CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA 16802

Nonbridging Ligand Effects in the Reactions of *cis*- and *trans*-$Cr(en)_2Cl_2^+$ and *cis*- and *trans*-$Cr(en)_2OH_2Cl^{2+}$ with Chromium(II)[1a]

BY DAVID E. PENNINGTON AND ALBERT HAIM[1b]

Received June 22, 1966

Chromium(II) catalyzes the dissociation of *cis*- and *trans*-$Cr(en)_2XCl^{n+}$ ($X = Cl, H_2O$) by electron transfer *via* chloride-bridged transition states. The reactions obey the rate law $-d[Cr(en)_2XCl^{n+}]/dt = k[Cr^{2+}][Cr(en)_2XCl^{n+}]$. Values of k in M^{-1} sec^{-1} (enthalpies of activation in kcal/mole follow in parentheses) at 25° and $\Sigma[ClO_4^-] = 1.0\ M$ are: 3.90×10^{-2} (9.0), 1.18 (8.7), 1.16×10^{-2} (10.2), and 0.434 (8.0) for *cis*-$Cr(en)_2Cl_2^+$, *trans*-$Cr(en)_2Cl_2^+$, *cis*-$Cr(en)_2OH_2Cl^{2+}$, and *trans*-$Cr(en)_2OH_2Cl^{2+}$, respectively. The results are used to discuss the nonbridging ligand effects of Cl^- and H_2O in *cis* and *trans* positions relative to the bridging ligand.

Introduction

The role of bridging ligands in electron-transfer reactions is well documented.[2] Various observations on the effects of nonbridging ligands have also been made,[3] but it is only recently that the role of nonbridging ligands directly bound to the oxidant has been examined systematically.[4-6]

In the present paper we report the results of a kinetic study of the reactions of *cis*- and *trans*-$Cr(en)_2Cl_2^+$ and of *cis*- and *trans*-$Cr(en)_2OH_2Cl^{2+}$ with chromium(II).

$$Cr(en)_2XCl^{n+} + Cr^{2+} + 2H^+ \longrightarrow CrCl^{2+} + Cr^{2+} + X + 2enH^+ \quad (X = Cl, H_2O) \quad (1)$$

As observed previously for the analogous reactions of halogenopentaamminechromium(III) complexes,[7] chromium(II) acts as a catalyst for the dissociation of the chromium(III) complexes. Since the chromium(II)-catalyzed dissociations proceed *via* chloride-bridged transition states, the present measurements provide information regarding the role of water and chloride ion as nonbridging ligands.

Experimental Section

Materials.—Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate with amalgamated zinc and were stored in serum bottles under prepurified argon. The chromium(II) concentration was determined by reaction with an excess of iron(III), followed by titration of the iron(II) produced with a standard potassium dichromate solution.[8] The total chromium content was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[9] The chromium(II) solutions contained less than 1% chromium(III).

Sodium perchlorate solutions were prepared by neutralization of sodium carbonate with perchloric acid.

All other chemicals were reagent grade. Triply distilled water was used for measurements at low ($<0.02\ M$) chromium(II) concentrations.

Preparation of Complexes.—*cis*$[Cr(en)_2Cl_2]ClO_4$ was prepared from the corresponding chloride monohydrate[10] according to the method of Linhard and Weigel.[11]

Repeated attempts to prepare *trans*-$[Cr(en)_2Cl_2]Cl$ from *trans*-$[Cr(en)_2(NCS)_2]SCN$ following published procedures[12,13] failed. Since we have found that the reaction of *trans*-$Co(en)_2Br_2^+$ with chlorine yields *trans*-$Co(en)_2Cl_2^+$ quantitatively,[14] the following alternate preparation was devised. Treatment of a suspension of 6 g of *trans*-$[Cr(en)_2Br_2]Br \cdot HgBr_2$[15] in 30 ml of water (0°) with hydrogen sulfide yielded a residue of mercury(II) sulfide and a dark green solution containing *trans*-$Cr(en)_2Br_2^+$. The solution was mixed with 60 ml of saturated (0°) sodium perchlorate solution, and the resulting precipitate of *trans*-$[Cr(en)_2Br_2]ClO_4$ was separated by filtration and then washed successively with 95% ethanol, acetone, and ether; yield 1.4 g. This product was suspended in 20 ml of water (0°) and treated with chlorine for 15–20 min. Recrystallization of the resulting solid was effected by dissolution in 175 ml of water at room temperature followed by addition of 50 ml of saturated sodium perchlorate solution and cooling to 0°; yield 0.7 g of *trans*-$[Cr(en)_2Cl_2]ClO_4$.

