Inorganica Chimica Acta, 29 (1978) L278–L280
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The Effect of Pressure on the Thermally-Induced Aquation of Hexathiocyanatochromate(III)

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Received June 5, 1978

Both the thermally [3] and photochemically [4, 5] induced aquation reactions of $Cr(NCS)_6^{3-}$ have been studied in detail. The net reaction for the loss of the first thiocyanate ligand is indicated by the equation:

$$Cr(NCS)_6^{3-} + H_2O \rightarrow Cr(NCS)_5OH_2^{2-} + NCS^- \quad (1)$$

Langford and coworkers [3, 6] have interpreted the thermal reaction in terms of a dissociative interchange mechanism (I_d-type). This conclusion was based on the observation that the solvolysis rate is about the same in a number of "potentially good coordinating" solvents (alcohols, dimethylformamide, water, and pyridine). In water–acetonitrile mixtures, the solvolysis rates parallel the encounter probability with water molecules in the second coordination sphere.

A high pressure kinetic study of this same reaction by Gay and Nalepa [7] also resulted in the assignment of an I_d mechanism for thermal aquation. The large positive volume of activation [$\Delta V^{\neq}_{exp}$ = (+16 ± 2) cm^3 mol^{-1}] and the marked pressure dependence of $\Delta V^{\neq}_{exp}$ reported by these authors, appear more consistent with a limiting dissociative mechanism (D-type). Furthermore, the high pressure data are incompatible with preliminary photochemical data [8] obtained in our laboratory. Therefore, we have reinvestigated the pressure dependence of the aquation kinetics of this system which is currently of special interest in view of the controversy [9–12] concerning the nature of the mechanism for the reaction of cationic chromium(III) complexes.

Experimental

The complex $K_3[Cr(NCS)_6]\cdot 4H_2O$ was prepared by a standard procedure [13]. Purity was confirmed by analysis of the total thiocyanate content using the method outlined below for the kinetic measurements. The absorption spectrum maxima (wavelength, nm) [14] were found at 564(155), 420(128), 307(22900) and 234(24300), respectively.

Kinetic runs were monitored using normal sampling techniques. The high pressure sampling device has been described elsewhere [15]. Each aliquot was analyzed spectrophotometrically for thiocyanate [4] after precipitating the unreacted complex by addition of tetramethylammonium chloride, filtering and diluting with an acidified solution of $Fe(NO_3)_3$. The absorption of each aliquot so treated was measured at 450 nm where the iron-thiocyanate complex has a molar absorptivity of 3980 M^{-1} cm^{-1} as determined from solutions of known SCN^- concentration (Wegner and Adamson [4] report 4300 M^{-1} cm^{-1}).

The pressure dependence study was conducted in 0.1 N NaOH solution. Under these conditions it can be assumed that deprotonation of the expected aquation product $Cr(NCS)_5OH_2^{2-}$ will result in the very rapid and complete aquation of this species and hence the rate determining loss of the first SCN^- ligand results in the complete loss of all six coordinated thiocyanate ions. This method not only avoids the problem of subsequent aquation of $Co(NCS)_5OH_2^{2-}$ interfering with the kinetics, but also provides for increased accuracy of each thiocyanate determination. First-order rate plots of the appropriate data were linear for at least three half-lives. It is essential to the above technique that no base catalysis of reaction (1) be possible and this was confirmed in additional kinetic experiments over a range of solution pH values.

TABLE I. First-Order Rate Constants for the Aquation of $Cr(NCS)_6^{3-}$ at 25 °C and μ = 0.1 *M* (NaOH).[a]

P, bar	10^5 k, sec^{-1}
1	2.43 ± 0.03
250	2.30 ± 0.13
500	2.26 ± 0.05
750	2.20 ± 0.02
1000	2.19 ± 0.04
1250	2.01 ± 0.15
1500	2.06 ± 0.05

[a] The complex concentration was in the range (1.17–2.18) × 10^{-3} *M*.

Results and Discussion

The first-order rate constants, given in Table I as a function of pressure and at 25 °C, represent the average of two independent kinetic runs. Within the given error limits, no curvature could be detected in the lnk *vs.* pressure plots and a linear least-squares analysis of the data resulted in $\Delta V^{\neq}_{exp}$ = (2.9 ± 0.8) cm^3 mol^{-1}. This value is in sharp contrast to that previously reported [7]. Before discussing the mecha-

TABLE II. First-Order Rate Constants for the Aquation of $Cr(NCS)_6^{3-}$ at Atmospheric Pressure and 25 °C.

$[H^+]$, *M*	$[OH^-]$, *M*	μ, *M*	10^5 k, sec^{-1}	N[a]
b	b	~0	2.60	2
b	b	0.1($LiClO_4$)	2.79	2
0.1	–	0.1($HClO_4$)	2.48	1
0.02	–	0.1($HClO_4$, $LiClO_4$)	2.52	1
–	0.1	0.1(NaOH)	2.43	6

[a] N is the number of mol of SCN^- assumed lost per mol of $Cr(NCS)_6^{3-}$ reacted. [b] Water solution with no acid or base added.

nistic implications of the sign and magnitude of this volume of activation, it is of interest to consider the probable cause for the discrepancy between the two investigations.

