TABLE IV

VIBRATIONAL DATA (CM^{-1}) FOR $SeCl_4$ AND RELATED SPECIES

$SeCl_4$ (solid)[a] Raman	$SeCl_6^{2-}$ (aqueous)[b] Raman	$SeCl_4$ (solid)[c] Infrared	
[560] (0–1)			
[515] (0)			
474 (1−)			
ca. 441 (1−)			
388 (15)		371, vs; ν_1 (a_1)	
346 (15)	346, ν_1 (a_1)	348, vs; ν_2 (e)	
ca. 258 (1−)	273, ν_2 (e)	275, m, br	
206 (3–4)		205, w	br ν_2 (a_1), ν_4 (e)
164 (1–2)	166, ν_5 (f_{2g})	190, s	
127 (2)		165, m	
96 (4)		145, m	
69 (1)		80, m, br, lattice	

[a] Reference 7. [b] Reference 28. [c] This work.

possible presence of $SeCl_5^-$ ions, because of the small number of Raman lines of sufficient intensity to be considered fundamentals. The infrared spectrum is ambiguous in this regard. In their discussion Gerding and Houtgraaf did not consider the possibility of $SeCl_6^{2-}$ ions, a much more likely species than $SeCl_5^-$. The observed Raman fundamentals[28] for octahedral $SeCl_6^{2-}$ at 346 and 166 cm^{-1} are readily accommodated by the Raman results for $SeCl_4$, but the other allowed $SeCl_6^{2-}$ fundamental at 273 cm^{-1} would have to experience a shift to about 258 cm^{-1} in $SeCl_4$ if $SeCl_6^{2-}$ were to be considered present in the solid tetrachloride. Infrared examination[14] of $[(CH_3)_4N]_2SeCl_6$ yields absorption at 294 and 182 cm^{-1}, the former of which could be shifted to 275 cm^{-1} in the infrared spectrum of solid $SeCl_4$. Thus, the available vibrational data are in accord with the presence of $SeCl_3^+$ species in solid $SeCl_4$ but are inconclusive regarding the nature of the anionic species.

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A Kinetic Study of the Reactions of Chromium(II) and the Isomeric Dichlorotetraaquochromium(III) Ions[1a]

BY JAMES H. ESPENSON AND SALLY G. SLOCUM[1b]

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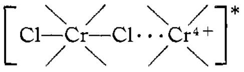
Measurements using the stopped-flow technique were carried out on the rate of the chromium(II)-catalyzed aquation reactions of *trans*- and *cis*-dichlorotetraaquochromium(III) ions which produce monochlorochromium(III) ion. Each reaction is first-order with respect to the chromium(III) complex and with respect to chromium(II). Both reactions proceed by a chloride-bridged Cr(II)–Cr(III) exchange process that leads to chromium exchange and accompanying aquation of the nonbridging chloride ion. The reaction rates were studied as a function of temperature to determine the activation parameters. For *trans*, $k = 401 \pm 33\ M^{-1}\ \text{sec}^{-1}$ at 25.0°, with $\Delta H^* = 4.9 \pm 0.5$ kcal mole^{-1} and $\Delta S^* = -30.2 \pm 1.8$ cal mole^{-1} deg^{-1}; for *cis*, $k = 288 \pm 11\ M^{-1}\ \text{sec}^{-1}$ at 25.0°, with $\Delta H^* = 5.7 \pm 0.3$ and $\Delta S^* = -28.2 \pm 1.0$. The mechanism is discussed and compared to some related Cr(II)–Cr(III) electron-transfer processes.

Introduction

The reaction of dichlorochromium(III) and chromium(II) ions was one of the first electron-transfer reactions shown by Taube and Myers[2] to proceed by an "inner-sphere" or "bridged" transition state



$$\left[\text{Cl—Cr—Cl}\cdots\text{Cr}^{4+}\right]^*$$

on the basis of formation of the monochlorochromium(III) ion in a reaction (eq 1) in which chromium(II) acts

$$trans\text{-}CrCl_2^+ = CrCl^{2+} + Cl^- \qquad (1)$$

as a rather efficient catalyst for the partial aquation of *trans*-$CrCl_2^+$. The feature of net aquation allows the reaction rate to be followed by virtue of the chemical change without resort to isotopic labeling.

