

cathodic current-time curves follow neither the original Ilkovic equation nor the modified equation of the type of eq. 1 with a plus sign replacing the minus sign, even for the first drop, and hence in the absence of the depletion effect.¹⁵ Our results also do not agree with those of Kůta and Smoler, who, from the "average" slope of $\log i - \log t$ plots conclude that in the absence of the "Spüleffekt" the Koutecky equation holds. However, this equation (see eq. 1) does not predict a straight line for such a plot. On the other hand, at slow dropping rates we found, in accordance with the Ilkovic equation, a straight-line relation. For example, the current-time curve corresponding to curve 5 of Figure 9 gave a linear $\log i - \log t$ plot within the time range of 0.7 to 15.9 sec., with a slope of 0.177. This value compares favorably with the value of $1/6$ (0.167) given in the simple Ilkovic equation.

It is of interest to note that the capillaries used to obtain curves 5 and 7 in Figure 8 had practically the same drop time (15.3 and 15.9 sec.), but their m values were considerably different (0.742 and 1.943 mg. sec.⁻¹). These results clearly indicate that, for dropping amalgam oxidations, it is the flow rate m and not the drop time t that is responsible for the deviation from the Ilkovic equation. Thus, there is little doubt that the greater deviation at higher flow rates is due to the "Spüleffekt."

The diffusion coefficient of copper in mercury calculated from the value of $i/Cm^{2/3}t^{1/6} = 3.45$, where i is the maximal current at the moment the drop falls, at

(15) J. M. Los and D. W. Murray, "Advances in Polarography," ref. 1, Vol. 2, p. 408.

$h = 40$ cm. (curve 5 in Figure 9) by using the original Ilkovic equation, is equal to 5.95×10^{-6} cm.² sec.⁻¹. Furman and Cooper³ reported the value of 1.06×10^{-5} cm.² sec.⁻², but this value must be too high because they used capillaries with short drop times (1.4–5.0 sec.) and large m values (1.1–1.4 mg. sec.⁻¹) and did not consider the "Spüleffekt." The diffusion coefficient calculated from the value of $i_d(\text{av.})/Cm^{2/3}t^{1/6} = 3.55$ reported by Schupp, Youness, and Watters⁶ by using the Ilkovic equation becomes equal to 8.55×10^{-6} cm.² sec.⁻¹. Apparently this value is also too high because the characteristics of their capillary ($m = 0.636$ mg. sec.⁻¹, $t = 11.10$ sec.) do not assure complete absence of the "Spüleffekt." The diffusion coefficient of cadmium in mercury calculated from $i/Cm^{2/3}t^{1/6} = 4.45$ at $h = 40$ cm. (curve 5 in Figure 8) is equal to 9.80×10^{-6} cm.² sec.⁻¹ as compared to the value 1.68×10^{-5} cm.² sec.⁻¹ reported by von Stackelberg and Toome⁸ and 1.520×10^{-5} cm.² sec.⁻¹ chosen by Furman and Cooper.³

In conclusion it may be stated that the extent of stirring decreases with decreasing m , decreasing amalgam concentration, increasing supporting electrolyte concentration, and presence of a suitable surface-active substance. For studies of anodic dropping amalgam electrode reactions, it is recommended to eliminate stirring effects by using a capillary with an m value not greater than 0.5 mg. sec.⁻¹, by working with very dilute amalgams, and by adding supporting electrolyte in large concentration and a suitable surfactant which does not affect adversely the rate of the electrode reaction.

The Thermodynamics of Ionization of Cyanocarbon Acids

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The relationship between acid strength and heats and entropies of ionization in water of five cyanocarbon acids whose pK covers the range 11 to -6 has been investigated. The heats of ionization of four of the acids [malononitrile, *p*-(tricyanovinyl)phenyldicyanomethane, methyl dicyanoacetate, and bis(tricyanovinyl)amine] were measured in the present work. The first one was determined calorimetrically and the others from a spectroscopic study of the temperature dependence of the protonation equilibria in sulfuric acid solutions. The latter two acids required acidity function techniques. A method was used for the determination of ΔH° that is based on a simple relation between the heat of ionization in a given acid solution and the temperature derivative of the indicator ratio. This heat is extrapolated by the overlap technique to estimate ΔH° . The entropies were calculated from ΔH° and pK . The temperature dependence of the pK of *p*-nitroaniline has also been determined by spectroscopic methods and used along with activity coefficient data to extrapolate ΔH for *p*-(tricyanovinyl)phenyldicyanomethane to dilute solution. It was found that most of the variation of pK with

structure for the cyanocarbon acids comes through variation of ΔH° . The entropies are rather small in absolute value ranging from ~ -7 to ~ 0 e.u. The correlation with the entropies of other acid ionizations is also discussed.

