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Solvent Exchange in the Chromium(II)–Methanol System

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Solvent proton relaxation times (T_1 and T_2) have been measured between +40 and −95 °C for solutions of chromium(II) trifluoromethanesulfonate dissolved in CH_3OD. The variation of the rotating-frame relaxation time ($T_{1\rho}$) with the magnitude of the spin-locking field at −80 °C indicates that there are two exchanging solvent molecules. The temperature dependence of T_1 and T_2 gives the following kinetic parameters for exchange per methanol molecule: $\Delta H^{\ddagger} = 7.61 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = 4.0 \pm 1.8$ cal mol^{-1} deg^{-1}, and $k = 1.2 \times 10^8$ s^{-1} at 25 °C. The $T_{1\rho}$ results require that axial–equatorial interconversion in the tetragonally distorted $Cr(CH_3OD)_6^{2+}$ ion must have a rate constant $<7.4 \pm 10^4$ s^{-1} at −80 °C.

Introduction

Chromium(II) has been widely used as a reducing agent for mechanistic studies of electron-transfer reactions since the classic studies by Taube and co-workers.[1,2] However it has been difficult to estimate the energetic contributions to inner-sphere electron-transfer reactions with chromium(II) because of the paucity of quantitative information on the substitution lability of chromium(II). There is no doubt that it is one of the most labile transition-metal ions.

The structure and dynamics of the solvated chromium(II) ion have not been established. Evidence from solid-state structures[3] and electronic spectroscopy[4] is consistent with a Jahn–Teller effect in this d^4 system causing a tetragonal distortion with two axial ligands displaced further from the metal than the four equatorial ligands. A recent EXAFS study[5] is consistent with this view and also implies that axial–equatorial interconversion has a significant energy barrier.

In this study, the temperature dependence of the solvent proton nuclear relaxation rates has been used to determine the solvent exchange rate in the $Cr(O_3SCF_3)_2$–CH_3OD system by following methods initially described by Swift and Connick.[6] In addition, rotating-frame relaxation rates have been used to determine the number of exchanging solvent molecules as described recently by Chopra, McClung, and Jordan.[7]

Results and Discussion

The temperature dependences of the bulk solvent–CH_3 longitudinal (R_1) and transverse (R_2) relaxation rates have been corrected for the pure solvent relaxation rate[8] and normalized according to eq 1,[9] where (CH_3OD) and (Cr(II)) represent the

$$R_{ip} = \frac{(CH_3OD)}{(Cr(II))}(R_{iobsd} - R_{isolv}) \qquad (1)$$

molal concentrations. It should be noted that the solvation number (n) has been omitted from the normalization procedure (i.e., eq 1 assumes $n = 1$) because of uncertainties about the correct value.

The temperature dependencies of R_{1p} and R_{2p} are shown in Figure 1. The results for four samples with (Cr(II))/(CH_3OD) in the range of 2.9×10^{-4} to 11.4×10^{-4} conform to the normalization given by eq 1. The results in Figure 1 are typical of many previous such studies. For $10^3/T < 4$ the solvent exchange is fast and controlled by the inner-sphere relaxation rate (R_{im}) and outer-sphere effects (R_{2o}). As the temperature decreases, R_{2p} increases more rapidly than R_{1p} because of the contribution of chemical shift dephasing ($\Delta\omega_m^2/r_m$). When $10^3/T > 5.1$, the solvent exchange rate (r_m) becomes slow enough to control the nuclear relaxation and R_{2p} and R_{1p} approach each other in magnitude.

Table I. Proton Chemical Shifts for Solutions of $Cr(O_3SCF_3)_2$ in CH_3OD

temp, °C	$\Delta\nu$,[a] Hz	$10^{-3}(\Delta\nu)T$,[a] Hz K	$10^7 nC_\omega$[b]
36.5	12.60	3.90	1.75
14.8	13.45	3.87	1.74
3.9	14.05	3.89	1.75
−6.6	14.65	3.90	1.75
−16.4	15.10	3.87	1.74
−26.0	15.70	3.88	1.75
−36.4	16.40	3.88	1.75
−45.2	16.95	3.86	1.74
−55.9	17.80	3.86	1.74

[a] Values at 80 MHz versus internal cyclohexane for a solution with (Cr(II))/(CH_3OD) = 1.56×10^{-3}. [b] $nC_\omega = 2\pi\Delta\nu T(CH_3OD)/(Cr(II))$ and was corrected to 89.5 MHz by multiplying by (89.5/80).

