

procedure.<sup>21</sup> The final spectra of the hydrolysis products were found to be unaffected by the presence of the buffer ions. To determine the stereochemical course of the hydrolysis reactions, *trans*-Na<sub>3</sub>[Cr(ox)<sub>2</sub>(OAc)<sub>2</sub>] was dissolved in a solution (10<sup>-2</sup> M) of HClO<sub>4</sub> at 0°; after 5 min (100% of the first reaction) the recorded spectrum of the solution was found to be identical, in both molar absorptivities and λ<sub>max</sub> values, with that of an authentic specimen of *trans*-Na<sub>2</sub>[Cr(ox)<sub>2</sub>(OH)<sub>2</sub>OAc]. This result was confirmed by the quantitative isolation of *trans*-Ba[Cr(ox)<sub>2</sub>(OH)<sub>2</sub>OAc], as obtained on precipitation of the latter from the reaction solution of *trans*-Na<sub>3</sub>[Cr(ox)<sub>2</sub>(OAc)<sub>2</sub>] with a CH<sub>3</sub>COOH-Ba(OAc)<sub>2</sub> mixture.

In the case of base hydrolysis, the complex in the reaction solution was first converted into the aquo form by acidification. The spectra of the acidified solutions of the complete acid and

(21) H. T. S. Britton, "Hydrogen Ions," Chapman and Hall, London, 1965, p 361.

base hydrolysis products of *trans*-Cr(ox)<sub>2</sub>(OAc)<sub>2</sub><sup>3-</sup> were found to be identical with that of the *cis*-Cr(ox)<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup> complex. The spectra of the solutions of *trans*-Cr(ox)<sub>2</sub>(OH)<sub>2</sub>OAc<sup>2-</sup> on acid hydrolysis (2 M ≥ [H<sup>+</sup>] ≥ 1 × 10<sup>-5</sup> M) were found to be identical with that of *cis*-Cr(ox)<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>. Under basic conditions (1 × 10<sup>-11</sup> M ≥ [H<sup>+</sup>] ≥ 1 × 10<sup>-9</sup> M), the spectra were identical with those of *cis*-Cr(ox)<sub>2</sub>(OH)<sub>2</sub><sup>3-</sup>, and this result was confirmed by conversion of *cis*-Cr(ox)<sub>2</sub>(OH)<sub>2</sub><sup>3-</sup>, as produced during the reaction, into the corresponding diaquo form. The hydrolysis of *cis*-Na<sub>3</sub>[Cr(ox)<sub>2</sub>(OAc)<sub>2</sub>] and *cis*-Na<sub>2</sub>[Cr(ox)<sub>2</sub>(OH)<sub>2</sub>OAc] did not proceed with the formation of well-defined reaction products, in accordance with the early findings of Werner.<sup>9c</sup>

The hydrolysis rate constants (10<sup>4</sup>k, sec<sup>-1</sup>) at diverse temperatures (given in parentheses as °C) are as follows, except for those in Tables III and V: *trans*-Cr(ox)<sub>2</sub>(OAc)(OH)<sub>2</sub><sup>2-</sup> at pH 3, 2.15 (16.0), 2.76 (18.5), 9.85 (30.5); *trans*-Cr(ox)<sub>2</sub>(OAc)(OH)<sub>2</sub><sup>3-</sup> at pH 11, 160 (14.0), 231 (21.0); *trans*-Cr(ox)<sub>2</sub>(py)<sub>2</sub><sup>-</sup>, 0.98 (35.6), 13.8 (56.0).

