

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

## Mechanism of the Reduction of Chromium(VI) by Hexachloroiridate(III) in Acidic Aqueous Solution

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The kinetics of the reduction of  $\text{HCrO}_4^-$  by  $\text{IrCl}_6^{3-}$  have been studied at 25.0°, 0.40 M  $\text{H}^+$ , and 0.50 M ionic strength in perchlorate solutions. The reaction follows the rate equation  $-d[\text{HCrO}_4^-]/dt = (a[\text{IrCl}_6^{3-}] + b[\text{IrCl}_6^{3-}]^2(1 + c[\text{IrCl}_6^{3-}]^{-1}))[\text{HCrO}_4^-]/[\text{IrCl}_6^{3-}]$ . Values of the parameters are  $a = (4.85 \pm 0.81) \times 10^{-6} \text{ sec}^{-1}$ ,  $b = 0.147 \pm 0.017 \text{ M}^{-1} \text{ sec}^{-1}$ , and  $c = 123 \pm 25 \text{ M}^{-1}$ . This rate equation is consistent with several mechanisms in which the second step in the reduction of chromium(VI) is rate determining and which require the existence of more than one form of chromium(V). The reaction products are  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and  $\text{IrCl}_6^{2-}$ , with no evidence for formation of a binuclear product or for transfer of  $\text{Cl}^-$  from Ir to Cr.

### Introduction

The reduction of chromium(VI) by one-electron metal ion reducing agents has generally been proposed to occur by three successive one-electron-transfer steps involving unstable intermediate oxidation states of chromium. Depending on the reductant used, either the first (reduction of Cr(VI)) or second step (reduction of Cr(V)) has been rate determining. It has been proposed<sup>1,2</sup> that the distinguishing factor is the substitution lability of the reducing agent—substitution-inert reducing agents having the first step rate determining. The distinction was thought to arise from the inner-sphere or outer-sphere nature of the reduction. The reductions by  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$  (bipy = 2,2'-bipyridyl), and  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  were shown<sup>2</sup> to occur by inner-sphere processes in the third step (reduction of Cr(IV)), however, and evidence was advanced that the first step (reduction of Cr(VI)) is also inner-sphere in these reactions. These conclusions have now received support from studies of the inner-sphere reductions of vanadium(V) by these complexes.<sup>3,4</sup> The factors which influence the identity of the rate-determining step are thus not well understood. The reduction of chromium(VI) by substitution-inert hexachloroiridate(III) was studied in an attempt to examine more fully those factors which may influence the mechanism.

The reductions of Cr(VI) and of V(V) by the above Fe(II) complexes are of special interest since they represent the first proven examples of inner-sphere processes in which the bridging ligand is supplied by the reducing agent. The reduction of Cr(VI) by  $\text{IrCl}_6^{3-}$  was thought to be a useful test of the postulates that the "reverse ligand-transfer" mechanism would occur if the reducing agent were substitution inert and contained relatively good bridging ligands and if the oxidizing agent were either substitution labile or if it expanded its coordination sphere upon reduction.<sup>3</sup>

### Experimental Section

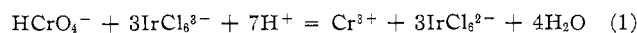
Sodium dichromate, lithium perchlorate, and perchloric acid solutions were prepared, purified, and analyzed as previously described.<sup>2</sup> Sodium hexachloroiridate(III) was prepared by the method of Poulsen and Garner<sup>5</sup> from the iridium(IV) salt (Johnson, Matthey and Co.), which was used without further purification.

The iridium(III) was stored as the dihydrate over  $\text{CaSO}_4$  in a vacuum desiccator and was shielded from light. Solutions of the iridium complexes were prepared by weight and concentrations were checked spectrally.<sup>5,6</sup> A volumetric flask containing the solid was purged with deoxygenated nitrogen and an appropriate volume of nitrogen-flushed distilled water was added. Solutions were protected from light and were stored in an ice bath between experiments. Experiments carried out with two different preparations of the iridium(III) salt gave identical results within experimental uncertainty.

