with a mean of 3.108 Å. At these long distances there can be scarcely any donor bonding by sulfur to molybdenum, since Mo–S single bond lengths are typically about 2.45 Å.

Only a few thiocyanato complexes of quadruply bonded M_2 moieties have previously been reported, and only one has been examined by X-ray crystallography, namely, $Mo_2(Ph_2PCH_2PPh_2)_2(NCS)_4$.[7] The thiocyanate ions were shown to be linear and N bonded (mean Mo–N distance = 2.06 Å), and infrared data have suggested that this is true in other cases as well.[8-11]

Compounds of Mo_2^{4+} and Re_2^{6+} containing two bridging ligands and four unidentate ligands have also been reported before. Two stereochemical arrangements have been observed. A transoid arrangement, first observed in $Re_2(O_2CPh)_2I_4$,[12] has been frequently seen subsequently, and a cisoid arrangement, first observed in $Re_2(O_2CCH_3)_2Cl_4$,[13] has not been reported subsequently. Thus, these molecules have structures of a type that has previously been uncommon. The factors which might favor the cisoid and transoid arrangements are obscure.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. 1, 69596-93-6; 2, 69532-08-7; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: Tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Notes

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Activation Parameters in Electron-Transfer Reactions. The System $Co(phen)_3^{3+}$–Ferrocene in Water/Propan-1-ol Mixture

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Received October 13, 1978

Among the several theories available for treating the outer-sphere electronic-transfer reactions,[1] the Marcus theory[2] is the most useful, allowing the calculation of cross-reaction activation free energy (ΔG^*_{12}) through eq 1. $k_{12} =$

$$\Delta G^*_{12} = w_{12} + \frac{\lambda_{12}}{4}\left(1 + \frac{\Delta G^\circ{}_{12}{}'}{\lambda_{12}}\right)^2 \qquad (1)$$

$Z \exp(-\Delta G^*_{12}/RT)$ (k_{12} is the cross-reaction rate constant, Z the collision frequency in solution, assumed 10^{11} M^{-1} s^{-1}), $\Delta G^\circ{}_{12}{}' = \Delta G^\circ + w_{21} - w_{12}$, w_{12} and w_{21} being the work terms involved in bringing together the reactants and products, respectively; λ_{12} equals $2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22})$, where ΔG^*_{11} and ΔG^*_{22} represent the self-exchange activation energies and w_{11} and w_{22} the related work terms.

For reactions in which the work terms are negligible (e.g., when at least one of the reactants is uncharged or the medium is at high ionic strength) and the free energy variation is small, the expression is greatly simplified, giving eq 2, where K_{12} is

$$k_{12} \simeq (k_{11}k_{22}K_{12})^{1/2} \qquad (2)$$

the equilibrium constant and k_{11} and k_{22} are the two self-exchange rate constants.

Recently, Marcus and Sutin[3] showed that the activation parameters for an electron-transfer reaction can be derived by differentiating eq 1 with respect to temperature[4] (eq 3–5).

$$\Delta H^*_{12} = \left(\frac{\Delta H^*_{11}}{2} + \frac{\Delta H^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta H^\circ{}_{12}}{2}(1 + 2\alpha) \qquad (3)$$

$$\Delta S^*_{12} = \left(\frac{\Delta S^*_{11}}{2} + \frac{\Delta S^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta S^\circ{}_{12}}{2}(1 + 2\alpha) \qquad (4)$$

$$\alpha = \Delta G^\circ{}_{12}/4(\Delta G^*_{11} + \Delta G^*_{22}) \qquad (5)$$

Equations 3–5 have recently received some experimental verification,[5] and, while in some cases there is a good agreement, in other systems the difference between the calculated and experimental enthalpies is within 2–3 kcal mol^{-1} and for the entropies within 10 cal deg^{-1} mol^{-1}. Explanations which account for these discrepancies have been advanced.[5a]

The application of the Marcus equations is also sometimes limited, by the uncertainty in some of the parameters and by the difficulty in the evaluation of the work terms.[6] The importance of the data reliability has been recently underlined by Wherland and Gray.[7]

In order to test with more accuracy the application of eq 1–5, we have decided to investigate reactions 6 and 7 in 50:50

$$Co(phen)_3^{3+} + Fe(cp)_2 \rightleftharpoons Co(phen)_3^{2+} + Fe(cp)_2^+ \qquad (6)$$

$$Co(phen)_3^{3+} + Fe(mcp)_2 \rightleftharpoons Co(phen)_3^{2+} + Fe(mcp)_2^+ \qquad (7)$$

v/v water/propan-1-ol. In fact the self-exchange rate constants and related activation parameters can be calculated for $Fe(cp)_2^{+/0}$ system in the present medium,[8] the analogous data for $Co(phen)_3^{3+/2+}$ can be determined by polarimetry, and the equilibrium quotients for reaction 6 can be obtained spectrophotometrically at different temperatures.