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## Substitution Reactions of Oxalato Complex Ions. X. The Kinetics and Mechanism of Electron Transfer between the Chromium(II) Aquo Cation and Some Aquooxalatochromium(III) Complex Ions

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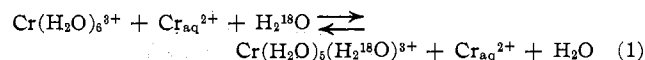
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Electron transfer in the system Cr(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>4</sub><sup>+</sup>-Cr<sub>aq</sub><sup>2+</sup> occurs with no net chemical change but can be observed by use of chromium-51 labeling. The reaction is first order in each species and is independent of acid concentration up to 2.0 M HClO<sub>4</sub>. At 25° and I = 2.0 M, the values of k, ΔH<sup>‡</sup>, and ΔS<sup>‡</sup> are 0.13 M<sup>-1</sup> sec<sup>-1</sup>, 11 kcal/mol, and -26 cal/deg mol, respectively. In contrast, the reaction between *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> and Cr<sub>aq</sub><sup>2+</sup> is first order in acid concentration as well as in each of the other two reactants. Electron transfer is accompanied by transfer of a single oxalate ligand so that in effect catalyzed aquation of the Cr(III) complex occurs. At 25°, I = 2.0 M, and [H<sup>+</sup>] = 1.0 M, the values of k, ΔH<sup>‡</sup>, and ΔS<sup>‡</sup> are 0.04 M<sup>-2</sup> sec<sup>-1</sup>, 12 kcal/mol, and -24 cal/deg mol, respectively. Mechanisms involving an intermediate with oxalate doubly bridged between the two chromium ions provide a satisfactory explanation of the observations.

### Introduction

The aqueous solution chemistry of the chromium(III) oxalato complex ions of the type [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>6-2n</sub>]<sup>3-2n</sup> has been extensively investigated, with much of the recent attention focused on the kinetics of aquation,<sup>1-3</sup> aquation,<sup>4-6</sup> isomerization,<sup>7-9</sup> and oxygen exchange.<sup>10,11</sup> All of these reactions are relatively slow, attesting to the considerable resistance of either the water or the oxalate ligand to displacement from a chromium(III) ion coordination site. However, early oxygen-18 studies of the water-exchange reaction of the Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion demonstrated an appreciable accelerat-

ing influence by chromium(II) aquo cation. Thus, the reaction



has a half-time of 2.1 hr at 27° in 0.33 M HClO<sub>4</sub> and with chromium(III) and chromium(II) concentrations of 1.05 and 0.16 M, respectively, while in the absence of chromium(II) but with other conditions nearly identical a 35-hr half-time is observed.<sup>12</sup> Furthermore, the second-order rate constant for reaction 1, deduced on the assumption of first-order catalysis by Cr<sub>aq</sub><sup>2+</sup>, is 4.7 × 10<sup>-4</sup> M<sup>-1</sup> sec<sup>-1</sup>. This is almost identical with the rate constant for electron transfer according to the reaction



for which the value can be calculated to be 4.5 × 10<sup>-4</sup> M<sup>-1</sup> sec<sup>-1</sup> under similar conditions on the basis of recorded data.<sup>13</sup> This comparison indicates that chromium(II)-catalyzed water exchange as symbolized by eq 1 probably occurs by a ligand-bridge electron-transfer mechanism of the type now so familiar for many inor-

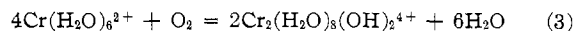
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ganic redox systems.<sup>14</sup> A recent report<sup>15</sup> suggests that similar but much more rapid electron-transfer-promoted reactions take place in the aqution of  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$  ion and in the isomerization of *trans*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  in the presence of  $\text{Cr}_{\text{aq}}^{2+}$ . This finding again demonstrates the efficiency of oxalate as a ligand for mediating electron transfer, as is also observed in studies of the reduction of oxalatocobalt(III) complex ions by chromium(II).<sup>16,17</sup> The present work extends our understanding of oxalatochromium(III)-chromium(II) reactions by a kinetic and mechanistic investigation of electron transfer in the system  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+ - \text{Cr}_{\text{aq}}^{2+}$  where there is no net chemical change over long periods and in the system *cis*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^- - \text{Cr}_{\text{aq}}^{2+}$  where the major net process is catalyzed aqution of the bis(oxalato)chromium(III) species.<sup>18</sup>

