Table III. Summary of Spectral Data for the Three Oxopentahalouranate(V) Species

	Best-fit parameters, cm^{-1}			Electronic transitions obsd, cm^{-1}					
	ζ	Δ	θ	$\Gamma_6(\Gamma_8)$	$\Gamma_7(\Gamma_8)$	$\Gamma_7(\Gamma_7')$	$\Gamma_6(\Gamma_8')$	$\Gamma_7(\Gamma_8')$	$\Gamma_6(\Gamma_6)$
UOF_5^{2-}	1850	4630	6540	2380	6792	6837	11,448	12,420	18,660
$UOCl_5^{2-}$	1770	3810	3110	1555	5050	6161	8,584	10,616	16,835
$UOBr_5^{2-}$	1750	4070	2150	1490	4880	6080	8,163	10,460	16,194

Table IV. Epr Data for Uranium(V) Complexes

Complex	$\langle g \rangle$	peak-to-peak signal width, G
UF_6^-	*a*	*a*
UOF_5^{2-}	0.58	~8000
UCl_6^-	1.12	~1200
$UOCl_5^{2-}$	1.09	~1400
UBr_6^-	1.21	850
$UOBr_5^{2-}$	1.24	~1600

[a] Values of the average *g* tensor for polycrystalline MUF_6 (M = Li, Na, Cs) at 77°K have been reported[9] as −0.768, −0.748, and −0.709, respectively.

pounds and that the spin-orbit coupling constants for the compounds decrease in the order $F^- > Cl^- > Br^-$. We suggest that the symmetry of UOX_5^{2-} should not be characterized as strongly axially distorted (note that the tetragonal distortion parameter $\tau = 700$ cm^{-1} is adequate to account for the electronic spectral bands) in the same way that NpO_2^{2+} and other *trans*-dioxoactinyl species are. For example, the first excited level in $5f^1$ $RbNpO_2(NO_3)_3$ is probably below 1000 cm^{-1}. This low-lying level apparently shortens the longitudinal relaxation time T_1 sufficiently to require very low temperatures for epr signal observation of the NpO_2^{2+} species. Although one might expect relatively shorter relaxation times (due to the Γ_8 splitting into higher and lower levels) and larger *g* anisotropies in the oxo species relative to the hexahalo species, these factors do not appear to be sufficient to eliminate (but only greatly broaden) room-temperature epr signals, as has been suggested by Lewis, Hecht, and Eastman.[6] Their theoretical predictions in this regard simply are not borne out by the experimental facts illustrated in Figures 5 and 6.

Acknowledgment. The authors are grateful for a grant from the National Science Foundation (GP-30661x1) (to J. S.) which supported this research.

Registry No. $(Et_4N)_2UOF_5$, 30917-64-7; $(Et_4N)_2UOBr_5$, 30917-62-5; UCl_6^-, 44491-58-9; $UOCl_5^{2-}$, 41677-65-0; UBr_6^-, 44491-06-7; $(C_2H_5)_4NF$, 665-46-3; $(C_2H_5)_4NUCl_6$, 17141-96-7; $UCl_5 \cdot TCAC$, 20574-41-8.

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Stoichiometry and Kinetics of the Reduction of $Cr(OH_2)_5CH_2I^{2+}$ by Chromium(II)[1]

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The stoichiometry of the reaction between Cr(II) and $Cr(OH_2)_5CH_2I^{2+}$ was found to be $2Cr^{2+} + 2H^+ + CrCH_2I^{2+} = CrI^{2+} + 2Cr^{3+} + CH_4$. The rate law for the disappearance of Cr(II) was $(-{}^1/_2 d[Cr^{2+}]/dt = k_1[Cr^{2+}][CrCH_2I^{2+}]$; at 25° $k_1 = 2.9 \pm 0.2 \times 10^{-2}$ l. mol^{-1} sec^{-1} with $\Delta H^\ddagger = 7.7$ kcal/mol, and $\Delta S^\ddagger = -39$ eu. The rate law for the appearance of CH_4 was found to be $d[CH_4]/dt = k_4[I][H^+]$, where I is a long-lived organochromium intermediate; k_4 at 25° was $5.2 \pm 0.3 \times 10^{-3}$ l. mol^{-1} sec^{-1}. Evidence is presented that I was $CrCH_3^{2+}$, and a possible mechanism is proposed.

