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Chlorine Atom Abstraction Reaction of Dichloromethylchromium(III) Ions with Chromium(II). Kinetics and Radiotracer Determinations[1]

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Reaction with Cr^{2+} in aqueous $HClO_4$ converts the complex $CrCHCl_2{}^{2+}$ to $CrCH_2Cl^{2+}$, with accompanying formation of Cr^{3+} and $CrCl^{2+}$ in equivalent amounts. Kinetic data indicate that the first and rate-limiting step ($k = 0.016$ dm^3 mol^{-1} s^{-1}, 25.1 °C) is a bimolecular halogen atom abstraction reaction of $CrCHCl_2{}^{2+}$ and Cr^{2+}, forming $CrCl^{2+}$ and $Cr\dot{C}HCl^{2+}$. The latter intermediate, according to chromium-51 tracer results, rapidly exchanges with Cr^{2+} via an intermediate Cr_2CHCl^{4+}, the latter subsequently being converted to Cr^{3+} and $CrCH_2Cl^{2+}$ in a protonolysis step. The chemistry of these reactions is discussed, and reference is made to the observation of an intensely absorbing transient formed at lower $[H^+]$ (0.01–0.05 M), which is believed to be a nonproductive intermediate lying off the main reaction pathway. A mechanism to account for these observations is proposed.

Introduction

One of the first known complexes of chromium(III) containing a metal–carbon σ bond was the dichloromethyl complex $(H_2O)_5Cr{-}CHCl_2{}^{2+}$ prepared by Anet[2] in the heterogeneous reaction of aqueous Cr^{2+} and chloroform (eq 1). Dodd and

$$2Cr^{2+}(aq) + CHCl_3 = (H_2O)_5CrCl^{2+} + (H_2O)_5CrCHCl_2{}^{2+} \qquad (1)$$

Johnson[3] found it convenient to utilize this same reaction under homogeneous conditions (acetone consolvent), and also prepared the monochloromethyl complex by the analogous reaction of Cr^{2+} with methylene chloride (eq 2). They suc-

$$2Cr^{2+}(aq) + CH_2Cl_2 = (H_2O)_5CrCl^{2+} + (H_2O)_5CrCH_2Cl^{2+} \qquad (2)$$

cessfully separated the highly water-soluble organochromium complexes from the other components of the reaction mixture using cation-exchange chromatography.[3,4]

Dodd and Johnson also noted that when reaction 1 was carried out with large molar excesses of Cr^{2+}, a lower yield of the dichloromethyl complex resulted, with monochloromethylchromium(III) formed instead. They attributed this to the conversion of the one complex to the other by reaction with excess Cr^{2+}, which was confirmed by direct observation of this reaction (eq 3).

$$(H_2O)_5CrCHCl_2{}^{2+} + 2Cr^{2+}(aq) + H^+ = (H_2O)_5CrCH_2Cl^{2+} + Cr(H_2O)_6{}^{3+} + (H_2O)_5CrCl^{2+} \qquad (3)$$

In relation to this, Castro and Kray[5] observed the stepwise reduction of haloforms and methylene halides by $CrSO_4$; in DMF–H_2O these reactions proceed eventually to methane and undoubtedly proceed through a series of organochromium intermediates—$CrCHX_2{}^{2+}$, $CrCH_2X^{2+}$, and $CrCH_3{}^{2+}$—each in turn formed from the preceding halide by a reaction with Cr^{2+} analogous to eq 1–3. In contrast to the results in DMF–H_2O and in the presence of sulfate ions, the only reaction we found to occur in perchlorate solution is that given by eq 3.

In the present work we report the results of a mechanistic study of this reaction including a determination of the reaction kinetics and isotopic studies to investigate further steps in the mechanism. The study of a related reaction of the iodomethylchromium complex with Cr^{2+} was reported recently.[6] In this case the products include liberated methane, presumably arising from acidolysis of an unstable methylchromium[7] intermediate (eq 4).

$$(H_2O)_5CrCH_2I^{2+} + 2Cr^{2+}(aq) + 2H^+ = 2Cr(H_2O)_6{}^{3+} + (H_2O)_5CrI^{2+} + CH_4 \qquad (4)$$

Experimental Section

Materials. The organochromium complexes were prepared and isolated as described in the literature,[1,2] with certain variations to ensure the recovery of a pure compound. The procedure used for $(H_2O)_5CrCHCl_2{}^{2+}$ was a follows. A 50-cm^3 sample of an aqueous solution of 0.1 M Cr^{2+} and 0.1 M H^+ was mixed with ca. 10 cm^3 of chloroform under nitrogen. After ca. 30 min of vigorous stirring the excess chloroform was removed and the solution made ca. 0.1 M in Hg^{2+} by addition of a concentrated solution of mercuric perchlorate.[8] After 15 min, HCl was added to provide a solution ca. 0.2 M, and the solution was filtered. The filtrate was placed on a column (30 × 1.5 cm) of Dowex 50W-X8 cation-exchange resin. The column was eluted with 0.1 M HCl until the eluate gave a negative test for Hg(II) with Na_2S and then with water until a negative test for Cl^- was obtained. Finally, the column was eluted with 1.0 M $HClO_4$ to collect $CrCHCl_2{}^{2+}$ leaving Cr^{3+} on the resin. In some instances separation of the desired complex was achieved without addition of Hg^{2+}, eluting first the green $CrCl^{2+}$ from the resin column with 0.5 M perchloric acid and then the orange $CrCHCl_2{}^{2+}$ with 1.0 M perchloric acid or lithium perchlorate. For some experiments the eluted solutions of $CrCHCl_2{}^{2+}$ in $LiClO_4$ were concentrated by lyophilization, first freezing them in dry ice–acetone and then evacuating to ca. 0.01 Pa for 8–12 h. The deuterio complex $CrCDCl_2{}^{2+}$ was prepared in an analogous fashion using $CDCl_3$, and the ^{51}Cr-labeled complex was prepared starting with $^{51}Cr^{2+}$.