Kinetic experiments were carried out with a Cary 14 recording spectrophotometer, using conventional syringe techniques and previously described thermostating arrangements.<sup>2</sup> Solutions complete but for one reactant were purged with a stream of purified nitrogen and all operations were carried out under a nitrogen atmosphere. The initial concentration ratio of reactants  $[\text{IrCl}_6^{3-}]/[\text{HCrO}_4^-]$  was maintained at  $\geq 30$  to prevent appreciable changes in  $[\text{IrCl}_6^{3-}]$  during the reaction. Most experiments were carried out at 487 nm, but a few experiments at other wavelengths gave identical results.

### Results

**Stoichiometry and Products.**—The consumption of three  $\text{IrCl}_6^{3-}$  per  $\text{HCrO}_4^-$  (eq 1) was confirmed by the



attainment of the correct final absorbance in kinetic experiments at 487 nm, an absorbance maximum for  $\text{IrCl}_6^{2-}$ . The products were examined particularly to determine the possible presence of a binuclear complex,  $\text{CrClIrCl}_5^+$ , or the possible transfer of chloride to give  $\text{CrCl}^{2+}$  and  $\text{IrCl}_5\text{OH}_2^-$ . The spectrum of a solution containing equivalent concentrations of Cr(VI) and Ir(III) was measured as a function of time. Spectra at all times were consistent with  $\text{IrCl}_6^{2-}$  as the only Ir(IV) species present. Equivalent concentrations were used to prevent the reduction by excess  $\text{IrCl}_6^{3-}$  of any  $\text{IrCl}_5\text{OH}_2^-$  produced, to give  $\text{IrCl}_5\text{OH}_2^{2-}$  which would be more difficult to detect spectrally. The chromium(III) product was identified as  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  by ion-exchange separation of the products on Dowex 50W-X8  $\text{H}^+$  resin. No other Cr(III) species were isolated and  $\text{Cr}^{3+}$ , which was identified spectrally, was recovered in ~95% of the theoretical yield. Experiments with Amberlite CG-400  $\text{NO}_3^-$  resin and Dowex 1-X8  $\text{Cl}^-$  and  $\text{ClO}_4^-$  resins were not conclusive due to apparent reaction of the iridium species with the resin—some  $\text{IrCl}_5\text{OH}_2^-$  was found, even though the Cr(III) product was entirely  $\text{Cr}^{3+}$ . The chromium(III) was retained somewhat by the  $\text{NO}_3^-$  resin, apparently due to an interaction with the resin. The Cr(III) band moved

(1) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963).  
 (2) J. P. Birk, *ibid.*, **91**, 3189 (1969).  
 (3) J. P. Birk, *Inorg. Chem.*, **9**, 125 (1970).  
 (4) J. P. Birk and S. V. Weaver, to be submitted for publication.  
 (5) I. A. Poulsen and C. S. Garner, *J. Amer. Chem. Soc.*, **84**, 2032 (1962).

(6) J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

only slowly with 0.3 *M* HNO<sub>3</sub> but was eluted readily with 1.0 *M* HNO<sub>3</sub> and was spectrally identical with Cr<sup>3+</sup>.

**Kinetics.**—The kinetics of the reaction between IrCl<sub>6</sub><sup>3-</sup> and HCrO<sub>4</sub><sup>-</sup> were studied at 25.0°, 0.40 *M* H<sup>+</sup>, and 0.50 *M* ionic strength, maintained with LiClO<sub>4</sub>, over the initial concentration ranges 1.0 × 10<sup>-4</sup>–1.6 × 10<sup>-2</sup> *M* IrCl<sub>6</sub><sup>3-</sup>, 6.0 × 10<sup>-6</sup>–1.3 × 10<sup>-4</sup> *M* HCrO<sub>4</sub><sup>-</sup>, and 0–3.6 × 10<sup>-4</sup> *M* IrCl<sub>6</sub><sup>2-</sup>. Although [IrCl<sub>6</sub><sup>3-</sup>]<sub>0</sub> was maintained at ≥30[HCrO<sub>4</sub><sup>-</sup>]<sub>0</sub> in an attempt to ensure pseudo-first-order conditions, plots of log (*D*<sub>∞</sub> – *D*<sub>*t*</sub>) vs. time (where *D* is the absorbance at the indicated time) were curved upward when no IrCl<sub>6</sub><sup>2-</sup> was added initially. This curvature indicated a pseudo-first-order rate constant which decreased with increasing time, consistent with inhibition by a product

