Inorg. Chem. **1992**, *31*, 3695-3696

High-Pressure Kinetic Evidence for a Dissociative Interchange (I_d) Substitution Mechanism for Aquated Chromium(II)

Rudi van Eldik,[*,†] Wolfgang Gaede,[†] Haim Cohen,[‡,§] and Dan Meyerstein[*,§]

Institute for Inorganic Chemistry, University of Witten/Herdecke, 5810 Witten, FRG, Nuclear Research Centre Negev, Beer-Sheva, Israel, and R. Bloch Coal Research Center and Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel

Received May 27, 1992

Solvent exchange and ligand substitution reactions of transition metal ions and complexes form the basis for understanding many chemical and biochemical processes that involve the interaction with metal ions and complexes. For this reason, much fundamental research has been devoted to reveal the intimate nature of solvent exchange and ligand substitution processes.[1] The application of high-pressure kinetic techniques has played a crucial role in the elucidation of the different mechanisms according to which such processes can occur, ranging from limiting dissociative (D) to interchange (I_d and I_a) and limiting associative (A) mechanisms.[2-7] Symmetrical solvent and ligand exchange reactions and nonsymmetrical solvent and ligand displacement reactions have been demonstrated to exhibit very characteristic volumes of activation. Such data are presently available for solvent exchange and complex formation reactions of the divalent first-row transition metal ions V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} and demonstrate a gradual changeover in mechanism from I_a for the larger metal ions (V^{2+} and Mn^{2+}) to I_d for the smaller metal ions (Fe^{2+}, Co^{2+}, and Ni^{2+}) in aqueous medium.[3,6] Although it is of fundamental importance to have similar data for solvent exchange reactions of Cr^{2+} and Cu^{2+}, such measurements are complicated by Jahn–Teller distortions and associated relaxations. A recent ^{17}O NMR study[8] shows that the rate of inversion of the Jahn–Teller distortion (2.0×10^{11} s^{-1} at 298 K) is rapid compared to the intermolecular water exchange rate (4.4×10^{9} s^{-1} at 298 K) for Cu^{2+}. This leads to the conclusion that the exchange occurs at the elongated axial site through a dissociative interchange or even a limiting dissociative mechanism. Furthermore, preliminary studies[9] show a small positive ΔV^{*} value for the water exchange process, which will favor an I_d mechanism. However, no such detailed insight into the solvent exchange and complex formation mechanism of aquated Cr^{2+} is presently available.

Data are reported herein which we believe indirectly confirm the operation of an I_d ligand substitution mechanism for aquated Cr^{2+}. We have for this purpose studied the pressure dependence of the rates of reaction of various aliphatic free radicals $^{\bullet}R$ with $Cr(H_2O)_6^{2+}$ to produce $Cr(H_2O)_5R^{2+}$ (reaction 1), which involves

$$Cr(H_2O)_6^{2+} + {}^{\bullet}R \rightarrow Cr(H_2O)_5R^{2+} + H_2O \qquad (1)$$

the formation of a chromium–carbon σ bond.[10,11] Formally these products are considered to be Cr^{III}–R^{-} species, but originate from the reaction of the organic radical with Cr^{2+}. Thus the substitution of a water molecule in the coordination sphere by an aliphatic radical does involve a change in the nature of the metal–ligand bond. In general, these reactions occur with rate constants between 2×10^{7} and 3×10^{8} M^{-1} s^{-1} at 25 °C, and exhibit only a weak dependence of steric factors on $^{\bullet}R$.[10,11] The quoted rate constants are close to that reported for the complex formation between Cr^{2+} and bipyridine, viz. 3.5×10^{7} M^{-1} s^{-1}.[12] Furthermore, these rate constants seem nearly invariant when compared with the rate constants reported for the reverse homolysis reactions which vary over many orders of magnitude.[10,11] Reaction 1 involves the formation of a Cr–C σ bond and includes the release of a solvent molecule, as mentioned above. The quoted rate constants are very close to that reported for solvent exchange on $Cr(H_2O)_6^{2+}$ as obtained from complex formation studies, viz. 7×10^{9} s^{-1}, i.e. 1.3×10^{8} M^{-1} s^{-1}.[1,3,11] Thus solvent exchange may be an integral part of metal–carbon bond formation in these systems.

