

and no chloride dioxide was detected even in 0.5 M $HClO_4$. The chromium(II)–chlorine dioxide reaction (see Table VII) is probably slightly faster than the chromium(II)–chlorite reaction. The data of Emmenegger and Gordon³⁶ indicate that the reaction between 10^{-3} M chlorine and 10^{-3} M chlorine(III) in 0.5 M perchloric acid to produce chlorine dioxide has a half-life greater than 6×10^{-2} sec. The corresponding second-order reaction between similar concentrations of chromium(II) and chlorine(III) is at least 10 times faster. The maximum chlorine concentration in the chromium(II)–chlorite reaction is surely several orders of magnitude less than the above estimate. Therefore, no significant production of chlorate ion or chlorine dioxide would be expected in the presence of such a potent reducing agent as chromium(II).

A similar calculation for the apparent half-lives in the hypochlorite–chromium(II) and the hypochlorite–chloride reaction³⁷ (to form chlorine) indicates that the former is at least 10 times faster than the latter in the absence of initial chloride ion. These considerations also rule out the possibility of chlorine(I)–chloride ion reaction in any of the other reactions studied. In the absence of chlorine–chlorine interactions, a comparison of the stoichiometry of the various chlorine oxidant–chromium(II) reactions is justified.

In light of this interpretation, a mechanism which consists of step-by-step reductions of chlorate ion with the other chlorine species as intermediates can prob-

(36) G. Gordon and F. Emmenegger, to be published.

(37) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).

ably be discarded on the basis of marked inconsistencies with the stoichiometric data. Conversely, a mechanism which involves chromium(II)–chlorine oxidant intermediates is consistent with the stoichiometric data if it is assumed that the stoichiometry of subsequent chromium(II) reductions with these intermediates yields different ratios of products than those resulting from the reaction of the uncomplexed oxidizing agent and chromium(II). Further, there does seem to be direct evidence of a complex of this type in the chlorine dioxide–chromium(II) reaction.

In conclusion, the observed rates for the ClO_2 , ClO_2^- , OCl^- , and Cl_2 reactions with chromium(II) are several orders of magnitude greater than the corresponding chlorate reaction. However, all seem to occur *via* an inner-sphere mechanism since considerable chlorine and oxygen³⁸ from the oxidizing agent is transferred to the chromium(III) products. The mechanism of these reactions probably involves the formation of chromium(II)–oxidizing agent intermediates which are unstable with respect to further reduction by the excess chromium(II) present. The reactions do not seem to be complicated by other chlorine reactions or interactions.

Acknowledgments.—The authors wish to express their appreciation to the Atomic Energy Commission for its generous support of this research through Grant No. AT-(40-1)-2858 and to Mr. Bassam Z. Shakhshiri for his help and suggestions on the tracer experiments.

(38) At least in the chlorate–chromium(II) reaction.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH

Thermodynamics of Proton Dissociation in Dilute Aqueous Solution. IV. pK , ΔH° , and ΔS° Values for Proton Ionization from $[1,12-B_{12}H_{10}(COOH)_2]^{2-}$ ^{1a}

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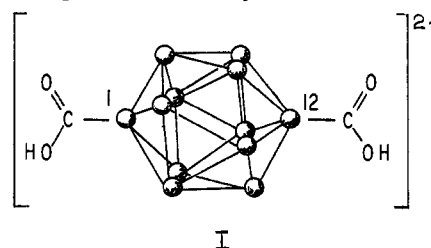
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Consecutive pK , ΔH° , and ΔS° values valid at 25° and $\mu = 0$ are reported for proton ionization from the $[1,12-B_{12}H_{10}(COOH)_2]^{2-}$ ion in aqueous solution. The ΔH° values were determined calorimetrically. The thermodynamic data indicate that the ionic charges on the B_{12} cage are localized in the vicinity of the carboxyl groups and that the second proton ionization is largely unaffected by the increased negative charge resulting from ionization of the first proton.