The chemical shift results are given in Table I and show the usual temperature dependence described by eq 2. The value of

$$\Delta\omega_m = \frac{n(Cr(II))C_\omega}{(CH_3OD)T} \qquad (2)$$

$nC_\omega(\sim 2 \times 10^7$ rad s$^{-1})$ is consistent with a qualitative analysis of the R_{2p} results. In the region where R_{2p} is a maximum, the theory for R_{2p} predicts that $r_m \sim \Delta\omega_m \sim 2R_{2p} \sim 1.2 \times 10^4$ s^{-1} at $10^3/T = 5.2$. Therefore the R_{2p} data predict $nC_\omega \sim (1.2 \times 10^5)/(5.2 \times 10^{-3}) = 2.3 \times 10^7$. This analysis simply shows that the exchange and chemical shifts are apparently originating from the same exchange site on the metal ion. Although this is often an assumed condition, the possibility of different sites on the tetragonally distorted chromium(II) ion make the point important for the analysis here. However, one cannot entirely exclude the possibility that the shifts and relaxation are caused by two different sites that just happen to have a combination of populations and coupling constants which makes them appear to be the same.

It is noteworthy that the values of R_{1p} and R_{2p} are the same in the high-temperature region. This implies that there is no significant scalar contribution to R_{2m} and that a dipolar relaxation mechanism is responsible for the R_{1m} and R_{2m} inner-sphere relaxation processes. Because this region is defined over a much longer temperature region for the R_{1p} data, the latter has been used to determine the activation energy for the observed relaxation in this region. The results give (E_{1m} ($=E_{2m}$) = 1.15 ± 0.05 kcal mol^{-1}. This value is well-defined but lower than that of ~2.5–3 kcal mol^{-1} observed previously for vanadyl complexes[10] and Co-

(1) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 4118.
(2) Taube, H.; Myers, H. *J. Am. Chem. Soc.* **1954**, *76*, 2103.
(3) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Wells, A. F. *Structural Chemistry*, 4th ed.; Clarendon: Oxford, England, 1975.
(4) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.
(5) Sham, T. K.; Hastings, J. R.; Perlman, M. L. *Chem. Phys. Lett.* **1981**, *83*, 391.
(6) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.
(7) Chopra, S.; McClung, R. E. D.; Jordan, R. B. *J. Magn. Reson.* **1984**, *59*, 361.
(8) Values of R_1 and R_2 for pure CH_3OD were found to be equal between +26 and −85 °C, and the temperature dependence is given by $R_{solv} = 1.46/T \exp(1800/RT)$.
(9) Detailed expressions are given in the Experimental Section.
(10) Angerman, N. S.; Jordan, R. B. *Inorg. Chem.* **1969**, *8*, 1824.

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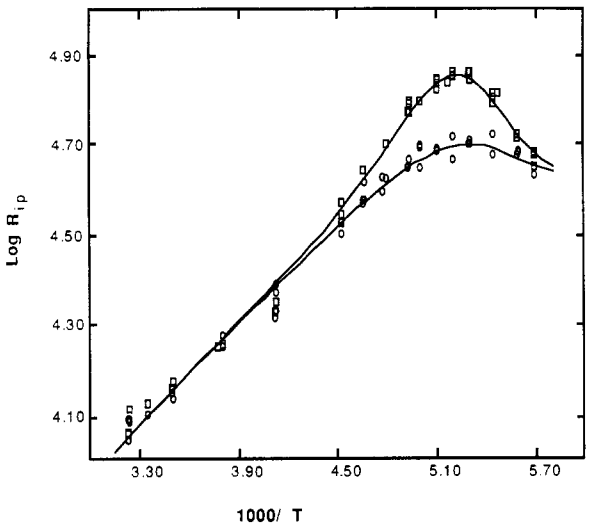

Figure 1. Temperature dependence of proton relaxation rates, log R_{1p} (O) and log R_{2p} (□), for chromium(II) trifluoromethanesulfonate in CH_3OD. Only alternate points from various samples have been plotted for clarity. Curves are calculated from parameters given in the text.

(trans[14]diene)$^{2+}$ [11] in methanol. This difference may be explained by a relatively short electron spin relaxation time (τ_e) being the controlling correlation time for nuclear relaxation in the chromium(II) system.