The preparation of $CrCH_2Cl^{2+}$ was performed similarly except that CH_2ClBr was used as the reactant (eq 5), and the reaction time

Table I. Absorption Spectra of Chloromethyl- and Dichloromethylchromium(III) Ions

Complex	λ_{max}/nm (ϵ/(dm^3 mol^{-1} cm^{-1}))			Ref
$CrCH_2Cl^{2+}$	517 (20)	391 (204)	262 (3500)	3
	517 (23.4)	393 (225)	265 (3600)	10
	517 (23)	391 (224)	256 (3620)	This work
$CrCHCl_2^{2+}$	514 (22.8)	396 (115)	265 (2450)	3
	514 (38.7)	396 (157)	266 (4290)	10
	515 (38.2)	396 (156)	266 (4010)	This work

$$2Cr^{2+}(aq) + CH_2ClBr = (H_2O)_5CrCH_2Cl^{2+} + (H_2O)_5CrBr^{2+} \qquad (5)$$

was 2 h. The product was isolated as a pure chromatographic fraction from Dowex 50W-X8 resin, from which it is eluted more slowly than $CrBr^{2+}$ by 1 M $HClO_4$.

The chromium concentrations of these complexes were determined spectrophotometrically as chromate in alkaline solution after oxidation with hydrogen peroxide (ϵ_{372} 4.83 × 10^3 M^{-1} cm^{-1}).[9] The uv–visible spectra of these complexes are in good agreement with literature values[3,10] for $CrCH_2Cl^{2+}$. The wavelengths but not the molar absorptivities for $CrCHCl_2^{2+}$ agree with the reported values (Table I).

Chromium(III) perchlorate was prepared from the trioxide by reduction with hydrogen peroxide in perchloric acid. The crystallized salt was reduced with amalgamated zinc or electrolytically in a nitrogen atmosphere to provide stock solutions of $Cr(ClO_4)_2$. In experiments where ^{51}Cr-tagged stock solutions were needed, a very small quantity of the isotopic tracer (purchased as a solution of $CrCl_3$ in HCl) was added to the Cr^{2+} solution stored over amalgamated zinc.

Lithium perchlorate and barium perchlorate were recrystallized twice. The complex $CrCl^{2+}$ was prepared by the Cr^{2+}-catalyzed aquation of *trans*-$CrCl_2^+$ (from commercial $CrCl_3 \cdot 6H_2O$) and purified by ion exchange.[11] The complex $[Co(NH_3)_5Br]Br_2$ was prepared by a standard method.[12]

Analyses and Techniques. Concentrations of $CrCH_2Cl^{2+}$ and of $CrCHCl_2^{2+}$ were determined spectrophotometrically using extinction coefficients (Table I) based on the spectra of freshly purified solutions. Chromium(II) analyses were determined by reaction with a 15–30% excess of $Co(NH_3)_5Br^{2+}$; for higher Cr^{2+} concentrations the Co^{2+} produced was determined spectrophotometrically as $Co(NCS)_4^{2-}$ in 50% aqueous acetone at λ 623 nm (ϵ 1842), and for lower Cr^{2+} concentrations the consumption of the cobalt complex, relative to an otherwise identical blank solution, was determined spectrophotometrically using the absorption maximum of $Co(NH_3)_5Br^{2+}$ at λ 253 nm (ϵ 16 700).

The counting rate of samples containing ^{51}Cr was determined with a well-type NaI γ-ray scintillation counter with a 400-channel analyzer in which the sample vials could be positioned through a styrofoam block to ensure uniform counting geometry.[13] Only those channels representing the energies around the peak in the ^{51}Cr γ-ray spectrum were tallied. Each sample was counted to attain at least 10^4 total counts.

Mass spectral determinations[14] were carried out by Ames Laboratory. Spectrophotometric analyses and kinetics determinations were carried out using a Cary Model 14 spectrophotometer equipped with an accurately thermostated cell holder. At the completion of each kinetic run, samples were withdrawn for Cr^{2+} analysis.

Stoichiometry. Several experiments were performed to establish the occurrence of reaction 3 as written. One pair of experiments determined the reaction ratio of Cr^{2+} and $CrCHCl_2^{2+}$: a solution of 3.1 × 10^{-2} M Cr^{2+} and 6.9 × 10^{-3} M $CrCHCl_2^{2+}$ in 1.0 M $HClO_4$ was allowed to react under nitrogen for 7 h, after which 1.7 × 10^{-2} M Cr^{2+} remained; a solution of 2.6 × 10^{-2} M Cr^{2+} and 4.9 × 10^{-3} M $CrCHCl_2^{2+}$ in 0.03 M $HClO_4$–0.97 M $LiClO_4$ was allowed to react under nitrogen for 9 h, after which 1.7 × 10^{-3} M Cr^{2+} remained. In both cases the results correspond to the reaction of 2.0 mol of Cr^{2+}/mol of $CrCHCl_2^{2+}$, in accordance with eq 3.

One experiment was designed to measure the relative yields of dipositive ($CrCl^{2+}$ + $CrCH_2Cl^{2+}$) and tripositive (Cr^{3+}) ions. In this experiment a solution which was initially 3.8 × 10^{-2} M in Cr^{2+} and 1.8 × 10^{-2} in M $CrCHCl_2^{2+}$ was allowed to react for 2.0 h (2 half-time periods) under nitrogen. A 1.0-cm^3 aliquot was delivered under nitrogen into a solution containing excess $Co(NH_3)_5Br^{2+}$, thereby oxidizing the excess of Cr^{2+} to $CrBr^{2+}$. This solution was quantitatively transferred to a 30 × 1 cm column of Dowex 50W-X8 50–100 mesh cation-exchange resin. The sample was eluted successively with 0.5, 1.0, and 2.0 M $HClO_4$, collecting the eluent in 8-cm^3 fractions using an automatic fraction collector. Each fraction was analyzed for total chromium.[9] The elution profile (chromium concentration vs. fraction number) gave two peaks. The earlier, larger peak, after correction for the $CrBr^{2+}$ formed (0.2 × 10^{-2} mmol) contained 3.7 × 10^{-2} mmol of dipositive ions (theoretical value for eq 3, 3.6 × 10^{-2} mmol) and the later peak contained 1.4 × 10^{-2} mmol of Cr (theoretical Cr^{3+} value from eq 3, 1.8 × 10^{-2} mmol). These values are adequately consistent with reaction 3, especially considering the reaction was carried to only 75% completion.