Introduction

Values of ΔH° and ΔS° for proton ionization from several carboxylic acids of general type $(RR'R'')C-COOH$ have been reported.² A major conclusion in both studies was that for the acids involved pK was a linear function of ΔS° ; ΔH° being approximately constant at -0.4 ± 1.0 kcal/mole. A recently re-

ported acid,³ $[1,12-B_{12}H_{10}(COOH)_2]^{2-}$ (H_2A^{2-} , I), provides an example of a carboxylic acid in which boron



(1) (a) Supported by National Institutes of Health Grant No. RG-9430-04. (b) National Defense Education Act Pre-doctoral Fellow, 1962–1965.

(2) (a) L. D. Hansen, Ph.D. Dissertation, Brigham Young University; (b) L. Ebersson and I. Wadso, *Acta Chem. Scand.*, **17**, 1552 (1963).

(3) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

rather than carbon is attached to the carboxyl group. It is of interest, therefore, to study this acid to determine whether it fits the previously found relationship between pK and ΔS° .

Further, because of the fixed distance between the carboxyl groups, this acid should provide useful data on electrostatic effects involved in the ionization of dicarboxylic acids. Thermodynamic data for proton ionization from I could be useful in elucidating the microscopic dielectric constant, D , of the acid environment⁴ and the change of D with temperature.

This system is also of interest because the ΔH° and ΔS° values for proton ionization should give insight concerning the distribution of charges in the boron-hydrogen cage.

There are presented in the present study pK , ΔH° , and ΔS° values valid at 25° and ionic strength $\mu = 0$ for stepwise proton ionization from $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$.

Experimental Section

Materials.—A stock $\text{B}_{12}\text{H}_{10}(\text{COOH})_2^{2-}$ solution was prepared from $\text{B}_{12}\text{H}_{10}(\text{CO})_2^{3-}$ by reaction with H_2O ; *i.e.*, $\text{B}_{12}\text{H}_{10}(\text{CO})_2 + 2\text{H}_2\text{O} \rightarrow \text{B}_{12}\text{H}_{10}(\text{COOH})_2^{2-} + 2\text{H}^+$. The solution was standardized by titration of the two strongly acidic protons formed in the reaction of the dicarbonyl with water. Reagent grade NaOH (Baker Analyzed) and HCl (E. I. du Pont de Nemours and Co.) were used in the pH and thermometric titrations, respectively. The pH meter was standardized with a phosphate buffer (pH 6.865) prepared using reagents obtained from the National Bureau of Standards. All solutions were prepared, stored, and used under a pure nitrogen atmosphere.

pH Determinations.⁶—Solutions of $\text{H}_2[\text{B}_{12}\text{H}_{10}(\text{COOH})_2]$ were titrated with 0.3067 *F* NaOH under a nitrogen atmosphere and at least twelve pH measurements were made covering the region of proton ionization using a Beckman Research pH meter (Model 1019) equipped with Beckman glass and saturated calomel electrodes. A total of five runs were made at four different total acid concentrations, covering a μ range of 0.0045 to 0.045.

Heat Determinations.⁵—The ΔH° values were determined using a precision thermometric titration calorimeter.⁷ The procedure was to titrate $\text{Na}_4[\text{B}_{12}\text{H}_{10}(\text{COO})_2]$ solutions with HCl. Four titrations were made at a μ value of approximately 0.05. The ΔH values obtained were assumed to be valid for a standard state of an ideal 1 *M* solution and are referred to as ΔH° values.

pK Calculations.⁸—Appropriate combination of Q_1 and Q_2 with the charge and mass balance relationships for the system results in eq 1

$$\bar{n} = \frac{(1 - \bar{n})[\text{H}^+]}{Q_2} + \frac{(2 - \bar{n})[\text{H}^+]^2}{Q_1 Q_2} \quad (1)$$

where

$$\bar{n} = \text{bound H}^+/\text{total A} =$$

$$\frac{4[\text{A}_{\text{total}}] - [\text{Na}^+] - [\text{H}^+] + [\text{OH}^-]}{[\text{A}_{\text{total}}]}$$

(4) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(5) The authors gratefully acknowledge a gift from Dr. Earl L. Meutteries, E. I. du Pont de Nemours Co., Wilmington, Del., of 10 g of this material which was used without further purification.