### Experimental Section

Labeled mono(oxalato)tetraaquo chromium(III) perchlorate was prepared by adding chromium-51, in the form of  $\text{CrCl}_3$  in 0.5 *M* HCl, to a 1:1 mixture of reagent grade  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{Cr}(\text{ClO}_4)_3$  and heating the solution at 50° for several days. It was then adsorbed on a column of Dowex 50W-X8 50-100 mesh cation-exchange resin in the hydrogen form, and the  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$  complex was selectively eluted with perchloric acid. Sodium *cis*-bis(oxalato)diaquo chromium(III) was prepared by the method of Werner.<sup>19</sup> The absorption maxima (molar extinction coefficient ( $M^{-1} \text{cm}^{-1}$ ) in parentheses) for the chromium(III) complexes were 407 nm (16.7) and 573 nm (13.8) for the hexaquo, 417 nm (40.7) and 557 nm (35.5) for the mono(oxalato), and 417 nm (66.7) and 562 nm (50.8) for the bis(oxalato) species, respectively, in very good agreement with published values.<sup>2,16,15,20</sup> The purity of the complexes was also checked by chemical determination of the  $\text{C}_2\text{O}_4$ :Cr ratio, analyzing for the oxalate by permanganate titration and for the chromium as chromate. The average value obtained in five different mono(oxalato) preparations was  $1.00 \pm 0.03$ , while for the one bis(oxalato) preparation, the ratio was 2.03. The ionic strength of 2.0 *M* was established by additions of  $\text{NaClO}_4$ , produced by neutralization of reagent grade  $\text{Na}_2\text{CO}_3$  with  $\text{HClO}_4$ . Chromous perchlorate was prepared from reagent grade chromic perchlorate by the zinc amalgam method.<sup>21</sup> Chromium(II) was determined by injecting an aliquot of the solution to be analyzed into a previously deoxygenated solution containing a slight excess of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , converting the resultant Co(II) into the thiocyanato complex by adding a large excess of  $\text{NH}_4\text{NCS}$  in 50:50 water-acetone solution, and using spectrophotometry to obtain the Co(II) concentration.<sup>22,23</sup> Perchloric acid concentration in the chromous perchlorate solutions was determined by passing an air-oxidized aliquot into the cation-exchange resin of the type mentioned above and titrating the liberated acid with standard base. The air oxidation is independent of acidity in the range  $0.1 \text{ M} < [\text{H}^+] < 0.4 \text{ M}$  and proceeds to completion<sup>24</sup> according to a reaction which apparently has no appreciable effect on the acidity,<sup>25</sup> viz.



It can be assumed that the zinc amalgam reduction of the chromic perchlorate is complete and yields 0.5 equiv of  $\text{Zn}_{\text{aq}}^{2+}$ , so that it can be deduced that  $[\text{H}^+]_{\text{Cr(II) soln}} = [\text{H}^+]_{\text{effluent}} - 3[\text{Cr}_{\text{aq}}^{2+}]$ . Most of the acid (usually >90%) was introduced into the reaction mixtures as part of the oxalatochromium(III) component in which it could be accurately titrated, so the errors inherent in the acid determination in the Cr(II) component were not very significant.

The chromous perchlorate solutions were prepared, stored, and handled under an argon atmosphere at a slight positive pressure. All transfers and sampling were achieved by use of rubber-serum-cap-hypodermic syringe technique, using calibrated glass syringes fitted with platinum-ruthenium hypodermic needles. Rubber-serum-capped bottles served as reaction vessels for studying the  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+ - \text{Cr}_{\text{aq}}^{2+}$  electron exchange, the rate data being obtained by measuring the change of chromium-51 activity of the mono(oxalato) species as a function of time. This was accomplished by air oxidation of periodically withdrawn samples of the reaction mixture, adsorption on the cation-exchange column, and elution of the singly charged oxalatochromium(III) cation with 1 *M* HClO<sub>4</sub> while the air-oxidation product (see reaction 3) remains firmly bound on the column. The fact that no activity was lost from a zero-time sample subjected to this separation procedure. The eluted samples were loaded into a Packard Auto Gamma spectrometer and counted sequentially three times to within a 1% standard deviation. The rate of reaction was deduced from the standard McKay plot of  $\ln(1 - F)$  vs. *t*, where *F* is the fraction of exchange at time *t*, and the rate *R* is readily determined from the expression

$$R = \frac{0.693[\text{Cr}_{\text{aq}}^{2+}][\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+]}{t_{1/2}\{[\text{Cr}_{\text{aq}}^{2+}] + [\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+]\}} \quad (4)$$

