easily accept and distribute a positive charge than can B_2H_6, and $B_7H_7^{2-}$ can more easily carry its dianionic charge than can $B_4H_4^{2-}$. No such pattern is discernible among the carboranes, however.

A variety of protonation types were observed. (The abstract summarizes our findings.) Some patterns emerge. Face protonation occurred always and only on closo compounds with available BBB faces. In the carborane series $C_2B_nH_{n+2}$ (n = 3, 4, 5, 10) BB edge or BBB face protonation occurs for all but n = 3.

Protonation tends to occur at the most negatively charged atoms in the substrate molecule. However, the percent character of the HOMO also serves as a good predictor of the site of proton attack. In fact, for B_6H_{10} percent HOMO character and not charge provides the best predictor. The most negatively charged atoms are often apical, and 2-CB_5H_9 is the only molecule where a two-center bond is formed at an equatorial atom, that atom being carbon. B–H_2 bonds are observed but never C–H_2 bonds, and B–H_2 bonds are not observed upon protonation of closo compounds. These compounds undergo little structural distortion as a result of protonation.

The proton affinity results presented in Table I show significant disagreement for 1,6-$C_2B_4H_6$. Given our interest in the reported experimental[7] high proton affinity, we decided to do extensive ab initio 3-21G calculations on 1,6-$C_2B_4H_6$ and $C_2B_4H_7^+$. With optimization of both structures (except for terminal BH and CH bonds) we obtain a calculated proton affinity of 157 kcal/mol. This is close to the MNDO results but 50 kcal/mol less than that reported experimentally. At the present we have no explanation for this wide discrepancy.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Part of this work was conducted at the University of Notre Dame; the authors acknowledge the hospitality of the Department of Chemistry and the Computer Center and useful discussions with Professor T. P. Fehlner. Dr. D. M. Chipman was very helpful in the use of the GAUSSIAN 76 ab initio computer program.

Registry No. B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; 1,5-$C_2B_3H_5$, 20693-66-7; 1,6-$C_2B_4H_6$, 20693-67-8; 2,4-$C_2B_5H_7$, 20693-69-0; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; 2-CB_5H_9, 12385-35-2; $B_4H_4^{2-}$, 12429-81-1; $B_6H_6^{2-}$, 12429-97-9; $B_7H_7^{2-}$, 12430-07-8.

Supplementary Material Available: A listing of calculated MNDO heats of formation and a figure showing classical structures (3 pages). Ordering information is given on any current masthead page.

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Use of Balanced-Like-Charges Approach to Metal–Bicarbonate Reactions

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Formation reactions for several metal–bicarbonate ion pairs were written as $M^{2+} + H_2CO_3 = MHCO_3^+ + H^+$. Values of the equilibrium constants as a function of temperature could then be fit to a two-parameter equation of the form $\log K = A + B/T$. The resulting equations reproduce selected published experimental formation constants to an average of ±0.5% for the following ions: Mn, Mg, Ca, Zn, and Cu.

Introduction

The temperature dependence of formation constants for metal–bicarbonate systems are important to seawater chemistry,[1] geothermal energy studies,[2] and nuclear waste disposal.[3] Usually the temperature dependence is described by fitting to nonlinear equations such as $\log K_f = A + B/T + C \ln T + DT^2$ in which either C or D may be zero.[1,2] An example is that of Lesht and Bauman,[1] who were unable to find a two-parameter equation consistent with their experimental $\log K_f$ values. We report here an approach whereby selected formation constants are fit to a two-term linear equation that permits estimating values at high temperatures by extrapolation. The approach is based on that recently used by Lindsay,[4] Cobble et al.,[5] and Phillips and Silvester,[9] in which the charges on both sides of a chemical reaction are of like sign and are equal in number.