(6) Material supplementary to this paper in the form of (a) IBM FORTRAN IV computer programs, (b) pH and thermometric titration data, and (c) pQ , pK , and ΔH results has been deposited as Document No. 8817 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$3.75 for the photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

$$Q_1 = \frac{[\text{H}^+][\text{HA}^{3-}]}{[\text{H}_2\text{A}^{2-}]}; \quad Q_2 = \frac{[\text{H}^+][\text{A}^{4-}]}{[\text{HA}^{3-}]}$$

In order that only concentration quantities appear in (1), the pH and ion product of water were converted to the corresponding concentration quantities at each experimental point with activity coefficient, γ , values calculated using eq 2, where the several terms have their usual significance.⁸

$$\log \gamma = \frac{-AZ^2\sqrt{u}}{1 + B\bar{a}\sqrt{u}} \quad (2)$$

The procedure previously used in this laboratory to calculate equilibrium constants from the experimental data involved the simultaneous solution of appropriate sets of equations of the form given in (1) to obtain concentration quotients which were then converted to thermodynamic equilibrium constants using appropriate γ corrections. In order to solve these sets of equations for the several Q values it must be assumed that each Q_n value is the same in the first \bar{n} region ($\bar{n} \sim 0.5$) as it is in each of the other \bar{n} regions ($\bar{n} \sim 1.5, 2.5$, etc.). This condition will be met only if (1) the Q values are not a function of μ , or (2) the effect on Q_n of changing μ throughout the run is negligible. In the present study, however, neither condition was true. The Q_n values are a function of μ , and due to the high charges on the anions being produced in the solution during a run (*e.g.*, $\text{B}_{12}\text{H}_{10}(\text{COO})_2^{4-}$) μ changed by more than a factor of 2 in going from one \bar{n} region to the other in some of the runs.

To overcome this problem the thermodynamic dissociation constants K_1 and K_2 were substituted for Q_1 and Q_2 in eq 1 to give eq 3

$$\bar{n} = \frac{(1 - \bar{n})[\text{H}^+]\gamma_2}{K_2} + \frac{(2 - \bar{n})[\text{H}^+]^2\gamma_{12}}{K_1 K_2} \quad (3)$$

where

$$\gamma_2 = \frac{\gamma_{\text{H}^+}\gamma_{\text{A}^{4-}}}{\gamma_{\text{HA}^{3-}}}; \quad \gamma_{12} = \frac{\gamma_{\text{H}^+}\gamma_{\text{A}^{4-}}}{\gamma_{\text{H}_2\text{A}^{2-}}}$$

$K_2 = \gamma_2 Q_2$ and $K_1 K_2 = \gamma_{12} Q_1 Q_2$. The only unknowns in eq 3 are K_1 and K_2 and these are constant at *all* experimental points in a run.

It was necessary to know μ in order to calculate the values of γ_1 and γ_2 used in eq 3. However, K_1 and K_2 must be known in order to calculate the species distribution required to obtain μ . Therefore, a series of successive approximations was made until successive γ values agreed within 0.1%. Values of \bar{a} from 4.5 to 9.3 Å were tried in eq 2 to calculate γ values for use in eq 3. The best "fit" of the data was obtained when $\bar{a} = 8$ Å was used, and this \bar{a} value was subsequently used for all calculations.

The pK_n values calculated using eq 3 showed much greater precision through a run than did those obtained using eq 1 with subsequent correction of the Q_n values. This would be expected since nonvalid assumptions were made in the simultaneous solution of equations of the form of eq 1. It was also observed that the pK_n values calculated using eq 3 were slightly higher (*e.g.*, 9.07 compared to 9.00 for pK_1) than those obtained using eq 1.

ΔH° Calculations.—The method of thermometric titration chart and data analysis has been described.^{2a,9} Heat of dilution data were taken from the literature.¹⁰

The calculations for this study were aided by an IBM 7040 computer.

