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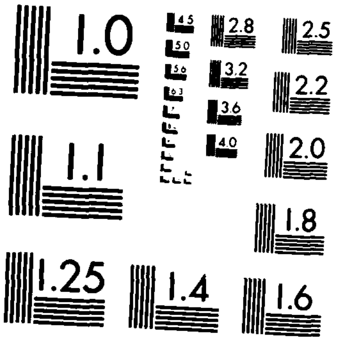
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CHEMICAL SYSTEMS LABORATORY

US Army Armament Research and Development Command
Aberdeen Proving Ground, Maryland 21010

TECHNICAL REPORT ARCSL-TR-82089

ON THE TEMPERATURE DEPENDENCE OF THE FORMATION OF THIOCYANATOPENTAAQUOCHROMIUM (III) IN ACIDIC SOLUTION

by

J. Richard Ward

Chemical Branch
Research Division

April 1983

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
ARCSL-TR-82089

2. GOVT ACCESSION NO.
AD-A128 420

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
ON THE TEMPERATURE DEPENDENCE OF THE FORMATION CONSTANT OF THIOCYANATOPENTAAQUOCHROMIUM (III) IN ACIDIC SOLUTION

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
J. Richard Ward

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Commander, Chemical Systems Laboratory
ATTN: DRDAR-CLB-CA
Aberdeen Proving Ground, Maryland 21010

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
1L161101A71A Research In Defense Systems

11. CONTROLLING OFFICE NAME AND ADDRESS
Commander, Chemical Systems Laboratory
ATTN: DRDAR-CLJ-R
Aberdeen Proving Ground, Maryland 21010

12. REPORT DATE
April 1983

13. NUMBER OF PAGES
34

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
NA

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Formation constants for metal ion complexes
Blandamer's method
Chromium (III) complexes
Heat capacity of activation
Equilibrium and kinetics of reactions in solution

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The equilibrium constants for the ionization of carboxylic acids in water pass through a maximum as temperature changes. If the equilibrium constant represents a one-step process, then the attendant thermodynamic properties such as enthalpy and entropy are also temperature dependent.

Blandamer and co-workers in the United Kingdom and Canada have recently concluded that the ionization of the carboxylic acids is a multistage process and the temperature dependence of the observed equilibrium (Continued)

20 ABSTRACT (Cont'd)

constant can be fit by combination of the equilibrium constants of the individual steps, each such equilibrium constant having temperature-independent enthalpy. Blandamer and his co-workers also derived an expression to test the temperature dependence of the enthalpy.

Temperature dependent enthalpies of reaction are less common in inorganic systems. In 1955, however, Postmus and King noted that the equilibrium constant for the association of thiocyanatopentaaquochromium (III), $Cr[H_2O]_5NCS^{2+}$, passed through a minimum temperature over the temperature range from 14° to 95° C. Blandamer's equation is used in this report to test the temperature dependence of the heat capacity. Application of Blandamer's equation to Postmus and King's data revealed that the heat capacity was temperature-independent (-66 cal/mole-K) implying that the equilibrium constant for association of $Cr[H_2O]_5NCS^{2+}$ is a unitary process. This suggests that many other equilibrium and kinetic constants for inorganic ions should also show this temperature behavior, and failure to see it rests on the limited temperature range over which most measurements are made. This also suggests that it is dangerous to extrapolate equilibrium or rate data far outside the range of measurements.

PREFACE

This work was performed under Project 1L161101A71A, Research in Defense Systems, Scientific Area B, during the author's residence at CSL in FY82 as part of cooperative program between BRL and the Research Division at CSL.

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CONTENTS

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ON THE TEMPERATURE DEPENDANCE OF THE FORMATION CONSTANT OF THIOCYANATOPENTAAQUOCHROMIUM (III) IN ACIDIC SOLUTION