Rubber-serum-capped spectrophotometer cells were used as the reaction vessels in following the *cis*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^- - \text{Cr}_{\text{aq}}^{2+}$  reaction, the absorbance measurements being made on a Cary Model 15 spectrophotometer with time-drive chart recording at 417 nm. Temperature control in the rate studies was achieved by use of a thermostat with circulating-pump attachment enabling control of the reaction vessel temperature fluctuation to within  $\pm 0.1^\circ$ .

### Results and Discussion

Preliminary experiments showed no spectral change in the visible region in acidified mixtures of  $\text{Cr}_{\text{aq}}^{2+}$  and  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$  during a period of nearly 20 hr at 25°. Furthermore, chemical analyses for chromium(II) and oxalate 1 hr after mixing of the reactants indicated no decrease in the concentration of either of these constituents. These findings are in agreement with the results of Price and Taube<sup>16</sup> in their study of the chemistry of the  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^- - \text{Cr}_{\text{aq}}^{2+}$  system, where the reduction of oxalate ligand was negligible, though there is some earlier evidence of fairly rapid glycolate formation<sup>26</sup> in mixtures of  $\text{Cr}_{\text{aq}}^{2+}$  and free oxalate under acidic conditions.<sup>27</sup>

The results of our measurements of the rate constant of isotopic exchange in the mono(oxalato)chromium(III)-chromium(II) system are presented in Table I, where  $k_m$  is the second-order rate constant derived from the relation

$$R = k_m[\text{Cr(II)}][\text{Cr(III)}] \quad (5)$$

with *R* as defined in eq 4. It is clear from the data that the second-order relationship holds well over a reason-

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(23) We used the value  $\epsilon = 1843 \text{ M}^{-1} \text{cm}^{-1}$  at 625 nm for  $\text{Co}(\text{SCN})_4^{2-}$ , as given by J. H. Espenson and D. W. Carlsyle, *Inorg. Chem.*, **5**, 586 (1966).

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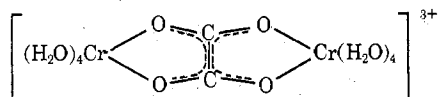
TABLE I  
RATE DATA FOR THE  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+-\text{Cr}_{\text{aq}}^{2+}$   
CHROMIUM-EXCHANGE REACTION AT  $20.0^\circ$  AND  $I = 2.0 M$

Expt no.	$[\text{HClO}_4], M$	$10^3[\text{Cr}(\text{III})], M$	$10^3[\text{Cr}(\text{II})], M$	$k_m, M^{-1} \text{sec}^{-1}$
1	1.00	1.13	2.24	1.0
2	1.00	1.70	2.26	0.95
3	1.00	2.26	2.33	0.81
4	1.05	2.83	2.17	1.1
5	1.00	3.40	2.25	0.96
6	1.00	1.86	1.63	1.2
7	1.00	1.86	1.95	0.85
8	1.00	1.86	4.84	0.97
9	1.00	1.86	8.73	0.93
10	1.00	1.86	9.55	0.92
11	0.014	1.86	2.26	0.60
12	0.014	1.86	2.20	0.72
13	0.014	1.86	2.32	0.66
14	0.015	1.86	1.51	0.64
15	0.015	1.86	1.26	0.61
16	0.03	1.86	1.69	0.88
17	0.05	1.86	2.00	0.73
18	0.08	1.86	1.94	0.69
19	0.10	1.86	2.09	0.90
20	0.50	2.83	2.10	0.86
21	2.08	2.83	2.28	1.2
22 <sup>a</sup>	1.00	1.86	2.15	0.46
23 <sup>a</sup>	1.00	1.86	1.88	0.47
24 <sup>a</sup>	1.00	1.86	1.75	0.58
25 <sup>b</sup>	1.00	1.86	2.21	1.5
26 <sup>b</sup>	1.00	1.86	1.96	1.6
27 <sup>b</sup>	1.00	1.86	1.90	1.7
28 <sup>c</sup>	1.00	1.86	1.80	3.6
29 <sup>c</sup>	1.00	1.86	1.80	4.0
30 <sup>c</sup>	1.00	1.86	1.88	3.3