Introduction

Chromium(II) has been widely used as a reducing agent for a variety of organic compounds,[2] and organochromium species have been proposed as intermediates in some of these reactions.[3,4] Castro and Kray[5] report that some polyhalomethanes are reduced to methane by excess chromium(II), and they suggest "chromium-complexed carbenes" as intermediates. We find that methane is also produced when iodomethylpentaaquochromium(III) ion, $CrCH_2I^{2+}$, is allowed to react with chromium(II). This paper presents the results of our study of this reaction, and a mechanism is proposed.

Experimental Section

Reagents. Reagent grade diiodomethane (MCB) was used without further purification, as was reagent grade perchloric acid. $NaClO_4$ was prepared by the neutralization of Na_2CO_3 (Baker Analyzed Reagent) with $HClO_4$. Stock solutions of $NaClO_4$ were analyzed by passing an aliquot through a cation-exchange column in the H^+ form and titrating the liberated H^+ with standard base. Cr(II) solutions were prepared by dissolving electrolytic grade Cr metal (~99.999% pure, Apache Chemicals) in deoxygenated perchloric acid solutions. All solutions were prepared using H_2O which had been deionized and then distilled using an all-glass still (Corning Model 1-a).

Analysis. Chromium(III) or total chromium content was determined using H_2O_2 in base as an oxidant and measuring chromium as chromate ion (CrO_4^{2-}, ϵ_{372} 4815).[6] Cr(II) was measured by determining the decrease in absorbance of acidic chromium(VI) solutions (λ 348 nm) after reaction with Cr(II).[7] Carbon present in gaseous compounds was measured by absorption of CO_2 on an Ascarite tube after catalytic (CuO) combustion at 930°. (Control experiments were run to ensure that complete combustion occurred under these conditions.) Gravimetric AgI analyses were made for I^-.

$Cr(OH_2)_5CH_2I^{2+}$. Iodomethylpentaaquochromium(III) ion, ($CrCH_2I^{2+}$), was prepared, after the method of Anet,[8] by adding Cr(II) solutions to CH_2I_2. The reactants were stirred for a 2-hr period

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(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

(2) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, 7, 247 (1968).

(3) K. D. Kopple, *J. Amer. Chem. Soc.*, **84**, 1586 (1962).

(4) J. K. Kochi and P. E. Mocadlo, *J. Amer. Chem. Soc.*, **88**, 4094 (1966).

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(6) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

(7) R. V. James and E. L. King, *Inorg. Chem.*, **9**, 1301 (1970).

(8) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959).

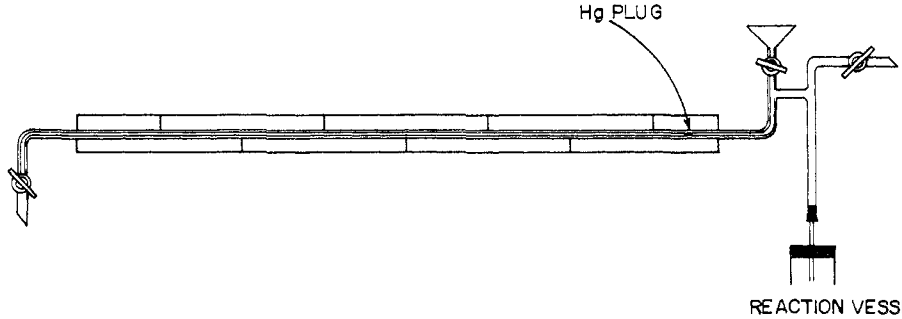

Figure 1. Apparatus for measuring small changes in gas volumes.

and then separated on a Dowex 50W-X8 (Bio-Rad Laboratories) ion-exchange column. The brownish-orange 2+ ion was removed by $NaClO_4$-$HClO_4$ mixtures ($I = 1.00$ *M*). The average of several independent analyses gave a Cr:C:I ratio of 1.00:0.98:0.99. Spectral measurements made on freshly prepared solutions with a Cary Model 14 spectrophotometer gave the following molar absorbancy indices for the maxima in the spectrum ($\lambda_{max}{}^{nm}$; ϵ mol^{-1} cm^{-1}): 524, 34.2; 396, 322; 296, 3430; 264, 3350.[9] $CrCH_2I^{2+}$ differs from most species having a chromium-carbon bond in that it does not undergo a rapid reaction with oxygen.[11]