cis- and *trans*-$Cr(en)_2OH_2Cl^{2+}$ were prepared in solution by ion-exchange separation of the aquation products of *cis*- and *trans*-$Cr(en)_2Cl_2^+$, respectively.[16]

The purity of the complexes was ascertained by comparing the absorption spectra measured in the present work with the spectra reported in the literature. Table I lists the wavelengths of the absorption maxima and the corresponding molar absorbancy indeces for the complexes investigated.

Stoichiometric Measurements.—Reaction vessels were serum bottles covered with self-sealing rubber caps. All manipulations were performed under an atmosphere of prepurified argon. The desired volumes of chromium(II) solutions were added by means of calibrated hypodermic syringes with steel needles to the solutions of the chromium(III) complexes containing the desired amounts of sodium perchlorate and/or perchloric acid. After completion of the reactions (1–3.5 hr at room temperature), oxygen was admitted to oxidize the excess chromium(II). Separation of the $CrCl^{2+}$ produced was achieved by ion exchange on

---

(1) (a) This work was supported by Grant GP-2001 from the National Science Foundation. (b) Fellow of the Alfred P. Sloan Foundation.

(2) For a recent review see N. Sutin, *Ann. Revs. Phys. Chem.*, in press.

(3) Some of these observations have been summarized by H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(4) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(5) R. D. Cannon and J. E. Earley, *ibid.*, **87**, 5264 (1965); *ibid.*, **88**, 1872 (1966).

(6) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

(7) (a) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958). (b) In contrast to the spontaneous aquation which involves replacement of Cl^- by H_2O, $Cr(en)_2XCl^{n+} + H_2O = Cr(en)_2OH_2X^{n+1} + Cl^-$, the chromium(II)-catalyzed dissociation results in replacement of ethylenediamine and X by water, as shown in eq 1.

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 579.

(9) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(10) W. C. Fernelius, *Inorg. Syn.*, **2**, 200 (1946).

(11) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 119 (1952).

(12) P. Pfeiffer, P. Koch, T. G. Lands, and M. Frieschman, *Ber.*, **37**, 4255 (1904).

(13) G. Schlesinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962, p 223.

(14) J. F. Remar, D. E. Pennington, and A. Haim, *Inorg. Chem.*, **4**, 1832 (1965).

(15) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(16) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

TABLE I

SPECTRAL DATA FOR $Cr(en)_2XCl^{n+}$ COMPLEXES

Complex	λ, mμ[a]	A[b]	Ref
cis-$Cr(en)_2Cl_2^+$	530, 401	76.0, 75.6	*c*
	530, 401	83.2, 77.6	*d*
	527, 402	70.6, 68.5	*e*
trans-$Cr(en)_2Cl_2^+$	587, 450, 396	22.6, 23.1, 32.9	*c*
	579, 444, 395	25.7, 30.0, 35.5	*d*
	578, 453, 396	24.5, 22.8, 34.0	*e*
cis-$Cr(en)_2OH_2Cl^{2+}$	512, 390	71.9, 58.4	*c*
	510, 385	71.4, 55.7	*e*
	512, 387	73.8, 60.3	*f*
trans-$Cr(en)_2OH_2Cl^{2+}$	540, 455, 382	22.9, 25.8, 46.0	*c*
	546, 448, 380	20.5, 24.4, 45.4	*e*

[a] Wavelengths for absorption maxima. [b] Molar absorbancy indeces at maxima. [c] This work. [d] M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt), **5**, 20 (1955). [e] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964). [f] D. A. House and C. S. Garner, *J. Inorg. Nucl. Chem.*, **28**, 904 (1966).