Introduction

One of the more interesting aspects of the study of the relationship between molecular structure and equilibria is the relation between structure and acid strength. According to a simplified picture, variations in acid strength from variations in structure should result from variations of the vapor phase ionic dissociation free energy of the H-A bond (or stability of the anion) and variations in the difference in free energy of hydration of the anion and the neutral molecule. The bond dissociation (or anion stabilization) free energy should be primarily an enthalpy effect, the changes in intramolecular entropy being rather small. According to the Born model, in aqueous solution, the hydration

Table I. Log of Indicator Ratio (R_I) in Sulfuric Acid at Various Temperatures and Concentrations^a

Wt. % sulfuric acid	Log R_I						
	Temp., °C.						
	-5	1	10	25	40	50	60
<i>p</i> -(Tricyanovinyl)phenyldicyanomethane							
1.03		0.440	0.441	0.434	0.435	0.437	
1.67	0.288	0.287	0.286	0.310	0.282	0.287	
2.44	0.096	0.120	0.126	0.131	0.129	0.128	
2.92	0.058	0.056	0.055	0.047	0.052	0.058	
4.18	-0.075	-0.070	-0.083	-0.080	-0.080	-0.070	
5.07	-0.255	-0.252	-0.237	-0.242	-0.240	-0.240	
6.30	-0.370	-0.365	-0.359	-0.346	-0.373	-0.370	
8.50	-0.618	-0.600	-0.615	-0.608	-0.602	-0.608	
9.50	-0.690	-0.689	-0.684	-0.681	-0.690	-0.680	
10.54	-0.830	-0.825	-0.827	-0.823	-0.826	-0.825	
11.20	-0.869	-0.869	-0.873	-0.870	-0.860	-0.869	
12.00	-0.960	-0.956	-0.942	-0.932	-0.926	-0.910	
14.00	-1.160	-1.140	-1.122	-1.102	-1.085	-1.060	
18.00	-1.53	-1.48	-1.47	-1.43	-1.39	-1.36	
21.40	-1.79	-1.76	-1.69	-1.67	-1.64	-1.62	
25.80	-2.19	-2.13	-2.11	-2.07	-1.99	-1.98	
Methyl Dicyanoacetate							
30.1	1.05		1.00	0.92	0.87		
34.1	0.62		0.57	0.51	0.46		
39.2	0.16		0.122	0.011	0.043		
43.7	-0.344		-0.354	-0.387	-0.424		
48.5	-0.821		-0.826	-0.826	-0.822		
52.9	-1.30		-1.316	-1.282	-1.280		
57.5	-1.77		-1.84	-1.84	-1.82		
61.7	-2.23		-2.38	-2.42	-2.39		
Bis(tricyanovinyl)amine							
52.9	1.762		1.69	1.512	1.512	1.402	1.132
57.5	1.262		1.208	1.142	1.048	0.98	0.77
61.7	0.863		0.79	0.684	0.64	0.566	0.456
67.2	0.162		0.132	0.104	0.052	0.03	0.034
71.9	-0.43		-0.44	-0.427	-0.446	-0.455	-0.49
75.2	-0.87		-0.873	-0.874			
<i>p</i> -Nitroaniline							
	1	10	20	25	30	40	50
1.67	-0.62	-0.51	-0.41	-0.38	-0.33	-0.24	-0.16
2.92	-0.91	-0.80	-0.71	-0.67	-0.63	-0.53	-0.46
4.18	-1.04	-0.92	-0.84	-0.79	-0.75	-0.67	-0.58
6.30	-1.31	-1.18	-1.08	-1.04	-1.02	-0.93	-0.85
9.5	-1.57	-1.48	-1.39	-1.34	-1.29	-1.22	-1.14
10.54	-1.66	-1.57	-1.49	-1.44	-1.40	-1.32	-1.25
11.20	-1.68	-1.60	-1.52	-1.49	-1.46	-1.35	-1.28
14.00	-1.96	-1.87	-1.80	-1.77	-1.74	-1.65	-1.57

^a $R_I = C_A/C_{HA}$ or C_B/C_{BH^+} .

enthalpy contribution should be negative and rather small (0 to -2 kcal.) for ions with radii of physical interest ($>2/3$ Å). The entropy contribution should be negative and lie between 0 and -25 e.u. Thus over-all changes in acidity (pK) resulting from structure changes such as changes in resonance stabilization of anions should show up as an enthalpy effect. Changes in the size of the ion (and also the charge distribution) will result in changes in entropy, although the range available is definitely limited.