Replacement of chloride ion by water in the dichloro complexes is quite favorable thermodynamically,[3] with <0.1% of the dichloro species remaining at equilibrium in a solution initially 0.01 *M*. Spontaneous aquation proceeds slowly,[4] however, and metastable dichloro species have been isolated and their geometrical isomers separated.[5] In a single rate measurement on the very rapid chromium(II) catalysis, Taube and Myers[2] found that the rate constant (presuming a rate law first order in each component) was $1.7 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ at 0.2° in 1 *F* perchloric acid.

Again in a single rate experiment, Johnson and Rey-

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(1) (a) This work was performed at the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2001. (b) Undergraduate research participant, summer 1966.

(2) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

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(4) J. Salzman and E. L. King, *Inorg. Chem.*, **6**, 426 (1967).

(5) E. L. King, Sr. M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

nolds[6] found a rate constant of $\sim 1 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, under unspecified conditions of temperature and medium, for the analogous reaction (eq 2) of the *cis* complex catalyzed by chromium(II).

$$cis\text{-}\mathrm{CrCl_2}^+ = \mathrm{CrCl}^{2+} + \mathrm{Cl}^- \qquad (2)$$

We have carried out a detailed study of the kinetics of chromium(II) catalysis of the aquation reactions of the isomeric dichlorochromium(III) ions, using the stopped-flow technique with a spectrophotometric detection system. The half-times of the reactions studied here under the various conditions examined lay between 0.03 and 1.1 sec.

Experimental Section

Reagents.—Solutions of *trans*-$\mathrm{CrCl_2}^+$ were prepared by dissolving reagent grade green chromium(III) chloride, $[\mathrm{Cr(OH_2)_4Cl_2}]\mathrm{Cl \cdot 2H_2O}$, in 1 *F* perchloric acid. Such solutions contain the *trans* complex as the only chromium(III) species.[5,7] The *cis* complex was prepared and separated in pure form by ion exchange according to the procedure of King, Woods, and Gates.[5] The absorbance ratio D_{4500}/D_{6350} provides a convenient criterion for isomeric purity.[5] Fractions with ratios ≥ 1.40 were used for *cis*, and most of the *cis* material used had values 1.44–1.46. The purified *cis* isomer was obtained as a dilute solution (*ca.* 0.01 *M*) in 0.1 *F* perchloric acid. These solutions were frozen and stored at −78° until use.

Chromium(II) perchlorate solutions in perchloric acid were prepared by electrolytic reduction of chromium(III) perchlorate and stored and analyzed as described previously.[8] Stock solutions of chromium(II) were diluted for use as needed in the kinetic runs by transferring aliquots of the solution, using a syringe, into a solution containing the requisite amounts of perchloric acid, lithium perchlorate, and water. The solutions were continuously swept with nitrogen gas from which traces of oxygen had been removed by chromium(II) wash solutions. Each diluted solution was individually analyzed for chromium(II) taking advantage of its rapid oxidation by a slight excess of pentaamminechlorocobalt(III) ion.[9] Lithium perchlorate was prepared by dissolving the carbonate in perchloric acid. The solid was crystallized from this solution and recrystallized twice more. Reagent grade perchloric acid was used without purification, and conductivity water distilled from alkaline permanganate was used in all solutions.