A final stoichiometry experiment was designed to determine the relative yield of $CrCl^{2+}$ and $CrCH_2Cl^{2+}$. A solution of 0.10 M Cr^{2+} and 5.0 × 10^{-3} M $CrCHCl_2^{2+}$ in 1.0 M $HClO_4$ was allowed to react essentially to completion (1 h). The excess Cr^{2+} was air oxidized, and 10.0 cm^3 of the solution was transferred to a 30 × 1 cm column of Dowex 50W-X8 50–100 mesh cation-exchange resin. The column was eluted with 0.47 M NaSCN, which by virtue of a fairly rapid equilibrium (eq 6),[10] converts the organochromium complex largely

$$(H_2O)_5CrCHCl_2^{2+} + SCN^- \rightleftharpoons trans\text{-}(H_2O)_4(SCN)CrCHCl_2^+ \qquad (6)$$

to a unipositive form, leaving $CrCl^{2+}$ unaffected. The elution profile gave two peaks, which although not completely resolved, had nearly equal areas, indicating the production of equal amounts of $CrCl^{2+}$ and $CrCH_2Cl^{2+}$ as required by eq 3.

Isotopic Tracer Experiments. Three types of ^{51}Cr radiotracer determinations along with appropriate blanks were carried out in an attempt to learn the origins of the chromium atoms in the three different chromium-containing products of reaction 3. It is worth noting at the outset that chromium exchange between Cr^{2+} and $CrCl^{2+}$ is virtually instantaneous on the time scale of this reaction,[15] whereas that between Cr^{2+} and Cr^{3+} is entirely negligible.[16] We carried out an experiment to study possible chromium exchange between $CrCH_2Cl^{2+}$ (2.4 × 10^{-3} M) and $^{51}Cr^{2+}$ (2.4 × 10^{-2} M) in 1.0 M $HClO_4$. After 1.5 h at 25 °C, the solution was air oxidized and the organochromium complex separated from $Cr_2(OH)_2^{4+}$ by ion-exchange chromatography using NaNCS elution as described above. The activity of $CrCH_2Cl^{2+}$ above background was negligible, establishing negligible exchange between Cr^{2+} and $CrCH_2Cl^{2+}$ on the time scale of this experiment. A second blank experiment was carried out to learn whether exchange occurs between Cr^{2+} and $CrCHCl_2^{2+}$, the reactant organochromium complex. A solution of $CrCHCl_2^{2+}$ (6 × 10^{-3} M) and $^{51}Cr^{2+}$ (1.3 × 10^{-2} M) in 1.0 M $HClO_4$ was allowed to react for 1.5 h (a time during which reaction 3 occurs to ca. 50% completion as established by kinetics experiments), following which the remaining Cr^{2+} was air oxidized and the products $CrCl^{2+}$ and $CrCH_2Cl^{2+}$ converted to Cr^{3+} by reaction with excess Hg^{2+}.[8] The solution was treated with HCl, filtered, and passed through an ion-exchange column. The unreacted $CrCHCl_2^{2+}$ was isolated by elution with 1.0 M $HClO_4$ and found to contain no chromium-51 activity. This establishes that chromium exchange between Cr^{2+} and $CrCHCl_2^{2+}$ is negligible during the course of reaction 3.

Two radiotracer experiments were performed on the reaction of $CrCHCl_2^{2+}$ with $^{51}Cr^{2+}$, and one experiment was done with the reverse isotopic labeling. The general procedure was the following. After a selected period of time the reaction was quenched by addition of excess $Co(NH_3)_5Br^{2+}$, converting the remaining Cr^{2+} to $CrBr^{2+}$, and the solution was then transferred to an ion-exchange column. The resin was eluted with increasing concentrations of perchloric acid, 0.5, 1.0, and (in one case) 2.0 M, the eluent being collected automatically in 8-cm^3 fractions in which the specific activity[17] of each fraction was determined using the counting rate[18] and the total chromium analysis.[9] The early fractions (typically no. 1–5) contained the product $CrCl^{2+}$ as well as $CrBr^{2+}$ from unreacted Cr^{2+}, the middle fractions (no. 6–12) contained the product $CrCH_2Cl^{2+}$ along with unreacted $CrCHCl_2^{2+}$, and the final fractions (no. 19–23, taken in only one of the three experiments) contained Cr^{3+}.

The conditions, reaction times, and specific activities for these experiments are summarized in Table II. Included in the table is a comparison of the numerical results of these determinations with a mechanistic model which is presented in the Interpretation and Discussion. The agreement with this model can be seen to be within the limits of the experimental error.

A different type of isotopic tracer determination was performed using the deuterated complex $CrCDCl_2^{2+}$. The reaction of this complex (3.9 × 10^{-3} M) with Cr^{2+} (0.12 M) was carried to completion, following which the known reaction[19] with aqueous bromine was used to dealkylate the chloromethylchromium complex. The mass spectrum

Table II. Results of ^{51}Cr Isotopic Tracer Experiments on the Reaction[a] of Cr^{2+} and $CrCHCl_2^{2+}$

	Expt 1	Expt 2	Expt 3
$[Cr^{2+}]_0$/M	0.038	0.038	0.061
$[CrCHCl_2^{2+}]_0$/M	0.017	0.017	0.029
% reaction	75	50	75
Specific activities[b,c]			
Initial Cr^{2+}:	5.3	5.1	0
Initial $CrCH_2Cl^{2+}$:	0	0	6.2
Fraction 1, $CrCl^{2+}$ + $CrBr^{2+}$	4.3 ± 0.4 (3.5)	3.8 ± 0.1 (4.0)	2.2 ± 0.03 (2.2)
Fraction 2, $CrCH_2Cl^{2+}$ + $CrCHCl_2^{2+}$	3.5 ± 0.1 (3.3)	2.3 ± 0.2 (2.3)	2.2 ± 0.15 (2.4)
Fraction 3, Cr^{3+}	4.5 ± 0.2 (4.4)	Not determined (4.5)	Not determined (1.1)

[a] At 25.0 °C, 1.00 M $HClO_4$. [b] Given as 10^{-6} × cpm/molarity of Cr. [c] The values in parentheses are those calculated for the model in reaction a of Scheme I; see Appendix.