(7) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instr.*, **36**, 779 (1965).

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 165.

(9) L. D. Hansen, J. J. Christensen, and R. M. Izatt, *J. Phys. Chem.*, in press.

(10) J. M. Sturtevant, *J. Am. Chem. Soc.*, **62**, 3265 (1940).

Results

In Table I are given the pH titration data from which Q₁ and Q₂ values were calculated.

TABLE I
pH TITRATION DATA USED TO CALCULATE Q₁ AND Q₂^a

ml. 0.3067 F NaOH	pH	\bar{n}	$-\log [A^{4-}]$
RUN 1			
4.130	8.344	0.725	4.374
4.386	8.574	0.585	4.470
4.638	8.762	0.446	4.569
4.816	8.878	0.349	4.669
4.945	8.961	0.278	4.768
5.000	8.936	0.000	4.868
6.090	8.650	0.655	4.968
6.249	8.749	0.570	5.068
6.474	8.902	0.452	5.168
6.631	8.016	0.371	5.268
6.769	8.128	0.302	5.368
RUN 3			
4.185	8.510	0.696	4.679
4.304	8.616	0.631	4.774
4.415	8.708	0.570	4.869
4.535	8.798	0.504	4.964
4.650	8.883	0.442	5.059
4.765	8.959	0.379	5.154
4.845	8.800	0.001	5.249
5.960	8.688	0.741	5.344
6.127	8.787	0.656	5.439
6.325	8.908	0.557	5.534
6.515	8.029	0.466	5.629
6.667	8.126	0.397	5.724
RUN 4			
2.030	8.386	0.765	5.229
2.190	8.705	0.591	5.324
2.265	8.820	0.510	5.419
2.339	8.929	0.430	5.514
2.410	8.025	0.354	5.609
2.443	8.073	0.319	5.704
2.462	8.584	0.881	5.799
2.938	8.668	0.805	5.894
3.017	8.756	0.727	5.989
3.089	8.835	0.658	6.084
3.166	8.922	0.588	6.179
3.239	8.004	0.523	6.274
3.310	8.082	0.463	6.369
RUN 5			
3.985	8.316	0.808	5.693
4.100	8.472	0.746	5.788
4.269	8.646	0.656	5.883
4.438	8.789	0.566	5.978
4.567	8.899	0.497	6.073
4.746	8.013	0.403	6.168
4.910	8.694	0.827	6.263
5.070	8.778	0.756	6.358
5.278	8.822	0.666	6.453
5.440	8.960	0.584	6.548
5.610	8.038	0.541	6.643
5.776	8.115	0.485	6.738

^aRuns 1 and 2 are duplicates, therefore, only run 1 is given here. Initial solution volume and A_{total} concentration, respectively, are 99.96 ml. and 0.005570 F (run 1 & 2), 252.2 ml. and 0.002207 F (run 3), 227.2 ml. and 0.001225 F (run 4), and 849.7 ml. and 0.0006553 F (run 5).

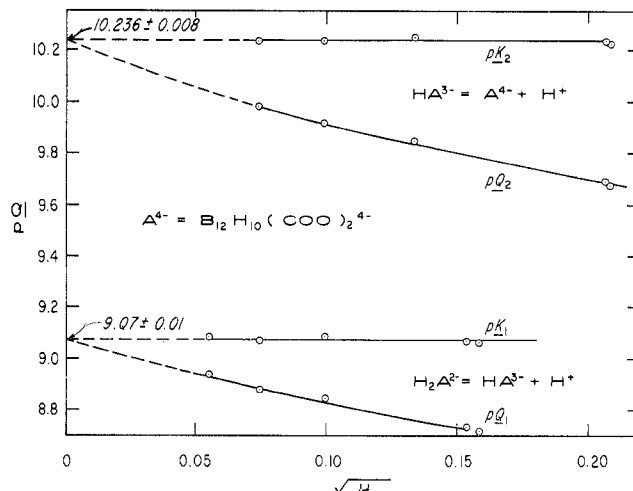


Figure 1.—Plot of pQ_n and pK_n vs. μ^{0.5} for proton ionization from H₂A²⁻. The plotted pQ_n values are those at $\bar{n} = 1/2$ and $1 1/2$. The uncertainties are given as standard deviations of the pK_n values.