Table I. Rate Constants and Activation Volumes for the Reaction[a]

$$Cr(H_2O)_6^{2+} + {}^{\bullet}R \rightarrow (H_2O)_5CrR^{2+} + H_2O$$

$^{\bullet}R$	kK,[b] M^{-1} s^{-1}	ΔV^{*},[c] cm^3 mol^{-1}
$^{\bullet}CH_3$	2.2×10^{8}	+6.3
$^{\bullet}CH_2CH_2OH$	9.9×10^{7}	+4.0
$^{\bullet}CH(CH_3)OH$	1.1×10^{8}	+3.5
$^{\bullet}C(CH_3)_2OH$	6.4×10^{7}	+5.7
$^{\bullet}CH(CH_3)CH_2OH$	1.1×10^{8}	+3.9
$^{\bullet}CH_2C(CH_3)_2OH$	1.0×10^{8}	+3.4
$^{\bullet}CH_2C(CH_3)_2NH_3$	1.6×10^{7}	+3.6
$^{\bullet}CH(OH)CH_2OH$	1.0×10^{8}	+4.8
$^{\bullet}CH(CH_3)OCH_2CH_3$	3.4×10^{7}	+4.3
$^{\bullet}CH(CH_3)CH(CH_3)OH$	9.8×10^{7}	+3.9

[a] Experimental conditions: $[Cr^{2+}] = 1 \times 10^{-3}$ M; [RH] = 0.5–1.0 M; pH ≈ 3; T = 20 °C. [b] Observed second-order rate constant in terms of the interchange mechanism outlined in (3). [c] Error limits are ±1 cm^3 mol^{-1}.

Pulse radiolysis of aqueous solutions containing organic molecules RH and saturated with N_2O result in the following set of rapid reactions (2), which are completed in less than 1 μs

$$\begin{gathered} H_2O \xrightarrow{\gamma,\, e^-} e_{aq}^-, {}^{\bullet}OH, {}^{\bullet}H, H_2O_2, H_3O^+, OH^- \\ e_{aq}^- + N_2O \xrightarrow{H^+} {}^{\bullet}OH + N_2 \\ RH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H_2O \\ (CH_3)_2SO + {}^{\bullet}OH \rightarrow CH_3SOOH + {}^{\bullet}CH_3 \\ R^1R^2C{=}CR^3R^4 + {}^{\bullet}OH \rightarrow {}^{\bullet}CR^1R^2CR^3R^4(OH) \qquad (2) \end{gathered}$$

following the electron pulse.[10] These are then followed by the

---

[†] University of Witten/Herdecke.

[‡] Nuclear Research Centre Negev.

[§] Ben Gurion University of the Negev.

(1) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. *Coordination Chemistry, Vol. 2*; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; p 1.

(2) van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; Elsevier: Amsterdam, 1986.

(3) Ducommun, Y.; Merbach, A. E. Reference 2, Chapter 2.

(4) van Eldik, R. Reference 2, Chapter 3.

(5) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(6) Akitt, J. W.; Merbach, A. E. *NMR: Basic Princ. Progr.* **1990**, *24*, 189.

(7) van Eldik, R.; Merbach, A. E. *Comments Inorg. Chem.* **1992**, *12*, 341.

(8) Powell, D. H.; Helm, L.; Merbach, A. E. *J. Chem. Phys.* **1991**, *95*, 9258.

(9) Powell, D. H.; Pittet, P. A.; Merbach, A. E. Private communication.

(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(11) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.

(12) Diebler, H. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 268.

0020-1669/92/1331-3695$03.00/0

rate-determining step (1) to produce $Cr(H_2O)_5R^{2+}$. Such experiments were performed for a series of $^{\bullet}R$ at pressures up to 150 MPa,[13-15] and the corresponding volumes of activation are summarized in Table I. Throughout the series of investigated free radicals, there is no correlation of $\Delta V^{\ddagger}$ with the nature, especially size, of $^{\bullet}R$, and it remains small positive with an average value of $+4.3 \pm 1.0$ cm^3 mol^{-1}. This nearly constant activation volume cannot be correlated with a simple σ-bond formation process, since this would result in a negative intrinsic volume of activation and in a further volume decrease due to an increase in electrostriction.[5,7] Thus, the small positive volumes of activation rather suggest that solvent dissociation, in terms of an I_d mechanism outlined in (3), is the main contributor to the observed

$$Cr(H_2O)_6^{2+} + {}^{\bullet}R \overset{K}{\rightleftharpoons} [Cr(H_2O)_6^{2+}\cdot{}^{\bullet}R] \xrightarrow{k} Cr(H_2O)_5R^{2+} + H_2O \quad (3)$$