Method of Calculation

The formation of a metal–bicarbonate ion pair for a divalent metal ion is written as

$$M^{2+} + HCO_3^- = MHCO_3^+ \qquad (1)$$

where

$$K_f = \frac{[MHCO_3^+]}{[M^{2+}][HCO_3^-]} \qquad (2)$$

Adding the dissociation reaction for H_2CO_3

$$H_2CO_3 = HCO_3^- + H^+ \qquad (3)$$

to eq 1 gives

$$M^{2+} + H_2CO_3 = MHCO_3^+ + H^+ \qquad (4)$$

It is seen that eq 4 has ions of identical sign on each side of the equation

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Table I. Equilibrium Constants for Eq 4 Calculated from Data in Ref 1, 6, and 7

	log *K* at indicated temp, °C							
species	5	10	15	25	40	55	70	90
$MnHCO_3^+$	−5.252	−5.222	−5.187	−5.081	−4.966	−4.892		
$CaHCO_3^+$		−5.23		−5.13	−5.04	−4.97	−4.91	−4.85
$CuHCO_3^+$		−4.55		−4.28	−3.98	−3.69		
$ZnHCO_3^+$		−5.04		−4.96	−4.83	−4.71	−4.66	
$MgHCO_3^+$		−5.413		−5.290	−5.188	−5.117	−5.061	−5.016
H_2CO_3[a]	−6.513	−6.464	−6.422	−6.356	−6.296	−6.277	−6.291	−6.353

[a] Equation 3; calculated from eq 12.

Table II. Enthalpy, Entropy, and *A*, *B* Coefficients for Reactions according to Eq 4 Based on the Fit to Eq 5

species	$\Delta H_{298.15}$, cal/mol	$\Delta S_{298.15}$, cal/(deg mol)	log $K = A + B/(T(K))$ *A*	*B*	r^a
$MnHCO_3^+$	3160	−12.7	−2.773	−691.58	0.996
$CaHCO_3^+$	2240	−15.9	−3.479	−492.24	0.997
$CuHCO_3^+$	8130	7.8	1.717	−1780.15	0.998
$ZnHCO_3^+$	3000	−12.5	−2.739	−654.98	0.993
$MgHCO_3^+$	2350	−16.3	−3.567	−514.77	0.988

[a] Correlation coefficient.

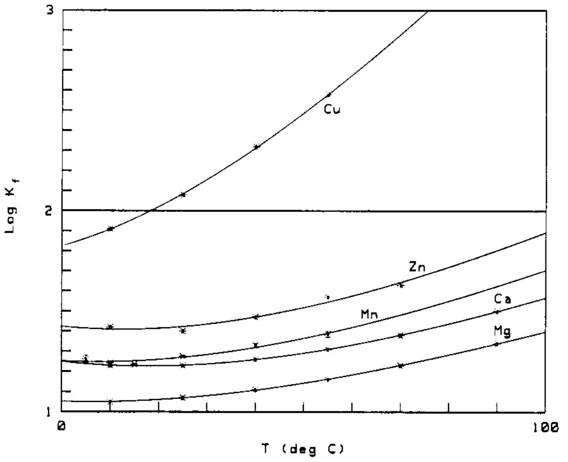

Figure 1. Effect of temperature on ion-pair formation constants for the reactions $M^{2+} + HCO_3^- = MHCO_3^+$. The lines are fits to experimental values.

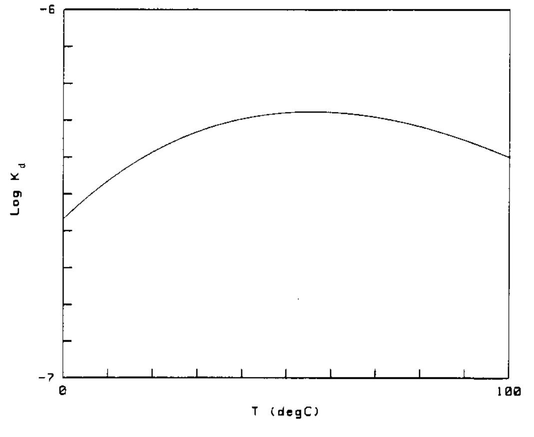

Figure 2. Dissociation constants for $H_2CO_3 = HCO_3^- + H^+$ over the temperature range 0–100 °C.

and an equal number of charges. On the other hand, eq 1 has ions with unlike charges on the left-hand side.