Kinetic Measurements

The kinetics of the reaction between Cr(II) and $CrCH_2I^{2+}$ were followed by a titrimetric procedure. Preequilibrated solutions of Cr(II) and $CrCH_2I^{2+}$ were mixed in a jacketed buret and temperatures were maintained by passing water from a Lauda K4-R constant temperature circulator through the jacket. (Temperature control was estimated at ±0.08°.) Measured aliquots from the reaction buret were added to measured, deareated portions of acidic Cr(VI) solutions. The decrease in absorbance of the Cr(VI) solutions was used to calculate the concentration of unreacted Cr(II) in the reaction solution. Due to complications caused by the reduction of Cr(VI) by I^-,[12] it was necessary to add Ag^+ (~0.00015 *M*) to the Cr(VI) solution in order to precipitate the I^- as AgI. Under the conditions of the experiment, the solubility of Ag_2CrO_4 was not exceeded. $CrCH_2I^{2+}$ has an appreciable absorbance at 348 nm, the wavelength at which the Cr(VI) was measured; therefore, the quenched aliquot was passed through a cation-exchange column to remove any unreacted $CrCH_2I^{2+}$. The ion-exchange column also acted as an effective filter for the AgI precipitate. The absorbancies of the Cr(VI) solutions were measured on a Gilford-modified Beckman DU spectrophotometer (accuracy $> \pm 1\%$ in absorbance). Blank experiments were run which demonstrated the accuracy and reproducibility of the technique.

Kinetic measurements were also made on the production of gases during the course of the reaction. The volume of gases produced under the concentrations and conditions of the experiments was small (<5 ml) so an apparatus for measuring small volume changes under conditions of atmospheric pressure was devised. The apparatus is shown in Figure 1. It consisted of a capillary tube, 1.4 m long with a uniform 2.0-mm i.d., and connecting tubes fitted with an addition funnel (to introduce the mercury plug) and a nitrogen outlet. The volume of the connecting tube was 30.1 ml. The connecting tube was joined to a 100- or 250-ml reaction vessel through a gas tight 18 G needle-serum stopper connection. The reaction vessel was placed in a thermostated water bath and the reaction solutions were continuously agitated. The change in position of the mercury plug (which could be converted to change in volume) was measured as a function of time.

Results Section

Stoichiometry. The stoichiometry of the reduction of $CrCH_2I^{2+}$ by Cr(II) was established under conditions which were similar to those of the kinetic studies. The procedure was to determine the initial amounts of Cr(II) and $CrCH_2I^{2+}$, mix and allow the reaction to proceed, and quench the reaction by Cr(VI) or by exposing it to air. The chromium products were determined by separating the species on a cation-exchange column maintained at 0°, identifying the products spectrophotometrically, and analyzing the fractions for total chromium. Methane was identified as the organic product by retention time on two different glc columns and estimated by combustion to CO_2 and subsequent gravimetric measurements after absorption on Ascarite. Table I presents the result.

The average ratio of Cr(II) reacted:$CrCH_2I^{2+}$ reacted is 2.03, and the sum of the moles of Cr(II) and $CrCH_2I^{2+}$ reacted agrees very well with the sum of the moles of CrI^{2+} and Cr^{3+}. The half-time for aquation of CrI^{2+} to Cr^{3+} at 25° ($t_{1/2} = 98$ min)[12] is quite appreciable compared to the average length of reaction time (120 min) in the experiments, and some of the CrI^{2+} initially formed is converted to Cr^{3+}. In those experiments in which the initial Cr(II) concentration was high and the reaction time was short, the amount of CrI^{2+} found more nearly equaled the amount of $CrCH_2I^{2+}$ reacted. The initial yield of CrI^{2+} was calculated for several of the experiments using the known rates of formation and aquation, and the values support the conclusion that one CrI^{2+} is formed for every $CrCH_2I^{2+}$ reacted. The average per cent conversion of $CrCH_2I^{2+}$ to methane found was 98%. The small discrepancy from 100% conversion is due to the slow thermal aquation of $CrCH_2I^{2+}$ which produces other products.[13] The stoichiometry of the reaction is represented by the following.

$$2Cr(II) + CrCH_2I^{2+} + 2H^+ = CrI^{+2} + 2Cr^{3+} + CH_4$$

Kinetic Results. Disappearance of Cr(II). The method for following the disappearance of Cr(II) involved taking aliquots of the reaction mixture and oxidizing the remaining Cr(II) with Cr(VI). It was observed that the rate was dependent on [Cr(II)] and [$CrCH_2I^{2+}$] and independent of [H^+]. It

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[9] The molar absorbancy indices which were determined in this study are appreciably higher than those obtained by Dodd and Johnson[10] for the same ion. However, these authors report an iodine:chromium ratio of 0.82 ± 0.2:1, and we suspect that their solutions contained some hexaaquochromium(III) ions.