$$-d[\text{HCrO}_4^-]/dt = k_0[\text{HCrO}_4^-]/[\text{IrCl}_6^{3-}] \quad (2)$$

Data were plotted according to the integrated form of this rate law

$$\ln \{ (D_\infty - D_t)/(D_\infty - D_0) \} - \{ 3[\text{Cr(VI)}]_0/([\text{Ir(IV)}]_0 + 3[\text{Cr(VI)}]_0) \} \{ 1 - (D_\infty - D_t)/(D_\infty - D_0) \} = \{ -k_0/([\text{Ir(IV)}]_0 + 3[\text{Cr(VI)}]_0) \} t \quad (3)$$

Such plots were generally linear through ≥95% reaction, demonstrating the validity of the assumed inverse dependence on [IrCl<sub>6</sub><sup>2-</sup>] (eq 2). Further support for this rate equation was obtained from experiments in which IrCl<sub>6</sub><sup>2-</sup> was present initially—the degree of curvature in first-order plots decreased with increasing [IrCl<sub>6</sub><sup>2-</sup>]<sub>0</sub> and excellent linearity was obtained at the highest concentrations. Most experiments were carried out without added IrCl<sub>6</sub><sup>2-</sup> because of its intense absorption in the wavelength range where reasonable absorbance changes could be obtained and because of the high noise level associated with measurements under these conditions. Values of *k*<sub>0</sub> determined over a range of [HCrO<sub>4</sub><sup>-</sup>] and [IrCl<sub>6</sub><sup>3-</sup>] are given in Table I.

TABLE I  
VALUES OF RATE CONSTANTS FOR THE REACTION OF  
HCrO<sub>4</sub><sup>-</sup> WITH IrCl<sub>6</sub><sup>3-</sup> AT 25°, 0.40 *M* H<sup>+</sup>, AND  
0.50 *M* IONIC STRENGTH

10 <sup>6</sup> [HCrO <sub>4</sub> <sup>-</sup> ] <sub>0</sub> , <i>M</i>	10 <sup>4</sup> [IrCl <sub>6</sub> <sup>3-</sup> ] <sub>0</sub> , <i>M</i>	10 <sup>4</sup> <i>k</i> <sub>0</sub> , <sup>a</sup> <i>M</i> sec <sup>-1</sup>	
		Obsd <sup>b</sup>	Calcd <sup>c</sup>
0.40	1.23	0.85 (1)	0.82
0.60	2.45	2.18 ± 0.18 (2)	2.05
1.20	4.91	5.62 ± 0.51 (4)	5.69
2.40	9.78	16.7 ± 0.6 (4)	17.2
6.71	15.9	38.0 (1)	38.7
6.71	19.3	58.4 ± 10.4 (4)	53.4
13.4	32.2	142 (1)	125
13.4	38.9	265 ± 38 (8)	170
13.4	64.3	345 (1)	371
13.4	77.8	465 ± 28 (3)	492
13.4	96.5	719 ± 1 (2)	673
13.4	117	861 ± 50 (4)	880
13.4	155	1540 ± 190 (3)	1290
13.4	160	1110 (1)	1340

<sup>a</sup> Defined by eq 2. <sup>b</sup> Determined from eq 3; numbers in parentheses are the number of duplicate experiments under the same conditions. <sup>c</sup> Calculated from eq 4 and values of the parameters given in the text.

