ was calculated as described below.

To calculate the spectrum of $HR \cdot DNP^-$ in mixtures of DNP^- and HR, those spectra are considered that pass through the isosbestic point at 453 mμ, where the concentration of $(HR)_2DNP^-$ can be neglected as compared to that of $HR \cdot DNP^-$ (curves 1–6 in Figure 1). The equilibrium concentration of DNP^- is calculated, knowing the analytical concentrations C_{HR} and C_{DNP^-} and the value of the formation constant $K^f_{HR \cdot DNP^-}$. Knowing $[DNP^-]$, the absorbance of DNP^- at a given wavelength is calculated from the absorbance index of DNP^-[5,9] and this absorbance of DNP^- subtracted from the experimental absorbance to obtain that due to $HR \cdot DNP^-$. As an example, consider curve 5 in Figure 1 at 400 mμ: $C_{HR} = 1.56 \times 10^{-3}$ M, $C_{DNP^-} = 1.23 \times 10^{-4}$ M, $K^f_{HR \cdot DNP^-} = 1.3 \times 10^3 = x/(1.23 \times 10^{-4} - x)(1.56 \times 10^{-3} - x)$, or $x = [HR \cdot DNP^-] = 0.80 \times 10^{-4}$, $[DNP^-] = 0.43 \times 10^{-4}$, and $[HR] = 1.48 \times 10^{-3}$ M. The absorbance due to 0.43×10^{-4} M DNP^- at 400 mμ is 0.060, the absorbance index being 1.4×10^3. Since the experimental absorbance is 0.246 (curve 5), the difference due to the absorbance of 0.80×10^{-4} M $HR \cdot DNP^-$ is 0.186. Hence the absorbance of 1.23×10^{-4} M $HR \cdot DNP^-$ at 400 mμ is 0.286.

The formation constant $K^f_{(HR)_2DNP^-}$ is then found from the absorbances at wavelengths where the absorbance by DNP^- can be neglected as compared to those of $HR \cdot DNP^-$ and $(HR)_2DNP^-$ and where the absorbance of $(HR)_2DNP^-$ is very small. This is the situation in curves 8–12 in Figure 1 at 440 mμ. Neglecting the absorbance of $(HR)_2DNP^-$ at this wavelength, $[HR \cdot DNP^-]$ is readily calculated from the observed absorbance, knowing the absorbance index at 440 mμ. The value of $[(HR)_2DNP^-]$ is then found from the relation $C_{DNP^-} = [HR \cdot DNP^-] + [(HR)_2DNP^-]$ and the forma-

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(9) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *Anal. Chem.*, **39**, 315 (1967).