Furthermore, since the terms w_{12} and w_{22} can be neglected when one reactant is uncharged, these systems are particularly versatile for the application of the Marcus equations.

Experimental Section

Materials. $Co(phen)_3(ClO_4)_3$[9] and $(+)Co(phen)_3(ClO_4)_3$[10] were prepared according to the literature procedure. $Co(phen)_3^{2+}$ was prepared in situ by the reaction of $Co(NO_3)_2$ with excess phenanthroline (from 3.2 up to 10 molar ratio). Ferrocenes were Alfa products. All other chemicals were of the highest quality available. Doubly distilled water was used.

Table II. Kinetic Data for $Co(phen)_3{}^{3+}$ Oxidation of Ferrocenes[a]

ferrocene	rate const, $M^{-1}\ s^{-1}$ 9.0 °C	25.0 °C	39.0 °C	$\Delta H^{‡}$, kcal mol^{-1}	$\Delta S^{‡}$, cal $deg^{-1}\ mol^{-1}$
$Fe(cp)_2$	$(8.0 \pm 1.7) \times 10^2$	$(2.3 \pm 0.3) \times 10^3$	$(6.6 \pm 1.3) \times 10^3$	11.7 ± 1.5	-4 ± 5
$Fe(mcp)_2$	$(2.5 \pm 0.3) \times 10^3$	$(1.0 \pm 0.2) \times 10^4$	$(2.5 \pm 0.2) \times 10^4$	12.9 ± 1.7	$+3 \pm 5$

[a] 50:50 v/v water/propan-1-ol; $[KNO_3] = 0.02$ M.

Equilibrium Measurements. The equilibrium quotient for reaction 6 was determined by a spectrophotometric technique at 15.0, 25.0, and 31.0 °C ($\mu = 0.02$ M (KNO_3), 50:50 v/v water/propan-1-ol), following the absorbance at 620 nm, the wavelength where $Fe(cp)_2{}^+$ is the only species which absorbs significantly. The concentration of ferricenium ion was calculated from its molar absorptivity coefficient, measured at the same wavelength by oxidation of ferrocene with iron(III) perchlorate (this reaction has been proven to be quantitative)[8] ($\epsilon = 4.0 \times 10^2\ M^{-1}\ cm^{-1}$, while for the other species $\epsilon \leq 5\ M^{-1}\ cm^{-1}$).

The equilibrium quotients were then calculated from the known initial concentrations of $Co(phen)_3{}^{3+}$, $Co(phen)_3{}^{2+}$, and $Fe(cp)_2$ and the calculated equilibrium concentration of $Fe(cp)_2{}^+$.

Self-Exchange Rate Measurements. The measurements of self-exchange rates at $\mu = 0.02$ M (KNO_3) and 25.0, 35.0, and 45.0 °C in 50:50 water/propan-1-ol for the $Co(phen)_3{}^{3+/2+}$ couple were carried out in a 10-cm cell by following the decrease of the optical activity (α) of the Co(III) complex with time. Measurements were carried out at 340 nm with a Perkin-Elmer polarimeter. The initial concentrations were 2×10^{-4} M and $(1-2) \times 10^{-5}$ M, respectively. Plots of log α_t vs. time were linear, and the second-order rate constants were derived according to the treatment proposed by Im and Busch.[11]

Kinetic Measurements of Reactions 6 and 7. The kinetic runs were followed at 620 nm by means of a Durrum-Gibson stopped-flow spectrophotometer. The initial concentration of ferrocenes was $(3-5) \times 10^{-5}$ M, while $[Co(phen)_3{}^{3+}]$ was in the range of $(1-7) \times 10^{-4}$ M ($\mu = 0.02$ M (KNO_3), 50:50 v/v water/propan-1-ol at different temperatures). Conditions were chosen in order to shift the reactions toward completion. Both second-order constants and the method proposed by Corbett[12] gave satisfactory results. When the reverse reaction can be significant, i.e., in reaction 6, the data were also computed with the kinetic equations derived for equilibrium reactions.[5c]

Results

Equilibrium Quotients. The data referring to $Co(phen)_3{}^{3+}$–$Fe(cp)_2$ at 25.0 °C are summarized in Table I. The following equilibrium quotients for reaction 6 were determined: 0.92 ± 0.12 at 15.0 °C (18 measurements), 2.1 ± 0.2 at 25.0 (18), 2.9 ± 0.5 at 31.0 (20). The related $\Delta H^\circ = 12.5 \pm 2.2$ kcal mol^{-1} and $\Delta S^\circ = 43 \pm 7$ cal $deg^{-1}\ mol^{-1}$ were estimated.

