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ON THE TEMPERATURE DEPENDENCE OF THE FORMATION CONSTANT OF $Cr(H_2O)_5NCS^{2+}$ IN ACIDIC SOLUTION

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ABSTRACT

The equilibrium constants derived by Postmus and King were treated with Blandamer's expression to test the temperature-dependence of ΔC_p^0 for the formation of the thiocyanatopentaaquochromium(III) ion. The results revealed temperature-dependent enthalpies and temperature-independent ΔC_p^0 (66 Cal mole^{-1} K^{-1}) implying that the equilibrium constant for association of $Cr(H_2O)_5NCS^{2+}$ represents a unitary process.

INTRODUCTION

The ionization constants for the reversible dissociation of carboxylic acids pass through a minimum as the temperature varies [1]. If the ionization is regarded as a one-step or unitary process, then the heat capacity at constant pressure, ΔC_p^0, must be negative. Numerous investigators have tried to find expressions to fit the experimentally observed temperature dependence in order to compute ΔC_p^0 which is regarded as a measure of solute–solvent interactions [2]. Timimi reviewed these empirical expressions [3].

More recently, Blandamer et al. [4] have re-examined the interpretation of negative heat capacities for the ionization of carboxylic acids using Albery and Robinson's proposal [5] that such non-zero heat capacities are artefacts caused by the presence of intermediates. Starting with a suggestion by Eigen [6] that diffusion-controlled intermediates are formed in the ionization of carboxylic acids, Blandamer and co-workers postulated [7,8] that the dissociation of carboxylic acids could be written as

$$\mathrm{RCOOH} + 2\,\mathrm{H_2O} \overset{K_1}{\rightleftharpoons} [\mathrm{RCOOH{-}H_2O\,H_2O}] \overset{K_2}{\rightleftharpoons} [\mathrm{RCOO{-}H_2O{-}H_3O^+}] \overset{K_3}{\rightleftharpoons} \mathrm{RCOO^-} + \mathrm{H_2O} + \mathrm{H_3O^+} \qquad (1)$$

where the intermediates are hydrogen-bonded, diffusion-controlled, "encounter" complexes with K_1 and K_3 values near unity. Since $K_2 << 1$ for

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carboxylic acids, the observed dissociation constant, K_0, is

$$K_0 = \frac{K_1 K_2 K_3}{1 + K_1} \tag{2}$$

Blandamer showed that the observed temperature dependence of K_0 arose from using temperature-independent enthalpies for the individual equilibria, K_1, K_2 and K_3.

Blandamer and co-workers [9–17] have also shown that the solvolysis of many organic compounds with non-zero heat capacities of activation which had been treated as unitary reactions [18] may also be multi-step reactions with rapid pre-equilibria. Blandamer and colleagues have labelled such temperature-dependent activation energies arising from the presence of pre-equilibria as "spurious" or "anomalous". Blandamer noted that "spurious" heat capacities are themselves temperature-dependent [5,19] and an expression that he derived to compute enthalpies and heat capacities of activation also gave a temperature-dependent ΔC_p^0, if pre-equilibria were present [13]. Albery and Robinson [5] chided earlier investigators for fitting rate or equilibrium constants to expressions with temperature-independent heat capacities.

In contrast to the wealth of information on organic compounds with temperature-dependent activation energies, there are far fewer examples in the inorganic chemistry literature, particularly for formation constants of strong complexes which one can liken to the formation of carboxylic acids [reverse of eqn. (2)] [20]. A notable exception is the formation of thiocyanatopentaaquochromium (III)

$$\mathrm{Cr(H_2O)_6^{3+} + NCS^- \overset{K}{\rightleftharpoons} Cr(H_2O)_5NCS^{2+} + H_2O} \tag{3}$$

Postmus and King [21,22] found the equilibrium constant vs. temperature curve for reaction (3) passed through a minimum in accord with the behavior of the observed association constant for carboxylic acids. Postmus and King computed a value of ΔC_p^0 for reaction (3), but they used an expression which assumed a temperature-independent heat capacity.