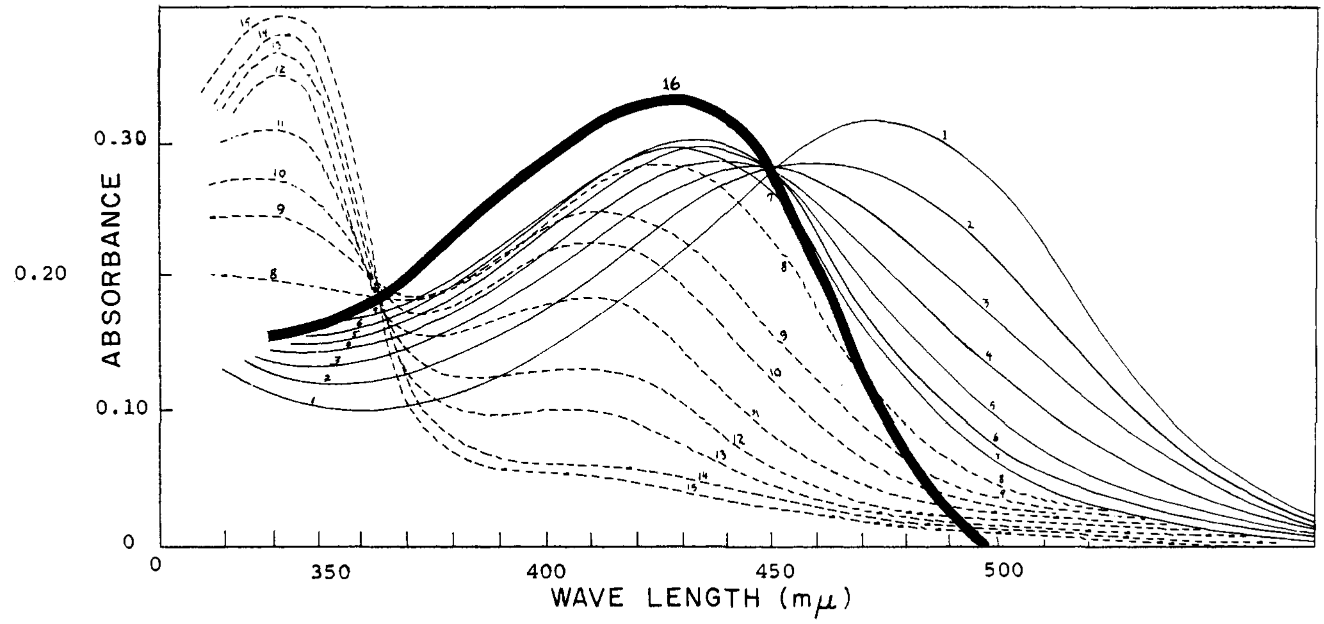

Figure 1. Spectra of 1.23×10^{-4} M tetraethylammonium 3,5-dinitrophenolate in the presence of *p*-bromophenol: (1) no *p*-bromophenol added; (2) in the presence of 1.95×10^{-4} M *p*-bromophenol; (3) 3.90×10^{-4} M HR; (4) 7.80×10^{-4} M HR; (5) 1.56×10^{-3} M HR; (6), 3.12×10^{-3} M HR; (7) 4.68×10^{-3} M HR; (8) 1.74×10^{-2} M HR; (9) 4.92×10^{-2} M HR; (10) 9.10×10^{-2} M HR; (11) 1.70×10^{-1} M HR; (12) 3.38×10^{-1} M HR; (13) 5.75×10^{-1} M HR; (14) 1.25×10^{-1} M HR; (15 and 16) calculated spectra of 1.23×10^{-4} M $(HR)_2DNP^-$ and $HR \cdot DNP^-$, respectively.

tion constant $K^f{}_{(HR)_2DNP^-}$ evaluated, taking the equilibrium concentration of HR equal to the analytical concentration, since it is in large excess. As an example, consider curve 10 in Figure 1, where $C_{HR} = 9.10 \times 10^{-2}$ M. The observed absorbance at 440 mμ is 0.154, from which $[HR \cdot DNP^-] = 6.10 \times 10^{-5}$ since $a_{HR \cdot DNP^-}$ at 440 mμ is 2.52×10^3. $[(HR)_2DNP]^-$ is then equal to $1.23 \times 10^{-4} - 0.61 \times 10^{-4} = 0.62 \times 10^{-4}$ M. Hence $K^f{}_{(HR)_2DNP^-} = 6.2 \times 10^{-5}/(9.10 \times 10^{-2})(6.1 \times 10^{-5}) = 1.1 \times 10^1$.