TABLE II

YIELD OF $CrCl^{2+}$ IN THE REACTIONS OF *cis*- AND *trans*-$Cr(en)_2XCl^{n+}$ WITH CHROMIUM(II) (ROOM TEMPERATURE)[a]

Complex[b]	$[Cr^{2+}]$, *M*	$[H^+]$, *M*	% $CrCl^{2+}$ [c]
cis-$Cr(en)_2Cl_2^+$	0.098	0.68	84
	0.098	0.10	40
trans-$Cr(en)_2Cl_2^+$	0.037	0.97	92[d]
	0.037	0.10	85[d]
cis-$Cr(en)_2OH_2Cl^{2+}$	0.10	0.73	82
	0.10	0.03	12
trans-$Cr(en)_2OH_2Cl^{2+}$	0.010	0.88	91
	0.010	0.03	75
$CrCl^{2+}$	0.10	0.70	83
	0.10	0.10	21

[a] Reaction time was 3.5 hr except where noted. [b] Concentration range 1.2–1.8 × 10^{-3} *M*. [c] Yield of $CrCl^{2+}$ calculated from moles of $CrCl^{2+}$ produced/moles of starting complex. [d] Reaction time was 1 hr.

Dowex 50-X8, 50–100 mesh, H^+ form. Elution of the $CrCl^{2+}$ fraction was accomplished with 1 *M* perchloric acid, and the chromium content of this fraction was determined.[9]

Kinetic Measurements.—The desired amounts of the chromium(III) complex, sodium perchlorate, and/or perchloric acid were added to a cylindrical spectrophotometric cell of appropriate length. The cell was covered with a self-sealing rubber cap, and oxygen was removed by means of a stream of prepurified argon. The cell was then placed in the thermostated (±0.1°) cell compartment of a Cary Model 15 recording spectrophotometer. After temperature equilibration was reached, the desired amount of chromium(II) solution was added by means of a calibrated syringe, and a recording of absorbance *vs.* time at the desired wavelength was obtained. This procedure was satisfactory for all the complexes except *cis*-$Cr(en)_2Cl_2^+$. For this complex the spontaneous aquation was not negligible compared to the catalyzed dissociation (*vide infra*), and therefore the following procedure was adopted in order to minimize the spontaneous aquation. The solid salt *cis*-$[Cr(en)_2Cl_2]ClO_4$ was weighed directly into the dry cell. After removal of oxygen followed by temperature equilibration, the desired volume of perchloric acid and/or sodium perchlorate was injected into the cell. Following the dissolution of the solid, the chromium(II) solution was added. In this manner, aquation of *cis*-$Cr(en)_2Cl_2^+$ prior to addition of chromium(II) was minimized.

Since the reactions under study are catalytic (see eq 1), pseudo-first order rate constants k' were obtained from the slopes of plots of log $(D_t - D_\infty)$ *vs.* time. The absorbances at time t and after reaction is complete (measured after 7–10 half-lives) are D_t and D_∞, respectively. For the complexes investigated, with the exception of *cis*-$Cr(en)_2Cl_2^+$, the values of D_∞ remained essentially constant after 7 half-lives, and the plots of log $(D_t - D_\infty)$ *vs.* time were linear at least up to 80% reaction. For *cis*-$Cr(en)_2Cl_2^+$, however, the absorbance continued decreasing after 7 half-lives. The significance of the drift in absorbance at long times and the treatment of the data for this complex will be discussed later.

Results

The results of the experiments performed to establish the stoichiometries of the reactions under consideration are presented in Table II. According to eq 1 the expected yield of $CrCl^{2+}$ is 100%. An examination of column 4 of Table II shows widely variable yields, with values ranging from 12 to 92%. It is seen, however, that yields approaching the theoretical value of 100% were obtained at high $[H^+]$, low $[Cr^{2+}]$, and short reaction times. In contrast, poor yields of $CrCl^{2+}$ were obtained at low $[H^+]$, high $[Cr^{2+}]$, and long reaction times. Blank experiments were carried out with $CrCl^{2+}$, and it is seen (*cf.* the last two entries of Table II) that the recovery of $CrCl^{2+}$ decreases with decreasing $[H^+]$. The significance of these observations will be discussed later.