A preliminary analysis using computer simulations indicated that the low-temperature R_{1p} and R_{2p} data require an outer-sphere contribution (R_{io}) to be consistent. Otherwise the R_{1p} values should remain substantially below the R_{2p} values up to −95 °C. An earlier analysis[11] of outer-sphere effects indicates that the ratio of inner- to outer-sphere dipolar contributions for protons is given by eq 3, where n is the inner-sphere solvation number, S_0 and ρ are the

$$\frac{R_{2m}}{R_{2o}} = \frac{396nd_o^3}{(S_0)\rho r_i^6} \tag{3}$$

solvent molality and density respectively and d_o and r_i are the outer-sphere and inner-sphere interaction distances (Å). Previous studies[10,11] indicate that $r_i \sim 3.9$ and $d_o \sim 4.8$ for methanol CH_3 protons, and with $S_0 = 30.3$ and $\rho \sim 0.8$ g/mL for CH_3OD, one can estimate that $(R_{2m}/R_{2o}) \sim 0.5n$. Therefore it is not surprising that there should be some outer-sphere contribution.

The least-squares analysis[12] was done with fixed values of $E_m = E_o = 1.15$ kcal mol^{-1} as discussed above and initial guesses of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, C_{im}, and C_{om} determined from visual analysis. The R_{2p} results were used to get best-fit values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and then the $\Delta H^{\ddagger}$ was fixed in the R_{1p} analysis to give $\Delta S^{\ddagger}$, C_{1m}, and C_{0m}. The process was repeated several times to obtain self-consistency between the R_{2p} and R_{1p} fits. The self-consistent parameters are as follows:[13] $\Delta H^{\ddagger} = 7.61 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = 5.40 \pm 1.8$ cal mol^{-1} deg^{-1}; $C_{2m} = C_{1m} = (3.42 \pm 0.6) \times 10^5$ s^{-1} deg^{-1}; $C_0 = 1.9 \pm 0.5 \times 10^5$ s^{-1} deg^{-1} and $C_\omega = (1.7 \pm 0.05) \times 10^7$ rad s^{-1} deg. The values are based on a solvation number $n = 1$, and the curves in Figure 1 are calculated with these parameters.

Rotating Frame Relaxation ($R_{1\rho}$). The dependence of $R_{1\rho}$ on the magnitude of the spin-locking field H_1 ($\omega_1 = \gamma H_1$) can be used to determine the number of exchanging solvent molecules on a labile paramagnetic ion.[7] The study requires a significant difference between R_1 and R_2 and is best done in the temperature region below the maximum in R_2 because then the variation in $R_{1\rho}$ primarily depends on the relatively well-defined value of $\Delta\omega_m$.

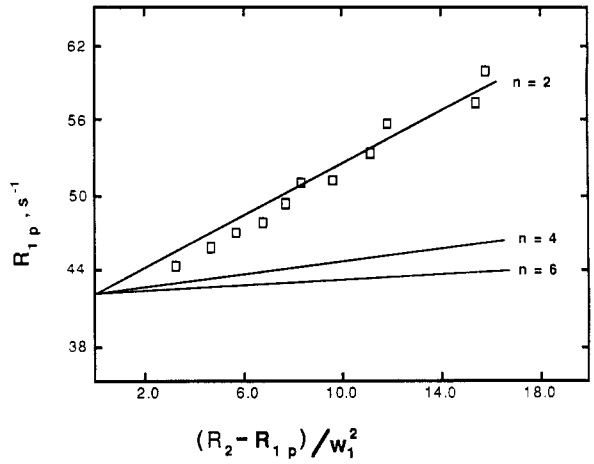

Figure 2. Variation of the rotating frame relaxation rate ($R_{1\rho}$) with $(R_2 - R_{1\rho})/\omega_1^2$ at −80 °C for chromium(II) trifluoromethanesulfonate in CH_3OD. Lines are calculated for two, four, and six exchanging solvent molecules.

In the chromium(II)–methanol system R_1 and R_2 rapidly come together in the optimum temperature region. Therefore, the study was done near the R_2 maximum, where R_1 and R_2 have their maximum difference.

The variation of $R_{1\rho}$ with ω_1 was studied at −80 °C. It has been shown[8] that the results should be described by eq 4, where $R^{\infty}_{1\rho}$

$$R_{1\rho} = R^{\infty}_{1\rho} + S_\rho^2(R_2 - R_{1\rho})\omega_1^{-2}$$
$$S_\rho^2 = \left(\frac{R_{1m} + r_m}{R_{2m} + r_m}\right)((R_{2m} + r_m)^2 + \Delta\omega_m^2) \tag{4}$$

is the limiting value as $\omega_1 \rightarrow \infty$. The results are plotted according to eq 4 in Figure 2 and show the predicted linear dependence.