The absorbances at 440 mμ have been corrected for that of $(HR)_2DNP^-$ in the following way. Considering the spectra in Figure 1 in such large excess of HR that $(HR)_2DNP^-$ is the predominant species (*i.e.*, curve 14), the concentration of $HR \cdot DNP^-$ is calculated using the preliminary value of $K^f{}_{(HR)_2DNP^-}$. From the value of the absorbance index of $HR \cdot DNP^-$ previously found, the absorbance of $HR \cdot DNP^-$ is calculated and is subtracted from the observed absorbance to obtain that due to $(HR)_2DNP^-$ and, in turn, the absorbance index of $(HR)_2DNP^-$. This procedure carried out at various wavelengths yielded the calculated spectrum of $(HR)_2DNP^-$ shown in Figure 1. The correction for the absorbance of $(HR)_2DNP^-$ at 440 mμ is then applied to the spectra in curves 8–12 in Figure 1; the corrected absorbance is used in the calculation of $[HR \cdot DNP^-]$ and in turn $[(HR)_2DNP^-]$; then finally $K^f{}_{(HR)_2DNP^-}$ is calculated. As an example, in curve 14 in Figure 1, $C_{HR} = 1.25$ M, $C_{DNP^-} = 1.23 \times 10^{-4}$ M, $K^f{}_{(HR)_2DNP^-} = 1.1 \times 10^1$ (first approximation), $[HR \cdot DNP^-] = (1.23 \times 10^{-4})/[1 + (1.1 \times 10^1)(1.25)] = 0.08 \times 10^{-4}$ M. The absorbance due to 0.08×10^{-4} M $HR \cdot DNP^-$ is equal to 0.020, the absorbance index being 2.54×10^3. The absorbance of 1.16×10^{-4} M $(HR)_2DNP^-$ is then equal to 0.039 (observed value) − 0.020 = 0.019, from which an absorbance index of 1.6×10^2 for $(HR)_2DNP^-$ at 440 mμ is derived. Next, curve 10 is corrected for the absorbance of $(HR)_2DNP^-$ at 440 mμ. Since $[(HR)_2DNP^-] = 0.62 \times 10^{-4}$ M, the absorbance at 440 mμ due to $(HR)_2DNP^-$ is $(1.6 \times 10^2)(0.62 \times 10^{-4}) = 0.010$; therefore the corrected absorbance at 440 mμ is equal to 0.154 − 0.010 = 0.144, from which a value of $[HR \cdot DNP^-]$ equal to 5.60×10^{-5} M is found.

As a check on the corrected value of $K^f{}_{HR \cdot DNP^-}$ the sum of the absorbances of $HR \cdot DNP^-$ and $(HR)_2DNP^-$ were calculated at 345 mμ and compared with the experimental values at concentrations of HR when $[DNP^-]$ is negligible (curves 8–12 in Figure 1), knowing the absorbance indices of $HR \cdot DNP^-$ and $(HR)_2DNP^-$ at this wavelength. Calculated spectra of $HR \cdot DNP^-$ and of $(HR)_2DNP^-$ are included in Figure 1. The absorbance indices of the various species at 345, 400, 428, 440, and 473 mμ are as follows: DNP^-, 0.82×10^3, 1.4×10^3, 1.87×10^3, 2.06×10^3, and 7.6×10^3 (max), respectively; $HR \cdot DNP^-$, 1.34×10^3, 2.64×10^3, 2.77×10^3 (max), 2.54×10^3, and 0.82×10^3, respectively; and $(HR)_2DNP^-$), 3.3×10^3 (max), 2.0×10^2, and 1.6×10^2 at 345, 400, and 440 mμ, respectively. Absorption spectra of 1.23×10^{-4} M tetraethylammonium 3,5-dinitrophenolate in the presence of 0–1.25 M *p*-bromophenol are also presented in Figure 1.

From the spectrophotometric data at 440 mμ in 1.23×10^{-4} M tetraethylammonium 3,5-dinitrophenolate solutions containing from 1.7×10^{-2} to 3.4×10^{-1} M *p*-bromophenol in Table VI, a value of 1.5×10^1 for $K^f{}_{(HR)_2DNP^-}$ was obtained. Calculated and experimental absorbances at 345 mμ in the above solutions are listed in Table VII.

Heteroconjugation of *p*-Bromophenol (HR) with Sulfate. In the absence of HR, 3.6×10^{-3} M tetraethylammonium sulfate was found to have no effect on the spectrum of 2.4×10^{-3} M tetraethylammonium 3,5-dinitrophenolate, indicating no measurable interaction between DNP^- and sulfate ions.