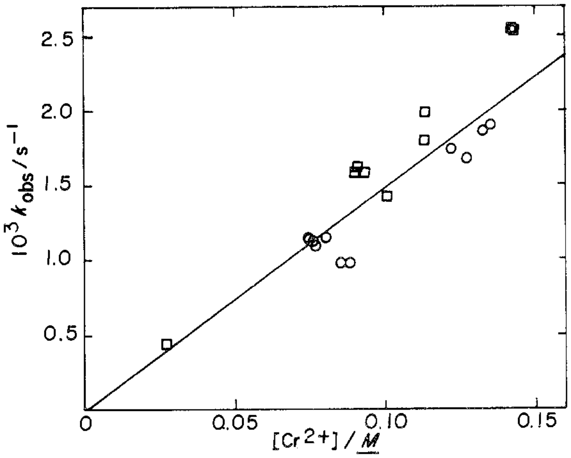


Figure 1. Plot of the pseudo-first-order rate constant vs. $[Cr^{2+}]$ for kinetics experiments at 1.00 M H^+ (25.0 °C, μ = 2.5 M) at λ 370–392 nm (squares) and λ 295–320 nm (circles).

showed only the presence of CDHBrCl, and in particular established the absence of CH_2BrCl. This experiment was performed twice with the same result, once at $[H^+]$ = 1.0 M and once at $[H^+]$ = 0.01 M. These results establish that exchange of the methyl hydrogen with solvent does not occur prior to or during the reaction, even at the lower $[H^+]$.

Kinetic Studies at High (1 M) $[H^+]$. A total of 28 spectrophotometric rate determinations were performed under a given set of conditions: 25.1 °C, 1.00 M $HClO_4$, with $[ClO_4^-]$ = 2.00 M and ionic strength 2.50 M, the last consisting of 0.500 M 2:1 $M(ClO_4)_2$ electrolytes, $CrCHCl_2(ClO_4)_2$ + $Cr(ClO_4)_2$ + $Ba(ClO_4)_2$.[20] The concentrations in these runs were such that $[Cr^{2+}]_0/[CrCHCl_2^{2+}]_0 \geq 10$ (usually ≥ 50). The pseudo-first-order rate plots for these runs were nicely linear, and the rate constants were independent of $[CrCHCl_2^{2+}]_0$ (variation 5×10^{-4}–5.3×10^{-3} M), thereby establishing the first-order dependence on $[CrCHCl_2^{2+}]$. Data are given in Table III. The plot of k_{obsd} against $[Cr^{2+}]$, Figure 1, shows a reasonably linear variation supporting the rate law in eq 7 with k_{Cr} = (1.60 ± 0.19) × 10^{-2} M^{-1} s^{-1} under the reaction conditions stated. The scatter in the data is fairly large, however, especially considering that $[Cr^{2+}]$ in each run was accurately determined and that large absorbance changes (0.5–1.5 absorbance units) were measured.

$$-d[CrCHCl_2^{2+}]/dt = k_{Cr}[CrCHCl_2^{2+}][Cr^{2+}] \qquad (7)$$

Closer inspection of the data suggests possible systematic wavelength dependence: the data taken from the absorbance decrease at λ 295–325 nm (mostly at 310 nm), which are shown as open circles in Figure 1, lie consistently below the line averaging all of the points, whereas data taken from the absorbance increase at longer wavelengths, λ 370–391 nm (usually 391 nm) lie consistently above this line. The respective values of $10^2 k_{Cr}/(M^{-1}\ s^{-1})$ for each wavelength region separately are 1.38 ± 0.13 and 1.66 ± 0.12. The difference is barely significant statistically, yet it may reflect the residual influence of the two-step rate process which is seen at lower $[H^+]$, described in a subsequent section.

In support of the possible wavelength dependence of k_{Cr}, some similar experiments at 1.00 M H^+ were conducted at λ 350 nm, a wavelength which is an isosbestic point for the overall reaction. A small, slow increase in absorbance was noted,[21] followed by a gradual decay back to the initial absorbance. This effect is greatly enhanced at very low $[H^+]$, but the small residual effect at 1.00 M H^+ may well account for the scatter in the kinetic data. Considering the absorbance decrease at λ 310 nm and the increase at λ 391 nm, the effect would be to decrease the apparent k_{Cr} in the former instance and increase it at the latter, consistent with our kinetic data.

Table III. Kinetic Data for Reaction of $CrCHCl_2^{2+}$ and Cr^{2+} at 1.00 M H^+, μ = 2.5 M, and T = 25.1 °C

Initial concn				Initial concn			
10^3-$[CrCHCl_2^{2+}]$/M	10^2-$[Cr^{2+}]$/M	λ/nm	$10^2 k_{Cr}/(M^{-1}\ s^{-1})$	10^3-$[CrCHCl_2^{2+}]$/M	10^2-$[Cr^{2+}]$/M	λ/nm	10^2-$k_{Cr}/(M^{-1}\ s^{-1})$
1.2	7.50	310	1.54	9.9	2.74	391	1.59
1.2	7.50	310	1.54	3.4	7.06	391	1.76
0.60	7.58	310	1.50	3.0	9.11	391	1.72
1.2	7.60	310	1.53	3.0	9.17	380	1.75
1.2	7.65	310	1.49	5.0	9.21	370	1.70
1.2	7.65	310	(1.66)[a]	1.2	10.1	392	1.41
0.60	7.72	310	1.44	2.5	10.1	392	1.42
1.2	7.74	310	1.42	2.5	11.4	391	1.74
0.60	7.77	310	1.42	2.5	11.4	391	1.57
0.60	8.08	310	1.42	5.3	14.2	370	1.80
0.50	8.70	310	1.11	5.3	14.2	370	1.79
0.50	8.90	300	1.09				
1.0	9.42	320	0.99	9.58	2.84	*b*	1.33
2.0	11.7	325	1.30	10.4	2.90	*b*	1.58
0.50	12.2	295	1.44	10.0	2.97	*b*	1.25
0.74	12.7	300	1.31				
0.60	13.3	310	1.41				
0.60	13.5	310	1.41				

[a] $[Cl^-]$ = 0.80 M. [b] Reaction rate monitored by Cr^{2+} analysis of periodically drawn samples; these runs had 0.05 M H^+.