μ value is of the order of ±0.005 pK unit. Two titrations were made at the highest μ value, which was approximately the same as that in the heat determinations. One titration was made at each of the other μ values.

In Table II is presented the quantity of heat evolved at several selected points on each thermometric titration curve corrected for the heat of stirring and the heat of dilution of the titrant.

In Table III are presented the ΔH₁^o and ΔH₂^o values obtained in the present study. The ΔH_n^o values are the averages of the ΔH_n^o values calculated from the data in Table II involving the sixteen possible combinations of four points from each of the two reaction regions (region 1: data points 2–5; region 2: data points 6–9) of the thermometric titration curves. The uncertainties in Table III are based on the sixteen possible combinations for each run and are given as standard deviations.

In Table IV is given a summary of the thermodynamic quantities valid at 25° and μ = 0 determined in

TABLE II^a
HEAT EVOLVED (Q_{cor}) AS A FUNCTION OF TITRANT ADDED (RUNS 1–4)^{a,b}

Data point	Moles of 0.3745 F HCl titrant × 10 ⁴	Δn _{HA} × 10 ⁴	Δn _{H₂A} × 10 ⁴	Q _{cor}			
				Run 1	Run 2	Run 3	Run 4
2	2.560	2.012	0.887	-0.858	-0.870	-0.873	-0.834
3	3.840	2.290	1.702	-1.258	-1.316	-1.295	-1.270
4	5.120	1.996	2.806	-1.690	-1.743	-1.727	-1.692
5	6.400	1.166	4.179	-2.089	-2.163	-2.148	-2.111
6	7.680	-0.098	5.769	-2.517	-2.589	-2.568	-2.540
7	8.960	-1.680	7.519	-2.937	-2.999	-2.989	-2.950
8	10.240	-3.484	9.381	-3.371	-3.406	-3.394	-3.351
9	11.520	-3.876	9.774	-3.371	-3.465	-3.449	-3.433

^a Δn_{HA} and Δn_{H₂A} refer, respectively, to the difference between the number of moles of HA and H₂A initially in solution and the number present at each data point. ^b Initial volume in each case 100.1 ml, total A present initially as H₄A 0.01002 F, total Na⁺ present initially (added as NaOH) 0.03578 F.

In Figure 1 the pQ_n and pK_n values calculated using the data in Table I are plotted vs. μ^{0.5}. The plotted Q_n values are those at $\bar{n} = 1/2$ and $1 1/2$. The total spread of the pK_n values in each determination at each

this study for H₂A²⁻ proton ionization. The uncertainties of the ΔG_n^o and ΔH_n^o values, given as standard deviations, are based on the values in Figure 1 (ΔG_n^o) and Table III (ΔH_n^o). The uncertainties of the

TABLE III
 ΔH_1° AND ΔH_2° VALUES FOR CONSECUTIVE PROTON IONIZATION
 FROM $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$

Run no.	ΔH_1° , kcal/mole $\text{H}_2\text{A}^{2-} = \text{HA}^{3-} + \text{H}^+$	ΔH_2° , kcal/mole $(\text{HA}^{3-} = \text{A}^{4-} + \text{H}^+)$
1	2.142 ± 0.026	2.256 ± 0.060
2	2.142 ± 0.014	2.370 ± 0.027
3	2.143 ± 0.012	2.342 ± 0.021
4	2.178 ± 0.016	2.242 ± 0.031

TABLE IV
 ΔG_n° , ΔH_n° , AND ΔS_n° VALUES VALID AT 25° AND $\mu = 0$ FOR
 CONSECUTIVE PROTON IONIZATION FROM $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$

Reaction	ΔG_n° , kcal/mole	ΔH_n° , kcal/mole	ΔS_n° , eu
$\text{H}_2\text{A}^{2-} = \text{HA}^{3-} + \text{H}^+$	12.37 ± 0.02	2.15 ± 0.02	-34.4 ± 0.1
$\text{HA}^{3-} = \text{A}^{4-} + \text{H}^+$	13.96 ± 0.01	2.30 ± 0.05	-39.1 ± 0.2

ΔS_n° values are estimated from those of the corresponding ΔG_n° and ΔH_n° values.