Rate Studies.—The stopped-flow apparatus and our procedures for rate measurements have been described in some detail.[10] Since the chromium(II) concentration remained constant during a particular run, the reaction followed pseudo-first-order kinetics. Conditions of concentration and wavelength were adjusted so that the absorbance change in a run was sufficiently large (>0.005) for accurate measurement of rates but sufficiently small (<~0.1) that absorbance and transmittance remained closely proportional.[10] The relevant molar absorbancy indices for the dichloro ions were taken from the literature.[5] These values were not needed in computations involving the kinetic data since first-order kinetics were obeyed but were useful in selecting appropriate reaction conditions.

Solutions of the *cis* and *trans* complexes were prepared shortly before use to avoid interference from spontaneous aquation or isomerization. The available kinetic data[4] indicate that, during the preparation of solutions and the rate measurements, inappreciable aquation or isomerization occurred at the hydrogen ion concentrations and temperatures employed. The solutions were thoroughly bubbled out with purified nitrogen before and during their use in the rate studies.

Results and Discussion

Kinetic Results.—Most rate studies on *trans*-$\mathrm{CrCl_2}^+$ were made at a wavelength corresponding to one or the other of its two visible peaks,[5] 4480 and 6350 A. The concentration ranges covered in the study of the *trans* isomer were as follows: chromium(II), 0.005–0.05 *M;* *trans*-$\mathrm{CrCl_2}^+$, 2×10^{-4}–0.036 *M;* and hydrogen ion, 0.02–0.96 *M*. Most experiments were carried out at the higher acid concentrations, $[\mathrm{H}^+] > 0.8\ M$. The data at 25° summarized in Table I are consistent with a single-term rate law, eq 3, with $k_t = 401 \pm 33\ M^{-1}\ \text{sec}^{-1}$ at 25.0°. Within experimental error this value is independent of $[\mathrm{H}^+]$.

$$-\mathrm{d}[trans\text{-}\mathrm{CrCl_2}^+]/\mathrm{d}t = k_t[\mathrm{Cr}^{2+}][trans\text{-}\mathrm{CrCl_2}^+] \qquad (3)$$

The scarcity of *cis*-$\mathrm{CrCl_2}^+$ ion and the difficulty in preparing in quantity solutions containing only this species prompted us to confine our kinetic studies to concentrations of *cis* $0.2\text{–}1.0 \times 10^{-3}\ M$. The reaction was followed exclusively in the ultraviolet region, 2450–2600 A, where the extinction coefficient difference between *cis* and monochloro leads to a larger absorbance change. The range of chromium(II) concentration covered was 0.002–0.02 *M*, but hydrogen ion was not varied substantially in our study of the *cis* complex. The kinetic data are summarized in Table II, and the value of k_c (defined by eq 4) is $288 \pm 11\ M^{-1}\ \text{sec}^{-1}$ at

$$-\mathrm{d}[cis\text{-}\mathrm{CrCl_2}^+]/\mathrm{d}t = k_c[cis\text{-}\mathrm{CrCl_2}^+][\mathrm{Cr}^{2+}] \qquad (4)$$

25.0°. By analogy with the behavior of *trans*, we assumed no dependence upon $[\mathrm{H}^+]$, but sought no experimental confirmation of this point.

Temperature Dependence and Activation Parameters.—A number of runs for both isomers were performed also at 16.0 and 34.2°. The values are summarized in Tables I and II.

The absolute rate theory expression was applied to the rate constants for each complex at these temperatures. The values of the activation parameters are $\Delta H^*_t = 4.9 \pm 0.5$ kcal mole^{-1} and $\Delta S^*_t\ (\kappa = 1) = -30 \pm 1.8$ cal mole^{-1} deg^{-1}; the corresponding values for the *cis* isomer are 5.7 ± 0.3 and -28.2 ± 1.0. Observed and calculated rate constants at the temperatures studied are: 16.0°, $k_t = 345$ (obsd), 319 (calcd); $k_c = 211$, 209; 25.0°, $k_t = 401$, 425; $k_c = 288$, 291; 34.2°, $k_t = 588$, 560; $k_c = 400$, 399 M^{-1} sec^{-1}.