$\Delta V^{\ddagger}$.[3,6] This will account for the fact that the observed second-order rate constant (kK) does not exhibit a strong dependence on the nature of $^{\bullet}R$ and is in good agreement with that inferred from ligand substitution reactions for solvent exchange on $Cr(H_2O)_6^{2+}$.[1,3,11] The small positive $\Delta V^{\ddagger}$ is very typical for I_d substitution processes and will mainly represent $\Delta V^{\ddagger}(k)$, since $\Delta V(K)$ will be small for precursor formation involving a neutral molecule.[2,5] Again, in terms of a dissociative interchange step, $\Delta V^{\ddagger}(k)$ will mainly depend on the degree of $Cr-H_2O$ bond breakage in the transition state, with no significant dependence on the nature and size of $^{\bullet}R$. A large volume collapse resulting from the formation of the Cr–R bond and contraction of the metal center due to $Cr^{II}-{}^{\bullet}R \rightarrow Cr^{III}-R^{-}$, occurs following the transition state, as can be clearly seen from the volume profile given in Figure 1 for $R = C(CH_3)_2OH$. In this case, the volume of activation for the reverse homolysis reaction is available from the literature.[16] It follows that substitution of a coordinated water molecule by $C(CH_3)_2OH$ results in a volume collapse of 9.4 cm^3 mol^{-1}.

Does the assignment of an I_d mechanism for solvent exchange and complex formation reactions of aquated Cr^{2+} fit the results reported previously for the other first-row transition metal ions? On the basis that such reactions for $V^{2+}(t_{2g}^3)$ and $Mn^{2+}(t_{2g}^3e_g^2)$ have been shown to be I_a in character,[3,6] it may be reasonable to expect that $Cr^{2+}(t_{2g}^3e_g^1)$ must also undergo substitution according to an I_a mechanism. However, this ion is known to undergo Jahn–Teller distortion, which causes metal–ligand bond lengthening in a particular direction and may induce an I_d mechanism.[8,9] XAFS measurements on $Cr(H_2O)_6^{2+}$ suggest a tetragonal distortion with Cr–O = 1.99 Å (equatorial) and Cr–O = 2.30 Å (axial).[17,18] This also accounts for the fact that water exchange on Cr^{2+} is as fast as water exchange on Cu^{2+} (which presumably follows an I_d mechanism[9]) and is significantly faster than water exchange on Mn^{2+} and V^{2+}.[3,11] We conclude that all the indirect evidence supports the operation of an I_d solvent exchange and complex formation mechanism for aquated Cr^{2+}.

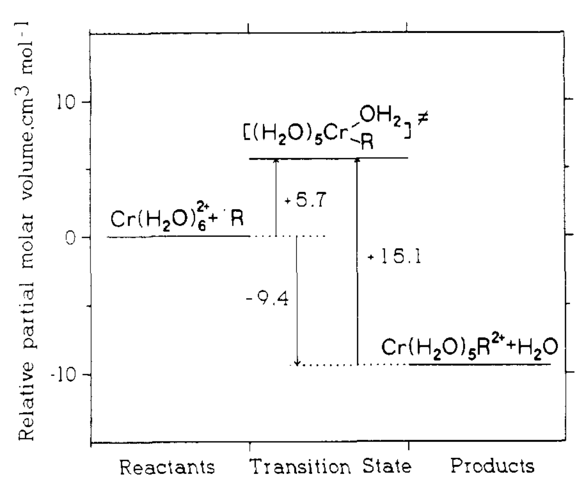

Figure 1. Volume profile for the reaction $Cr(H_2O)_6^{2+} + {}^{\bullet}R \rightleftharpoons Cr(H_2O)_5R^{2+} + H_2O$ ($R = C(CH_3)_2OH$).

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Volkswagen-Stiftung, and the German-Israeli Foundation for Scientific Research. D.M. thanks Mrs. Irene Evens for her continuous support and interest. Technical assistance by S. Cohen, Y. Nehemia, and D. Carmi is kindly acknowledged. We appreciate critical comments and a preprint of ref 8 from Professor A. E. Merbach.

---

(13) van Eldik, R.; Cohen, H.; Meshulam, A.; Meyerstein, D. *Inorg. Chem.* **1990**, *29*, 4156.

(14) van Eldik, R.; Cohen, H.; Meyerstein, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1158.

(15) Wishart, J. F.; van Eldik, R. *Rev. Sci. Instrum.* **1992**, *63*, 3224.

(16) Sisley, M. J.; Rindermann, W.; van Eldik, R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 7432.

(17) Sham, T. K.; Hastings, J. B.; Perlman, M. L. *Chem. Phys. Lett.* **1981**, *83*, 391.

(18) Micskei, K.; Nagypál, I. *J. Chem. Soc., Dalton Trans.* **1990**, 1301.