(10) D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 34 (1968).

(11) (a) A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc. A*, 1927 (1970); (b) R. G. Coombes and M. D. Johnson, *J. Chem. Soc.*, 177 (1966).

(12) D. C. Gaswick and J. H. Krueger, *J. Amer. Chem. Soc.*, 91, 2240 (1969).

(13) The results of our study of the kinetics of aquation of $CrCH_2I^{2+}$ and other haloalkylchromium(III) ions will be reported elsewhere.

Table I. Stoichiometric Measurements on the Reaction between Cr(II) and $CrCH_2I^{2+}$ [a]

$[H^+]$	mol Cr(II) reacted	mol $CrCH_2I^{2+}$ reacted	mol CrI^{2+} produced	mol Cr^{3+} produced	mol CH_4
1.0	0.184	0.090	0.0304	0.244	0.088
1.0	0.285	0.142	0.0906	0.336	0.140
1.0[b]	0.560	0.269	0.105	0.724	0.261
0.5	0.651	0.323	0.259	0.700	0.317
0.1	0.404	0.201	0.163	0.440	0.199
0.1	0.610	0.306	0.290	0.620	

[a] Experimental ionic strength maintained at 1.0 *M* by $NaClO_4$, *T* 25° except as noted. [b] Run at 45°.

was experimentally difficult to follow the kinetics under pseudo-first-order conditions so the data were plotted using various forms of integrated rate laws. If the rate law

$$1/2\,\frac{-d[Cr(II)]}{dt} = k_1[Cr(II)][CrCH_2I^{2+}]$$

is integrated using the above reaction stoichiometry, the result is

$$k_1t = \frac{1}{2A_0 - B_0}\ln\frac{B_0(A_0 - x)}{A_0(B_0 - 2x)} \qquad (1)$$

where A_0 = initial $[CrCH_2I^{2+}]$, B_0 = initial [Cr(II)], and $2x$ = [Cr(II)] which has reacted. The data obeyed this rate law over more than 95% of the reaction. A typical plot (being neither the best nor the worst) is shown in Figure 2. A summary for the kinetic data for the disappearance of Cr(II) is found in Table II. The activation parameters were calculated to be $\Delta H^\ddagger = 7.7$ kcal/mol and $\Delta S^\ddagger = -39$ eu.

Spectroscopic Evidence for an Intermediate. Attempts were made to follow the reaction kinetics using spectroscopy. Since CrI^{2+} is formed and undergoes subsequent aquation to Cr^{3+} at a rate similar to that of the disappearance of $CrCH_2I^{2+}$, the absorbance changes were measured at 524 mμ, an isosbestic point for CrI^{2+} and Cr^{3+}. In these experiments, the absorbance increased to a maximum (the time to reach maximum absorbance decreased as the $[Cr(II)]/[CrCH_2I^{2+}]$ ratio increased) and then decreased. These observations were taken as evidence that a long-lived organochromium intermediate was formed in the reaction sequence.

Kinetics of Methane Production. The kinetics of the production of methane were followed using the apparatus shown in Figure 1. A plot of the change in the position, *L*, of the mercury plug for a specific time interval $\Delta L/\Delta t = (L_t - L_{t'})/(t - t')$ *vs.* time for an experiment in which the initial [Cr(II)] was about eight times the initial $[CrCH_2I^{2+}]$ is shown in Figure 3. $\Delta L/\Delta t$ is proportional to the rate of production of methane, $d[CH_4]/dt$. The appearance of this plot again suggests that a long-lived organochromium intermediate is formed which decomposes to produce methane and the final chromium products.

The concentrations of the reactants were adjusted such that initial [Cr(II)] ≫ initial $[CrCH_2I^{2+}]$ in attempts to make the formation of the intermediate much faster than its subsequent disappearance, but it was experimentally impossible to achieve true limiting conditions. However, the formation of the intermediate does become pseudo-first order in $[CrCH_2I^{2+}]$ when initial [Cr(II)] ≫ initial $[CrCH_2I^{2+}]$. If it is then assumed that the rate of production of methane is first order (or pseudo-first order) in the intermediate, the system can be treated as one of consecutive first-order reactions

$$A \xrightarrow{k_A} I \xrightarrow{k_I} C$$

where A = $CrCH_2I^{2+}$, $k_A = k_1[Cr^{2+}]_0$, k_I = first-order rate constant, I = intermediate, C = CH_4. For consecutive irreversible first-order reactions in which there is no change in the number of molecules, *viz.*, one $CrCH_2I^{2+}$ (A) produces one intermediate (I) which produces one CH_4 (C), the solution for [C] of the simultaneous differential equations is[14]