Also shown in Table III are three kinetic runs followed by a different analytical technique—analysis of Cr^{2+} using $Co(NH_3)_5Br^{2+}$ as described above. These runs at 0.050 M H^+ had comparable values of reactant concentrations, and a second-order treatment of the rate data gave the values of k_{Cr} shown in Table III. These results are in reasonable agreement with the spectrophotometric values at 1 M H^+ especially those at the lower wavelengths.

Independent experiments demonstrated that the products are stable to decomposition and that Cr^{2+} does not react with $CrCH_2Cl^{2+}$ under these conditions.

Regardless of the origin of the scatter of k_{Cr} values, it seems clear that the data are in accord with eq 7 and that the value of k_{Cr} is known within a 12% average deviation.

Kinetic Studies at Low (0.01–0.10 M) $[H^+]$. Rate determinations at $[H^+]$ < 0.1 M were carried out under conditions similar to those employed in the earlier runs, using $LiClO_4$ and $Ba(ClO_4)_2$ to maintain a constant ionic medium.[20] The spectrophotometric results were more complicated: instead of the single-stage pseudo-first-order change in absorbance found at 1.00 M H^+, a two-step reaction was observed. The rapid but easily measured rise in absorbance at λ 391 nm was followed by a smaller, slower decrease. The wavelength λ 350 nm proved convenient for exact studies, as this is an isosbestic point in the overall reaction, thereby rendering the rise and fall of absorption quite pronounced. Figures 2 and 3 show the magnitude of this effect in several kinetic runs at this wavelength.

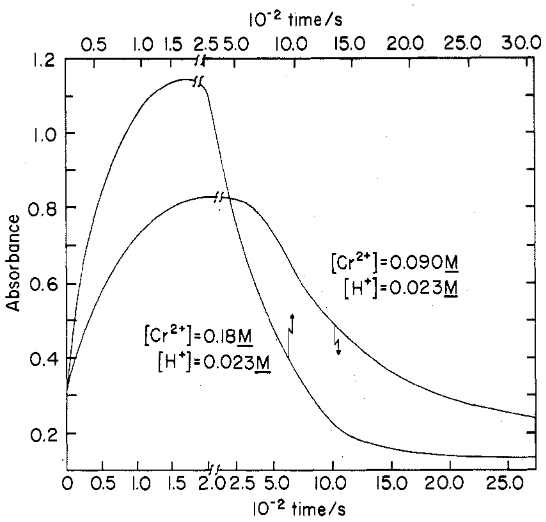


Figure 2. Plots of absorbance (b = 2.4 cm) vs. time for runs at low and constant [H$^+$] illustrating the effect of varying [Cr^{2+}].

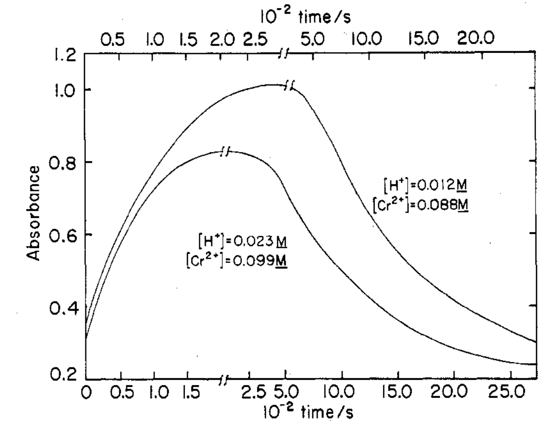


Figure 3. Plots of absorbance (b = 2.4 cm) vs. time for runs at low [H$^+$] and constant [Cr^{2+}] illustrating the effect of varying [H$^+$].

The two rate processes were sufficiently separated in time that they could be treated largely independently. The first-stage rate data were treated by the Guggenheim method[22] which gave linear rate plots

$$-d[CrCHCl_2^{2+}]/dt = k^I[CrCHCl_2^{2+}] \tag{8}$$

Values of k^I, tabulated in Table IV, proved roughly independent of [Cr^{2+}] (0.036–0.18 M) and mildly dependent on [H$^+$] (0.012–ca. 0.05 M); the data give $10^2k^I/s^{-1} = 1.45 \pm 0.29$.

The rate data for the second step showed a pseudo-first-order dependence on the concentrations of the absorbing "intermediate" (=A),[23] the rate constant for which, k^{II}, proved to be *independent* of [H$^+$] over the same range, but showed a first-order dependence upon [Cr^{2+}] over the fivefold range studied. These data (Table IV) permit the formulation of a rate law for the second-stage process as given in eq 9, where $k_A = k^{II}/[Cr^{2+}]$, with $10^2k_A = 1.25 \pm 0.06$ M^{-1} s^{-1}.

$$d[CrCH_2Cl^{2+}]/dt = k_A[A][Cr^{2+}] \tag{9}$$

The higher precision of this rate constant compared to that of k_{Cr} should be noted. Moreover, the agreement of the kinetic form and the numerical agreement (within experimental error) between the values of the rate constants for the two Cr^{2+}-dependent reactions should be noted: $k_{Cr} \simeq k_A$.

Noted in the preceding section were three kinetic determinations at 0.05 M H$^+$, in which the rate was determined by Cr^{2+} analysis (last three entries in Table III). The data for these runs were taken over a time period which would correspond to the second stage of spectrophotometric determinations. The concentration of Cr^{2+} fell smoothly from its initial value, suggesting that the first stage of reaction did not consume appreciable Cr^{2+}. These data conformed well to a second-order kinetic expression, suggesting further that [$CrCHCl_2^{2+}$] was not appreciably lowered from its initial value by the formation of A.