A plot of log *k*<sub>0</sub> vs. log [IrCl<sub>6</sub><sup>3-</sup>]<sub>0</sub> indicated an apparent order in [IrCl<sub>6</sub><sup>3-</sup>] of 1.58 throughout the concentration range. This suggests a complex dependence on [IrCl<sub>6</sub><sup>3-</sup>], but the exact nature of the dependence is not indicated since it was not possible to determine whether

the plot contained downward curvature or upward curvature. A possible rate law is one containing a sum of terms in the numerator—one first order and the other second order in [IrCl<sub>6</sub><sup>3-</sup>].

A plot of *k*<sub>0</sub>[IrCl<sub>6</sub><sup>3-</sup>]<sup>-1</sup> vs. [IrCl<sub>6</sub><sup>3-</sup>] which is suggested by such a rate law is given in Figure 1. The non-

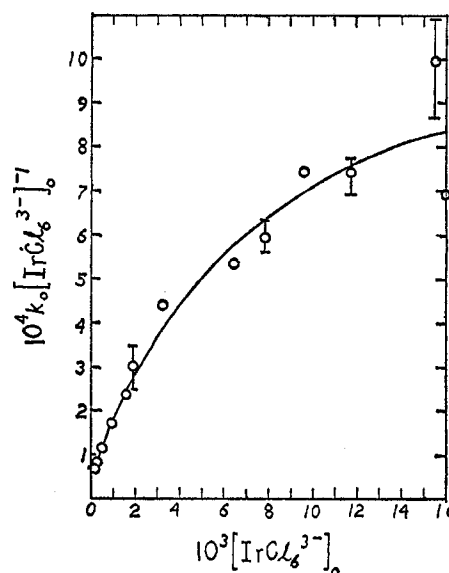


Figure 1.—A plot of *k*<sub>0</sub>[IrCl<sub>6</sub><sup>3-</sup>]<sup>-1</sup> vs. [IrCl<sub>6</sub><sup>3-</sup>], showing conformity of data to eq 4.

zero intercept indicates that the rate law does indeed contain a sum of terms in the numerator, while the downward curvature at high [IrCl<sub>6</sub><sup>3-</sup>] indicates that a sum of terms in the denominator is also required

$$k_0 = a[\text{IrCl}_6^{3-}] + b[\text{IrCl}_6^{3-}]^2(1 + c[\text{IrCl}_6^{3-}])^{-1} \quad (4)$$

Data were fit to this equation with a nonlinear least-squares computer program,<sup>7</sup> with each data point weighted as *k*<sub>0</sub><sup>-2</sup>. Values of the rate parameters are *a* = (4.85 ± 0.81) × 10<sup>-5</sup> sec<sup>-1</sup>, *b* = 0.147 ± 0.017 *M*<sup>-1</sup> sec<sup>-1</sup>, and *c* = 123 ± 25 *M*<sup>-1</sup>. These values of the parameters reproduce the values of *k*<sub>0</sub> (see Table I) with an average deviation of 12%. The agreement between the data and the line calculated from these parameters (Figure 1) further substantiates the form of the rate equation (eq 4). Attempts to fit data to eq 4 with *a* = 0 resulted in systematic trends and a poor fit of the data.

A limited amount of data was also collected with IrCl<sub>6</sub><sup>2-</sup> added initially. Values of *k*<sub>0</sub> as a function of [IrCl<sub>6</sub><sup>2-</sup>]<sub>0</sub> are given in Table II. There does appear to

TABLE II  
VALUES OF RATE CONSTANTS IN EXPERIMENTS WITH  
ADDED IrCl<sub>6</sub><sup>2-</sup>