The results of the kinetic measurements at 15, 25, and 35° are summarized in Table III. Under the experimental conditions used, the spontaneous aquations of *trans*-$Cr(en)_2OH_2Cl^{2+}$ and *trans*-$Cr(en)_2Cl_2^+$ are too slow[17] to interfere with the chromium(II)-catalyzed dissociations. In these cases, the second-order rate constants for the Cr(II)–Cr(III) reactions were calculated from the expression $k = k'/[Cr^{2+}]$. The spontaneous aquations of *cis*-$Cr(en)_2OH_2Cl^{2+}$ and *cis*-$Cr(en)_2Cl_2^+$, although slower than the corresponding chromium(II)-catalyzed dissociations, are sufficiently important to interfere with the rate measurements.[19] In the case of *cis*-$Cr(en)_2OH_2Cl^{2+}$, the product of the spontaneous aquation, *cis*-$Cr(en)_2(OH_2)_2^{3+}$,[16] is inert with respect to further reaction with chromium(II). Under these circumstances, it can be shown[4] that $k' = k_a + k/[Cr^{2+}]$, where k_a is the known[16,20] first-order rate constant for spontaneous aquation and k is the second-order rate constant (to be evaluated) for the catalyzed dissociation. The spontaneous aquation of *cis*-$Cr(en)_2Cl_2^+$ produces *cis*-$Cr(en)_2OH_2Cl^{2+}$,[16] which also reacts with chromium(II). The observed drift in absorbance at long times (see Experimental Section) can therefore be ascribed to the latter reaction. The kinetic scheme

$$\begin{tikzcd}
cis\text{-}Cr(en)_2Cl_2^+ \arrow[r] \arrow[d, "Cr^{2+}"'] & cis\text{-}Cr(en)_2OH_2Cl^{2+} + Cl^- \arrow[d, "Cr^{2+}"'] \\
\text{products} & \text{products}
\end{tikzcd}$$

is analogous to the one previously encountered in the *cis*-$Co(en)_2Cl^{2+}$–Fe^{2+} system.[4] The absorbance measurements were carried out at 510 mμ, an isosbestic point

---

(17) Values of the first-order rate constants for spontaneous aquation at 35° are ~5 × 10^{-6} and 8.02 × 10^{-5} sec^{-1}, respectively.[16,18]

(18) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

(19) The first-order rate constants for spontaneous aquation at 35° are 9.23 × 10^{-5} and 1.11 × 10^{-3} sec^{-1}.[16]

(20) J. Selbin and J. C. Bailar, *J. Am. Chem. Soc.*, **79**, 4285 (1957).

TABLE III

RATE CONSTANTS FOR THE REACTIONS OF *cis*- AND *trans*-$Cr(en)_2XCl^{n+}$ WITH CHROMIUM(II) (25°, $[ClO_4^-] = 1.0\ M$)

Complex[a]	$[Cr^{2+}]$, M	$[H^+]$, M		k, $M^{-1}\ sec^{-1}$ [b]
cis-$Cr(en)_2Cl_2^+$ [c]	0.061	0.540		3.85×10^{-2}
	0.100	0.100		3.93×10^{-2}
	0.100	0.500		3.95×10^{-2} [d]
	0.100	0.690		3.79×10^{-2}
	0.150	0.791		4.04×10^{-2}
			Av	$(3.90 \pm 0.12) \times 10^{-2}$
	0.100–0.232	0.094–0.700		$(2.22 \pm 0.10) \times 10^{-2}$ [e]
trans-$Cr(en)_2Cl_2^+$ [f]	0.0100	0.970		1.14
	0.0114	0.100		1.16
	0.0141	0.954		1.30
	0.0189	0.981		1.15
	0.0200	0.940		1.15
			Av	1.18 ± 0.07
	0.0095–0.020	0.954–0.981		0.68 ± 0.01[e]
cis-$Cr(en)_2OH_2Cl^{2+}$ [g]	0.100	0.031		1.16×10^{-2}
	0.100	0.100		1.13×10^{-2} [d]
	0.100	0.698		1.16×10^{-2} [d]
	0.280	0.100		1.18×10^{-2}
			Av	$(1.16 \pm 0.02) \times 10^{-2}$
	0.116–0.220	0.100–0.380		$(6.05 \pm 0.15) \times 10^{-3}$ [e]
	0.116–0.220	0.100–0.380		$(2.08 \pm 0.17) \times 10^{-2}$ [h]
trans-$Cr(en)_2OH_2Cl^{2+}$ [f]	0.0050	0.100		0.440
	0.0100	0.100		0.430
	0.0100	0.963		0.430
	0.0301	0.100		0.433
			Av	0.434 ± 0.007
	0.0100–0.0200	0.100		0.264 ± 0.002[e]
	0.0100–0.0200	0.100		0.707 ± 0.018[h]