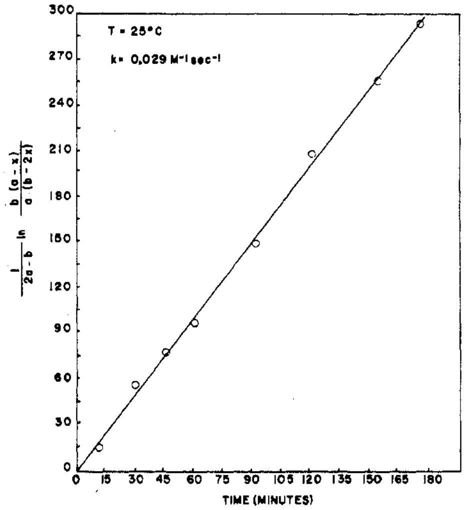

Figure 2. Integrated second-order plot for the reduction of $CrCH_2I^{2+}$ by Cr(II): *a* = initial $[CrCH_2I^{2+}]$; *b* = initial [Cr(II)]; $2x$ = [Cr(II)] which has reacted.

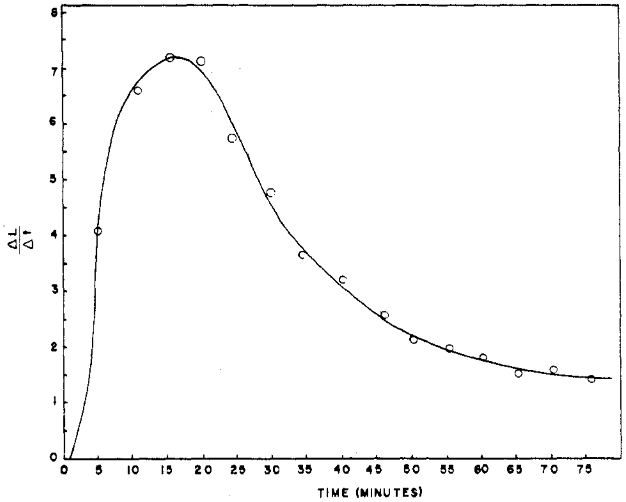

Figure 3. Rate of production of methane with time at 25° for the reduction of $CrCH_2I^{2+}$ by Cr(II). $\Delta L/\Delta t = (L_t - L_{t'})/(t - t')$ where *L* is the position of the mercury plug (Figure 1). $\Delta L/\Delta t \propto d[CH_4]/dt$.

Table II. Rate Constants for the Disappearance of Cr(II)[a]

T, °C	$[H^+]$, *M*	$k_1 \times 10^2$, l. mol^{-1} sec^{-1} [b]
45	0.1	6.6 ± 0.2
45	0.5	6.8 ± 0.2
45	1.0	6.7 ± 0.1
35	0.1	4.4 ± 0.1
35	0.5	4.5 ± 0.1
35	1.0	4.5 ± 0.1
25	0.1	2.9 ± 0.2
25	0.5	2.9 ± 0.2
25	1.0	2.9 ± 0.1
15	1.0	1.9 ± 0.2

[a] *I* maintained at 1.00 *M* by $NaClO_4$. [b] Rate constants evaluated by a linear least-squares computer program fit of eq 1.

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[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 33.

$$[\mathrm{C}] = [\mathrm{A}]_0\left[1 - \frac{k_{\mathrm{I}}e^{-k_{\mathrm{A}}t}}{k_{\mathrm{I}} - k_{\mathrm{A}}} + \frac{k_{\mathrm{A}}e^{-k_{\mathrm{I}}t}}{k_{\mathrm{I}} - k_{\mathrm{A}}}\right]$$