Self-Exchange Rates. At 25.0 °C, the value for $Co(phen)_3{}^{3+/2+}$ self-exchange of $1.1 \pm 0.1\ M^{-1}\ s^{-1}$ (averaged over eight measurements) has been determined. From four measurements at 35.0 °C ($1.5 \pm 0.2\ M^{-1}\ s^{-1}$) and 45.0 °C ($2.5 \pm 0.3\ M^{-1}\ s^{-1}$), the activation parameters $\Delta H^{‡} = 7.2 \pm 1.6$ kcal/mol and $\Delta S^{‡} = -34 \pm 5$ cal $mol^{-1}\ deg^{-1}$ can be calculated.

Electron-Transfer Rates. The electron-transfer rate constants for reactions 6 and 7 and the related activation parameters are collected in Table II.

Discussion

K_{12}, k_{11}, and k_{22} for reaction 6 are known. Since the free energy change involved is small, eq 2 can be applied: a value of $3.6 \times 10^3\ M^{-1}\ s^{-1}$ (25.0 °C) can be compared with the experimental value of $2.3 \times 10^3\ M^{-1}\ s^{-1}$ (a value of $5.7 \times 10^6\ M^{-1}\ s^{-1}$ has been used for the $Fe(Cp)_2{}^{+/0}$ self-exchange rate).[8] If the more general expression (1) is adopted, a value of $6.2 \times 10^3\ M^{-1}\ s^{-1}$ is obtained.[13] The equilibrium quotient for reaction 7 can be estimated from the difference in the reduction potentials between the $Fe(cp)_2{}^{+/0}$ and $Fe(mcp)_2{}^{+/0}$ systems in 50:50 v/v water/propan-1-ol;[8] this calculation leads to a value 48 (at 25.0 °C). Then eq 2 gives k_{12}(calcd) = $3.1 \times 10^4\ M^{-1}\ s^{-1}$ ($k_{11} = 6.6 \times 10^6\ M^{-1}\ s^{-1}$ for the $Fe(mcp)_2{}^{+/0}$ self-exchange rate) in agreement with k_{12}(exptl) = $1.0 \times 10^4\ M^{-1}\ s^{-1}$.

In order to verify the applicability of eq 3–5, the activation parameters concerning $Fe(cp)_2{}^{+/0}$ have been derived from the literature data by averaging the results concerning two different systems:[16] the values derived are $\Delta H_{11}{}^{‡} = 3.8$ kcal mol^{-1} and $\Delta S_{11}{}^{‡} = -14$ cal $deg^{-1}\ mol^{-1}$.

Due to the small value of α, eq 3 and 4 can be simplified to

$$\Delta H^*{}_{12} = \tfrac{1}{2}(\Delta H^*{}_{11} + \Delta H^*{}_{22} + \Delta H^\circ{}_{12})$$

and

$$\Delta S^*{}_{12} = \tfrac{1}{2}(\Delta S^*{}_{11} + \Delta H^*{}_{22} + \Delta S^\circ{}_{12})$$

These expressions lead to a $\Delta H_{12}{}^{‡}$(calcd) = 11.8 kcal mol^{-1} and $\Delta S_{12}{}^{‡}$(calcd) = -3 cal $deg^{-1}\ mol^{-1}$ for reaction 6, to be compared with $\Delta H_{12}{}^{‡}$(exptl) = 11.7 kcal mol^{-1} and $\Delta S_{12}{}^{‡}$(exptl) = -4 cal $deg^{-1}\ mol^{-1}$.

Then, for the present system, there is good agreement between experimental results and calculated values.

Registry No. $Fe(cp)_2$, 102-54-5; $Fe(mcp)_2$, 1291-47-0; $Co(phen)_3{}^{3+}$, 18581-79-8.

Supplementary Material Available: Table I containing equilibrium quotients for reaction 6 (1 page). Ordering information is given on any current masthead page.

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