The analysis of the temperature dependence of R_1 and R_2 assumed in effect that there was one exchanging solvent molecule ($n = 1$) because of the normalization factor used (see eq 1). Therefore the least-squares parameters describing R_{1m}, R_{2m}, $\Delta\omega_m$, and r_m give values that are n times larger than the true values i.e., $R^1_{im} = nR_{im}$, $r^1_m = nr_m$, $\Delta\omega^1_m = n\Delta\omega_m$, where the nonsuperscripted values should be used in eq 4. Substitution of the known values into eq 4 gives

$$S^2_\rho = \frac{1}{n^2}\{(R^1_{2m} + r^1_m)^2 + (\Delta\omega^1_m)^2\} \tag{5}$$

where the simplification resulting from $R_{1m} = R_{2m}$ has also been made. Rearrangement of eq 5 relates n to the known parameters as follows:

$$n = \left(\frac{(R^1_{2m} + r^1_m)^2 + (\Delta\omega^1_m)^2}{S_\rho^2}\right)^{1/2} \tag{6}$$

The results plotted in Figure 2 give a slope of $S^2_\rho = 1.0 \times 10^{10}$, and substitution into eq 6 gives

$$n = \left(\frac{(1.47 \times 10^5 + 0.35 \times 10^5)^2 + (0.85 \times 10^5)^2}{1.0 \times 10^{10}}\right)^{1/2} = 2.01 \tag{7}$$

The conclusion from this analysis is that there are two exchanging solvent molecules.

As can be seen from eq 7, r^1_m is the dominant factor in the calculation of n. However r^1_m must be 2.6×10^5 s^{-1} for $n = 4$, and 4.6×10^5 for $n = 6$. An analysis similar to that applied previously to the maximum R^1_{2p} value (Figure 1) and $\Delta\omega_m$ shows that r^1_m must be $<2 \times 10^5$ at −80 °C; therefore, larger solvation

(11) Rusnak, L. L.; Jordan, R. B. *Inorg. Chem.* **1976**, *15*, 709.
(12) Nonlinear least-squares analysis was done with a locally modified version of the IBM Share Library program SDA3094 (1964) running on a Macintosh computer.
(13) Extra "significant figures" are included to avoid round off errors in recalculations.

numbers would not be consistent with the R_{2p} data.

The simplest explanation for the two exchanging solvent molecules would be to assign them to the axial solvent molecules in the tetragonally distorted complex $Cr(CH_3OH)_6^{2+}$. The remaining four equatorial ligands might be exchanging much more rapidly, but that seems inconsistent with the shorter bond lengths. The equatorial ligands might be exchanging too slowly to be observed and/or R_{2m} and $\Delta\omega_m$ of the equatorial positions could be much smaller than those for the axial positions so that the equatorial ligands are essentially transparent to the nuclear relaxation measurements. However the results do require that the axial–equatorial interconversion is slow on our NMR time scale. Otherwise, all the coordinated solvent molecules would equilibrate to give effectively six exchanging solvent ligands as opposed to the two observed.

Conclusions

With the known number of exchanging ligands, it is possible to calculate the kinetic parameters for exchange of one CH_3OD. The values are $k = 1.2 \times 10^8\ s^{-1}$ (25 °C), $\Delta H^{\ddagger} = 7.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 4$ cal mol deg^{-1}.

The great lability of chromium(II) has the effect of preventing analogous solvent exchange studies in water over the available liquid range. Studies on iron(II), cobalt(II), and nickel(II) indicate that the activation enthalpy is about 2 kcal mol^{-1} less in water than in methanol.[14] Therefore one can estimate an activation enthalpy of ~6 kcal mol^{-1} for chromium(II) in water, but this extrapolation must be viewed with caution because of the tetragonal distortion of the solvated chromium(II) species.

Experimental Section

Materials. The solutions of chromium(II) trifluoromethanesulfonate in CH_3OD were prepared on a standard vacuum line by distilling CH_3OD and F_3CSO_3H onto a weighed amount of chromous acetate (prepared by standard methods). The solvent containing acetic acid was removed by vacuum distillation and the process was repeated twice. The final blue solution was sealed under vacuum in a 10 mm flat-bottomed tube. The final amount of CH_3OD in the sample was determined by weight. The four samples used were in the range of 0.96×10^{-3} to 4×10^{-3} *m* in chromium(II).