Mechanism and Rate Comparisons.—Our kinetic results show that the chloride-bridged reduction of the *trans* isomer occurs at a slightly higher rate than that of *cis*. In related chloride-bridged inner-sphere reactions, chromium(II) exchanges with $\mathrm{Cr(OH_2)_5Cl}^{2+}$ [11] more rapidly than it does with $\mathrm{Cr(NH_3)_5Cl}^{2+}$.[12] Ogard and Taube[12] attributed the lower rate of the ammine complex to the greater ligand field strength of $\mathrm{NH_3}$ com-

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TABLE I

KINETIC DATA[a] FOR *trans*-$CrCl_2^+ + Cr^{2+}$

Temp, °C	$[Cr^{2+}]$, *M*	$[trans]_0$, *M*	$[H^+]$, *M*	k_t, M^{-1} sec^{-1} [b]
16.0	0.010	0.025	0.935	335 ± 9 (5)
16.0	0.021	0.025	0.855	359 ± 9 (4)
16.3	0.025	0.007	0.890	326 ± 19 (5)
15.9–16.1	0.025	0.025	0.855	354 ± 10 (4)
16.0	0.021	0.025	0.12	379 ± 8 (6)
16.0	0.011	0.025	0.11	356 ± 7 (5)
16.0	0.005	0.01	0.02	311 ± 19 (5)
25.0	0.005	0.0021	0.934	430 ± 12 (6)
25.0	0.005	0.0043	0.953	360 ± 8 (5)
25.0	0.005	0.0082	0.948	397 ± 15 (6)
25.0	0.005	0.032	0.908	350 ± 15 (11)
25.0	0.010	0.0002	0.960	408 ± 34 (5)
25.0	0.010	0.0034	0.913	384 ± 25 (9)
25.0	0.010	0.017	0.895	385 ± 16 (6)
25.0	0.010	0.019	0.893	442 ± 10 (4)
25.0	0.010	0.036	0.870	446 ± 11 (6)
25.0	0.015	0.018	0.914	437 ± 21 (4)
25.0	0.025	0.015	0.796	390 ± 20 (2)
25.0	0.025	0.016	0.784	425 ± 9 (4)
25.0	0.025	0.018	0.756	448 ± 14 (17)
25.0	0.050	0.0073	0.801	350 ± 20 (4)
25.0	0.010	0.018	0.09	445 ± 17 (2)
34.2	0.006	0.025	0.951	602 ± 13 (5)
34.2	0.010	0.009	0.935	584 ± 39 (5)
34.2	0.016	0.025	0.915	576 ± 18 (17)
34.2	0.026	0.025	0.880	588 ± 12 (3)

[a] 1.00 *M* ionic strength maintained with lithium perchlorate. [b] Uncertainties represent the average deviation of individual values from the mean. The number of duplicate runs is shown in parentheses.

TABLE II

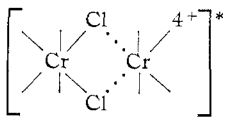
KINETIC DATA[a] FOR *cis*-$CrCl_2^+ + Cr^{2+}$

Temp, °C	$[Cr^{2+}]$, *M*	$[cis]_0$, *M*	$[H^+]$, *M*	k_c, M^{-1} sec^{-1} [b]
16.0	0.005	0.0005	0.976	208 ± 8 (3)
16.0	0.008	0.0005	0.968	213 ± 12 (3)
16.0	0.018	0.0005	0.940	211 ± 20 (4)
25.0	0.002	0.0005	0.988	305 ± 9 (4)
25.0	0.0065	0.001	0.973	277 ± 9 (4)
25.0	0.008	0.0005	0.968	298 ± 9 (4)
25.0	0.01	0.0002	0.960	283 ± 20 (4)
25.0	0.01	0.001	0.956	299 ± 11 (3)
25.0	0.02	0.001	0.916	275 ± 13 (6)
34.2	0.005	0.0005	0.980	392 ± 21 (3)
34.2	0.008	0.0005	0.968	422 ± 36 (6)
34.2	0.012	0.0005	0.952	392 ± 30 (5)
34.2	0.020	0.0005	0.920	393 ± 29 (7)