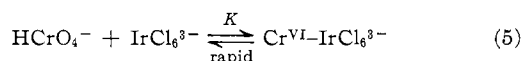
10 <sup>4</sup> [IrCl <sub>6</sub> <sup>2-</sup> ] <sub>0</sub> , <i>M</i>	10 <sup>7</sup> <i>k</i> <sub>0</sub> , <sup>b</sup> <i>M</i> sec <sup>-1</sup>	10 <sup>4</sup> [IrCl <sub>6</sub> <sup>3-</sup> ] <sub>0</sub> , <i>M</i>	
		<i>M</i>	10 <sup>7</sup> <i>k</i> <sub>0</sub> , <sup>b</sup> <i>M</i> sec <sup>-1</sup>
0.00	26.5 ± 3.8 (8)	2.70	34.9 (1)
0.92	28.4 ± 3.3 (6)	3.60	36.6 ± 4.3 (6)
1.82	30.6 (1)		

<sup>a</sup> At 25°, 0.40 *M* H<sup>+</sup>, *I* = 0.50 *M*, 3.88 × 10<sup>-3</sup> *M* IrCl<sub>6</sub><sup>3-</sup>, and 1.34 × 10<sup>-4</sup> *M* Cr(VI). <sup>b</sup> Defined in eq 2; numbers in parentheses are the number of duplicate experiments under the same conditions.

(7) The programs used were based on the reports from Los Alamos Scientific Laboratory, LA-2367 + addenda, and were modified to operate on the IBM 360/75 computer.

be a small trend in the data with increasing  $[\text{IrCl}_6^{2-}]$ . We hesitate to interpret this trend in terms of a more complex rate equation because of the possibility of inaccuracy in  $k_0$  due to the rather large noise level caused by the intense  $\text{IrCl}_6^{2-}$  absorption and because the effect is barely outside the experimental uncertainty. It is possible that the trend is due to a small amount of  $\text{IrCl}_6^{3-}$  impurity which would be formed in  $\text{IrCl}_6^{2-}$  solutions of low acidity.<sup>8</sup> The fair agreement between these data and values of  $k_0$  determined in the initial absence of  $\text{IrCl}_6^{2-}$  does indicate that the deviation from linearity in first-order plots was caused by an inverse dependence on  $[\text{IrCl}_6^{2-}]$ .

On the basis of several other studies of chromium(VI) oxidations,<sup>9-16</sup> it was felt that the sum of terms in the denominator of eq 4 probably arose from the formation of a  $\text{Cr}^{\text{VI}}\text{-Ir}^{\text{III}}$  binuclear complex (eq 5), with  $c = K$ .



A formula is not written for  $\text{Cr}(\text{VI})$  in this complex since we have not established the absence of a  $[\text{H}^+]$  dependence in this rate term. Confirmation of this interpretation was sought in the form of spectral interactions between  $\text{Cr}(\text{VI})$  and  $\text{Ir}(\text{III})$ . Experiments were carried out at very low  $[\text{H}^+]$ , where spectra could be measured before appreciable redox reaction occurred. Spectra of mixtures of  $\text{Cr}(\text{VI})$  and  $\text{Ir}(\text{III})$  could be accounted for as the sum of the individual spectra within experimental error. This does not rule out complexation such as eq 5 but does indicate that such complexation either must be accompanied by a  $[\text{H}^+]$  dependence or must occur with only a very small absorbance change. No evidence was found in the kinetics experiments for a rapid initial absorbance change however. The kinetics of the reaction were not determined as a function of  $[\text{H}^+]$  due to the complexity of the rate equation at constant  $[\text{H}^+]$  and the relatively low precision of the data. Spectral experiments were also carried out on mixtures of  $\text{Cr}(\text{VI})$  and  $\text{Ir}(\text{IV})$  over a range of  $[\text{H}^+]$ . Spectra were additive within experimental error, indicating that complexation between  $\text{Cr}(\text{VI})$  and  $\text{Ir}(\text{IV})$  is apparently not occurring.