[a] Concentration range 0.70 to $4.7 \times 10^{-3}\ M$. [b] Limits given are standard deviations. [c] Measured at 510 mμ. [d] Average of two measurements. [e] Measured at 15°. [f] Measured at 382 mμ. [g] Measured at 512 mμ. [h] Measured at 35°.

for *cis*-$Cr(en)_2Cl^{2+}$ and *cis*-$Cr(en)_2OH_2Cl^{2+}$. The data were treated as described previously,[4] except that the slopes of log $(D_t - D_\infty)$ *vs.* t plots after long times were biased to correspond to the known pseudo-first-order rate constant for the reaction of *cis*-$Cr(en)_2OH_2Cl^{2+}$ with Cr(II). This treatment is justified by the fact that the contribution of spontaneous aquation to the disappearance of *cis*-$Cr(en)_2Cl^{2+}$ is small, and consequently the small changes in optical density after long times do not accurately define the slope. Subsequent calculation of the rate constant is rather sensitive to this slope.

It is seen (*cf.* column 4 of Table III) that the values of k for each of the complexes investigated are independent of $[Cr^{2+}]$ and $[H^+]$, and we conclude that the reactions represented by eq 1 obey the second-order rate law

$$\text{rate} = k[\textit{cis-}\text{ or }\textit{trans-}Cr(en)_2XCl^{n+}][Cr^{2+}] \qquad (X = Cl, H_2O) \tag{2}$$

It is noteworthy that the rates for the aquo complexes are independent of $[H^+]$, and the significance of this observation will be discussed below.

The rate constants at 25° and the corresponding activation parameters for the reactions investigated are presented in Table IV. In order to compare the rates for the dichloro species with those for the aquochloro species, the rate constants for *cis*- and *trans*-$Cr(en)_2Cl_2^+$ have been corrected for the symmetry number factor.[21]

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR SOME REACTIONS OF CHROMIUM(III) COMPLEXES WITH CHROMIUM(II)

Complex	k, M^{-1} sec^{-1} [a]	ΔH^*, kcal mole^{-1}	ΔS^*, eu	Ref
cis-$Cr(en)_2OH_2Cl^{2+}$	1.16×10^{-2}	10.2 ± 1.2	-33 ± 4	b
cis-$Cr(en)_2Cl_2^+$	1.95×10^{-2} [c]	9.0 ± 1.7	-36 ± 6	b
trans-$Cr(en)_2OH_2Cl^{2+}$	4.34×10^{-1}	8.0 ± 0.4	-33 ± 2	b
trans-$Cr(en)_2Cl_2^+$	5.09×10^{-1} [c]	8.7 ± 1.2	-31 ± 4	b
$Cr(NH_3)_5Cl^{2+}$	5.14×10^{-2}	11.1 ± 0.2	-27[d]	e
$Cr(OH_2)_5Cl^{2+}$	9.1[f]	...	...	g

[a] At 25°. [b] This work. [c] Corrected for symmetry number factor. [d] Recalculated from the data of ref 7. [e] Ref 7. [f] At 0°. [g] Ref 22.

Values for the related reactions of $Cr(NH_3)_5Cl^{2+}$,[7] and $Cr(OH_2)_5Cl^{2+}$,[22] are also included in Table IV.

Discussion

The present observations on the chromium(II)-catalyzed dissociations of *cis*- and *trans*-$Cr(en)_2XCl^{n+}$ complexes can be readily understood on the basis of electron transfer *via* chloride-bridged transition states (eq 3).[23] Although the chromium(III) product pre-

$$\begin{aligned} &\textit{cis-}\text{ or }\textit{trans-}Cr(en)_2XCl^{n+} + Cr^{2+} \longrightarrow \\ &\qquad [\textit{cis-}\text{ or }\textit{trans-}Cr(en)_2XClCr^{n+2}]^* \longrightarrow \\ &\qquad\qquad Cr^{2+} + 2enH^+ + X + CrCl^{2+} \end{aligned} \tag{3}$$

dicted on the basis of eq 3 is $CrCl^{2+}$, it is seen (Table II) that yields much lower than theoretical were obtained.