The heat capacity change may be small for reactions such as those in eq 4, so that a plot of log *K* vs. $1/T$ closely approximates a straight line.[4,5,7,9] Extrapolation to high temperatures is thereby much facilitated.

Data on formation constants for metal bicarbonates from Lesht and Bauman[1] and Bauman[6] (Figure 1) and data on H_2CO_3 dissociation from Patterson et al.[7] (Figure 2) were used to construct Table I according to eq 4. Figure 3 is a plot of log *K* values in Table I as a function of temperature. The equilibrium constants in this table were fit to the equation[9,10]

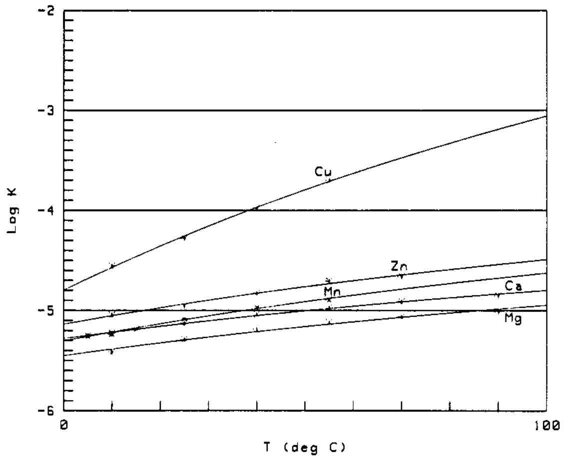

Figure 3. Variation in formation constants for the "balanced-charge" reactions $M^{2+} + H_2CO_3 = MHCO_3^+ + H^+$ over the temperature range 0–100 °C.

$$R \ln K = A + \frac{B}{T} + C \ln T + DT + ET^2 + FT^3 \qquad (5)$$

where

$$\begin{aligned} A = \Delta S°_\theta - \left(C_0 - \frac{\theta^2}{4}C_2 + \frac{10\theta^3}{72}C_3\right) - \\ \ln \theta\left(C_0 - \theta C_1 + \frac{\theta^2}{2}C_2 - \frac{\theta^3}{6}C_3\right) \end{aligned} \qquad (6)$$

$$B = -\Delta H°_\theta + \theta C_0 - \frac{\theta^2}{2}C_1 + \frac{\theta^3}{6}C_2 - \frac{\theta^4}{24}C_3 \qquad (7)$$

$$C = C_0 - \theta C_1 + \frac{\theta^2}{2}C_2 - \frac{\theta^3}{6}C_3 \qquad (8)$$

$$D = \frac{C_1}{2} - \frac{\theta}{2}C_2 + \frac{\theta^2}{4}C_3 \qquad (9)$$

$$E = \frac{C_2}{12} - \frac{\theta}{12}C_3 \qquad (10)$$

$$F = \frac{C_3}{72} \qquad (11)$$

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Table III. Comparison of Formation Constants (log K_f) Calculated from Eq 5 with Other Data

	log K_f				
temp, °C	eq 5	Bauman[6]	Siebert and Hostetler[8]	Lesht and Bauman[1]	Jacobson and Langmuir[12]
		$CuHCO_3^+$			
10	1.89	1.91[a]			
25	2.10	2.08			
40	2.33	2.32			
55	2.57	2.58			
		$ZnHCO_3^+$			
10	1.41	1.42[b]			
25	1.42	1.40			
40	1.47	1.47			
55	1.54	1.57			
70	1.65	1.63			
		$MgHCO_3^+$			
10	1.079		1.051		
25	1.062		1.066		
40	1.085		1.108		
55	1.141		1.160		
70	1.224		1.230		
90	1.369		1.337		
		$MnHCO_3^+$			
5	1.254			1.261	
10	1.249			1.242	
15	1.249			1.235	
25	1.263			1.275	
40	1.315			1.330	
55	1.397			1.385	
		$CaHCO_3^+$			
10	1.25	1.23[c]			0.81
25	1.23	1.23			1.01
40	1.24	1.26			1.21
55	1.30	1.31			1.41
70	1.38	1.38			
90	1.52	1.50			