### Discussion

Although it was expected that the reduction of  $\text{HCrO}_4^-$  by substitution-inert  $\text{IrCl}_6^{3-}$  would have the first step rate determining,<sup>1,2</sup> the observed rate equation (eq 2 and 4) is consistent with a rate-determining reduction of  $\text{Cr}(\text{V})$ . The sum of terms in the denominator, in accord with several other reactions,<sup>9-16</sup> can be interpreted in terms of complex formation between  $\text{Cr}(\text{VI})$  and  $\text{Ir}(\text{III})$  (eq 5). This interpretation becomes more obvious if the rate equation (eq 4) is rearranged to have a common denominator

$$k_0 = (a[\text{IrCl}_6^{3-}] + d[\text{IrCl}_6^{3-}]^2)(1 + c[\text{IrCl}_6^{2-}])^{-1} \quad (6)$$

(8) D. A. Fine, *Inorg. Chem.*, **8**, 1015 (1969).

(9) J. G. Mason and A. D. Kowalak, *ibid.*, **3**, 1248 (1964).

(10) G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *ibid.*, **3**, 1777 (1964).

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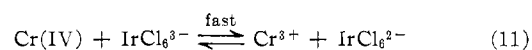
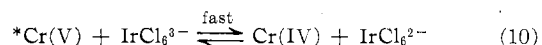
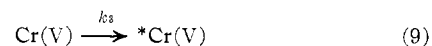
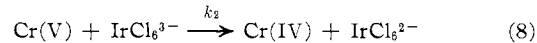
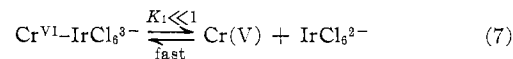
(13) G. P. Haight, Jr., M. Rose, and J. Preer, *ibid.*, **90**, 4809 (1968).

(14) S.-A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *ibid.*, **90**, 6018 (1968).

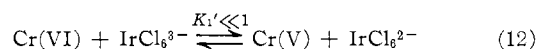
(15) I. Baldea and G. Niac, *Inorg. Chem.*, **7**, 1232 (1968).

(16) J. N. Cooper, *J. Phys. Chem.*, **74**, 955 (1970).

where  $d = b + ac = 0.153 \pm 0.017 M^{-1} \text{sec}^{-1}$ . A rate term of the type  $a[\text{IrCl}_6^{3-}][\text{HCrO}_4^-]/[\text{IrCl}_6^{2-}]$  has not previously been observed in reductions of  $\text{Cr}(\text{VI})$ . A possible interpretation of such a term would involve a rate-determining conversion of  $\text{Cr}(\text{V})$  to a more reactive form (possibly involving an expansion of the coordination number from 4 to 6 prior to reduction<sup>17</sup>)

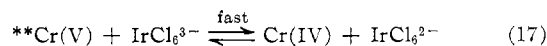
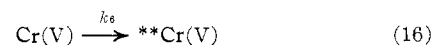
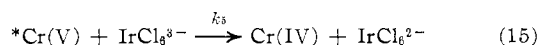
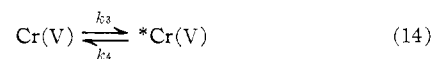
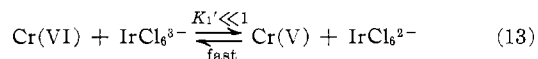


where  ${}^*\text{Cr}(\text{V})$  is a reactive form of  $\text{Cr}(\text{V})$ , and  $a = K_1 k_3 K$ ,  $d = K_1 k_2 K$ , and  $c = K$ . An indistinguishable mechanism involves the above sequence but with  $\text{Cr}(\text{VI})$  and  $\text{IrCl}_6^{3-}$  as the reactants in the first step