---

(21) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(22) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

(23) Direct evidence by means of chromium tracer studies cannot be obtained because the rate of equilibration between $CrCl^{2+}$ and Cr^{2+} is much faster than the rate of production of $CrCl^{2+}$.[7]

The dependence of the yield of $CrCl^{2+}$ upon $[Cr^{2+}]$, $[H^+]$, and reaction time, as well as the blank experiments with $CrCl^{2+}$ (see last two entries of Table II) suggest aquation[24] of $CrCl^{2+}$ by a path $k_1[CrCl^{2+}] \cdot [Cr^{2+}]/[H^+]$. Direct evidence for such a path was obtained by studying the disappearance of $CrCl^{2+}$ in the presence of chromium(II) at relatively low hydrogen ion concentrations. Preliminary experiments yield a value for k_1 of $\sim 4 \times 10^{-4}$ sec^{-1} at 25° and $\Sigma[ClO_4^-] = 1.0$ M. This value is sufficiently large to account for the low yields of $CrCl^{2+}$, and we conclude that the stoichiometric measurements are consistent with the consecutive reactions[25]

$$cis\text{- or } trans\text{-}Cr(en)_2XCl^{n+} \xrightarrow{Cr^{2+}} CrCl^{2+} \xrightarrow{Cr^{2+}} Cr^{3+} \quad (4)$$

The second step of the sequence represented by eq 4 demonstrates the increased lability of $CrCl^{2+}$ in the presence of chromium(II).[26]

Once it is established that the reactions represented by eq 1 proceed *via* chloride-bridged transition states, the observed variations in rates can be taken to represent nonbridging ligand effects.[4-6] These effects were previously classified in the following three categories:[4] (a) effects of geometry—relative rates of reduction of various pairs of *cis* and *trans* isomers; (b) effects of changing the nature of one nonbridging ligand—variation in rates along a series of constant geometry (*cis* or *trans*; (c) effects of chelation—change in rate upon substitution of ammonia by ethylenediamine. The results of the present investigation (see Table IV) indicate that, for Cl^- and H_2O, the geometrical position of the nonbridging ligand (effect a) rather than its identity (effect b) is the important factor in determining relative reactivities. The results for the *cis* isomers conform to those previously obtained[4] in the reduction of *cis*-$Co(en)_2XCl^{n+}$ (X = Cl, H_2O) by iron(II). For the *trans* isomers, however, it was previously found[4] that H_2O is considerably more effective than Cl^- in promoting electron transfer. In order to provide a more quantitative comparison of the nonbridging ligand effects of Cl^- and H_2O in the $Cr(en)_2XCl^{n+}$–Cr^{2+} and $Co(en)_2XCl^{n+}$–Fe^{2+} systems, relative rate constants are presented in Table V. It is seen that, except for the case of *trans* H_2O to be discussed below, there is a striking parallel in the relative rate constants for the two systems. As noted previously,[6] the similarity in trends may be taken as indirect support for the view that the Co(III)–Fe(II) reactions proceed *via* chloride-bridged transition states.

In the study of the reduction of $Co(en)_2XCl^{n+}$ complexes by iron(II),[4] the following order of reactivity for the *trans* ligands was observed: $NH_3 < NCS^- < Cl^- < Br^- < H_2O$. With the exception of H_2O, this order conforms to Orgel's prediction[27] regarding the dependence of rate on the crystal field strength of the *trans* ligand. In trying to rationalize the high rate of the *trans*-$Co(en)_2OH_2Cl^{2+}$–Fe^{2+} reaction, stretching of *trans* H_2O was invoked.[4]

TABLE V

COMPARISON OF RATES OF REDUCTION OF SOME $Cr(en)_2XCl^{n+}$ AND $Co(en)_2XCl^{n+}$ COMPLEXES BY IRON(II) AND CHROMIUM(II) AT 25°

X	Relative rate constants	
	$Cr(en)_2XCl^{n+}$ [a]	$Co(en)_2XCl^{n+}$ [b]
cis-OH_2	1.0	1.0
cis-Cl[c]	1.7	1.7
NH_3[d]	4.4	2.9
trans-Cl[c]	44	35
trans-OH_2	37	520

[a] Reduction by chromium(II), present work. [b] Reduction by iron(II), from ref 4. [c] Corrected for symmetry number factor. [d] The oxidant is $Cr(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5Cl^{2+}$.