Table VI. Calculation of $K^f_{(HR)_2DNP^-}$ from Spectrophotometric Data at 440 mμ[a]

Curve no. in Fig 1	C_{HR}, $M \times 10^2$	A_{440}	$[HR\cdot DNP^-]$, $M \times 10^5$	$[(HR)_2DNP^-]$, $M \times 10^5$	$K^f_{(HR)_2DNP^-} \times 10^{-1}$
8	1.74	0.249	9.8	2.5	1.5
9	4.92	0.185	7.3	5.0	1.4
10	9.10	0.142	5.6	6.7	1.3
11	17.0	0.099	3.9	8.4	1.3
12	33.8	0.040	1.6	10.7	2.0
					Av 1.5×10^1

[a] $C_{DNP^-} = 1.23 \times 10^{-4}$ M.

Table VII. Calculation of Absorbances of Mixtures of $HR\cdot DNP^-$ and $(HR)_2DNP^-$ at 345 mμ

Curve no. in Fig 1	C_{HR}, $M \times 10^2$	$[HR\cdot DNP^-]$[a] calcd, $M \times 10^4$	$[(HR)_2DNP^-]$[a] calcd, $M \times 10^4$	$A_{HR\cdot DNP^-}$ calcd	$A_{(HR)_2DNP^-}$ calcd	Total absorbance	
						A_{calcd}	A_{obsd}
8	1.74	0.97	0.25	0.131	0.081	0.212	0.199
9	4.92	0.73	0.50	0.098	0.161	0.259	0.247
10	9.10	0.56	0.67	0.075	0.217	0.292	0.275
11	17.0	0.39	0.84	0.052	0.271	0.323	0.310
12	33.8	0.16	1.07	0.021	0.347	0.368	0.351

[a] $K^f_{(HR)_2DNP} = 1.5 \times 10^1$ taken (see text).

Table VIII. Heteroconjugation of HR in Mixtures of Tetraethylammonium 3,5-Dinitrophenolate and *p*-Bromophenol (HR) in the Presence of Tetraethylammonium Sulfate[a]

$C_{SO_4^{2-}}$, $M \times 10^3$	C_{DNP^-}, $M \times 10^3$	A_{560}	$[DNP^-]$, $M \times 10^3$	$[HR\cdot DNP^-]$, $M \times 10^3$	[HR], $M \times 10^3$	$[SO_4^{2-}]$, $M \times 10^4$	$[(HR)_2SO_4^{2-}]$, $M \times 10^3$	$[(HR)_4SO_4^{2-}]$, $M \times 10^4$	C_{HR}, $M \times 10^3$	
									Calcd	Exptl
3.59	2.37	0.538	2.37	0	0	35.9	0	0	0	0
3.48	2.30	0.463	2.04	0.33	0.125	26.5	0.83	0.00084	2.1	3.4
3.45	2.27	0.412	1.91	0.46	0.19	20.5	1.40	0.031	3.5	4.7
3.41	2.22	0.344	1.52	0.85	0.43	6.9	2.71	0.34	6.7	6.0
3.38	2.20	0.293	1.29	1.08	0.64	3.6	2.95	0.79	7.9	6.9
3.34	2.18	0.232	1.03	1.34	1.01	1.5	3.00	1.98	9.1	8.1
3.26	2.15	0.195	0.86	1.51	1.36	0.76	2.80	3.33	9.6	9.0
3.22	2.11	0.153	0.68	1.69	1.94	0.34	2.57	6.25	11.2	10.2
1.80	2.37	0.547	2.37	0	0	18.0	0	0	0	0
1.73	2.32	0.448	1.94	0.43	0.17	11.2	0.61	0.012	1.9	2.4
1.71	2.30	0.374	1.62	0.75	0.35	4.8	1.22	0.10	3.6	3.4
1.69	2.28	0.303	1.31	1.06	0.62	1.9	1.46	0.37	4.7	4.4
1.68	2.27	0.257	1.11	1.26	0.87	1.0	1.51	0.74	5.4	5.0
1.67	2.25	0.217	0.94	1.43	1.17	0.54	1.49	1.32	6.1	5.7
1.66	2.22	0.187	0.81	1.56	1.48	0.33	1.43	2.0	6.7	6.3
1.65	2.19	0.151	0.66	1.72	2.03	0.16	1.29	3.46	7.7	7.2
1.64	2.17	0.125	0.52	1.83	2.61	0.084	1.13	5.0	8.7	8.1
1.62	2.14	0.101	0.44	1.93	3.39	0.04	0.93	6.9	9.9	9.3