$[\mathrm{A}]_0$ = initial $[\mathrm{CrCH_2I}]^{2+}$

In this equation the only unknown is k_{I}, since k_{A} is known from the data on disappearance of chromium(II) and [C] can be determined from the data on the volume changes over the reaction solution. The rate constant k_{I} was evaluated from a number of different points during a single kinetic experiment and the average values are reported in Table III.[15] The rate constant k_{I} shows a dependence on $[\mathrm{H^+}]$ and values of $k_{\mathrm{I}}' = k_{\mathrm{I}}/[\mathrm{H^+}]$ are also reported. The constancy of k_{I}' as the reactant concentrations vary is evidence that the assumption of first-order dependence (actually pseudo-first-order dependence) on I is correct. The rate law for the production of methane is then

$$\mathrm{d}[\mathrm{CH_4}]/\mathrm{d}t = k_{\mathrm{I}}'[\mathrm{I}][\mathrm{H^+}]$$

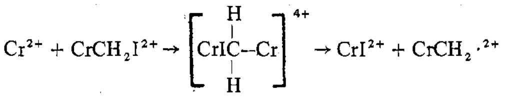
Discussion

The formation of iodomethylchromium(III) ion by reduction of diiodomethane with chromium(II) corresponds to that suggested for many reactive organic halides,[8,16,17] *i.e.*, the abstraction of an iodine atom by chromium(II) ion to give a radical which is captured by another chromium (II) ion.

$$\mathrm{Cr^{2+} + CH_2I_2 \rightarrow CrI^{2+} + \cdot CH_2I} \tag{2}$$

$$\mathrm{Cr^{2+} + \cdot CH_2I \rightarrow CrCH_2I^{2+}} \tag{3}$$

The further reaction of Cr(II) with $\mathrm{CrCH_2I^{2+}}$ produces methane as a final organic product. The observations that $\mathrm{CrI^{2+}}$ is a product and the reaction is first order in $\mathrm{CrCH_2I^{2+}}$ and in Cr(II) suggest that the initial step in the reduction of $\mathrm{CrCH_2I^{2+}}$ is analogous to eq 2. This step would involve the abstraction of an iodine atom by chromium(II) by means of a bridged transition state



$$\mathrm{Cr^{2+} + CrCH_2I^{2+}} \rightarrow \left[\mathrm{CrI}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}{-}Cr}\right]^{4+} \rightarrow \mathrm{CrI^{2+} + CrCH_2\cdot^{2+}} \tag{4}$$

The $\mathrm{CrCH_2\cdot^{2+}}$ would then react very rapidly with another Cr(II) ion. The value of 7.7 kcal for $\Delta H^{\ddagger}$ is consistent with a rate-determining step involving the breaking of the weak C–I bond. The negative value of $\Delta S^{\ddagger}$, −39 eu, is also consistent with a highly charged transition state formed by an aggregation of two ions.[18]

Comparison of the data on the production of methane, the final organic product, with that for the disappearance of Cr(II) shows that a long-lived organochromium intermediate is involved in the reaction sequence. At 25°, the second-order rate constant determined by following the disappearance of Cr(II) is $2.9 \pm 0.2 \times 10^{-2}$ l. mol^{-1} sec^{-1}, and the rate is independent of $[\mathrm{H^+}]$; the rate constant determined by following the appearance of methane is $5.3 \pm 0.3 \times 10^{-3}$ l. mol^{-1} sec^{-1}, and the reaction is first order in $[\mathrm{H^+}]$.

One obvious candidate for the organochromium intermediate is methylpentaaquochromium(III) ion, $\mathrm{CrCH_3^{2+}}$, which Schmidt, Swinehart, and Taube report[19] dissociates in aqueous acidic solutions to form methane and $\mathrm{Cr^{3+}}$. These authors report that the aquation of $\mathrm{CrCH_3^{2+}}$ is first order in $[\mathrm{CrCH_3^{2+}}]$ and in $[\mathrm{H^+}]$ with a rate constant at 25° of $5.2 \pm 0.2 \times 10^{-3}$ l. mol^{-1} sec^{-1}. There is good agreement between this value and the rate constant we determined by following $\mathrm{CH_4}$ production.

Table III. Rate Constants for the Production of Methane under Conditions of Excess Cr(II)[a]

$[\mathrm{H^+}]$	Initial $[\mathrm{CrCH_2I^{2+}}]$ $\times 10^3$	Initial $[\mathrm{Cr^{2+}}]$ $\times 10^2$	$k_{\mathrm{I}}{}^b \times 10^3$, l. mol^{-1} sec^{-1}	$k_{\mathrm{I}}/[\mathrm{H^+}] = k^1 \times 10^3$
0.46	0.945	5.66	2.3 ± 0.1	5.0
0.086	1.11	6.52	0.44 ± 0.02	5.1
1.00	1.23	6.54	5.5 ± 0.2	5.5
0.094	4.21	21.1	0.52 ± 0.02	5.5
0.093	2.38	21.3	0.50 ± 0.02	5.4
			Av	$5.3 \pm 0.3 \times 10^{-3}$

[a] Ionic strength maintained at 1.0 *M* by $\mathrm{NaClO_4}$, *T* 25°. [b] Each value is the average of at least *six* calculations at various points in the reaction.