Experimentally, it is found that there is often no clear-cut correlation between pK and enthalpy. In addition, the Born model is known to fail in detailed application to acid ionizations.¹ However, most of the data available for comparison between compounds of similar structure (such as the carboxylic acids) do not cover a very wide range in acid strength. Furthermore, reliable thermodynamic measurements on the

dissociation of the stronger acids such as the mineral acids are difficult or impossible to make. The availability of cyanocarbon acids²⁻⁴ presents the opportunity of examining this correlation over a much wider range of acid strength than previously available. In the present work we have determined the heats and entropies of ionization of several cyanocarbon acids covering a range in ionization constant of seventeen powers of ten (10^{-11} to 10^6). Such a study should lead to greater insight into the gross features of acid dissociations.

Malononitrile and hydrocyanic acid were chosen as representative of weak cyanocarbon acids, and the three acids upon which the H_- scale is based³ [*p*-(tricyanovinyl)phenyldicyanomethane (Williams Blue), methyl dicyanoacetate, and bis(tricyanovinyl)amine] as stronger ones. The heat of ionization of malononitrile was measured calorimetrically and literature

(1) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 15.

(2) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(3) R. H. Boyd, *ibid.*, **83**, 4288 (1961).

(4) R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

Table II. Log of Activity Coefficient in Aqueous Sulfuric Acid Solutions at Various Temperatures

Wt. % sulfuric acid	Temp., °C.					
	1	10	25	35	40	50
Anilinium Pentacyanopropenide						
0.38	-0.09 ^a	-0.106 ^a	-0.122 ^a		-0.14 ^a	
4.18	-0.17	-0.18	-0.190		-0.201	
6.30	-0.168	-0.170	-0.175		-0.184	
9.50	-0.125	-0.140	-0.145		-0.151	
10.54	-0.115	-0.125	-0.130		-0.141	
11.20	-0.100	-0.106	-0.144		-0.123	
14.00	-0.074	-0.082	-0.090		-0.101	
<i>p</i> -Chloro- <i>N</i> -(tricyanovinyl)aniline ^b						
0.38	0.0	0.0	0.0	0.0	0.0	
1.67	0.018	0.018	0.107	0.017	0.017	
4.18	0.043	0.042	0.042	0.041	0.040	
6.30	0.062	0.058	0.054	0.053	0.052	
9.50	0.086	0.082	0.077	0.073	0.071	
10.54	0.096	0.090	0.084	0.080	0.078	
11.20	0.101	0.096	0.090	0.85	0.092	
14.00	0.124	0.117	0.108	0.102	0.100	
2,6-Dichloro-4-nitroaniline						
0.0	0.0	0.0	0.0		0.0	0.0
1.67	0.008	0.008	0.007		0.007	0.006
4.18	0.470	0.036	0.024		0.018	0.008
6.30	0.050	0.044	0.030		0.020	0.008
9.50	0.062	0.053	0.037		0.021	0.009
10.54	0.069	0.057	0.040		0.022	0.009
11.20	0.070	0.059	0.041		0.022	0.010
14.00	0.080	0.068	0.050		0.023	0.011

^a Calculated from the Debye-Hückel theory; the activity coefficient is the mean ionic activity coefficient, f_{\pm} . ^b Compound ionizes in pure water.

data are available for HCN.⁵ For the two strongest acids it was necessary to study the temperature dependence of the protonation in sulfuric acid solutions using acidity function techniques. We are well aware of the possible difficulties in extending these techniques to determining heats and entropies, but we believe we have used a method that indicates to some extent the likely uncertainty.

Experimental Methods

1. *Indicator Studies in Concentrated Sulfuric Acid.* *p*-(Tricyanovinyl)phenyldicyanomethane (Williams Blue),⁶ methyl dicyanoacetate, and bis(tricyanovinyl)amine were studied in aqueous sulfuric acid solutions by indicator methods previously described.^{3,4} A Beckman Model DU spectrophotometer was used for quantitative optical density measurements. The spectrophotometer has a specially constructed thermostated cell holder in which water from a thermostat can be circulated through the walls of the cell holder. The temperature in the optical cell was measured by means of a mercury thermometer at each thermostat setting. Values of the indicator ratio for each of these indicators at a number of temperatures and acid concentrations are shown in Table I.

Indicator ratios were also measured for *p*-nitroaniline in sulfuric acid (Table I) and hydrochloric acid (Table III). The results agree reasonably well with previous data⁷ at 25° and with a study over a more limited temperature range,^{8a} but not with the data of Gelbstein,

(5) J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, **2**, 337 (1963).

(6) J. K. Williams, *J. Am. Chem. Soc.*, **84**, 3478 (1962).