Discussion

The data in Table IV show the magnitude of the ΔG° , and, thus, of the pK , values to be determined primarily by the ΔS° term in each reaction. However, the pK_n values for H_2A^{2-} proton dissociation are significantly larger than those reported previously for carboxylic acids.² The data in Table IV show the higher pK_n values in the case of proton ionization from H_2A^{2-} to result from the unusually (for carboxylic acids) large and positive contribution to pK_n of the respective ΔH_n° terms. Carboxylic acids studied previously which have ΔS° values for proton dissociation similar to those given in Table IV (e.g., the second ionization of disubstituted malonic acids and maleic acid) have negative ΔH° values.

A common feature of those carboxylic acids having large negative ΔS° values for proton ionization^{2a} is the close proximity of a formal negative charge to the ionizing proton. The similar magnitudes of the ΔS° values for proton ionization from $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$ and those for the second ionization of maleic acid ($\Delta S_2^\circ = -32$ eu) and the disubstituted malonic acids ($\Delta S^\circ \sim 36$ eu) indicate that a negative charge in the B_{12} cage is localized in the vicinity of each ionizing proton, resulting in each ionization being similar to the ionization of a proton from a monovalent anion. Thus, each carboxyl group behaves as though its proton ionization were being affected by one negative charge. If this were not the case, one would expect the ΔS° value for proton ionization from HA^{3-} to be much more negative than that for proton ionization from HA^{2-} .

For example, King¹¹ has shown that ΔS for reactions of the type $(\text{CH}_2\text{CO}_2)_2\text{H}_n^{n-2} = (\text{CH}_2\text{CO}_2)_2\text{H}_{n-1}^{n-3} + \text{H}^+$ ($n = 1, 2$) after correction for difference in symmetry numbers¹² conform to the equation $\Delta S_{\text{cor}}^\circ = -6.6 - 4.1\Delta Z^2$ where ΔZ^2 is the difference in the square of the charge on the products and reactants. This equation would predict that $\Delta(\Delta S_{\text{cor}}^\circ)/\Delta(\Delta Z^2)$ should be -4.1 whereas in the present case it is -2.35 .

(11) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959).

(12) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

Also, in the much smaller species $\text{H}_2\text{P}_2\text{O}_7^{2-}$, where the ionizing protons should be affected by the entire ionic charge, the ΔS° value for the second ionization is much more negative than is that for the first ionization,¹⁸ i.e., $\Delta S_1^\circ = -32$ eu, $\Delta S_2^\circ = -49$ eu. The difference between ΔS_1° and ΔS_2° for proton ionization from $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$ can be partially accounted for by statistical effects, i.e., $R \ln 4$ or 2.8 eu from a total difference of 4.7 eu. It apparently then is not the over-all ionic charge on the acid which largely determines the magnitude of ΔS° ; rather, it is the charge distribution in the near vicinity of the ionizing proton. Therefore, since ΔH° and ΔS° for both ionization steps are approximately equal, we conclude that the proton ionizations in H_2A^{2-} are largely independent.