1. INTRODUCTION

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

More recently, Blandamer[4] and coworkers in the United Kingdom and Canada have reexamined the interpretation of negative heat capacities for the ionization of carboxylic acids, using Albery and Robinson's idea[5] that such nonzero heat capacities are artificats 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 coworkers postualted[7,8] that the dissociation of carboxylic acids could be written as

$$\mathrm{RCOOH} + 2\mathrm{H_2O} \xrightleftharpoons{K_1} [\mathrm{RCOOH} \cdot \mathrm{H_2O} \cdot \mathrm{H_2O}] \xrightleftharpoons{K_2}$$

$$[\mathrm{RCOO^-} \cdot \mathrm{H_2O} \cdot \mathrm{H_3O^+}] \xrightleftharpoons{K_3} \mathrm{RCOO^-} + \mathrm{H_2O} + \mathrm{H_3O^+} \qquad (1)$$

where the intermediates are hydrogen-bonded, diffusion-controlled, "enounter" complexes with K_1 and K_3 values near unity. Since $K_2 << 1$ for carboxylic acids, the observed dissociation constant, K_0, is

$$K_0 = K_1K_2K_3/(1+K_1) \qquad (2)$$

Blandamer showed that the observed temperature dependence for K_0 arose from equation (2) using temperature-independent enthalpies for the individual equilibria K_1, K_2, and K_3.

Over the past three years, Blandamer [9-17] has also shown that the solvolysis of many organic compounds with nonzero heat capacities of activation which had been treated as unitary reactions[18] may also be multistep reactions with rapid preequilibria. Blandamer and colleagues have labeled such temperature-dependent activation energies, arising from the presence of preequilibria, 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 temperature-dependent ΔC_p^o, if preequilibria 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 equation 2).[20] A notable exception is the formation of thiocyanotopentaaquochromium (III), given below:

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

Postmus and King[21,22] found the equilibrium constant for equation 3 passed through a minimum in accordance with the behavior of the observed association constant for carboxylic acids. Postmus and King computed a value of ΔC_p° for equation 3, but they used an expression with a temperature-independent heat capacity.

In view of Blandamer's recent interpretation of carboxylic acid ionization, one wonders whether the ΔC_p° that Postmus and King measured is also "spurious." To this end, Blandamer's expression has been applied to Postmus and King's equilibrium constants to test the temperature-dependence of ΔC_p° for equation 3.

2. BLANDAMER'S METHOD FOR COMPUTING ACTIVATION PARAMETERS

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

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

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

The equation is obtained by the integration of the van't Hoff isochore between the temperature T_0 and T assuming ΔC_p° is independent of temperature. If ΔC_p° is dependent on temperature, equation 4 gives a poor fit and the ΔC_p° values as computed do predict the correct trend of the actual ΔC_p° dependence with temperature, though thermodynamically incorrect. For rate data, K and K_0 in equation 4 become k and $(k_0 \cdot T)/T_0$, respectively, and ΔH° and ΔC_p° 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 fit to equation 4 to give ΔH° and ΔC_p° 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° and ΔC_p° from which one determines whether ΔC_p° is zero, constant, or temperature dependent.

A nonlinear least-squares program[23] is used to find the best-fit values of ΔH° and ΔC_p° from a set of K,T data. The temperature, T, is the independent variable, K is the dependent variable, ΔH° and ΔC_p° are parameters to be fit, and K_0 and T_0 are fixed parameters. The program finds best-fit values of ΔH° and ΔC_p° and then computes the equilibrium constants with these best-fit values of ΔH° and ΔC_p° to compare the fit between sets of data.

3. RESULTS AND DISCUSSION

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

In table A-2, which illustrates typical results of the temperature fit with Blandamer's expression using 94.6°C as an example, one can see that the formation constants calculated with the best-fit values of ΔH° and ΔC_p° agree well with the experimental values. The results of the calculations at each of the other temperatures are listed in appendix B. Table A-3 summarizes the values of ΔH° and ΔC_p° from all the calculations, which seem to show that ΔC_p° is constant. To test this premise further, the enthalpies in table A-3 were fit linearly with temperature with the least-squares program. The results of this calculation are shown in table A-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-K.

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 A-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 A-6 where four temperature measurements are available, application of Blandamer's method (equation 4) revealed temperature-dependent enthalpies (tables A-6 and A-7). Postmus and King[21] also noted that the acid dissociation constant of $Cr(H_2O)_6{}^{3+}$ had a temperature-dependent ΔH°, though much smaller than that for the formation constant of $Cr(H_2O)_5NCS^{2+}$.

These results also caution against extrapolating rate or equilibrium data beyond the measured temperature range. Assume, for example, that one used only the three formation constants from the ratio of rate constants to compute ΔH° by the following:

$$K = e^{(-\Delta H^\circ/RT + \Delta S^\circ/R)} \tag{5}$$

Table 8 shows the fit obtained with the least-squares program. One would conclude that the fit is adequate over this temperature range, but it would be a mistake to extrapolate to 94.6°C with this value of ΔH°.