<sup>a</sup> Temperature  $10^\circ$ . <sup>b</sup> Temperature  $30^\circ$ . <sup>c</sup> Temperature  $40^\circ$ .

able range of chromium reactant concentration and that  $k_m$  is only slightly dependent on the acidity. A conventional Eyring-Polanyi plot of the data at various temperatures in 1 M acid enables evaluation of the activation parameters and their standard error limits by means of a least-squares computer program. This yields the figures  $\Delta H^\ddagger = 11 \pm 2.5$  kcal/mol and  $\Delta S^\ddagger = -26 \pm 5$  cal/deg mol. These values and the interpolated second-order rate constant at  $25^\circ$  and  $I = 2.0 M$  are recorded in Table IV for later comparison with related rate constants and temperature parameters.

Electron transfer in the  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+-\text{Cr}_{\text{aq}}^{2+}$  system can conceivably proceed either by an outer- or inner-sphere mechanism. The former can be excluded because of the absence of chemical change in the system as evidenced by its spectral stability, as also can reduction of oxalate or catalyzed aquation of the mono-oxalato chromium(III) species. Consequently, a completely symmetrical doubly coordinated oxalate-bridged transition state for the transfer is postulated, as has been recently proposed for the  $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{Cr}_{\text{aq}}^{2+}$  reaction.<sup>17</sup> Such a formulation precludes the necessity of prior oxalate ring-opening which is not observed to occur for  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$  at room temperature even in strong acid.<sup>6</sup> In the proposed doubly chelated transition state, *viz.*



there would be little strain in the bridging system so there can be firm bonding and a completely symmetrical, relatively rigid structure, as suggested by the

large negative entropy of activation. It is of interest that the initial product of the chromium(II) reduction of the glycolatopentaamminechromium(III) ion is a chelated complex which slowly changes to the more stable monodentate form.<sup>28</sup> Apparently this type of multifunctional bridging group can form a chelated structure even in those systems where additional transformations involving the bridging ligand take place subsequent to electron transfer.

Preliminary experiments at  $20^\circ$  with acidified mixtures of  $\text{Cr}_{\text{aq}}^{2+}$  and *cis*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  demonstrated several features of the reaction. In 1 M  $\text{HClO}_4$ , the optical spectrum rapidly changed (half-time of the order of minutes) from that of the bis(oxalato) complex to one approaching that of the mono(oxalato), but the decrease in absorbance stopped short of that expected for complete aquation to the  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$  ion, and in fact on long standing (hours) a slow increase in absorbance was observable. With the acid concentration reduced to 0.1 M, the initial absorbance decrease was much less rapid and pronounced, while the onset of the secondary processes which cause absorbance to increase was somewhat more noticeable. The nature of these secondary processes has not yet been elucidated but may well involve chromium(II)-oxalate interactions such as mentioned earlier.<sup>27</sup> In any case, it is apparent that an initially uncomplicated and vigorous chromium(II)-catalyzed aquation of the bis(oxalato) complex occurs in strongly acidic solution, since the half-time for the same reaction in absence of chromium(II) is of the order of days<sup>4,29</sup> rather than minutes.