Because of the fixed distances between the carboxyl groups, this system provides the opportunity to estimate the value of D for the B_{12} cage and its immediate environment. If one assumes that proton ionization from H_2A^{2-} can be accounted for entirely by statistical and electrostatic terms, D can be calculated using a form of the Born equation, eq 4,¹⁴ provided r , the interprotonic distance, is known.

$$\frac{rKT(\ln 10)(\Delta pK - \log 4)}{e^2} = \frac{1}{D} \quad (4)$$

k is the Boltzmann constant, T is the absolute temperature, e is the electronic charge, and ΔpK is $pK_2 - pK_1$. The C-C distance in this cage has been determined recently¹⁵ to be 8.5 Å. From this value, the value 11.4 Å is calculated for r using 1.45 Å as the average C-H distance in each carboxyl group.¹⁴ Substituting this value of r into eq 4 one obtains the value $D = 38$. This value is a reasonable one, being midway between the values observed for the dielectric constants of water (80)¹⁶ and of hydrocarbons (2).¹⁶ Substituting this value for D into eq 5 and 6¹⁷ one obtains $-2.47 \times$

$$\frac{[(\Delta S_2^\circ - \Delta S_1^\circ) + R \ln 4]Dr}{e^2} = (\partial \ln D / \partial T) \quad (5)$$

$$\frac{(\Delta H_2^\circ - \Delta H_1^\circ)Dr}{e^2} - 1/T = (\partial \ln D / \partial T) \quad (6)$$

10^{-3} and $-2.53 \times 10^{-3} \text{ deg}^{-1}$, respectively, for $(\partial \ln D / \partial T)$.

The agreement of the $(\partial \ln D / \partial T)$ values calculated using eq 5 and 6 indicates that the differences in the pK , ΔH° , and ΔS° values for the first and second ionizations result entirely from the electrostatic and statistical effects considered.

To the best of our knowledge, no experimental $(\partial \ln D / \partial T)$ values for any aqueous species have been re-

(13) J. J. Christensen and R. M. Izatt, *J. Phys. Chem.*, **66**, 1030 (1962).

(14) F. H. Westheimer and M. W. Shookoff, *J. Am. Chem. Soc.*, **61**, 555 (1939).

(15) Determined by Mr. Keith Babcock, E. I. du Pont de Nemours and Co., personal communication from Dr. Earl L. Muetterties.

(16) Digest of Literature on Dielectrics, Vol. 26, 1962, Publication 1139, National Academy of Sciences, National Research Council, Washington, D. C., 1963.

(17) J. L. Magee, T. Ri, and H. Eyring, *J. Chem. Phys.*, **9**, 419 (1941).

ported. In fact, no values calculated in the above fashion have been reported, probably because of the difficulty of determining r for a nonrigid structure. It is interesting that the $(\partial \ln D/\partial T)$ value obtained, $-2.5 \times 10^{-3} \text{ deg}^{-1}$, is of the same order of magnitude as that reported¹⁷ for bulk water, $-4.7 \times 10^{-3} \text{ deg}^{-1}$.

The thermodynamic values determined in this study for $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$ proton ionization were

found not to fit the same linear $\Delta G^\circ - \Delta S^\circ$ relation found for other carboxylic acids.² The two points for $[1,12\text{-B}_{12}\text{H}_{10}(\text{COOH})_2]^{2-}$ on a plot of ΔG° vs. ΔS° fall on a parallel line with a different intercept. It would now be of interest to study other boranocarboxylic acids to learn if this intercept is characteristic of the ΔH° values for ionization of carboxylic acids with the carboxyl group attached to a boron atom.

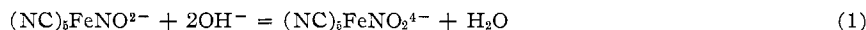
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA

The Equilibrium and Kinetic Properties of the Aqueous Hydroxide-Nitroprusside System

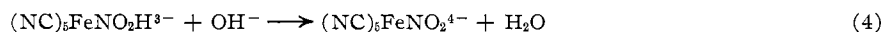
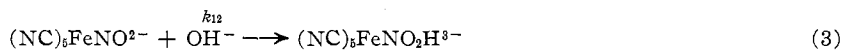
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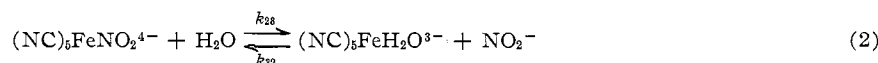
A complete thermodynamic and kinetic investigation of the aqueous hydroxide-pentacyanonitrosylferrate(II) (nitroprusside), $(\text{NC})_5\text{FeNO}_2^{2-}$, system has been carried out. For the equilibrium