Table IV. Kinetic Data for Reaction of $CrCHCl_2^{2+}$ and Cr^{2+} at 0.01–0.05 M H$^+$ (T = 25.1 °C, μ = 2.50 M, 2.0 × 10^{-3} M $CrCHCl_2^{2+}$)

[H$^+$]/M	[Cr^{2+}]/M	10^2k^I/ s^{-1}	10^3k^{II}/ s^{-1}	10^2k_A/ (M^{-1} s^{-1})	ΔD	ΔD[H$^+$]/ [Cr^{2+}]
0.012	0.090	1.1	1.12	1.25	0.76	0.10
0.021	0.051	1.1	0.61	1.18	0.37	0.15
0.023	0.088	1.4	1.01	1.15	0.66	0.17
0.023	0.179	1.7	2.35	1.31	0.96	0.12
0.025	0.180	1.6	2.40	1.33	1.03	0.14
0.031	0.093	1.8	1.15	1.23	0.45	0.15
0.034	0.100	2.0	1.36	1.36	0.54	0.18
a	0.0364	0.9	0.42	1.14	0.71	
a	0.0395	1.4	0.49	1.24	0.36	
a	0.0831	1.5	1.06	1.28	0.51	

[a] [H$^+$] is not known precisely but is approximately 0.02–0.05 M.

Experiments on the Nature of A. The absorbance–time traces, such as those shown in Figures 2 and 3, illustrate that the maximum concentration of intermediate[23] A increases with decreasing [H$^+$] and increases with increasing [Cr^{2+}]. Also included in Table IV are data showing the variation of the maximum absorbance of the intermediate at different concentrations of H$^+$ and Cr^{2+}. These data are given as ΔD $(=D_{max} - D_0 = D_{max} - D_\infty)$, λ 350 nm being an overall isosbestic point. The last column shows that the extent of intermediate formation is proportional to [Cr^{2+}] and inversely proportional to [H$^+$], in that the quantity $\Delta D[H^+]/[Cr^{2+}]$ is roughly constant.

Several experiments were done in an effort to determine further information about the composition of A and its role in the chemistry of this reaction, as follows. (1) The reaction of $CrCDCl_2^{2+}$ with Cr^{2+} at 1.0 and 0.01 M H$^+$ produces exclusively $CrCDHCl^{2+}$, as mentioned previously, indicating that C–H exchange does not accompany intermediate formations. (2) Injection of oxygen-free perchloric acid to raise [H$^+$] to 1 M, at the point at which the absorption maximum occurs, results in a virtually instantaneous drop in absorbance to the value expected had the run originally been carried out at 1 M H$^+$ (this in spite of the lack of effect of 0.01–0.05 M H$^+$ on k^{II}). (3) Kinetic data taken by Cr^{2+} sampling and analysis in a run with a *comparable* concentration of reactants (in contrast to the large Cr^{2+} excess in most of the spectrophotometric determinations) showed that, at 0.05 M H$^+$, as well as at 1.0 M H$^+$, consumption of 2 Cr^{2+} per $CrCHCl_2^{2+}$ occurs uniformly throughout the period from the start of the reaction until its completion (the bulk of the data, however, taken at $t > t_{max}$). The rate constant found in three such determinations, evaluated by second-order rate plots, was $10^2k_{Cr} = 1.2 \pm 0.1$ M^{-1} s^{-1}, in reasonable agreement with the more precise spectrophotometric runs. Clearly, formation of the species absorbing at λ 350 nm does not result in consumption of an appreciable quantity of Cr^{2+} (unless, of course, the product also rapidly reduced the analytical reagent $Co(NH_3)_5Br^{2+}$ to Co^{2+} as Cr^{2+} does). (4) Injection at t_{max} of deoxygenated Fe^{3+} in an amount insufficient to oxidize all of the Cr^{2+} present merely reduces the rate to the value corresponding to k_A considering the lower [Cr^{2+}]. (5) Injection at t_{max} of a reagent to destroy all of the Cr^{2+} (such as excess Fe^{3+} or bubbling the solution at this point with gaseous O$_2$), leads in each instance to the gradual decay of the λ 350 nm absorption at a rate *higher* than when Cr^{2+} was present; moreover, the rate is greater when Fe^{3+} is used for this purpose than when O$_2$ is used. (6) The rate of reaction of $CrCDCl_2^{2+}$ is very nearly the same as that of $CrCHCl_2^{2+}$: at 0.020 M H$^+$, $10^2k^I(D) = 1.21$ s^{-1} compared to 1.07, and $10^2k_A(D) = 1.15$ M^{-1} s^{-1} compared to 1.23.

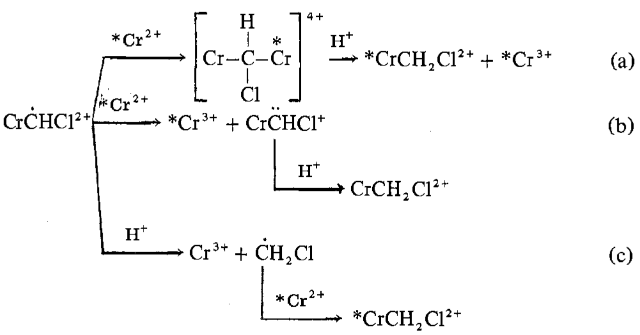
Interpretation and Discussion

Results at 1 M H$^+$. Consider first the mechanistic conclusions which can be drawn from the data at 1.00 M H$^+$, where the 350-nm absorption can largely be ignored. The kinetic expression of eq 7 supports the assignment of the first step as chlorine atom abstraction (eq 10) a conclusion which

$$Cr\text{–}CHCl_2^{2+} + Cr^{2+} \xrightarrow{k_{Cr}} CrCl^{2+} + Cr\text{–}CHCl^{2+} \tag{10}$$

seems to us eminently reasonable considering the multitude

Scheme I. Possible Reactions of the Intermediate $Cr\dot{C}HCl^{2+}$



of examples of reactions of alkyl and aralkyl halides with Cr^{2+} [2,3,5,24] and other one-electron metallic reducing agents.[25]

The mechanistic conclusions from the kinetic data are largely limited to the postulation of eq 10 as the rate-limiting step. Whatever subsequent reactions the presumed "dehalo" intermediate $Cr\dot{C}HCl^{2+}$ may undergo, giving eventually the products shown in eq 3, these necessarily occur more rapidly than eq 10 and are therefore not revealed by the rate data.

The ^{51}Cr radiotracer experiments can prove helpful in differentiating among a number of ways we might envisage by which the intermediate $Cr\dot{C}HCl^{2+}$ could be converted rapidly to the observed products. In Scheme I we indicate three such possibilities: (a) "radical coupling" between the coordinated radical and the one-electron reducing agent Cr^{2+}, a process for which wide precedent exists,[2,3,5,24,26] followed by a protonolysis reaction, a process well known for organochromium complexes,[7a,27] which yields the observed products of reaction; (b) outer-sphere electron transfer followed by protonation; (c) protonolysis of the Cr–C bond, followed by Cr^{2+}–radical recombination.