[a] D. Rages, M.S. Thesis, University of Missouri-Columbia, 1978. [b] From ref 13. [c] W. R. Almon, M.S. Thesis, University of Missouri-Columbia, 1973.

and $C_0 = \Delta C_{p\theta}$, $C_1 = (\mathrm{d}\Delta C_p/\mathrm{d}T)_\theta$, $C_2 = (\mathrm{d}^2\Delta C_p/\mathrm{d}T^2)_\theta$, and $C_3 = (\mathrm{d}^3\Delta C_p/\mathrm{d}T^3)_\theta$. $\theta = 298.15$.

Enthalpy and entropy values at 25 °C were obtained from the computer fit to eq 5; adding a heat capacity change term did not improve the fit, so that the *C*, *D*, *E*, and *F* coefficients were negligible. Table II summarizes the results.

Values of the dissociation constants for eq 3 were calculated from the following equation, which was obtained by fitting data from Patterson et al.[7] to eq 5:

$$\log K_d = 102.261 - \frac{5251.01}{T\ (\mathrm{K})} - 36.778 \log (T\ (\mathrm{K})) \qquad (12)$$

Equation 12 is valid only for 0–100 °C.

Results

Smoothed values were calculated at selected temperatures from eq 5 by using the coefficients in Table II. These were converted to formation constants by subtracting values for the dissociation of H_2CO_3 at these temperatures and compared with other values. Table III compares our results with those used to develop our correlation—Lesht and Bauman, Bauman, and Siebert and Hostetler—as well as earlier data published by Jacobson and Langmuir.[12]

Values of log K_f calculated from eq 5 agree to an average of better than ±1% with those of Lesht and Bauman for $MnHCO_3^+$ and with the tabulation for Mg, Ca, Cu, and Zn

Table IV. Enthalpy, Entropy, and Heat Capacity for Formation of Ion-Pair Species Shown and for Dissociation of H_2CO_3 (298.15 K): $M^{2+} + HCO_3^- = MHCO_3^+$

species	$\Delta H_{298.15}$,[b] cal/mol	$\Delta S_{298.15}$, cal/(deg mol)	C_p, cal/(deg mol)
$MnHCO_3^+$	985 (983)	9.1	56.6
$CaHCO_3^+$	412 (551)	7.0	53.9
$MgHCO_3^+$	785 (779)	7.5	41.9
$CuHCO_3^+$	5550 (5610)	28.1	127.9
$ZnHCO_3^+$	846	9.3	67.7
H_2CO_3[a]	2236	−21.6	−73.1

[a] Smith and Martell[11] select at 298.15 K, $\Delta H = 2000 \pm 100$ cal/mol, $\Delta S = -22$ cal/(deg mol); Patterson et al.[7] find $\Delta H = 2165.3$ cal/mol, $\Delta S = -21.8$ cal/(deg mol), $\Delta C_p = -80.8$ cal/(deg mol). [b] Calculated values by Bauman[6] given in parentheses.

Table V. Three-Parameter Fit to $\log K_f = A + B/(T\ (K)) + C \log (T\ (K))$[a]

species	*A*	*B*	*C*	σ[b]
$MnHCO_3^+$	−80.87 (−80.63)	3473.16 (3462)	28.49 (28.41)	0.015
$CaHCO_3^+$	−77.49 (−79.08)	3427.79 (3497)	27.17 (27.71)	0.0011
$CuHCO_3^+$	−181.09 (−168.7)	7122.87 (6560)	64.38 (60.13)	0.0089
$ZnHCO_3^+$	−97.03	4225.52	34.06	0.027
$MgHCO_3^+$	−59.64 (−59.85)	2556.59 (2567)	21.07 (21.14)	0.0023

[a] Coefficients calculated by Bauman are shown in parentheses. [b] Standard deviation of fit.