In view of Blandamer's interpretation of carboxylic acid ionization, it may be that the ΔC_p^0 value that Postmus and King measured is also "spurious", perhaps with participation of ion-pair formation prior to formation of the complex. To this end, Postmus and King's equilibrium constants have been treated with Blandamer's expression to test the temperature-dependence of ΔC_p^0 for reaction (3).

Blandamer's expression for calculating thermodynamic parameters from the temperature dependence of equilibrium data is

$$K = K_0 \exp\left\{ \frac{\Delta H^0}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{\Delta C_p^0}{R}\left[\ln\left(\frac{T}{T_0}\right) + \frac{T}{T_0} + 1\right]\right\} \tag{4}$$

where K = equilibrium constant at temperature T, K_0 = equilibrium constant at temperature T_0, ΔH^0 = enthalpy at T_0, and ΔC_p = heat capacity at T_0.

The equation is obtained by integration of the van't Hoff isochore between the temperatures T_0 and T assuming ΔC_p^0 is independent of temperature. If ΔC_p^0 values are so computed, though thermodynamically incorrect, they do predict the correct trend of the actual ΔC_p^0 dependence with temperature. For rate data, K and K_0 in eqn. (4) become k and $(k_0T)T_0$, respectively, and ΔH^0 and ΔC_p^0 become activation parameters. For a series of measurements at n pairs of K and T, any pair of K and T is set as K_0 and T_0, and all other values of K, T are fitted to eqn. (4) to give ΔH^0 and ΔC_p^0 at temperature T_0. The calculation is repeated with a different K, T set as K_0, T_0 until all values of T have been used as T_0. This results in n values of ΔH^0 and ΔC_p^0 from which we can determine whether ΔC_p^0 is zero, constant, or temperature dependent.

A non-linear, least-squares program [23] is used to find the best-fit values of ΔH^0 and ΔC_p^0 from a set of K, T data. The temperature, T, is the independent variable, K is the dependent variable, ΔH^0 and ΔC_p^0 are parameters to be fitted, and K_0 and T_0 are fixed parameters. The program finds best-fit values of ΔH^0 and ΔC_p^0 and then computes the equilibrium constants with these best-fit values of ΔH^0 and ΔC_p^0 in order to judge the goodness of fit.

RESULTS AND DISCUSSION

Table 1 lists the equilibrium constants as measured by Postmus and King for the formation constant of $Cr(H_2O)_5NCS^{2+}$ which were corrected to zero ionic strength with a modified Debye–Hückel equation. The three formation constants at 14.0, 25.1 and 30.0°C are the ratio of the forward and reverse rate constants. At 30°C the formation constant was measured both spectro-

TABLE 1

Formation constants for $Cr(H_2O)_5NCS^{2+}$ [a]

$K(M^{-1})\times10^{-3}$	T(°C)
1.24	94.6
1.15	84.8
1.06	73.7
1.04	63.6
1.03	46.2
1.10	30.0
1.12 [b]	30.0
1.23 [b]	25.1
1.38 [b]	14.0

[a] Taken from ref 21. Formation constants corrected to zero ionic strength.

[b] Ratio of forward and reverse rate constants (ref. 22).

TABLE 2

Temperature fit of formation constants at 94.6°C

T (°C)	$K \times 10^{-3}(\mathrm{M}^{-1})$	
	Expt.	Calcd.
84.8	1.15	1.14
73.7	1.06	1.06
63.6	1.04	1.03
46.2	1.03	1.03
30.0	1.10	1.13
30.0	1.12	1.13
25.1	1.23	1.19
14.0	1.38	1.38

TABLE 3

Summary of enthalpies and heat capacities for the formation constant of $Cr(H_2O)_5NCS^{2+}$