The radiotracer results indicate a considerable level of activity in all three reaction products, a finding which eliminates reactions b and c of Scheme I from further consideration.[28] The mathematical treatment of mechanism a does not yield specific activities agreeing with experiment unless the first step (eq 11) is assumed to be rapid and reversible,[29]

$$Cr\dot{C}HCl^{2+} + Cr^{2+} \rightleftarrows Cr_2CHCl^{4+} \qquad (11)$$

such that this reaction reaches isotopic equilibrium prior to the protonolysis step (eq 12). With this modification, the

$$Cr_2CHCl^{4+} + H^+ \rightarrow Cr^{3+} + CrCH_2Cl^{2+} \qquad (12)$$

mathematical model (see Appendix) of exchange gives results in reasonable accord with the experimental data, as summarized in Table I.

Results at Low $[H^+]$. The salient observations are these: A forms at a *rate* independent of $[Cr^{2+}]$ but to an *extent* directly proportional to Cr^{2+} and inversely proportional to $[H^+]$. One seemingly attractive proposal invokes an intensely colored substance, lying off the main reaction pathway, formed only in a small amount. Such a scheme might consist of rate-limiting proton transfer of a carbon proton to a solvent molecule from the starting dichloromethyl complex (eq 13)

$$CrCHCl_2^{2+} + H_2O \xrightarrow{k^I} CrCCl_2^{+} + H_3O^+ \qquad (13)$$

$$CrCCl_2^{+} + Cr^{2+} \xrightarrow{\text{fast}} Cr_2CCl_2^{3+}\ (= A) \qquad (14)$$

(note the slow proton transfer from $CHCl_3$ to OH^- [30]), followed by fast addition of Cr^{2+} (eq 14), forming the species $Cr_2CCl_2^{3+}$ to which in this model we attribute the λ 350 nm absorption. Whatever its other attributes or failings, such a mechanism accounts for the formal kinetics but is of course eliminated on the basis of the experiments utilizing $CrCDCl_2^{2+}$.

Another possibility is based on our earlier observation[10] that *one* of the five water molecules bound to the organochromium complexes is *much* more labile than the other four. The labile water molecule is presumably the trans H_2O, since its more rapid substitution is unique. Based on kinetic data for the anation of $(H_2O)_5CrCHCl_2^{2+}$ by SCN^- (eq 6), the rate-limiting step at low $[SCN^-]$ is inferred to be reversible unimolecular dissociation of the trans water molecule

$$(H_2O)_5CrCHCl_2^{2+} \overset{k_d}{\rightleftarrows} (H_2O)_4CrCHCl_2^{2+} + H_2O \qquad (15)$$

for which $k_d = 4.6 \times 10^{-2}\ s^{-1}$ at 25 °C and $\mu = 1.0$ M. Given the rather different reaction medium, this value is not in poor agreement with the present value of k^I for the formation of A at low $[H^+]$, $k^I = 1.5 \times 10^{-2}\ s^{-1}$ (25.0 °C, $\mu = 2.50$ M).

The formal kinetic parameters would be satisfied by completing the scheme with the reversible reaction

$$(H_2O)_4CrCHCl_2^{2+} + Cr^{2+}(aq) \overset{\text{fast}}{\rightleftarrows} \underset{A}{CrOHCrCHCl_2^{3+}} + H^+ \qquad (16)$$

where the OH^--bridged, "mixed-valence" dichromium complex (A) formed in small quantity is assigned to the λ 350 nm absorption.

In this model, the occurrence of reactions 15 and 16 produces a species which lies off the main reaction pathway (eq 10–12). Since the reversal of (15) and (16) are (in this model) fast, A, once formed, merely serves as an "indicator" for the progress of the overall reaction. That is, loss of $CrCHCl_2^{2+}$ by reaction with Cr^{2+} (eq 10) is accompanied by reversal of the equilibrium reactions 15 and 16. Thus in the second stage of reaction the observation that k_A(of eq 9) $\simeq$ k_{Cr}(of eq 7) is rationalized.

In fact, the reversible equilibria 15 and 16 can explain all observations we have made (although further oxidative cleavage steps may be needed to account for the data with excess O_2 or Fe^{3+}). Aside from the agreement and our inability to formulate an attractive or reasonable alternative, formation of species A remains without confirmation or, as far as we are aware, precedent.

Our mechanistic formulations for the main reaction pathway are the same as those of Spreer and Nohr[6] for the reaction of $CrCHI_2^{2+}$ with Cr^{2+}. These workers did not do spectrophotometric studies of the sort described here, nor did their work extend to low $[H^+]$. They consequently did not describe an intermediate analogous to A.

Appendix. Radiotracer Experiments[30]

The mechanism of reaction is taken to be

$$Cr^{2+} + CrCHCl_2^{2+} \xrightarrow{k_{Cr}} Cr\dot{C}HCl^{2+} + CrCl^{2+} \qquad (A\text{-}1)$$

$$Cr\dot{C}HCl^{2+} + Cr^{2+} \rightleftarrows Cr_2CHCl^{4+}\ \text{(very fast)} \qquad (A\text{-}2)$$

$$Cr_2CHCl^{4+} + H^+ \rightarrow CrCH_2Cl^{2+} + Cr^{3+} \qquad (A\text{-}3)$$

The following symbols and abbreviations are used

$x = [CrCl^{2+}] + [CrBr^{2+}] =$ "Cr^{2+} fraction"[31]