[a] $K^f_2 = 2 \times 10^7$, $K^f_4 = 1.3 \times 10^{12}$, $K_{HR\cdot DNP^-} = 1.3 \times 10^3$, $[(HR)_2DNP^-] = 0$.

In mixtures of tetraethylammonium 3,5-dinitrophenolate and HR in the presence of tetraethylammonium sulfate, values of [HR] were calculated from the absorbance of the red uncomplexed DNP^- ion at 560 mμ and using the expression for $K^f_{HR\cdot DNP^-}$. Reasonable agreement between the experimental and calculated values of C_{HR} in Table VIII was obtained by considering the formation of only two heteroconjugates, $(HR)_2SO_4^{2-}$ and $(HR)_4SO_4^{2-}$ and taking K^f_2 and K^f_4 equal to 2×10^4 and 1.3×10^{12} (potentiometric value), respectively. These values of K^f_2 and K^f_4 were introduced into eq 5 ($n = 2, 4$) along with the above values of [HR] to calculate m, and, in turn, C_{HR}. An example of the calculation of C_{HR} is given below. $C_{SO_4^{2-}} = 1.69 \times 10^{-3}$ *M*, $C_{DNP^-} = 2.28 \times 10^{-3}$ *M*, with an absorbance of 0.303 observed, corresponding to $[DNP^-] = 1.31 \times 10^{-3}$ *M*. Hence $[HR] = (C_{DNP^-} - [DNP^-])/K^f_{HR\cdot DNP^-}[DNP^-] = (2.28 \times 10^{-3} - 1.31 \times 10^{-3})/(1.3 \times 10^3)(1.31 \times 10^{-3}) = 6.2 \times 10^{-4}$ *M*. Substituting the value of [HR] into eq 5, we have $(6.2 \times 10^{-4})^2 \cdot (2 \times 10^7)[m - 2(1.69 \times 10^{-3})] + (6.2 \times 10^{-4})^4(1.3 \times 10^{12})[m - 4(1.69 \times 10^{-3})] + m = 0$, or $m = 3.04 \times 10^{-3}$ from which $C_{HR} = 3.04 \times 10^{-3} + 0.62 \times 10^{-3} + 1.06 \times 10^{-3} = 4.73 \times 10^{-3}$ *M*.

Experimental and calculated values of C_{HR} in solutions of 2.37×10^{-3} *M* tetraethylammonium 3,5-dinitrophenolate and 1.8×10^{-3} and 3.6×10^{-3} *M* tetraethylammonium sulfate are tabulated in Table VIII. Evidently the constants derived from the pa_H data (Table III) account satisfactorily for the concentrations of the various species calculated from the spectrophotometric measurements.

Discussion

Sulfuric acid as well as methanesulfonic acid[6] form monohydrates, while in addition the former forms a dihydrate, one water molecule coordinated to each -OH group. The formation constant of the monohydrate is about the same for both acids, being 1.0×10^1 and 1.4×10^1 for sulfuric and methanesulfonic acids, respectively, even though sulfuric acid as a monobasic acid is a stronger acid by 2.2 p*K* units than methanesulfonic acid ($pK^d_{MeSO_3H} = 10.0$,[10] $pK^d_{H_2SO_4} = 7.8$[2]). No indication has been obtained that the weak hydrogen bond *acceptor*, *p*-bromophenol, associates with sulfuric acid. On the other hand, *p*-bromophenol,

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[10] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 87, 4428 (1965).