T (°C)	$\Delta H^{0\,a}$ (cal mole^{-1})	$\Delta C_p^{0\,a}$ (cal mole^{-1} K^{-1})
94.6	2535 ± 150	64.7 ± 4
84.8	1991 ± 169	66.6 ± 5
73.7	1201 ± 182	66.2 ± 7
63.6	548 ± 132	62.6 ± 6
46.2	−580 ± 57	65.7 ± 4
30.0	−1765 ± 183	76.6 ± 8
30.0	−1693 ± 126	69.9 ± 8
25.1	−1998 ± 275	61.1 ± 12
14.0	−2668 ± 135	65.1 ± 5

[a] Error expressed as standard deviation of the mean.

TABLE 4

Linear fit of enthalpy vs. temperature

T (°C)	ΔH^0(cal mole^{-1})	
	Expt.	Calcd. [a]
94.6	2535	2579
84.8	1991	1934
73.7	1201	1203
63.6	548	538
46.2	−580	−608
30.0	−1765	−1675
30.1	−1693	−1675
25.1	−1998	−1998
14.0	−2668	−2728

[a] $\Delta H_0^0 = -21.7 \pm 0.2$ kcal mole^{-1}; $\Delta C_p^0 = 65.9 \pm 0.6$ cal mole^{-1} K^{-1}

TABLE 5

Temperature range for measuring some inorganic equilibria

Reaction	No. of measurements	Range (°C)	Ref.
$Fe^{3+} + NCS^- \rightleftharpoons FeNCS^{2+}$	3	11.4–28.5	24
$Fe^{3+} \rightleftharpoons FeOH^{2+} + H^+$	3	18 –32	25
$2\ FeOH^{2+} \rightleftharpoons (FeOH)_2^{4+}$	3	18 –32	25
$Co^{3+} \rightleftharpoons CoOH^{2+} + H^+$	4	12.5–28.2	26
$Ce^{2+} \rightleftharpoons CeOH^{3+} + H^+$	4	5 –35	27
$2\ CeOH^{3+} \rightleftharpoons [Ce\text{–}O\text{–}Ce]^{6+} + H_2O$	4	5 –35	27

photometrically and as a ratio of rate constants.

Table 2 illustrates typical results of the temperature fit with Blandamer's expression using 94.6°C as an example, where one can see that the formation constants calculated with the best-fit values of ΔH^0 and ΔC_p^0 agree well with the experimental values. Table 3 summarizes the values of ΔH^0 and ΔC_p^0 from all the calculations which seem to show that ΔC_p is constant. To test this further, the enthalpies in Table 3 were fitted linearly with temperature using the least-squares program. The results of this calculation are shown in Table 4. Again, agreement between experimental and computed enthalpies and the small standard deviations of the mean suggest that the fit is adequate and that ΔC_p can be considered constant at 66 cal mole^{-1} K^{-1}. This implies that the equilibrium constant for association of $Cr(H_2O)_5NCS^{2+}$ represents a unitary process.

These results suggest, then, that the ΔC_p for the formation constant of $Cr(H_2O)_5NCS^{2+}$ is not "spurious", and that temperature-dependent enthalpies should be much more common for inorganic reactions; one need only extend the temperature range to find the temperature dependence. As Table 5 shows, many inorganic equilibria [24–27] have been measured over narrow temperature ranges in contrast to Postmus and King's experiments. In all instances in Table 5 where four temperature measurements are available, application of Blandamer's method [eqn. (4)] revealed temperature-dependent enthalpies. Postmus and King [21] also noted that the acid dissociation constant of $Cr(H_2O)_6^{3-}$ had a temperature-dependent ΔH^0 though much smaller than that for the formation constant of $Cr(H_2O)_5$-NCS^{2+}.

Our results suggest that many other equilibrium and kinetic constants for inorganic ions should also show this temperature behavior: failure to observe such temperature behavior may be due to the limited temperature range over which most measurements are made.

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