(7) K. W. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(8) (a) A. I. Biggs, *ibid.*, 2572 (1961); (b) A. I. Gelbstein, G. G. Sheglova, and M. I. Temkin, *Zh. Neorgan. Khim.*, **1**, 282, 506 (1956); *Dokl. Akad. Nauk SSSR*, **107**, 108 (1956).

et al., as a function of temperature.^{8b} A more complete study of the temperature dependence of ionization of Hammett indicators would be worthwhile.

2. *Heat of Ionization of Malononitrile.* Pearson and Dillon⁹ have measured the *pK* of this acid by potentiometric titration, and we have repeated their work and found good agreement with their results. We determined the heat of ionization *via* a calorimetric measurement of the heat of neutralization. Approximately 0.1 *M* solutions of malononitrile were partially neutralized (one-third, one-half, and two-thirds neutralized) in a stoppered 1-l. dewar flask (600 ml. of solution) by breaking an ampoule containing 1 *N* sodium hydroxide. The contents of the flask were magnetically stirred. The temperature change was measured by means of a platinum resistance thermometer and a Mueller G-1 bridge. The calorimeter was calibrated by measuring the heat of neutralization of hydrochloric acid solution with sodium hydroxide. It is estimated that the accuracy of the method is $\sim \pm 1\%$.

It was found that apart from a slow temperature change, apparently due to a hydrolysis reaction, the temperature change due to neutralization was zero within experimental error. This places the heat of ionization equal to that of water at 13.4 kcal./mole.¹⁰

The malononitrile was purchased from Eastman Organic Chemicals Co. and purified by fractional distillation at 5 mm. It was stored at 0° until ready for use. Solutions of known concentration were made by weighing the malononitrile.

(9) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(10) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C.

3. *Activity Coefficients Used in the Determination of the pK of Williams Blue.* Mean activity coefficients of anilinium pentacyanopropenide, *p*-chloro-*N*-(tricyanovinyl)aniline, and 2,6-dichloro-4-nitroaniline were measured at a number of temperatures and acid concentrations by previously described methods.¹¹ They are tabulated in Table II.

Treatment of Results

1. *Heats of Ionization of Indicators Studied in Sulfuric Acid Solutions.* Standard-state heats of ionization can, in principle, be determined by first determining *pK* by the conventional overlap technique¹² and plotting¹³ *pK* vs. $1/T$. However, we prefer another method which we think displays the likely reliability of the method more satisfactorily. It is shown in the Appendix that the heat of ionization of an indicator in a given acid solution may be determined from the temperature variation of $\log R_I$ (where R_I is the indicator ratio = C_A/C_{HA}) as

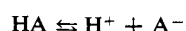
$$\Delta H(\text{ionization}) = -2.303R \frac{\partial \log R_I}{\partial (1/T)} \quad (1)$$

To determine ΔH° , ΔH may be plotted against acid concentration for a series of indicators and the overlap technique attempted on ΔH directly. The method has the advantage of carrying out the critical operation, *i.e.*, the extrapolation vs. acid concentration in the final step where it may be displayed more readily. Values of ΔH calculated from the slopes of $\log R_I$ plotted vs. $1/T$ for the three indicators studied here are plotted against sulfuric acid concentration in Figure 1. Just as in *pK* determinations, when the overlap method is applied to ΔH° determinations, all values are relative to a reference compound whose ΔH° must be determined by an independent method. This question is taken up in the next section.

It is to be expected that owing to the inaccuracies in determining a temperature derivative it will be more difficult to give an adequate test to the overlap technique applied to ΔH than for *pK*. It may be seen in Figure 1 that the curves are not far from parallel and that at least for the cyanocarbon acids studied here a useful estimate of ΔH° can be made. However, it is not difficult to imagine serious errors arising when a number of $\partial \log R_I / \partial (1/T)$ curves that are not quite parallel are overlapped.

2. *Determination of the pK and ΔH° of Williams Blue.* The H^- acidity function previously reported³ was based on the *pK* of Williams Blue. This was determined by extrapolation of the log of the equilibrium quotient against acid concentration,⁴ but since the extrapolation is not linear it is not an entirely satisfactory method. The following method was used in the present work to determine *pK* as a function of temperature to provide a reference for the ΔH° determinations above.

If we compare the unknown *pK_A* for



$$pK_A = -\log a_{H^+} - \log R_A - \log f_A/f_{HA} \quad (2)$$

(11) R. H. Boyd, *J. Am. Chem. Soc.*, **85**, 1555 (1963).

(12) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(13) E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.*, **86**, 1564 (1964).