Two recent papers provide information on this point. In a nitrogen (of ammonia) isotope fractionation study of the reactions of *cis*- and *trans*-$Co(en)_2NH_3X^{2+}$ ($X^- = Cl^-, OH^-$) with chromium(II), Green, Schug, and Taube[28] concluded that there is little stretching of Co–N bonds and none preferential to *cis* or *trans* positions. From a study of the rates of chromium(II) reduction of *cis*- and *trans*-$Co(en)_2XOH^{2+}$ (X = NH_3, H_2O), Cannon and Earley[5] suggested that outward motion of *trans* NH_3 or H_2O is of little importance in these systems.

Additional information on this question may be derived from the kinetic results of the present investigation. The observed order *cis*-$Cr(en)_2OH_2Cl^{2+}$ < *cis*-$Cr(en)_2Cl_2^+$ << *trans*-$Cr(en)_2OH_2Cl^{2+}$ < *trans*-$Cr(en)_2Cl_2^+$ would appear, at first glance, to conform to Orgel's predictions[27] regarding the relative rates of reactions of *cis* and *trans* isomers and the dependence of rate on the crystal field strength of the *trans* ligand. However, a closer examination indicates that this is not the case. In Table VI we present values of k_t/k_c (the ratio of the rate constant for the *trans* isomer to the rate constant for the corresponding *cis* isomer) for NH_3, Cl^-, and H_2O. The values of k_t/k_c represent a measure of the efficiency of the nonbridging ligand in promoting electron transfer in the *trans* position relative to the *cis* position. It is seen that k_t/k_c is larger for $Cr(en)_2OH_2Cl^{2+}$ than for $Cr(en)_2Cl_2^+$, whereas the opposite result would be predicted from the crystal field strengths of Cl^- and H_2O. Moreover, the difference in rate constants for *trans*-$Cr(en)_2Cl_2^+$ and *trans*-$Cr(en)_2OH_2Cl^{2+}$ (see Table V) is very small, whereas a substantial difference would be expected since the crystal field strength of Cl^- is considerably smaller than that of H_2O.

Arguments analogous to these were used previously[4] to assign a special role to *trans* H_2O in the $Co(en)_2OH_2Cl^{2+}$–Fe^{2+} reaction, and it was suggested that

---

(24) The low yields of $CrCl^{2+}$ cannot be explained as the result of spontaneous aquation. At the lowest $[H^+]$ used (0.030 M) the half-life for aquation of $CrCl^{2+}$ is $\sim 10^4$ min [T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965)].

(25) It might be argued, particularly for the aquo complexes, that the decrease in the yield of $CrCl^{2+}$ with decreasing $[H^+]$ is the result of an additional path (for example *via* a hydroxide-bridged transition state) that produces Cr^{3+}. However, this alternate explanation is ruled out in view of the hydrogen ion independence of the rates of these reactions (see Table III).

(26) Entirely similar effects have been observed for $CrNCS^{2+}$ and $CrSO_4^+$ (unpublished observations) and for CrI^{2+} and $CrBr^{2+}$ [D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3450 (1966)].

(27) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p 289.

(28) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

TABLE VI

THE *trans* EFFECTS OF NH_3, Cl^-, AND H_2O IN SOME ELECTRON-TRANSFER REACTIONS

Reaction	k_t/k_c[a] NH_3	Cl^-	H_2O	Mechanism	Ref
$Co(en)_2XOH^{n+} + Cr^{2+}$	1.1	...	3.3	Hydroxide bridge	*b*
$Co(en)_2XNCS^{n+}$ Cr^{2+}	1.2	...	30	Thiocyanate bridge	*c*
$Cr(en)_2XCl^{n+} + Cr^{2+}$	...	26	37	Chloride bridge	*d*
$Co(en)_2XCl^{n+} + Fe^{2+}$	3.7	20	520	Chloride bridge (?)	*e*
$Co(NH_3)_4XN_3^{n+} + Fe^{2+}$	...	...	68	Azide bridge (?)	*f*

[a] Ratio of rate constants (25°) of *trans* to *cis* complex. [b] Ref 5. [c] Ref 6. [d] This work. [e] Ref 4. [f] A. Haim, *J. Am. Chem. Soc.*, **86,** 2352 (1964).