[a,b] See footnotes of Table I.

pared to H_2O. A higher-field ligand *trans* to the bridging chloride ion raises the vacant e_g orbital on Cr(III) to a higher energy resulting in higher activation energy for reduction to Cr(II), with electronic structure $t_{2g}^3e_g^1$. This line of reasoning also has been applied to other reactions.[13,14] The lower rate of reaction of *cis*-$Cr(OH_2)_4Cl_2^+$ compared to *trans* is consistent with the lower ligand field strength of chloride compared to water. The slightly higher value of ΔH^* for the *cis* isomer was predicted by this model, and would, by itself lead to a ratio of ~4 for k_t/k_c. The values of ΔS^* oppose this effect, however, and the observed k_t/k_c ratio is only 1.4 at 25°. The rate effects are small, however, consistent with the relatively small difference in ligand field strength of chloride ion and water.

Our experiments do not settle the question of whether a "double-bridged" transition state attains importance relative to the single bridged path in the case of the *cis* isomer. Since the double-bridged reaction leads only to isotopic exchange rather than net aquation, we would not observe it by our methods of rate measurement. Available evidence suggests that only in the case of certain polyatomic ligands (azide ion[15,16] and perhaps hypophosphite ion[17]) can the rate of a double-bridged reaction compete with electron transfer by a single bridge; in other instances[18,19] where a search was made for this reaction with simple ligands its rate was immeasurably low relative to the single-bridged reaction.

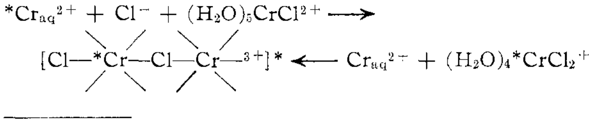


Recent experiments[20,21] have demonstrated the presence of a rate-law term $k[CrCl^{2+}][Cr^{2+}]/[H^+]$ resulting in the loss of Cl^- catalyzed by chromium(II). This reaction presumably corresponds to hydroxide-bridged electron transfer. Our data with *trans*-$CrCl_2^+ + Cr^{2+}$ indicate the analogous path is unimportant here, at $[H^+] \geq 0.02$ *M*, within the precision of the data; $[H^+]$ was not varied in our runs with the *cis* isomer.

The Reverse Reaction.—In their study of exchange of chromium(II) and monochlorochromium(III) ions, Taube and King[22] noted appreciable catalysis by chloride ion. The rate-law term for this path was of the form given in eq 5, with $k_{Cl} = 0.50\ M^{-2}\ sec^{-1}$ at 0° and 1.2 *M* ionic strength.

$$R_{ex} = k_{Cl}[Cr^{2+}][CrCl^{2+}][Cl^-] \qquad (5)$$

This transition state has a composition identical with that for chromium(II)-catalyzed aquation reactions of dichlorochromium(III) studied here, with the possible exception of a different number of solvent molecules. This alone does not prove they are identical; there could, for example, be a quite different geometrical arrangement of the chromium or chlorine atoms. Taube and King[22] suggest that these two processes are the forward and reverse of one another; this can be represented as in eq 6. On this basis the ratio of rate constants is the formation quotient Q_2



$$^*Cr_{aq}^{2+} + Cl^- + (H_2O)_5CrCl^{2+} \longrightarrow [Cl{-}^*Cr{-}Cl{-}Cr{-}^{3+}]^* \longleftarrow Cr_{aq}^{2+} + (H_2O)_4{}^*CrCl_2^+ \qquad (6)$$