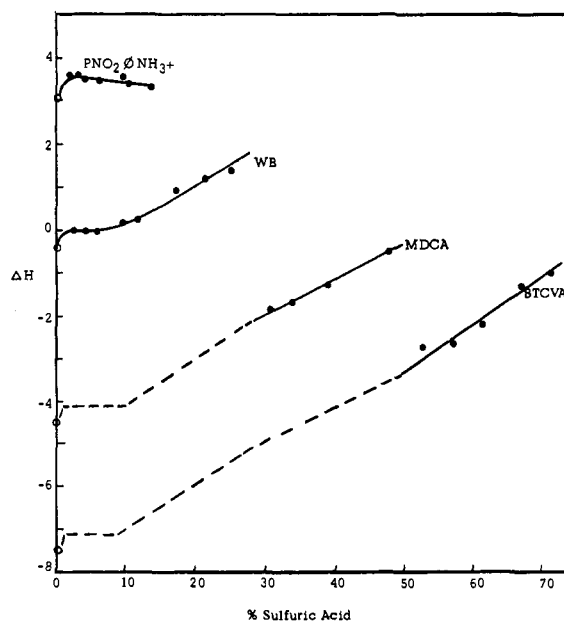
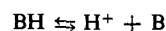


Figure 1. Heat of ionization plotted against acid concentration (25°). Dashed portions represent extrapolation by overlap technique. WB, Williams Blue (*p*-(tricyanovinyl)phenyldicyanomethane); MDCA, methylidyacyanoacetate; BTCVA, bis(tricyanovinyl)amine. Open circles are ΔH° values.

where $R_A = C_A/C_{HA}$, with a known *pK_B* for



$$pK_B = -\log a_{H^+} - \log R_B - \log f_B/f_{BH^+} \quad (3)$$

we find at the same concentration

$$pK_A = pK_B - \log R_A + \log R_B - \log f_{BH^+}f_{A^-} + \log f_{HA}f_B \quad (4)$$

We have taken *p*-nitroaniline as *B* and determined its *pK* at a number of temperatures by a linear extrapolation¹² of the equilibrium quotient vs. acid concentration in hydrochloric acid (see Table III). The $\log R_A$ and $\log R_B$ values are from Table I. For the activity coefficients in eq. 4, we have used data measured here on model compounds. $f_{\pm}^2(BH^+A^-)$ was taken as that for anilinium pentacyanopropenide, f_B from 2,6-dichloro-4-nitroaniline, and f_{HA} from *p*-chloro-*N*-(tricyanovinyl)aniline (Table II).

The *pK_A* values thus calculated are listed in Table IV. The calculated *pK_A* is seen to be substantially the same at each concentration indicating the method works satisfactorily. There is a small temperature variation in *pK* leading to $\Delta H^\circ = -0.4 \pm 0.3$ kcal. The *pK* arrived at here differs appreciably from the previous value^{3,4} (0.75 vs. 0.60), but it does not seem worthwhile to make changes in the H^- scale³ which is based on this *pK*.

It is of interest to compare the ΔH values at low concentration of sulfuric acid for Williams Blue and *p*-nitroaniline (Figure 1) with the ΔH° values (Tables III and V). Since the second ionization of sulfuric acid is important in the low concentration region, \bar{L}_{H^+} could be quite appreciable. ΔH° is less than ΔH by 0.6 and ~ 0.4 kcal./mole in these two cases, a rather small difference considering the substantial heat of dilution of sulfuric acid in this region. How-

Table III. $-\log$ Equilibrium Quotient [$-(\log C_B/C_{BH^+} + \log C_{H^+})$] of *p*-Nitroaniline in Aqueous Hydrochloric Acid Solutions at Various Temperatures^a

HCl, <i>M</i>	Temp., °C.							
	1	10	20	25	30	40	50	60
0.167	1.225	1.14	1.055	1.029	0.991	0.928	0.861	0.800
0.244	1.24	1.163	1.077	1.044	1.006	0.939	0.873	0.816
0.416	1.269	1.201	1.115	1.073	1.041	0.977	0.909	0.851
0.610	1.131	1.234	1.146	1.110	1.074	1.001	0.936	0.876
0.834	1.351	1.365	1.188	1.149	1.112	1.044	0.974	0.916
1.017	1.369	1.291	1.217	1.179	1.143	1.073	1.01	0.954
1.250	1.412	1.331	1.256	1.213	1.179	1.115	1.044	0.992
1.67	1.453	1.371	1.300	1.272	1.245	1.171	1.107	1.049
	p <i>K</i>							
	1.194	1.120	1.028	1.002	0.962	0.900	0.830	0.768

^a $\Delta H^\circ = 3.0$ kcal./mole, $\Delta S^\circ = 5.4$ e.u., and $\Delta C_p^\circ = 0$.