A comparison of the values of the rate constant at atmospheric pressure reported in the literature (1.62×10^{-5} sec^{-1} at $[H^+] = 6 \times 10^{-3}$ *M* and 50 °C [7], 5.25×10^{-5} sec^{-1} in water at 29 °C [3], and 2.72×10^{-5} sec^{-1} in water at 25 °C [4]), clearly indicate that the latter two values are in reasonable agreement with the first entry in Table I. The higher acidity used in the first study is unlikely to account for the much slower reaction rate because acid catalysis (if present at this acidity) should lead to a more *rapid* reaction than that observed in water.

With this comparison in mind, a number of kinetic runs were undertaken in an attempt to establish the effect of acidity and ionic strength on the observed rate constant. The results are summarized in Table II. Despite the differences in the solution compositions, little variation in the k_{obs} values is observed and a mean value of $(2.57 \pm 0.13) \times 10^{-5}$ sec^{-1} is calculated. In acidic solutions (0.1 and 0.02 *M*) it was assumed, as suggested by Wegner and Adamson [4], that only one SCN^- ion is lost per rate determining act and hence reactions in acidic solutions were followed only for about 25% of the initial reaction. On the other hand, at a pH of about 7, first-order rate plots were linear for at least 70% of the initial reaction based on the assumption that two mol of SCN^- ligand were lost per mol of reactant consumed. Presumaly in unbuffered solutions the *trans* effect of an OH^- ligand is responsible for the rapid loss of the second SCN^- ligand. Under the conditions used in the previous high pressure work [7], we surmise that between one and two ligands were lost in reaction (1). As this "equilibrium" is quite likely pressure dependent, the discrepancy between the $\Delta V^{\neq}_{exp}$ values can at least be rationalized.

Turning now to the mechanism of reaction (1), a positive $\Delta V^{\neq}_{exp}$ can only be interpreted in terms of a basically dissociative process. Conversely, bond making between the chromium center and a water molecule would result in a negative volume of activation, with a maximum conceivable value of -18 cm^3 mol^{-1} for the limiting associative (A-type) mechanism. Within the framework of a dissociative mechanism, solvation contributions to $\Delta V^{\neq}_{exp}$ would be expected to be positive due to the change in charge distribution. For comparison, it may be noted that the thermally-induced aquation [16] of $Co(CN)_5Cl^{3-}$ (μ = 0.1 *M*) exhibited a $\Delta V^{\neq}_{exp} = (9.1 \pm 0.3)$ cm^3 mol^{-1} at 25 °C. From competition studies [17], this reaction has been classified as dissociative (D mechanism). Thus the small absolute value of $\Delta V^{\neq}_{exp}$ found in the present investigation is more in keeping with an interchange process. Within the limits of the pressure range investigated and the experimental errors incurred, the apparent pressure independence of $\Delta V^{\neq}_{exp}$ provides additional support for an I_d mechanism based on the concepts developed by Swaddle [18] and Stranks [19].

High pressure measurements of the aquation reactions [9, 11, 20] of $Cr(NH_3)_5X^{2+}$ (where X^- = Cl^-, Br^-, I^-, and SCN^-) and of the solvent exchange reactions of $Cr(OH_2)_6^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$ in water [21], $Cr(DMSO)_6^{3+}$ in DMSO [22], and $Cr(DMF)_6^{3+}$ in DMF [23] all tend to establish an I_a mechanism. An I_d mechanism has been assigned [6] to the thermal aquation of *trans*-$Cr(NH_3)_2(NCS)_4^-$. There appear to be two major causes for the appearance of both I_a and I_d mechanisms. Firstly, it has been postulated that a dissociative mechanism may be important for chromium(III) complexes only in the presence of strong *trans*-labilizing groups. This explanation is consistent with the fact that both $Cr(NCS)_6^{3-}$ and *trans*-$Cr(NH_3)_2(NCS)_4^-$ react dissociatively whereas $Cr(NH_3)_5NCS^{2+}$ reacts via an associative mechanism. The negative charge carried by the former two complexes probably contributes to the *trans* effect. Secondly, Langford and Tong [6] invoked the role played by specific solvation in these systems. For the $Cr(DMSO)_6^{3+}$ system [24], one specific site seems to exist in the second coordination sphere in which a DMSO molecule more strongly interacts with the substrate ion thereby provoking a more associative type mechanism. Hydrogen bonding, particularly involving the NH_3 ligands as donors to the solvent, may be a strong factor in influencing the activation mode of these complex ions.

Acknowledgements

The authors wish to express their gratitude to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research.

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