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for $CrCl_2^+$. Since the observed k_{Cl} may consist of both *cis* and *trans* contributions, the ratios cannot be evaluated uniquely from these data alone. The individual contributions of each of the isomeric forms can be resolved from the kinetic results in combination with Salzman and King's equilibrium quotient[4] for *cis-trans* isomerization; at 35° and 0.2 M ionic strength, [*cis*]/[*trans*] is 1.2$_7$. This value undoubtedly is relatively insensitive to both temperature and ionic strength. Assuming this value at 0° and 1.0 M ionic strength and that the scheme in eq 6 holds for each isomer, the following values are derived: $k_{Cl}(trans) = 0.28\ M^{-2}\ sec^{-1}$, $k_{Cl}(cis) = 0.22\ M^{-2}\ sec^{-1}$, $k_{Cl}(trans)/k_t = Q_{2t} = 1.6 \times 10^{-3}\ M^{-1}$, and $k_{Cl}(cis)/k_c = Q_{2c} = 2.0 \times 10^{-3}\ M^{-1}$.

Equilibrium studies on the individual forms of $CrCl_2^+$ have not been carried out. Gates and King[3] determined the gross stability quotient for the equilibrium mixture of dichloro species. These experiments measured the *unweighted* sum $Q_{2c} + Q_{2t}$; at 4.4 m univalent anion concentration and 0° (extrapolated) the value is 0.015 M^{-1}. Our calculation gave 0.003$_6$ M^{-1} at $I = 1.0\ M$ and 0°. The substantial difference in ionic media being considered does not allow these two values to constitute the independent check they would otherwise provide, but the discrepancy appears not at all unreasonable.[23]

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[23] The effect of this medium change on a related reaction can be seen in a comparison of values of the first stability quotient of monochlorochromium(III) which was evaluated independently in each of these two media. At 30° the values are 0.27 M^{-1} at 4.4 m univalent anion concentration[3] and 0.086 M^{-1} at $I = 0.96\ M$: R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

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Extended Hückel Calculations of the Molecular Orbitals in Bis(β-ketoenolate) Complexes of Copper(II) and Nickel(II)

BY F. A. COTTON, C. B. HARRIS, AND J. J. WISE

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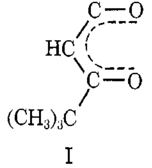
Extended Hückel-type MO calculations have been carried out on bis(β-ketoenolate) complexes of Cu(II) and Ni(II), taking these as planar molecules of D_{2h} symmetry, with the ring substituents as hydrogen atoms (to limit the size of the basis set of atomic orbitals). The Wolfsberg–Helmholz approximation was used to estimate off-diagonal matrix elements. The diagonal matrix elements for the metal orbitals were estimated by Ros' procedure in which VSIP's are corrected (substantially) for the influence of the ligand atoms. The coefficient of the d_{xy} orbital in one of the MO's was constrained to have a value similar to that indicated by esr data by adjustment of the H_{ii} terms of the oxygen atoms. The results of the calculation are in good agreement with esr data and the visible spectra and are useful in interpreting ultraviolet spectra, as shown in subsequent papers.

Introduction

The interpretation of the spectra and magnetic properties and, in general, understanding of the electronic structures and chemical bonding in transition metal complexes with β-ketoenolate anions are matters of some importance in coordination chemistry and have already received considerable attention.[1-13] Nonetheless, there still remain a number of unresolved questions concerning the assignment of spectral transitions and the validity of extended Hückel molecular orbital calculations in such molecules.

This is the second of several papers describing new studies of the compounds $Ni(DPM)_2$ and $Cu(DPM)_2$, where DPM is an abbreviation for the anion derived from dipivaloylmethane (I). The first paper[14] in the present series described the crystal structure of $Ni(DPM)_2$. It was found that the two compounds, $Cu(DPM)_2$ and $Ni(DPM)_2$, are crystallographically isomorphous and that the orientation of the planar molecules in the unit cells is very favorable for study of the polarization of absorption bands. The present paper describes molecular orbital calculations for these molecules. The calculations were influenced by and correlated with the results of the esr studies of $Cu(DPM)_2$



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