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bicarbonate complexes given by Bauman.[6]

Ion-pair formation constants according to eq 1 are recovered from eq 4 by subtracting equilibrium constants for the ionization of H_2CO_3 (eq 3). In this way, we have fit log K_f values to eq 5 to obtain the thermodynamic data given in Table IV.

We then calculate A, B, and C coefficients for a three-parameter equation, in which now the heat capacity change for eq 1 is not negligible. Table V compares our results with those published by Bauman.[6]

It is concluded that use of the balanced-like-charges approach permits linearization of the temperature dependence of formation constants for selected metal–bicarbonate reactions. The resulting two-parameter equation facilitates extrapolation of log K values to high temperatures and should simplify computer-assisted and other calculations for these reactions.

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Intramolecular Energy Transfer between Ligand Field Excited States in a Bimetallic System

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The bimetallic complex $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ (I) has been synthesized via the reaction of $Cr(NH_3)_5H_2O^{3+}$ with $Co(CN)_6^{3-}$ in 0.02 M $HClO_4$ solution (55 °C, 9 h). The UV–visible absorption spectrum of I reveals ligand field (LF) band maxima at 310 and 468 nm characteristic of the $Co–C_6$ and $Cr–N_6$ chromophores, respectively. Selective excitation of the $Co–C_6$ chromophore in 0.02 M $HClO_4$ solution using 313-nm irradiation results in bridging-cyanide labilization and the formation of $Co(CN)_5H_2O^{2-}$ ($\phi_{CN} = 0.08$). This cyanide quantum yield corresponds to a fourfold reduction in yield relative to that of the corresponding monometallic anion $Co(CN)_6^{3-}$, which is consistent with but not conclusive evidence for intramolecular $Co–C_6 \rightsquigarrow Cr–N_6$ energy transfer. More compelling evidence for such transfer is obtained from $Cr–N_6$ sensitization data. When absorbance-matched solutions of I are excited at 313 and 436 nm, the former wavelength yields a $Cr–N_6$ emission signal 76% as intense as that for 436-nm excitation. Furthermore, $Co–C_6$ irradiation is accompanied by a sensitized NH_3 ligand release yield of $\phi_{NH_3} = 0.16$, which is 73% of that obtained on direct $Cr–N_6$ excitation. The actual pathway for intramolecular energy transfer in I has not as yet been established, but the present data and possible symmetry requirements favor ${}^1T_{1g} \rightsquigarrow {}^4T_{2g}$ or ${}^3T_{1g} \rightsquigarrow {}^4T_{2g}$ transfer over a ${}^3T_{1g} \rightsquigarrow {}^2E_g$ pathway.

Introduction

Excitation energy transfer involving transition-metal (TM) complexes is presently an area of active theoretical and practical interest.[1-9] However, the energy-transfer systems studied so far have been primarily intermolecular in nature. Such processes generally occur via an exchange mechanism and necessitate collisional approach of donor and acceptor. In contrast, for the corresponding case of *intramolecular* energy transfer, the donor and acceptor species are in perpetual encounter and the probability of efficient transfer may therefore be significantly enhanced. This report describes the results of a study of intramolecular energy transfer between spectroscopically independent TM centers, where the chromophores are exclusively ligand field (LF) in character. The compound investigated was the bimetallic species $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ (I), which has been examined under conditions of normal photochemical interest, i.e., room-temperature aqueous solution.

Under ideal circumstances, energy-transfer efficiencies may be evaluated for bimetallic systems by selective excitation of one metal center (the donor) and by monitoring the extent of (1) quenching of donor emission and photoreaction and (2) sensitization of emission and photoreaction characteristic of the other metal center (the acceptor). It is important to note that although donor excited-state quenching (emission or reaction) may reveal which donor state is actually involved in energy transfer, it is not in itself definitive evidence for electronic energy transfer.[1] The observation of sensitized acceptor reaction is also inconclusive since it is possible the reaction is due to a chemical reaction between the excited donor and ground-state acceptor wherein no acceptor excited states are generated.[1] Unambiguous evidence for energy transfer is obtained, however, with the observation of *sensitized acceptor emission*, provided the donor and acceptor chromophores are

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