4. CONCLUSIONS

a. The heat capacity for the formation constant of $Cr(H_2O)_5NCS^{2+}$ is constant with temperature. This suggests that the heat capacity is not spurious, in the sense of arising from establishment of rapid preequilibria.

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*See appendix A for tables.

b. The formation constants of many inorganic equilibria should also have temperature-dependent enthalpies. Failure to see such temperature dependences may rest on the narrow temperature range over which most measurements have been made in comparison to Postmus and King's measurement with $Cr(H_2O)_5NCS^{2+}$.

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APPENDIX A

COLLECTED TABLES

Table A-1. Formation Constants for $Cr(H_2O)_5NCS^{2+}$[a]

K $M^{-1} \times 10^{-3}$	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

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

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

Table A-2. Temperature Fit of Formation Constant at 94.6° C

T °C	K, experimental $M^{-1} \times 10^{-3}$	K, calculated* $M^{-1} \times 10^{-3}$
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

*ΔH° = 2,535 ± 150 cal/mole; ΔC_p° = 64.7 ± 4; error expressed as standard deviation of the mean.

Table A-3. Summary of Enthalpies and Heat Capacities for Formation Constant of $Cr(H_2O)_5NCS^{2+}$

T	$\Delta H°$	$\Delta C_p°$
°C	cal/mole	cal/mole-K
94.6	2,535 ± 150*	64.7 ± 4*
84.8	1,991 ± 169	66.6 ± 5
73.7	1,201 ± 182	66.2 ± 7
63.6	548 ± 132	62.6 ± 6
46.2	-580 ± 57	65.7 ± 4
30.0	-1,765 ± 183	76.6 ± 8
30.0	-1,693 ± 126	69.9 ± 8
25.1	-1,998 ± 275	61.1 ± 12
14.0	-2,668 ± 135	65.1 ± 5

*Error expressed as standard deviation of the mean.

Table A-4. Linear Fit of Enthalpy versus Temperature

T °C	ΔH° cal/mole	ΔH° calculated* cal/mole
94.6	2,535	2,579
84.8	1,991	1,934
73.7	1,201	1,203
63.6	548	9,538
46.2	-580	-608
30.0	-1,765	-1,675
30.0	-1,693	-1,675
25.1	-1,998	-1,998
14.0	-2,668	-2,728

*ΔH° = -3,650 ± 36 cal/mole; ΔC_p^o = 65.9 ± 0.6 cal/mole-K

Table A-5. Temperature Range for Measuring Some Inorganic Equilibria

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

Table A-6. Enthalpy and Heat Capacity for Cobaltic Ion Dissociation Using Equation (4)

T	ΔH°	ΔC_p°
°C	kcal/mole	kcal/mole-K
12.5	10.3	-2.0
18.4	10.1	-2.0
23.6	2.0	-2.0
28.2	1.5	-0.7

---

*$Co^{3+} \rightleftharpoons CoOH^{2+} + H^+$

Table A-7. Enthalpy and Heat Capacities by Equation (4) for Ceric Ion Dissociation [a] and Dimerization[b]

Temperature	$\Delta H°^a$	$\Delta C_p°^a$	$\Delta H°^b$	$\Delta C_p°^b$
°C	kcal/mole	kcal/mole-K	kcal/mole-K	kcal/mole-K
5	11.8	0.30	42.4	-2.9
15	13.6	0.39	-10.8	-1.1
25	17.4	0.39	-19.5	-0.7
35	21.3	0.38	-31.3	-0.8

---

[a] $Ce^{4+} + H_2O \overset{K_1}{\rightleftharpoons} CeOH^{3+} + H^+$

[b] $2CeOH^{3+} \overset{K_2}{\rightleftharpoons} (Ce\text{-}O\text{-}Ce)^{6+} + H_2O$

Table A-8. Temperature Fit of Formation Constant Using Kinetic Data

Temperature °C	K, experimental $M^{-1} \times 10^{-3}$	K, fit* $M^{-1} \times 10^{-3}$
30.0	1.10	1.12
25.1	1.23	1.20
14.0	1.38	1.39

*$\Delta H = -2.3 \pm 0.5$ kcal/mole; $\Delta S = 6.5 \pm 1.7$ cal/mole-K.

