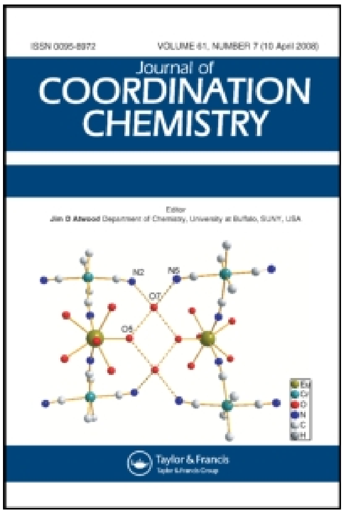

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SHORT COMMUNICATION
The Effect of Chromium-Carbon σ Bonds on the Rate of Ligand Exchange of Trivalent Chromium Ions in Aqueous Solutions

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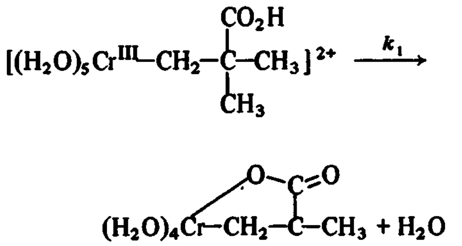
The formation of relatively stable compounds containing chromium-carbon σ bonds in aqueous solutions was reported.[1] Kinetic and spectroscopic data[1e] were interpreted as suggesting that the specific rate of the reaction:


$$[(H_2O)_5Cr^{III}{-}CH_2{-}C(CO_2H)(CH_3){-}CH_3]^{2+} \xrightarrow{k_1} (H_2O)_4Cr{-}CH_2{-}C(CH_3)(C(=O)O{-}) + H_2O \quad (1)$$

is $k_1 = (1.8 \times 10^2 + 6.0 \times 10^1 [H_3O^+])sec^{-1}$. This result indicates that the specific rate of exchange of a cis water molecule is orders of magnitude higher than that for most Cr(III) complexes. This conclusion was partially corroborated by the finding that the reactions:

$$(H_2O)_5CrCF_3^{2+} + X^- \longrightarrow (H_2O)_4Cr(CF_3)X^+ + H_2O \quad (2)$$

for $X = F^-, N_3^-, SCN^-$, occur within several minutes.[2]

It seemed of interest to obtain direct evidence for the high specific rates of ligand exchange in complexes of this type. We chose to study the kinetics of reactions of $(H_2O)_5CrCHCl_2^{2+}$ and $(H_2O)_5CrCHBr_2^{2+}$ (these complexes are stable for days in aerated aqueous solutions) with different simple ligands, e.g. Cl^-, Br^-, I^-, N_3^- and SCN^-. It was found that all these anions enhance the rate of decomposition of the chromium-carbon bonds. The kinetics of these reactions are rather complicated. We wish to report here the kinetics of the first reaction occurring upon mixing $(H_2O)_5Cr\,CHX_2^{2+}$ with SCN^-. This reaction is followed by two further reactions which are under investigation. The absorption spectra, 2–5 minutes after mixing indicate that the chromium–carbon bond is still intact.

The chromium–carbon compounds $(H_2O)_5CrCHBr_2^{2+}$ and $(H_2O)_5CrCHCl_2^{2+}$ were prepared according to the procedures reported by Johnson et al.[1c] The reaction of $(H_2O)_5CrCHX_2^{2+}$ with SCN^-(NH_4NCS, Merck Products AR) was studied in a motor driven stopped-flow apparatus built at the Hebrew University of Jerusalem.[3] The changes of absorption immediately after mixing the reactants were followed (in all experiments $[SCN^-] \gg [(H_2O)_5CrCHX_2^{2+}]$ was kept). The kinetics of reaction obeyed a pseudo first order

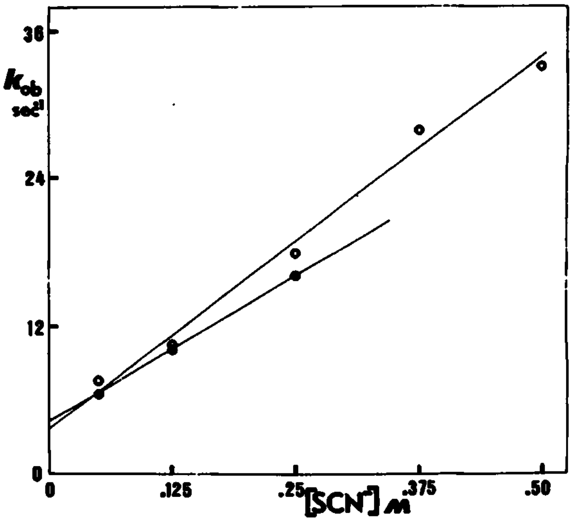


FIGURE 1 [SCN$^-$] dependence of the rate of formation of $[(H_2O)_4(SCN)CrCHX_2^+]$. ● – X = Cl^-; O–X = Br^-.