$\Delta H^\circ = -16.2 \pm 0.9 \text{ kcal/mole}$ and $\Delta S^\circ = -26.1 \pm 3.0 \text{ gibbs/mole}$. The equilibrium constant, K_{12} , at 298°K is $(1.5 \pm 0.3) \times 10^6$. The mechanism postulated for the nitroprusside-hydroxide reaction is



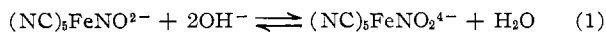
where (4) is a rapid acid-base reaction and (3) is rate-determining. For k_{12} , $\Delta H^* = 12.6 \pm 0.2 \text{ kcal/mole}$ and $\Delta S^* = -17.5 \pm 0.7 \text{ gibbs/mole}$. At 298°K $k_{12} = 0.55 \pm 0.01 \text{ M}^{-1} \text{ sec}^{-1}$. For the equilibrium



$\Delta H^\circ = +12.3 \pm 0.2 \text{ kcal/mole}$, $\Delta S^\circ = 25.2 \pm 0.7 \text{ gibbs/mole}$, and $\Delta G^\circ_{298} = 4.81 \text{ kcal/mole}$. The equilibrium constant, K_{23} , at 298°K is $(3.0 \pm 0.1) \times 10^{-4}$. For k_{23} , $(1.4 \pm 0.2) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ at 298°K , $\Delta H_{23}^* = 21.6 \pm 0.9 \text{ kcal/mole}$ and $\Delta S_{23}^* = -3.6 \pm 3.0 \text{ gibbs/mole}$. At 298°K $k_{32} = 0.46 \pm 0.07 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H_{32}^* = 9.3 \pm 1.1 \text{ kcal/mole}$, and $\Delta S_{32}^* = -28.8 \pm 3.7 \text{ gibbs/mole}$.

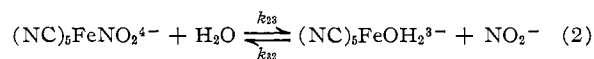
Introduction

Cambi and Szegő¹ in their investigation of the reaction between pentacyanonitrosylferrate(II) (nitroprusside), $(\text{NC})_5\text{FeNO}_2^{2-}$, and hydroxide ions reported the existence of the equilibrium



and obtained from spectrophotometric measurements $K_{12} = 0.74 \times 10^4$ (288°K). Kolthoff and Toren² re-investigated reaction 1 and obtained $K_{12} = 1.0 \times 10^6$ (298°K). The latter investigators also reported the decomposition of $(\text{NC})_5\text{FeNO}_2^{4-}$ to unspecified products and attempted to correct for this decomposition by extrapolation of their spectrophotometric data to zero time. Zuman and Kabát reported an equilibrium constant of 0.74×10^5 at 293°K .³ We have found in this investigation that the reaction between nitro-

prusside and hydroxide ions is not as simple as has been supposed and that in fact there are two important equilibria established in this system, the first being reaction 1 and the second being



We report here the results of a complete thermodynamic and kinetic investigation of reactions 1 and 2.

Experimental Section

Reagents.—Solutions were prepared from J. T. Baker reagent grade chemicals which were used without further purification; KCl (99.9%), NaNO_2 (98.9%), NaOH (98.7%), $\text{Na}_2\text{Fe}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$ (99.6%), and NaCl (99.5%). Stock nitroprusside solutions were stored in the dark and all operations were carried out in darkened rooms to prevent any light-catalyzed reactions.⁴ It was found that the presence of oxygen had no effect on the measurements made.

Instruments.—A Beckman Expandomatic pH meter and low

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(2) I. M. Kolthoff and P. E. Toren, *J. Am. Chem. Soc.*, **75**, 1197 (1953).

(3) P. Zuman and M. Kabát, *Chem. Listy*, **48**, 358 (1954).

(4) O. Baudish, *Science*, **108**, 443 (1948).