with  $a = K_1' k_3$ ,  $d = K_1' k_2$ , and  $c = K$ . Chromium(VI) is known to form binuclear complexes with a number of other species (with formation constants in parentheses):  $\text{HCrO}_4^-$  (98  $M^{-1}$ ),<sup>18</sup>  $\text{Cl}^-$  (17),<sup>10</sup>  $\text{HSO}_4^-$  (4.1),<sup>10</sup>  $\text{HSO}_3^-$  (36),<sup>11</sup>  $\text{HS}_2\text{O}_3^-$  ( $1.2 \times 10^4$ ),<sup>15</sup>  $\text{H}_2\text{AsO}_3^-$  (22),<sup>9</sup>  $\text{H}_3\text{PO}_4$  (9.4),<sup>19</sup>  $\text{H}_2\text{PO}_4^-$  (2.9, 6),<sup>14,19</sup>  $\text{H}_3\text{PO}_3$  (26, 12),<sup>12,13</sup>  $\text{H}_2\text{PO}_3^-$  (7),<sup>13</sup> and  $\text{H}_3\text{PO}_2$  (13).<sup>16</sup> With the exception of the  $\text{Cl}^-$  reaction, however, all the complexes are oxygen-bridged species, so it is difficult to make direct comparisons of the magnitude of the formation constants with that of  $K$  of eq 5 ( $K = 123$ ). Considering that the high charge on  $\text{IrCl}_6^{3-}$  would presumably be unfavorable to complex formation, this value does appear somewhat high however. Further doubt is cast on this interpretation by the absence of spectral evidence for such an interaction.

An alternate explanation can be proposed if it is assumed that the sum of terms in the denominator of the rate equation arises because of the occurrence of a steady-state intermediate,  ${}^*\text{Cr}(\text{V})$ , which again may be a form of  $\text{Cr}(\text{V})$  with an expanded coordination sphere. A third form,  ${}^{**}\text{Cr}(\text{V})$ , must also be proposed, however



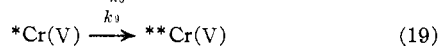
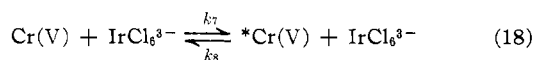
followed by eq 10, where  $a = k_6 K_1'$ ,  $b = k_3 k_2 K_1' / k_4$ , and  $c = k_5 / k_4$ . Although the three forms of  $\text{Cr}(\text{V})$  might have coordination numbers of 4, 5, and 6, the necessity of three forms is not an attractive feature of this mechanism. We tend to favor this mechanism out of a set of four *indistinguishable* mechanisms which can be pro-

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(18) J. Y. P. Tong and E. L. King, *ibid.*, **75**, 6180 (1953).

(19) F. Holloway, *ibid.*, **74**, 224 (1952).

posed readily by using electrical analogs to reaction rates.<sup>20,21</sup> The alternate mechanisms make use as well of eq 18 and 19 and are then composed of the following



sequences of steps: eq 13, 14, 19, 15, 17, and 11, with  $a = k_3k_9K_1'/(k_4 + k_9)$ ,  $d = k_3k_9K_1'/(k_4 + k_9)$ , and  $c = k_5/(k_4 + k_9)$ ; eq 13, 18, 19, 16, 17, and 11, with  $a = k_6K_1'$ ,  $b = k_7K_1'$ , and  $c = k_8/k_9$ ; eq 13, 18, 14, 19, 17, and 11, with  $a = k_3k_9K_1'/(k_4 + k_9)$ ,  $d = k_7k_9K_1'/(k_4 + k_9)$ , and  $c = k_8/(k_4 + k_9)$ . Although no previous study of Cr(VI) oxidations has yielded a rate equation which demands the existence of more than one form of Cr(V), it does not seem unreasonable to propose forms of Cr(V) with different states of coordination. Known compounds of Cr(V) are four-coordinate and of Cr(IV) are six-coordinate. On this basis, it has been proposed that the change in coordination number accompanying the reduction of Cr(VI) occurs at the Cr(V)-Cr(IV) step.<sup>17</sup> Although certain reducing agents may aid in changing the coordination number of chromium,<sup>1,2</sup> it should be possible for the adjustments in the coordination sphere of chromium to occur either before or after reduction to Cr(IV).