A test was made of the chemical separation procedure in the following manner. A solution  $4.45 \times 10^{-2} M$  in  $\text{Cr}_{\text{aq}}^{2+}$  and  $8.16 \times 10^{-2} M$  in  $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  at pH 3.4 was air oxidized 73 min after mixing and adsorbed on the cation-exchange resin. Successive elutions with water, 0.15 M  $\text{HClO}_4$ , and 4 M  $\text{HClO}_4$  produced fractions identifiable by their spectra and oxalate:chromium ratio determination to be solutions of *cis*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ ,  $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$ , and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  complex ions, respectively. The complete analytical data are presented in Table II, from which it can be seen

TABLE II  
ION-EXCHANGE CHROMATOGRAPHY OF THE AIR-OXIDIZED  
 $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^- - \text{Cr}_{\text{aq}}^{2+}$  REACTION MIXTURE AT  
 $20.0^\circ$  AND pH 3.4 (REACTION TIME 73 MIN)

Species determined	Concn $\times 10^3, M$		Ratio $[\text{C}_2\text{O}_4]/[\text{Cr}]$	Obsd spectro-photometric maxima <sup>c</sup>
	Initial	Final		
$\text{Cr}_{\text{aq}}^{2+}$	4.45 <sup>a</sup>	4.61 <sup>a</sup>	...	...
$\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$	8.16	5.97 <sup>b</sup>	2.04	417 (65.2), 562 (50.1)
$\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$	...	4.21 <sup>b</sup>	1.02	417 (40.3), 557 (34.6)
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	...	2.40 <sup>b</sup>	...	407 (16.0), 572 (12.9)
$\text{C}_2\text{O}_4^{2-}$	16.3	16.4	...	...

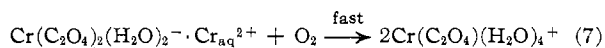
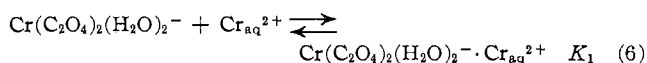
<sup>a</sup> Determined prior to air oxidation. <sup>b</sup> The sum of these quantities ( $12.58 \times 10^{-2}$ ) should and does equal the sum of the first two entries in column 2 ( $12.61 \times 10^{-2}$ ). <sup>c</sup> Wavelengths in nm; parenthesized values are the corresponding extinction coefficients ( $M^{-1} \text{cm}^{-1}$ ).

that only 73% of the initially present bis(oxalato) species is recovered in that form. Similar experiments were performed with air oxidation of the mixture carried out at periods of 36.5, 18.3, 9.0, and 0.25 min after mixing, for which the percentages of bis(oxalato) com-

(28) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

(29) D. Banerjee and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964).

plex recovered were 76, 77, 67, and 75, respectively. Prior to air oxidation, no chromium(II) is consumed (see first entry of Table II), and the percentage of bis-(oxalato) complex recovered from the air-oxidized mixtures is independent of the period of contact of the reactants even for very short reaction times. It is thus clear that it is the air-oxidation process itself which promotes the chemical changes at pH 3.4 which are apparent from the data of Table II: that is, *direct* Cr<sup>II</sup>-Cr<sup>III</sup> electron transfer is very slow at this low acidity. The observations may be conveniently explained in terms of an ion-pair preassociation and oxidation mechanism according to the following scheme



with the non-ion-paired Cr<sub>aq</sub><sup>2+</sup> simultaneously being rapidly oxidized according to eq 3, while the unpaired Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> remains unaffected. The average value for proportion of ion-pair formation in the several experiments mentioned above is thus 0.26, and one readily calculates the magnitude of the ion-pair formation constant to be about 15 M<sup>-1</sup> at 20°. This figure agrees well with the constant for similar (2+)(1-) outer-sphere ion pairs under comparable conditions.<sup>30</sup>