APPENDIX B

TEMPERATURE FIT OF FORMATION CONSTANT AT VARIOUS TEMPERATURES

Table B-1. Temperature Fit of Formation Constant at 84.8°C

Temperature	K, experimental	K, calculated*
°C	$M^{-1} \times 10^{-3}$	$M^{-1} \times 10^{-3}$
94.6	1.24	1.25
73.7	1.06	1.07
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	1.36

*ΔH° = 1,991 ± 169 cal/mole; ΔC_p^o = 66.6 ± 5 cal/mole-K.

Table B-2. Temperature Fit of Formation Constant at 73.7°C

Temperature °C	K, experimental $M^{-1} \times 10^{-3}$	K, calculated* $M^{-1} \times 10^{-3}$
94.6	1.24	1.24
84.8	1.15	1.14
63.6	1.04	1.02
46.2	1.03	1.02
30.0	1.10	1.13
30.0	1.12	1.13
25.1	1.23	1.19
14.0	1.38	1.39

---

*ΔH° = 1201 ± 182 cal/mole; ΔC_p° = 66.2 ± 7 cal/mole-K.

Table B-3. Temperature Fit of Formation Constant at 63.6°C

Temperature °C	K, experimental $M^{-1} \times 10^{-3}$	K, calculated* $M^{-1} \times 10^{-3}$
94.6	1.24	1.25
84.8	1.15	1.16
73.7	1.06	1.08
46.2	1.03	1.04
30.0	1.10	1.14
30.0	1.12	1.14
25.1	1.23	1.19
14.0	1.38	1.38

*ΔH° = 548 ± 132 cal/mole; ΔC_p° = 62.6 ± 6 cal/mole-K.

Table B-4. Temperature Fit of Formation Constant at 46.2°C

Temperature °C	K, experimental M^{-1} x 10^{-3}	K, calculated* M^{-1} x 10^{-3}
94.6	1.24	1.25
84.8	1.15	1.15
73.7	1.06	1.07
63.6	1.04	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

*ΔH° = -580 ± 57 cal/mole; ΔC_p° = 65.7 ± cal/mole-K.

Table B-5. Temperature Fit of Formation Constant at 30.0°C

Temperature	K, experimental	K, calculated	
°C	$M^{-1} \times 10^{-3}$	$M^{-1} \times 10^{-3}$	
94.6	1.24	1.29[a]	1.27[b]
84.8	1.15	1.16	1.15
73.7	1.06	1.06	1.07
63.6	1.04	1.01	1.02
46.2	1.03	1.00	1.02
25.1	1.23	1.16	1.18
14.0	1.38	1.37	1.38

a $\Delta H^{\circ} = -1{,}765 \pm 183$ cal/mole; $\Delta C_p^{\circ} = 76.6 \pm 8$ cal/mole-K

$(K_{30.0°C} = 1.10 \times 10^3 M^{-1})$

*b $\Delta H^{\circ} = 1{,}693 \pm 126$ cal/mole; $\Delta C_p^{\circ} = 69.9 \pm 6$ cal/mole-K

$(K_{30.0°C} = 1.12 \times 10^3 M^{-1})$

Table B-6. Temperature Fit of Formation Constant at 25.1°C

Temperature	K, experimental	K, calculated*
°C	$M^{-1} \times 10^{-3}$	$M^{-1} \times 10^{-3}$
94.6	1.24	1.22
84.8	1.15	1.14
73.7	1.06	1.07
63.6	1.04	1.04
46.2	1.03	1.06
30.0	1.10	1.17
30.0	1.12	1.17
14.0	1.38	1.43

*ΔH° = -1998 ± 275 cal/mole; ΔC_p° = 61.1 ± 12 cal/mole-K.

Table B-7. Temperature Fit of Formation Constant at 14.0°C

Temperature °C	K, experimental $M^{-1} \times 10^{-3}$	K, calculated* $M^{-1} \times 10^{-3}$
94.6	1.24	1.25
84.8	1.15	1.15
73.7	1.06	1.07
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

*ΔH° = -2668 $\pm$ 135 cal/mole; ΔC_p° = 65.1 $\pm$ 5 cal/mole-K.

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