Other observations have been made which support the choice of $\mathrm{CrCH_3^{2+}}$ as the intermediate. Castro and Kray[5] reported that both $\mathrm{CHCl_3}$ and $\mathrm{CH_2Br_2}$ are reduced to methane by excess Cr(II), and furthermore the rate of production of methane was the same for each. They interpreted this to mean there was a common intermediate which they believed to be $\mathrm{CrCH_3^{2+}}$. Dodd and Johnson[10] also suggested $\mathrm{CrCH_3^{2+}}$ as an intermediate in their investigations of some reactions of halomethylpentaaquochromium(III) ions.

One mechanism which can accommodate the formation of $\mathrm{CrCH_3^{2+}}$ and which is consistent with the data is

$$\mathrm{Cr^{2+} + CrCH_2I^{2+}} \xrightarrow{k_1} \mathrm{CrI^{2+} + CrCH_2\cdot^{2+}} \quad \text{rate determining} \tag{5}$$

$$\mathrm{Cr^{2+} + CrCH_2\cdot^{2+} + H^+ = CrCH_3^{2+} + Cr^{3+}} \quad \text{rapid net change} \tag{6}$$

$$\mathrm{CrCH_3^{2+} + H^+} \xrightarrow{k_2} \mathrm{Cr^{3+} + CH_4} \quad \text{rate determining} \tag{7}$$

Steps 5 and 7 would be considered to be slow compared to step 6 and would have the following rate laws associated with them.

$$(1/2)(-\mathrm{d}[\mathrm{Cr(II)}]/\mathrm{d}t) = k_1[\mathrm{Cr(II)}][\mathrm{CrCH_2I^{2+}}] \tag{8}$$

$$\mathrm{d}[\mathrm{CH_4}]/\mathrm{d}t = k_4[\mathrm{CrCH_3^{2+}}][\mathrm{H^+}] \tag{9}$$

Under conditions where $[\mathrm{Cr(II)}] \gg [\mathrm{CrCH_2I^{2+}}]$ this sequence can be treated as one of consecutive first-order reaction. The rate constant for the production of methane ($k_{\mathrm{I}}' = k_2$) was calculated from data taken under these conditions.

A number of experiments in which [Cr(II)] was not a great deal larger than $[\mathrm{CrCH_2I^{2+}}]$ were also done. If step 6 is fast compared to 5 and 7, the sequence under these conditions becomes one of consecutive reactions, the first, second order, the second, first order[20] (actually pseudo first order since $[\mathrm{H^+}] \gg [\mathrm{CrCH_3^{2+}}]$). It was assumed the relationship holds that

$$[\mathrm{CrCH_3}]_t = [\mathrm{CrCH_2I^{2+}}]_0 - [\mathrm{CrCH_2I^{2+}}]_t - [\mathrm{CH_4}]_t$$

where $[\ ]_0$ is initial concentration and $[\ ]_t$ is the concentration at time *t*. $[\mathrm{CrCH_2I^{2+}}]_t$ was evaluated from the inte-

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(15) Kinetic measurements on the production of methane were made by glc with qualitative agreement of the rate constants.

(16) J. K. Kochi and D. Buchanan, *J. Amer. Chem. Soc.*, **87**, 853 (1965).

(17) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).

(18) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 129.

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(20) We have obtained a useful analytical solution to the general case of irreversible, consecutive second-order, first-order reactions, which will be submitted for publication elsewhere.

grated rate law (eq 1), and d[CH_4]/dt and [CH_4]$_t$ were measured experimentally. The rate constant, k_4, could then be evaluated by substituting into eq 9. The value of k_2/[H^+] remained constant while [H^+] and [Cr^{2+}]/[$CrCH_2I^{2+}$] were independently varied and agreed very well with the experimental values (Table III) determined under conditions of excess Cr(II).