NMR Measurements. The R_1 and R_2 values were determined by 180–τ–90 and Carr–Purcell–Meiboom–Gill methods, respectively, on a Bruker SXP 4-100 pulsed spectrometer at 89.5 MHz. The instrumentation has been fully described elsewhere.[7,15] Relaxation rates are the average of at least five determinations for a particular sample and temperature. Chemical shifts were measured on a Bruker WP-80 spectrometer using cyclohexane as an internal standard.

Data Analysis. The relaxation rates were analyzed by eq 8,[6] where R_{2obsd} and R_{2solv} are the relaxation rates in the presence and absence of

$$R_{2p} = (R_{2obsd} - R_{2solv})\frac{(\text{solv})}{n(Cr^{2+})} = r_m\frac{R_{2m}(R_{2m} + r_m) + \Delta\omega_m^2}{(R_{2m} + r_m)^2 + \Delta\omega_m^2} + R_{2o} \quad (8)$$

chromium(II) respectively, (solv) and (Cr^{2+}) are the molality of the solvent and chromium(II), n is the number of exchanging solvent molecules, R_{2o} is the outer-sphere relaxation rate and the other terms have the usual meaning. A similar expression gives R_{1p} in terms of R_{1obsd} and R_{1solv} by substituting R_{1m} for R_{2m} and setting $\Delta\omega_m = 0$.

The temperature dependence of the terms in eq 1 are given by the following equations:[11]

$$R_{im} = C_{im}/T \exp(E_{im}/RT) \quad (9)$$

$$r_m = 2.083 \times 10^{10} T \exp(\Delta H^{\ddagger} - T\Delta S^{\ddagger}/RT) \quad (10)$$

$$\Delta\omega_m = C_\omega/T \quad (11)$$

The chemical shifts could be measured only in the fast-exchange region because the lines became too broad at lower temperatures. Therefore

$$\Delta\omega_{obsd} = -\frac{n(Cr^{2+})}{(\text{solv})}\Delta\omega_m = \frac{n(Cr^{2+})C_\omega}{(\text{solv})T} \quad (12)$$

Registry No. $Cr(O_3SCF_3)_2$, 99329-21-2; CH_3OD, 1455-13-6.

(14) (a) Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3696. (b) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 5588.

(15) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

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Facile Conversion of a Coordinated Nitro Group into an Aqua Group: Acid-Induced Nitro-to-Nitrito Rearrangement

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The nitro complex $(NH_3)_5CoNO_2^{2+}$ reacts rapidly and completely with neat anhydrous trifluoromethanesulfonic acid to generate the aqua species $(NH_3)_5CoOH_2^{3+}$. Oxygen-17 NMR results show that the oxygen in the bound water is derived from the original nitro group. A mechanism involving acid-catalyzed nitrogen-to-oxygen nitrite rearrangement is considered. The relationship between the mechanisms for oxygen scrambling and acid-catalyzed loss of NO^+ from the nitrito linkage isomer is discussed, together with the mechanism for the present reaction.

Introduction

The classic example of linkage isomerism in inorganic chemistry is the N-bound nitro and O-bound nitrito pair $(NH_3)_5Co–NO_2^{2+}$ and $(NH_3)_5Co–ONO^{2+}$, synthesized nearly a century ago.[1] Nonetheless, despite their extensive history, significant facts on their rearrangement chemistry continue to emerge,[2–6] and herein we report another.

We sought a means of rapidly generating *trans*-$Co(en)_2$(amine)$(O_3SCF_3)^{2+}$ from *trans*-$Co(en)_2$(amine)X^{n+} under ambient conditions. However, in the usual procedure[7,8] of heating

(1) Kauffman, G. B. *Coord. Chem. Rev.* **1973**, *11*, 161.
(2) (a) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 70. Pearson, R. G.; Henry, P. M.; Bergman, J. G.; Basolo, F. *J. Am. Chem. Soc.* **1954**, *76*, 5920.
(3) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Aust. J. Chem.* **1982**, *35*, 1561.
(4) Jackson, W. G.; Randall, M. L.; Sargeson, A. M.; Marty, W. *Inorg. Chem.* **1983**, *22*, 1013.
(5) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 904.
(6) van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* **1982**, *65*, L125.
(7) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.
(8) Dixon, N. E.; Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Synth.* **1983**, *22*, 103.

0020-1669/87/1326-3857$01.50/0 © 1987 American Chemical Society