$y = [Cr^{3+}] = [CrCH_2Cl^{2+}] = [CrCl^{2+}] = [Cr^{2+}]_0 - x$

$u =$ activity of the Cr^{2+} fraction, cpm

$v =$ activity of Cr^{3+} (or $CrCH_2Cl^{2+}$), cpm

$S_x = u/x =$ specific activity of Cr^{2+} fraction

$S_y = v/y =$ specific activity of Cr^{3+} and $CrCH_2Cl^{2+}$

$S_z =$ specific activity of $CrCHCl_2^{2+}$

The differential equations for this scheme are

$$dx/dt = -k_{Cr}[Cr^{2+}][CrCHCl_2^{2+}] \tag{A-4}$$

$$du/dt = k_{Cr}[Cr^{2+}][CrCHCl_2^{2+}](S_z - 2u/x) \tag{A-5}$$

Combining these equations, we have

$$du/dx = S_z - 2u/x \tag{A-6}$$

which yields

$$u/x = S_x = S_z + I_1 x \tag{A-7}$$

where the constant of integration I_1, is specified from the boundary conditions: (a) when Cr^{2+} is initially tagged, as in experiments RT-1 and -2, $S_z = 0$, $x_0 = [Cr^{2+}]_0$, and $I_1 = S_x^0/[Cr^{2+}]_0$; (b) when $CrCHCl_2^{2+}$ is initially tagged, as in experiment RT-3, $u^0 = 0$ and $I_1 = -S_z/[Cr^{2+}]_0$.

A similar development for S_y may be made

$$dy/dt = k_{Cr}[Cr^{2+}][CrCHCl_2^{2+}] \tag{A-8}$$

$$dv/dt = k_{Cr}[Cr^{2+}][CrCHCl_2^{2+}](u/x) \tag{A-9}$$

$$dv/dy = u/x = S_z + I_1 x = S_z + I_1([Cr^{2+}]_0 - y) \tag{A-10}$$

$$v = S_z y + I_1[Cr^{2+}]_0 y - {}^1/_2 I_1 y^2 + I_2 \tag{A-11}$$

The condition that, at $t_0 = 0$, $v = 0$ and $y = 0$ gives $I_2 = 0$. The expression for S_y is thus

$$S_y = v/y = S_z + I_1([Cr^{2+}]_0 - y/2) \tag{A-12}$$

for which the same values of I_1 as given above apply for the two types of experiments.

The values of S_x and S_y calculated from eq A-7 and A-12 are listed in Table I. In this calculation account must be taken of the fact that the reactions were quenched at a *known* extent of reaction and that the "CrR^{2+} fraction" is an unseparated mixture of unreacted $CrCHCl_2^{2+}$ and product $CrCH_2Cl^{2+}$.

Registry No. $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCHCl_2^{2+}$, 17477-10-0; Cr^{2+}, 22541-79-3.

References and Notes

(1) (a) Based in part on the Ph.D. Thesis of J.P.L., Iowa State University, Oct 1975. (b) Work performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

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(4) As yet these compounds have not been isolated as crystalline compounds, a situation however common to most known $(H_2O)_5CrX^{2+}$ complexes. C. T. Loo, L.-Y. Goh, and S. H. Goh, *J. Chem. Soc., Dalton Trans.*, 585 (1972), succeeded in isolating very low yields of two bis(ethylenediamine)organochromium complexes as the perchlorate salts, but they were quite impure, 27 and 40%.

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(8) Mercuric ion reacts rapidly with $CrCl^{2+}$ ($k = 0.2\ M^{-1}\ s^{-1}$) and $CrCH_2Cl^{2+}$ ($k = 6.8\ M^{-1}\ s^{-1}$) but only slowly with $CrCHCl_2^{2+}$, converting the former complexes to Cr^{3+}. This enables a purer sample of $CrCHCl_2^{2+}$ to be obtained because it is more easily separated from Cr^{3+} than from $CrCl^{2+}$ and $CrCH_2Cl^{2+}$.

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(12) H. Diehl, H. Clark, and H. H. Willard, *Inorg. Synth.*, **7**, 186 (1939).

(13) We are grateful to Professor D. S. Martin for use of the counting equipment and to Dr. E. Smith for assistance in its operation.

(14) We are grateful to Mr. G. D. Flesch for these determinations.

(15) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

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(17) Specific activity is reported in units of $10^{-6} \times$ cpm/molarity of chromium.

(18) A minimum of 10^4 counts was taken to reduce statistical errors in counting.

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(20) The relatively complicated nature of the reaction medium arises from the necessity of using fairly high $[Cr^{2+}]$, a consequence of which is that, with $[Cr^{2+}]$ variation, a 1:1 electrolyte such as $HClO_4$ cannot simultaneously maintain constant μ and constant $[ClO_4^-]$. (The latter is desirable for reactions between two highly charged cations: A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949)). The use of two inert electrolytes, $Ba(ClO_4)_2$ and $LiClO_4$, permits simultaneous control of both of these variables with variable $[H^+]$ and $[Cr^{2+}]$.

(21) $D_0 = 0.460$, $D_\infty = 0.460$, $D_{max} = 0.482$ ($b = 2$ cm).

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(23) We use the term "intermediate" advisedly: a likely interpretation of these data (see subsequent discussion) is that the absorption is due to a trace of intensely absorbing A, whose formation from reactants lies off the main reaction pathway for the overall reaction.

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(27) H. Cohen and D. Meyerstein, *Inorg. Chem.*, **13**, 2434 (1974).

(28) We are grateful to a referee for pointing out that mechanism b of Scheme I, appropriately modified, could also account for the data: the species $Cr\ddot{C}HCl^+$ could undergo exchange with Cr^{2+}, either via a dichromium complex or by dissociation. Although this is correct, it would require $Cr\ddot{C}HCl^+$ to survive sufficiently long in H_3O^+ solution to react other than by "instantaneous" protonation, which seems unlikely to us.

(29) This is evident from the data in Table II: note that the Cr^{2+} fraction is labeled in experiment 3 and that its specific activity is less than the initial value in experiments 1 and 2. These findings require a pathway for exchange of Cr^{2+} with the intermediate.

(30) J. Hine and K. Tanabe, *J. Am. Chem. Soc.*, **80**, 3002 (1958).

(31) We gratefully acknowledge the assitance of Professor D. S. Martin in the formulation of the mathematical model for this exchange process.

(32) Reactions were quenched by addition of $Co(NH_3)_5Br^{2+}$. The mixture of $CrCl^{2+}$ and $CrBr^{2+}$ was separated as a single fraction; moreover, isotopic exchange of Cr^{2+} and $CrCl^{2+}$ occurs rapidly on this time scale, so that both $CrCl^{2+}$ and $CrBr^{2+}$ have the same specific activity.