stretching of the Co–O bond was important. It must be noted, however, that these arguments are based on rate comparisons. Now the assignment of a certain effect on the basis of rate comparisons presupposes an ability to predict what the rates would have been in the absence of such an effect. In the above discussion it was assumed that a simple relation between crystal field strength of the *trans* ligand and rate of reaction held. Although gross reactivity features would appear to obey such a relation, we must admit that, at the present stage of development of the subject, predictions of detailed reactivity orders may be uncertain. We conclude, therefore, that, although stretching of the metal–oxygen bond in reductions of *trans*-$Co(en)_2OH_2Cl^{2+}$ or $Cr(en)_2OH_2Cl^{2+}$ provides a not unreasonable rationalization of the observed trends in reactivity, this suggestion must be considered tentative until direct evidence (such as oxygen isotopic fractionation studies[28]) either supports or refutes the suggestion.

The activation parameters measured in the present work (see Table IV) do not provide much information. The higher rates for the *trans* complexes are associated with slightly lower enthalpies of activation, whereas the entropies of activation remain approximately constant in the series (-33 ± 3 eu) and lie in the range (-25 ± 10 eu) observed for other electron-transfer reactions of a similar type.[7,29]

It is useful to contrast the behavior of the chromium(II)-catalyzed aquations of $Cr(en)_2OH_2Cl^{2+}$ and $CrCl^{2+}$. In the former case no acid dependence is observed, whereas in the latter case the dominant reaction proceeds *via* an inverse hydrogen ion path. At first glance it would appear that these results are contradictory. However, they can be readily understood by considering the relative efficiencies of Cl^- and OH^- as bridges and the nature of the reactions under consideration. Using the rate constants for the Cr^{2+}–$CrOH^{2+}$ ($k = 0.7\ M^{-1}\ sec^{-1}$ at 25°[30]) and Cr^{2+}–$CrCl^{2+}$ ($k = 9\ M^{-1}\ sec^{-1}$ at 0°[22]) reactions as a measure of the efficiency of OH^- and Cl^- bridges, we would conclude[31] that $Cr(en)_2OH_2Cl^{2+}$ and $Cr(en)_2OHCl^+$ react at rates that do not differ by more than 10^2. However, at the lowest $[H^+]$ used, the hydroxo species is approximately 10^{-4} less abundant than the aquo species. Therefore, the inverse acid path would be approximately 10^{-6} smaller than the acid independent path and obviously was not detected. Of course, the same considerations apply to $CrCl^{2+}$ and $CrOHCl^+$, but in this case the inverse hydrogen ion path was readily detected. The difference in the two systems is that for $Cr(en)_2OH_2Cl^{2+}$ reaction *via* a chloride bridge results in a net consumption of the reactant, whereas for $CrCl^{2+}$ reaction *via* a chloride bridge does not bring about any net reaction and can only be detected by radioactive exchange studies.[22]

(29) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86,** 1019 (1964).

(30) A. Anderson and N. A. Bonner, *ibid.*, **76,** 3826 (1954).

(31) It is assumed that the $1/[H^+]$ path corresponds to reaction *via* a hydroxide-bridged transition state.

CONTRIBUTION FROM THE MAX PLANCK INSTITUT
FÜR PHYSIKALISCHE CHEMIE, GÖTTINGEN, GERMANY

The Kinetics of Formation and Dissociation of the Monoammine Complexes of the Divalent, First-Row, Transition Metal Ions

BY D. B. RORABACHER[1]

Received March 10, 1966

The kinetics of formation and dissociation have been studied for the monoammine complexes of Co(II), Ni(II), and Zn(II) in aqueous solution using the temperature-jump relaxation method. The evaluated formation rate constants are shown to correspond to a mechanism involving the dissociation of water from the aquometal ion as the rate-determining step following the initial formation of an outer-sphere complex. To account for the much faster formation rates of the previously studied polyamine complexes, an internal conjugate base mechanism is proposed.

Introduction

In a previous paper[2] it was found that the formation rate constants for nickel polyamine complexes could be correlated with a mechanism involving the first nickel–nitrogen bond formation as the rate-determining step. However, a rate constant for the

(1) On leave from the Department of Chemistry, Wayne State University. Detroit, Mich. Correspondence to be sent to this address.

(2) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2,** 667 (1963).