Table IV. Calculated p*K* of *p*-(Tricyanovinyl)phenyldicyanomethane at Various Concentrations and Temperatures

Wt. % sulfuric acid	p <i>K</i>			
	Temp., °C.			
	1	10	25	40
4.18	0.65	0.72	0.74	0.77
6.30	0.70	0.74	0.74	0.78
9.50	0.71	0.74	0.75	0.76
10.54	0.75	0.77	0.77	0.79
11.20	0.75	0.76	0.74	0.76
Average	0.71 ± 0.04	0.75 ± 0.02	0.75 ± 0.01	0.77 ± 0.01

Table V. Thermodynamics of Ionization of Cyanocarbon Acids^a at 25°

	p <i>K</i>	ΔG° , kcal./mole	ΔH° , kcal./mole	$-T\Delta S^\circ$, kcal./ mole	ΔS° , e.u.
Malononitrile	11.20 ^b	15.28 ± 0.15	13.4 ± 0.3	1.9	-6.4 ± 1.5
HCN ^c	9.21	12.57 ± 0.01	10.4 ± 0.2	2.2	-7.4 ± 0.6
<i>p</i> -(Tricyanovinyl)phenyldicyanomethane	0.75	1.02 ± 0.05	-0.4 ± 0.3	1.4	-4.7 ± 1.0
Methyl dicyanoacetate	-2.8	-3.80 ± 0.1	-4.5 ± 1	0.7	-2 ± 3
Bis(tricyanovinyl)amine	-5.8	-7.9 ± 0.2	-7.5 ± 1.5	-0.4	1 ± 5

^a The uncertainties for the compounds measured in this work are estimates for ΔG° and ΔH° , and for ΔS° they are the uncertainties resulting from the first two. ^b Our value is in agreement with that in ref. 9. ^c From ref. 5.

ever, if one considers C_{H^+} in eq. A-4 to be the species concentration of hydrogen ions, we can suppose f_{H^+} to be similar to that in other strong acids. Thus in

$$\bar{L}_{H^+} = -RT^2 \left[\frac{\partial \ln C_{H^+}}{\partial T} + \frac{\partial \ln f_{H^+}}{\partial T} \right]$$

the derivative of the activity coefficient will contribute a few tenths of a kilocalorie to \bar{L}_{H^+} . C_{H^+} will change with temperature due to the second ionization equilibrium of sulfuric acid. A rough estimate of the magnitude of $\partial \ln C_{H^+}/\partial T$ can be made from the data of Young, *et al.*¹⁴ It would appear to contribute upwards of 1 kcal. to \bar{L}_{H^+} in the region 0–14% H_2SO_4 . Thus \bar{L}_{H^+} is of the right sign and approximate magnitude to account for the differences between ΔH° and ΔH as

$$\Delta H^\circ \cong \Delta H - \bar{L}_{H^+}$$

Discussion

1. Ionization of Cyanocarbon Acids. A complete tabulation of the thermodynamics of ionization of the cyanocarbon acids is given in Table V. ΔH° and $T\Delta S^\circ$ are plotted against p*K* in Figure 2. It may be seen that

there is a good correlation between ΔH° and p*K* and that the major contribution to the variation of p*K* is from the enthalpy. This is of course consistent with the idea discussed in the Introduction that large variations in acidity should be due primarily to variations in resonance stabilization of the anion and the effect of cyano-group electronegativity on the C–H bond strength. There also may be a slight trend in ΔS° towards larger (less negative) values as the acidity increases. This is consistent with the notion that increased anion-charge delocalization (and also size of the anion) attendant with increased acidity results in decreased solvent orientation. This trend, however, is very slight and it is somewhat surprising that malononitrile has such a small entropy loss on ionization. It would imply that there is considerable charge delocalization to the cyano groups. A Hückel molecular orbital calculation¹⁵ (for what it is worth) confirms this. It predicts about 0.4 of the negative charge on the central carbon and about 0.3 on each cyano group. The presence of large dipole moments on the cyano groups (~4 D.) should have a solvent-ordering effect. To a first approximation it should cancel between the neu-

(14) T. F. Young, L. F. Maranville, and H. S. Smith in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959.

(15) Using parameters previously adopted for calculations on cyanocarbon anions: R. H. Boyd, *J. Phys. Chem.*, **65**, 1834 (1961).