The data do not provide substantive information about the means by which $CrCH_2\cdot^{2+}$ is converted to $CrCH_3^{2+}$ (step 6). One two-step sequence which is consistent with the present study and the well-known tendency of aquochromium(II) to undergo inner-sphere electron-transfer reactions[18] is the following.

$$Cr^{2+} + CrCH_2\cdot^{2+} \rightarrow [CrCH_2Cr]^{4+}$$

$$[CrCH_2Cr]^{4+} + H^+ \rightarrow CrCH_3 + Cr^{+3}$$

In this sequence, a bridged dinuclear complex, [$CrCH_2Cr$]$^{4+}$, is formed. Attempts were made to separate the species present in the reaction solution on an ion-exchange column maintained at low temperatures and under an inert atmosphere. A species of charge 2+ other than $CrCH_2I^{2+}$, CrI^{2+}, or Cr^{2+} was detected, but an adequate separation was not achieved. No species of charge 4+ was detected, so that if a dichromiumalkyl species is formed it must rapidly dissociate. The agreement between values of the rate constant for the production of methane determined under various experimental conditions also supports the view that there is only one long-lived intermediate.

It is of course not necessary to invoke the alkyl-bridged species,[5] but it is analogous to other well-established bridged dichromium species.[21-23] Further work on chromium(II) reactions with other halomethylchromium(III) ions is in progress; we seek evidence pointing to existence of C-bridged dichromium intermediates.

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Registry No. Cr^{2+}, 22541-79-3; $CrCH_2I^{2+}$, 17477-14-4; $CrCH_3^{2+}$, 32108-96-6; CH_4, 74-82-8.

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Notes

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Ligand Field Theory of Metal Sandwich Complexes. d^4 Configurations

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The usefulness of the ligand field model for the assignment of low-energy d-d transitions of metal sandwich complexes is now widely realized[1] and this approach is also appropriate for the interpretation of magnetic susceptibilities[2] and magnetic resonance phenomena.[3] Scott and Matsen[4] showed that such species could be treated on the basis of an effective axial ($C_{\infty v}$) symmetry (as long as only d^n configurations were involved and a fivefold or higher rotation axis was present), and a complete strong-field treatment, including spin-orbit coupling, has recently been given for the d^1, d^2, and d^3 systems and their complementary configurations.[5] Partial strong-field treatments (excluding spin-orbit interactions) have also been reported for d^5 and d^6 systems,[6] but the lack of spectroscopic data has so far resulted in the complete neglect of d^4 configurations.

In the course of a full survey of the magnetic susceptibilities of metal sandwich complexes,[7] it became necessary to establish with greater certainty the probable ground state of chromocene ($3d^4$). The complete d^4 strong-field electrostatic repulsion matrices in $C_{\infty v}$ symmetry have been evaluated and are given in the Appendix,[8] in terms of the Racah parameters B and C and the axial field quantities[9] Ds and Dt. In such systems the fivefold degenerate d-orbital set is split into one nondegenerate (σ) and two twofold degenerate (π and δ) levels, the usual energetic order of these one-electron core terms being $\delta < \sigma \ll \pi$, where $E(\sigma) = 2Ds - 6Dt$, $E(\pi) = Ds + 4Dt$, and $E(\delta) = -2Ds - Dt$.

In all the metallocene systems for which ligand field fittings have been made ($V(Cp)_2$, $Cr(Cp)_2^+$, $Fe(Cp)_2^+$, $Fe(Cp)_2$, $Co(Cp)_2^+$, $Ni(Cp)_2$)[3,5,6,10] the Dt/Ds ratio lies between about 0.5 and 0.6, and the Tanabe-Sugano type d^4 diagram shown in Figure 1 was therefore calculated using the mean value $Dt/Ds = 0.55$, assuming $C/B = 4.0$. For the metallocenes listed above a range of Dt/B values have been derived, but none of these gives Dt/B as less than 3.5 and mostly they lie within the range 4.5-6.5. The results therefore show that at all normal field strengths the $^3\Delta$ ($\sigma\delta^3$) level will constitute the ground state. Increase of the C/B ratio to 4.4 (the Cr^{2+} free-ion value) has the effect of eliminating the small region in which $^3\Sigma^-$ ($\sigma^2\delta^2$) lies lowest and slightly raising the high-spin-low-spin crossover point to about $Dt/B = 3.2$. However, the $^1\Sigma^+$ (δ^4) level always lies substantially above $^3\Delta$ ($\sigma\delta^3$) and cannot be the ground state for any feasible field strength—it lies lowest only for $Dt/B > ca.$ 20.

For chromocene, molecular orbital calculations[11,12] also predict a $^3\Delta$ ($\sigma\delta^3$) ground state, and for this an orbital contribution to the magnetic moment is predicted. Thus one

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