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TABLE I
Kinetic data for the ligand exchange reaction of $(H_2O)_5CrCHX_2^{2+}$ with SCN^- [a]

$(H_2O)_5Cr{-}R^{2+}$	k_3 M^{-1} sec^{-1}	k_{-3} sec^{-1}	K_3^b M^{-1}	K_3^c M^{-1}
$(H_2O)_5Cr{-}CHBr_2^{2+}$ [d]	60.0	3.6	16.7	16
$(H_2O)_5Cr{-}CHCl_2^{2+}$ [e]	46.4	4.4	10.5	11

[a] The solutions contained 0.05 – 0.75 M of SCN^-, 8 – 40 x 10^{-4} M of $(H_2O)_5CrCHX_2^{2+}$ and 0.5 M $HClO_4$. The accuracy of the values of the specific rate constants is ±5%.

[b] $K_3^b = k_3/k_{-3}$.

[c] Calculated from A_∞, see footnote. The accuracy of K_3^c is ±20%.

[d] Measured at 505, 410 and 370 n.m.

[e] Measured at 505 and 410 n.m.

rate law d(Product)/dt = $k_{ob}[SCN^-]$. The value of k_{ob} was found to be independent of $[(H_2O)_5CrCHX_2^{2+}]$, and wavelength. The dependence of k_{ob} on $[SCN^-]$ is plotted in Figure 1. These kinetic results support the suggestion that the reactions observed are:

$$(H_2O)_5CrCHX_2^{2+} + SCN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{II}{(H_2O)_4(SCN)CrCHX_2^{+}} + H_2O \qquad (3)$$

where $k_{ob} = k_{-3} + k_3[SCN^-]$. The values of k_3 and k_{-3} (Table I) for X = Br, Cl were calculated from the slopes and intercepts in Figure 1. The equilibrium constants K_3 (Table I) were calculated from the kinetic data ($K_3 = k_3/k_{-3}$) and from the change in absorbance†. The values of K_3 obtained by the two independent techniques, Table I, are in very good agreement, thus supporting the suggested reaction mechanism.

The measured values of ligand exchange rate in these complexes are in agreement with those postulated for reaction (1). It is of interest to compare the effect of $:CHX_2^-$ as ligands on the specific rates of ligand exchange with the effect of common ligands. For isothiocyanate, chloride and iodide as ligands the specific rates of water exchange trans to the ligands are, 1.5 x 10^{-5}, 2.4 x 10^{-5} and 2.7 x 10^{-4} M^{-1} sec^{-1} respectively.[4] (The rate for the exchange at the cis position is 3 x 10^{-6} M^{-1} sec^{-1} for all these ligands.) Thus the results indicate that the effect of $:CHX_2^-$ is five orders of magnitude larger than that of iodide.

The effect of $:CF_3^-$ on the rate of ligand exchange is considerably smaller than that of $:CHCl_2^-$ or $:CHBr_2^-$. This observation suggests that the labilization of the water molecules in the inner coordination sphere of $(H_2O)_5Cr\,CR_1R_2R_3^{2+}$ depends on the "softness" of the $:CR_1R_2R_3^-$ ligand. The very large effect of the later ligands on the ligand exchange rates indicates that the $:CR_1R_2R_3^-$ ligands affect the electronic structure of the $3d^3Cr^{III}$ cation to a much larger degree than common σ donor ligands. This conclusion is in agreement with the observation that one of the d–d absorption bands of $(H_2O)_5CrCR_1R_2R_3^{2+}$ complexes has a relatively large oscillator strength.

Furthermore, similar conclusions are obtained from preliminary E.P.R. data.[5]

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† K_3 was calculated using the equation

$$K_3 = \frac{C_{II}}{(Co - C_{II})[SCN^-]} \quad \downarrow \quad K_3 = \frac{A_\infty/\Delta\epsilon \cdot 1}{(Co - A_\infty/_{\Delta\epsilon \cdot 1})[SCN^-]}$$

where Co – the initial concentration of $(H_2O)_5CrCHX_2^{2+}$, A_∞ – the change in absorbance due to reaction (3); $\Delta\epsilon = \epsilon_{(H_2O)_4(SCN)CrCHX_2^+} - \epsilon_{(H_2O)_5CrCHX_2^{2+}}$ 1 – optical path (0.15 cm in these experiments). The calculations were carried in the following sequence. *a* As a first approximation K_3 was assumed to have the value obtained from the kinetic study and Δε for a given wavelength was calculated from this value (of K_3) and the measured value of A_∞ for a given solution composition. *b*. Using the calculated value of Δε, K_3 was calculated for the other solutions. *c* The average value of K_3 thus obtained was introduced into the calculations as the assumed value in step *a*. *d* This procedure of itterations was continued till a constant value was obtained. *e* These calculations were repeated at two different wavelengths.

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