Various other possibilities for the interpretation of eq 2 and 4 were considered without success—e.g., the term first order in  $[\text{IrCl}_6^{3-}]$  was assumed to arise from a reaction between two different oxidation states of chromium or from a disproportionation of Cr(V) or Cr(IV),<sup>22</sup> but a rate equation of the correct form could not be derived. Attempts were also made to attribute the observed variation in the order of  $[\text{IrCl}_6^{3-}]$  to medium effects by making Harned's rule type corrections,<sup>23</sup>

(20) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, **No. 71**, 268 (1967).

(21) J. P. Birk, *J. Chem. Educ.*, **47**, 805 (1970).

(22) The authors are grateful to Professor G. P. Haight, Jr., for suggesting these possibilities.

(23) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1965, Chapter 15.

but the correct functional dependence was not obeyed so it appears that a true mechanistic effect is involved.

The products of the reaction were found to consist entirely of  $\text{Cr}^{3+}$  and  $\text{IrCl}_6^{2-}$ , with no evidence for a binuclear complex  $\text{CrIrCl}_6^+$  or for transfer of  $\text{Cl}^-$  from Ir to Cr. The absence of either of these effects precludes the classification of the reaction as inner or outer sphere. A binuclear complex may have been formed if it decomposed sufficiently rapidly with Cr-Cl bond breaking. A related binuclear complex  $\text{CrIrCl}_6$  containing Ir(III) decomposes within a few seconds with Ir-Cl bond breaking.<sup>24</sup> Since  $\text{IrCl}_6^{2-}$  aquates more slowly than  $\text{IrCl}_6^{3-}$ ,<sup>5,25</sup> a  $\text{Cr}^{\text{III}}-\text{Ir}^{\text{IV}}$  binuclear complex should decompose more slowly than  $\text{CrIrCl}_6$ , but even an order of magnitude difference in rates would still result in complete decomposition during the time of our experiments. Further, since  $\text{CrCl}_6^{2+}$  aquates more rapidly than  $\text{IrCl}_6^{2-}$ ,<sup>25,26</sup> the decomposition would be expected to occur with Cr-Cl bond breaking, and no evidence for a binuclear complex is likely to appear. Thus the identity of the products is consistent with either an inner-sphere or an outer-sphere reaction, and this reaction may possibly be of the "reverse ligand-transfer" type as was expected for reasons discussed in the Introduction. This system now provides an example of a reaction with a substitution-inert reducing agent in which the second step is rate-determining, indicating that previous explanations<sup>1,2</sup> for the identity of the rate-determining step were probably overly simplified. However, it does not appear to be possible at this time to advance an alternate explanation.

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(24) A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc. A*, 232 (1970).

(25) M. R. Martinez, Ph.D. Thesis, University of California, Los Angeles, Calif., 1958; quoted in ref 5.

(26) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

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## Halogen Perchlorates. Vibrational Spectra

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The infrared spectra of gaseous, solid, and matrix-isolated  $\text{ClOClO}_3$  and the Raman spectrum of liquid  $\text{ClOClO}_3$  have been measured. All 12 fundamentals expected for symmetry  $C_s$  were observed and assigned. The infrared spectra of gaseous and matrix-isolated  $\text{BrOClO}_3$  have also been recorded. Some vibrational force constants and the thermodynamic properties have been computed.

### Introduction

Recently, the existence of the two novel halogen oxides,  $\text{ClOClO}_3$  and  $\text{BrOClO}_3$ , has been discovered.<sup>1,2</sup> Their chemical and physical properties<sup>1,2</sup> were in ac-

cordance with covalent halogen perchlorate structures. In this paper we wish to present spectroscopic data supporting these suggested structures.

### Experimental Section

The preparation, purification, and handling of  $\text{ClOClO}_3$  and  $\text{BrOClO}_3$  have been reported elsewhere.<sup>1,2</sup> The apparatus used

(1) C. J. Schack and D. Pilipovich, *Inorg. Chem.*, **9**, 1387 (1970).

(2) C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, *ibid.*, **10**, 1078 (1971).