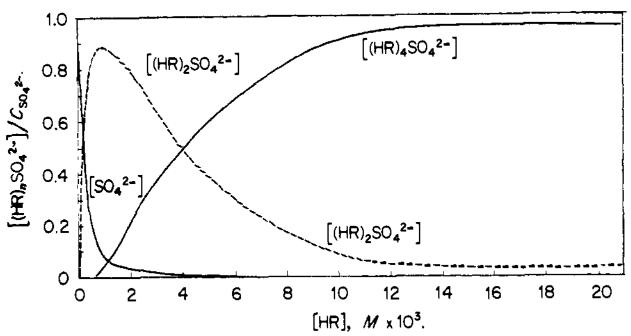

Figure 2. Plot of calculated values of $[(HR)_nSO_4^{2-}]/C_{SO_4^{-2}}$ *vs.* [HR]. HR = *p*-bromophenol.

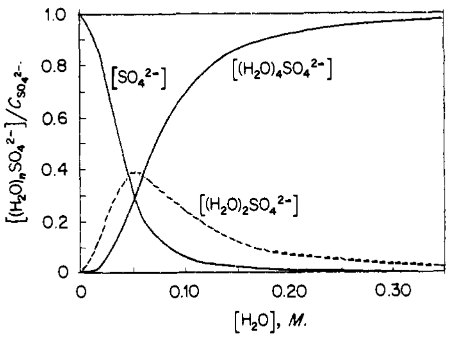

Figure 3. Plot of calculated values of $[(H_2O)_nSO_4^{2-}]/C_{SO_4^{2-}}$ *vs.* $[H_2O]$.

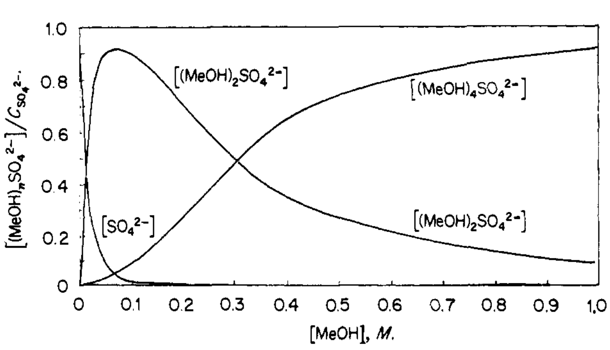

Figure 4. Plot of calculated values of $[(MeOH)_nSO_4^{2-}]/C_{SO_4^{2-}}$ *vs.* [MeOH].

being a much stronger hydrogen bond donor than water, conjugates the bisulfate ion while water does not. Evidently the phenolic –OH group coordinates with the $\geqslant S^{2+}–O^-$ group rather than with the –OH group of the bisulfate ion.

It is interesting to note that addition of water to an equimolar (5×10^{-3} *M*) mixture of sulfuric acid and tetraethylammonium bisulfate increases the pa_H considerably (Table II). For example, the presence of 0.4 *M* water increases the pa_H by 0.9 unit, as a result of its association with sulfuric acid. On the other hand, addition of *p*-bromophenol to a mixture which has a tenfold excess of sulfuric acid over bisulfate results in a pronounced decrease in the pa_H (Table I), because it associates only with the anion. In mixtures containing a fair excess of sulfuric acid over bisulfate *p*-bromophenol hardly decreases the pa_H (Table I), since the homoconjugation of bisulfate with sulfuric acid is much more extensive than its heteroconjugation with *p*-bromophenol. The heteroconjugate of bisulfate with *p*-bromophenol is considerably less stable than those of HR with 3,5-dinitrophenolate and benzoate. The following formation constants were reported previously: $K^f_{HR \cdot DNB^-} = 3.6 \times 10^2$,[7] $K^f_{(HR)_2DNB^-} = 3.9 \times 10^3$,[7] $K^f_{HR \cdot Bz^-} \sim 0$,[4] $K^f_{HR_2Bz^-} = 3.3 \times 10^4$,[4] as compared to $K^f_{HR \cdot HSO_4^-} = 2.7 \times 10^1$. As was to be expected the bisulfate ion, being a Brønsted acid, is a much weaker hydrogen bond acceptor than the two aromatic anions. No indication has been obtained that the bisulfate ion conjugates with more than one molecule of HR.