Returning now to the strongly acidic solutions where the chromium(II)-catalyzed aquation is spectrophotometrically observable and approaches completion, the data for individual runs generate satisfactorily linear pseudo-first-order plots when subjected to conventional ln(1 - F) vs. time analysis.<sup>31</sup> A series of runs was made in which both chromium reactant concentrations were varied at constant acidity and in which acid concentration was varied between the lowest limit at which the catalyzed aquation rate constant is accurately measurable (0.70 M) up to a maximum of 1.92 M. Temperature variation data were also obtained, as shown in the presentation of results in Table III. The values for k<sub>b</sub><sup>'</sup>, the experimental second-order rate constant, are derived by dividing the observed pseudo-first-order constants by the chromium(II) concentration, which is constant during a given run. It is obvious from the results for runs 1-5 and 21-27 that the second-order assumption is correct at constant acidity and that the rate of reaction is given by R = k<sub>b</sub><sup>'</sup>[Cr(II)][Cr(III)] under such circumstances. However, unlike the mono-(oxalato) reaction described earlier, in this system there is an acid dependence as is readily shown by the linearity of a plot of k<sub>b</sub><sup>'</sup> vs. [HClO<sub>4</sub>] of the data at 20°. There is considerable experimental scatter, but the first-order dependence on [H<sup>+</sup>] is clearly evident, and a least-squares analysis of such a plot indicates the slope of the line to be 0.027 ± 0.002 M<sup>-2</sup> sec<sup>-1</sup> and the intercept to be zero within the experimental error. The conventional temperature dependence plot of the results at 1.00 M acidity yields the parameters ΔH<sup>‡</sup> = 12 ± 1 kcal/mol and ΔS<sup>‡</sup> = -24 ± 4 cal/deg mol and enables the extrapolation of the rate constant to 25°, as recorded in Table IV.

(30) G. Nancollas, "Interactions in Electrolyte Solutions," Elsevier, New York, N. Y., 1966, Table A-1, p 179.

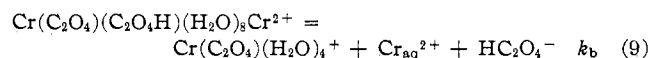
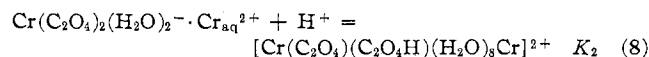
(31) In this treatment, F is defined as the fractional approach to complete aquation according to the stoichiometry Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> + H<sup>+</sup> + Cr<sup>2+</sup> → Cr(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>4</sub><sup>+</sup> + HC<sub>2</sub>O<sub>4</sub><sup>-</sup> + Cr<sup>2+</sup>. Such plots were linear for about 2 half-times in most experiments.

TABLE III  
RATE DATA FOR THE Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>-Cr<sub>aq</sub><sup>2+</sup>  
CATALYZED AQUATION AT 20.0°,  
I = 2.0 M, AND [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>] = 4.42 × 10<sup>-3</sup> M

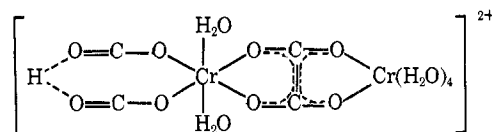
Expt no.	[HClO <sub>4</sub> ], M	10 <sup>3</sup> [Cr(II)], M	10 <sup>3</sup> k <sub>b</sub> <sup>'</sup> , M <sup>-1</sup> sec <sup>-1</sup>
1	1.00	1.42	2.5
2	1.00	5.93	3.0
3	1.00	7.26	3.0
4	1.00	15.1	2.6
5	1.00	19.2	2.7
6, 7	0.70	15.7	2.3 <sup>a</sup>
8	1.10	16.2	2.2
9	1.20	16.2	3.7
10	1.40	16.2	3.2
11, 12	1.50	16.1	3.7 <sup>a</sup>
13, 14	1.60	16.2	4.5 <sup>a</sup>
15, 16	1.70	15.9	4.8 <sup>a</sup>
17, 18	1.80	16.2	4.9 <sup>a</sup>
19, 20	1.92	15.9	5.4 <sup>a</sup>
21 <sup>f</sup>	1.00	16.4	3.9 <sup>b</sup>
22 <sup>f</sup>	1.00	16.4	4.2 <sup>c</sup>
23-25 <sup>f</sup>	1.00	15.9	4.0 <sup>c</sup>
26 <sup>f</sup>	1.00	16.4	4.2 <sup>d</sup>
27 <sup>f</sup>	1.00	16.4	4.3 <sup>e</sup>
28-30 <sup>g</sup>	1.00	16.1	6.0 <sup>a</sup>
31-34 <sup>h</sup>	1.00	15.9	11.2 <sup>a</sup>