Table VI. Thermodynamics of Acid Dissociations at 25°

$HA \rightleftharpoons A^- + H^+$						
Acid	pK	ΔG° , kcal./ mole	ΔH° , kcal./ mole	$-T\Delta S^\circ$, kcal./ mole	ΔS° , e.u.	Ref.
Carboxylic acids						
Formic	3.75	5.12	-0.02	5.14	-17.3	a, b
Acetic	4.76	6.49	-0.09	6.58	-22.1	a
Propionic	4.87	6.65	-0.16	6.81	-22.8	a
Butyric	4.82	6.57	-0.69	7.28	-24.4	a
Chloroacetic	2.87	3.91	-1.09	5.00	-16.8	c
Cyanoacetic	2.47	3.37	-0.83	4.20	-14.1	d
Fluoroacetic	2.58	3.53	-1.38	4.91	-16.5	c
Benzoic	4.20	5.74	0.09	5.65	-18.9	e
Cyanocarbon acids						
Malononitrile	11.20	15.28	13.4	1.9	-6.4	f, g
Hydrocyanic acid	9.21	12.57	10.4	2.2	-7.4	h
p-(Tricyanovinyl)phenyldicyanomethane	0.75	1.02	-0.4	1.4	-4.7	f
Methyl dicyanoacetate	-2.8	-3.80	-4.5	0.7	-2	f
Bis(tricyanovinyl)amine	-5.8	-7.95	-7.5	-0.4	1	f
Nitric acid	-1.3	-1.8	-3.5	1.7	-5	l, j
Boric acid (K_1)	9.24	12.60	3.33	9.27	-31.1	a
Phosphoric acid (K_1)	2.15	2.94	-1.82	4.76	-16.0	k
Phenols						
Phenol	10.02	13.67	5.66	8.01	-26.9	l
o-Cresol	10.33	14.10	5.73	8.37	-28.1	l
m-Cresol	10.10	13.78	5.52	8.26	-27.7	l
p-Cresol	10.28	14.02	5.50	8.52	-28.6	l
p-Nitrophenol	7.15	9.75	4.73	5.07	-17.0	m
Hydrofluoric acid	3.17	4.33	-3.05	7.38	-24.8	n

^a See ref. 1, p. 667. ^b H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934). ^c D. J. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955). ^d F. S. Feates and D. J. G. Ives, *ibid.*, 2798 (1956). ^e R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, Inc., New York, N. Y., 1959, Appendix 12.1. ^f This work. ^g See ref. 9. ^h See ref. 14. ⁱ G. C. Hood, O. Redlich, and C. A. Reilly, *J. Chem. Phys.*, **22**, 2067 (1954). ^j See ref. 14. ^k R. Bates, *J. Res. Natl. Bur. Std.*, **47**, 127 (1951). ^l D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58**, 480 (1962). ^m G. F. Allen, R. A. Robinson, and V. E. Bower, *J. Phys. Chem.*, **66**, 171 (1962). ⁿ H. H. Broene and T. DeVries, *J. Am. Chem. Soc.*, **69**, 1644 (1947).

tral molecule and the anion, although in HCN the cancellation might not be as effective.⁵

It might be supposed that for a large anion with delocalized charge the absolute entropies of HA and A^- would be rather similar and thus ΔS° for $HA \rightleftharpoons H^+ + A^-$ would approach the absolute entropy of the hydrogen ion. Since a number of estimates of the latter¹⁶⁻²¹ lie between -5 and -2 e.u., this would appear to be the case here.

2. *Comparison with Other Acid Ionizations.* Table VI gives thermodynamic data for a number of acid ionizations in which the protonated form is uncharged. It may be seen that the entropy of ionization of cyanocarbon acids is greater (less negative) than most acids of this type. This is probably the result of lessened ion-solvent interaction due to greater charge delocalization. Nitric acid, a relatively strong acid, presumably has a highly delocalized charge distribution, and it also has a relatively small entropy loss on ionization. The carboxylic acids with the charge localized on the acid oxygens have a greater entropy loss. The phenols with the charge largely localized on one oxygen have an even larger entropy loss, although the presence of a delocalizing group (such as p-nitro) causes a significant decrease in the entropy

loss. Hydrofluoric acid has a large entropy loss, but not as large as it might be (considering the small size of the fluoride ion) if there were not some ordering due to the polar HF molecule.

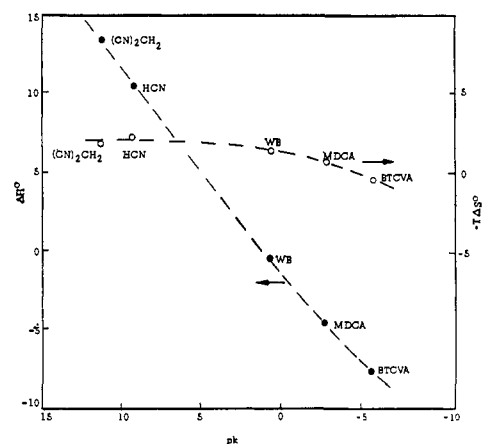


Figure 2. Correlation of ΔH° and $T\Delta S^\circ$ for ionization of cyanocarbon acids with pK (25°). Filled circles are ΔH° and are plotted on left-hand ordinate; open circles are $-T\Delta S^\circ$ and are plotted on right-hand ordinate (see Figure 1 for abbreviations).