The electronic structure of the sulfonate ion as deduced from the rate of hydrolysis of potassium 1-ethoxycarbonylethane-2-sulfonate[11] is thought to consist of a double positive charge on the sulfur atom and three equivalent negatively charged oxygen atoms. An analogous electronic structure of the sulfate ion has been postulated.[12] In accord with the postulated structure of the sulfate ion, a stable heteroconjugate species, $(HR)_4SO_4^{2-}$, presumably possessing one HR molecule hydrogen-bonded to each of the oxygen atoms of the sulfate is formed at sufficiently high concentration of *p*-bromophenol, water, and methanol. The stability constant, K_4, decreases in this order, *i.e.*, with decreasing hydrogen bond donating power.

Analysis of the data in Tables IV and V shows evidence of the presence of a stable diheteroconjugate, $(HR)_2SO_4^{2-}$, at small and intermediate concentration of water or methanol. The spectrophotometric data in Table VIII clearly indicate *p*-bromophenol also forms a diheteroconjugate at low concentrations of HR. The formation of fairly stable diheteroconjugates may be attributed to a possible contribution of a structure of the sulfate ion having two dative S→O bonds and two $S–O^-$ bonds, with an HR molecule hydrogen bonded to each of the latter. The experimental results cannot be interpreted on the basis of additional formation of mono- and triheteroconjugates, although presence of these forms as minor constituents cannot be excluded.

In Figures 2–4 are plotted the fractions of sulfate ion present in its simple form and in the forms of the di- and tetraheteroconjugates at given equilibrium concentrations of *p*-bromophenol [HR], water, and methanol. From Figure 2 it is evident that at an equilibrium concentration of 0.01 *M* *p*-bromophenol practically all sulfate is present as $(HR)_4SO_4^{2-}$.

Quite generally the effect of hydrogen bond donors is small in systems of uncharged acids with their anions when the acid is in large excess over salt (see Table I). This is not true in systems of a univalent anion acid with its divalent anion, like bisulfate-sulfate (Table III). The reason is that here the homoconjugation is small ($K^f_{H(SO_4)_2^{3-}} = 3 \times 10^1$).

The results presented in this paper are of direct analytical importance. Titrations of acids in AN are usually carried out with standard solutions of a tetraalkylammonium hydroxide. Such a solution always contains methanol or a higher alcohol. Moreover, water is formed during the neutralization. Water and alcohols decrease the pa_H of sulfate and its mixtures with bisulfate (see Tables III–V). For example, the presence of 0.1 *M* water or methanol decreases the pa_H

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(11) R. P. Bell and G. A. Wright, *Trans. Faraday Soc.*, 57, 1377 (1961).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 243.

of a mixture 2.01×10^{-3} *M* in sulfate and 3.63×10^{-4} *M* bisulfate by about 1.5 units. With stronger hydrogen bond donors, like *p*-bromophenol, the effect is much greater. This phenol is such a weak acid that it cannot react with sulfate by proton transfer. Here the acid–base reaction is due practically entirely to hydrogen bonding. The presence of 0.1 *M* *p*-bromophenol in the above mixture decreases the pa_H by 7.5 units. Hence the shape of the neutralization curve of bisulfate with tetraalkylammonium hydroxide is affected by water and alcohol and to a much greater extent by *p*-bromophenol or phenol. In the presence of a carboxylic acid proton transfer with the sulfate ion occurs. However, heteroconjugation will be the most important reaction. It can be predicted that a carboxylic acid not only greatly affects the neutralization curve of a bisulfate but that the sulfate formed will greatly affect the neutralization curve (or the effective strengths) of the carboxylic acid. At present we are studying the systems bisulfate–sulfate–acetic acid and sulfate–acetic acid–acetate. The results will be communicated in a subsequent paper.