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Appendix

The Relation between the Temperature Derivative of the Indicator Ratio and Heat of Ionization. The

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(17) K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

(18) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, *ibid.*, **72**, 4411 (1950).

(19) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

(20) K. J. Laidler, *Can. J. Chem.*, **34**, 1107 (1956).

(21) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

equilibrium constant for the ionization $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ is

$$K = \frac{C_{\text{H}^+} C_{\text{A}^-} f_{\text{H}^+} f_{\text{A}^-}}{C_{\text{HA}} f_{\text{HA}}} \quad (\text{A-1})$$

where C represents molar concentration and f represents the activity coefficient relative to a reference state of infinite dilution in pure water. The heat of ionization in the standard state (hypothetical ideal molar solutions of HA , A^- , and H^+) appropriate to this reference state is

$$\Delta H^\circ = RT^2 \frac{\partial \ln K}{\partial T} = RT^2 \frac{\partial \ln R_I}{\partial T} + \frac{\partial \ln f_{\text{H}^+} C_{\text{H}^+}}{\partial T} + \frac{\partial \ln (f_{\text{A}^-} / f_{\text{HA}})}{\partial T} \quad (\text{A-2})$$

where R_I is the indicator ratio $C_{\text{A}^-} / C_{\text{HA}}$. Under the usual indicator conditions H^+ is in great excess, and A^- and HA are very dilute. Thus H^+ does not change appreciably with changes in equilibrium position and $f_{\text{H}^+} C_{\text{H}^+}$ depends only on the properties of the acid solvent. In addition, f_{A^-} and f_{HA} are independent of C_{A^-} and C_{HA} . The changes in chemical potentials of the reactants and products on transfer from the standard states to the acid solution at concentrations C_{H^+} , C_{A^-} , and C_{HA} are

$$\begin{aligned} \mu_{\text{H}^+} - \mu_{\text{H}^+}^\circ &= RT \ln f_{\text{H}^+} C_{\text{H}^+} \\ \mu_{\text{A}^-} - \mu_{\text{A}^-}^\circ &= RT \ln f_{\text{A}^-} C_{\text{A}^-} \\ \mu_{\text{HA}} - \mu_{\text{HA}}^\circ &= RT \ln f_{\text{HA}} C_{\text{HA}} \end{aligned} \quad (\text{A-3})$$

The partial molar heats of transfer from the standard states to the acid solution at unit concentrations of A^- and HA and hydrogen ion at C_{H^+} are

$$\begin{aligned} \bar{L}_{\text{H}^+} &= -RT^2 \frac{\partial \ln f_{\text{H}^+} C_{\text{H}^+}}{\partial T} \\ \bar{L}_{\text{A}^-} &= -RT^2 \frac{\partial \ln f_{\text{A}^-}}{\partial T} \end{aligned} \quad (\text{A-4})$$

$$\bar{L}_{\text{HA}} = RT^2 \frac{\partial \ln f_{\text{HA}}}{\partial T}$$

Under the indicator conditions stated above, the temperature derivatives appearing in eq. A-4 are the same as in eq. A-2. Substituting eq. A-4 in A-2 we find

$$RT^2 \frac{\partial \ln R_I}{\partial T} = \Delta H^\circ + \bar{L}_{\text{H}^+} + \bar{L}_{\text{A}^-} - \bar{L}_{\text{HA}} \quad (\text{A-5})$$

but the right-hand side of (A-5) is just the heat of ionization in an acid solution at C_{H^+} which we call ΔH . Thus

$$\Delta H = RT^2 \frac{\partial \ln R_I}{\partial T} \quad (\text{A-6})$$

The right-hand side of eq. A-5 extrapolates to $\Delta H^\circ - RT^2 \partial \ln C_{\text{H}^+} / \partial T$ in very dilute solution which differs slightly from ΔH° owing to thermal expansion.

The overlap method¹² for $\text{p}K$ determination which utilizes

$$\text{p}K_1 - \text{p}K_2 = \log R_1 - \log R_2 \quad (\text{A-7})$$

is based on cancellation of the appropriate activity coefficient ratios. If this cancellation occurs over a range in temperature, then differentiation of (A-7) with respect to temperature results in

$$\Delta H_1^\circ - \Delta H_2^\circ = RT^2 \left[\frac{\partial \ln R_1}{\partial T} - \frac{\partial \ln R_2}{\partial T} \right] \quad (\text{A-8})$$

and the use of (A-6) leads to

$$\Delta H_1^\circ - \Delta H_2^\circ = \Delta H_1 - \Delta H_2 \quad (\text{A-9})$$

Thus the overlap technique may be attempted on the temperature derivatives of $\log R_I$ to determine heats of ionization.