Equilibrium Measurements in the Molybdenum–Carbon–Hydrogen System

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Abstract: Equilibrium values for the reaction of molybdenum with methane to form Mo_2C and hydrogen have been determined over the temperature range 450–650°. The results yield values for the free energy of formation of Mo_2C in good agreement with those reported by Gleiser and Chipman. The data previously reported by Browning and Emmett are in error, apparently because of contamination of the equilibrating system with a small amount of molybdenum oxide.

The equilibrium for the reaction

$$2Mo + CH_4 \rightleftharpoons Mo_2C + 2H_2 \qquad (1)$$

was measured by Browning and Emmett[1] on a sample of Mo_2C prepared by carbiding molybdenum with carbon monoxide. The resulting data are shown by curve 2 of Figure 2. A few years ago Gleiser and Chipman[2] pointed out that the data of Browning and Emmett lead to an impossibly high entropy change (about 26 eu) for the reaction

$$2Mo + C \rightleftharpoons Mo_2C \qquad (2)$$

They also showed that equilibrium measurements in a system containing Mo_2C, MoO_2, CO, and CO_2 in the temperature range 1200–1300° gave values for the free energy of formation of Mo_2C involving a small reasonable entropy change. In view of these facts we decided to redetermine the equilibrium for reaction 1.

The most obvious source of error in the measurements of Browning and Emmett was the possible contamination of the carbide sample with molybdenum oxide with the resulting inclusion of some water vapor, carbon dioxide, or carbon monoxide in the fraction called methane in the analysis of the final methane–hydrogen mixture. Accordingly, it was decided to prepare the Mo_2C by carbiding with methane under such partial pressure conditions as to exclude the formation of free carbon and also with the complete absence of any contamination due to oxygen.

Experimental Section

The equipment used is drawn schematically in Figure 1. It was so arranged that a methane–hydrogen mixture of known composition could be circulated over a sample of Mo or a mixture of Mo_2C and Mo. The molybdenum was obtained by reducing in hydrogen a sample of molybdenum trioxide powder (Baker "Analyzed" reagent). The powdered trioxide was supported on a quartz sinter in a quartz reactor. A quartz rod loosely fitting in a hole bored through the sinter was flattened on top to close off the hole during the reduction of the oxide and the equilibration of the metal–metal carbide system with the circulating methane–hydrogen mixture. In the bottom of the rod at a point below the furnace was imbedded a piece of soft iron. It was then possible, by use of a magnet, without interrupting the gas circulation to shake down samples of the molybdenum and its various compounds into a Pyrex capillary for X-ray examination. The temperature in the reactor could be closely controlled by a platinum resistance wire feeding a thyratron unit. Temperature was measured by a Pt—Pt-10% Rh thermocouple unit. It was controlled during a run to an accuracy of ±1°.

A four-way stopcock made it possible to close off the reactor from the exterior system. The latter consisted of the related circulating pump, inlet valves for hydrogen and methane, a vacuum line, manometer, trap, and a system of stopcocks which made it possible to flush a small constant volume of the gas mixture being circulated to a thermal conductivity cell without interrupting the circulation. The separation of the reactor and the exterior system in this way enabled one to mix methane and hydrogen in any desired concentration before bringing the gas mixture into contact with the molybdenum sample.

The hydrogen gas was diffused through a palladium-silver alloy thimble before entering the apparatus; the methane was taken directly from a tank (Matheson CP quality).

A liquid nitrogen trap was introduced into the circulating system to remove any traces of water vapor or carbon dioxide that might arise from traces of oxygen present as impurities. If any carbon monoxide were present it would be removed by reactions with the metallic molybdenum to form carbon dioxide and molybdenum carbide. The continual freezing out of any carbon dioxide would assure the absence of carbon monoxide since the reaction of carbon monoxide and Mo is known to be rapid over the temperature range

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[1] L. C. Browning and P. H. Emmett, *J. Amer. Chem. Soc.*, **74**, 4773 (1952).

[2] M. Gleiser and J. Chipman, *J. Phys. Chem.*, **66**, 1539 (1962).