<sup>a</sup> Average value for the experiments indicated. <sup>b</sup> [Cr(III)] = 1.11 × 10<sup>-3</sup> M. <sup>c</sup> [Cr(III)] = 2.21 × 10<sup>-3</sup> M. <sup>d</sup> [Cr(III)] = 7.37 × 10<sup>-3</sup> M. <sup>e</sup> [Cr(III)] = 8.84 × 10<sup>-3</sup> M. <sup>f</sup> Temperature 25°. <sup>g</sup> Temperature 30°. <sup>h</sup> Temperature 40°.

The rate data for this reaction are satisfactorily interpreted by a mechanism consisting of the ion-pair association step of reaction 6 followed by the reactions



The intermediate proposed in reaction 8 is conceived of as being similar in form to the transition state proposed for the mono(oxalato) exchange reaction above, again with the doubly coordinated oxalate bridge between the Cr ions and with the proton coordinated to the nonbridging oxalate, *viz.*<sup>32</sup>



With K<sub>1</sub> = 15 M<sup>-1</sup>, K<sub>2</sub> assumed to be quite small,<sup>33</sup> and the low magnitudes of the chromium ion concentrations in these experiments, the rate law for the overall reaction (the sum of eq 6, 8, and 9) takes the form

$$\text{rate} = k_b K_1 K_2 [\text{Cr(III)}][\text{Cr(II)}][\text{H}^+] \quad (10)$$

It is seen that k<sub>b</sub> = k<sub>b</sub><sup>'</sup>/K<sub>1</sub>K<sub>2</sub>[H<sup>+</sup>], and since K<sub>1</sub> ≈ 15 M<sup>-1</sup> and K<sub>2</sub> can be assigned an upper limit<sup>34</sup> of between 10<sup>-3</sup> and 10<sup>-2</sup> M<sup>-1</sup>, the lower limit on the value of k<sub>b</sub> is of the order of 1 sec<sup>-1</sup> at 25° and I = 2.0 M.

(32) One might question our earlier concept of this species as an "ion pair" (eq 6). However, since Cr<sub>aq</sub><sup>2+</sup> is exceedingly labile, the displacement of some of its associated water molecules in forming the structured "ion pair" suggested herewith does not present a difficulty.

(33) Chelated oxalate is known to be an extremely weak base: S. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966). There is little likelihood of the presence of ring-opened oxalate due to the high resistance of this complex to acid-catalyzed aquation.<sup>4,29</sup>

(34) At 50° and I = 1.0 M, a value of 5 × 10<sup>-2</sup> M<sup>-1</sup> has been deduced<sup>9</sup> for the association of a proton with Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>. This can reasonably be taken as an upper limit for protonation of the Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>Cr<sup>2+</sup> ion pair at 20° and I = 2.0 M.

TABLE IV  
 RATE PARAMETERS FOR VARIOUS OXALATOQUOCHROMIUM(III) REACTIONS AT 25° AND 1.0 < I < 2.0 M

Reaction <sup>a</sup>	$k, M^{-1} \text{ sec}^{-1}$	$\Delta H^\ddagger,$ kcal/mol	$\Delta S^\ddagger,$ cal/deg mol	Ref
(i) <sup>b</sup> $*Cr^{3+} + Cr^{2+} \rightarrow Cr^{3+} + *Cr^{2+}$	$1.2 \times 10^{-4}$	22	-2	13
(ii) <sup>c</sup> $*Cr(C_2O_4)^+ + Cr^{2+} \rightarrow Cr(C_2O_4)^+ + *Cr^{2+}$	0.13	11	-26	This work
(iii) <sup>d,e</sup> $cis-*Cr(C_2O_4)_2^- + Cr^{2+} \rightarrow cis-Cr(C_2O_4)_2^- + *Cr^{2+}$	0.17	...	...	15
(iv) <sup>f</sup> $trans-Cr(C_2O_4)_2^- + H^+ \rightarrow cis-Cr(C_2O_4)_2^- + H^+$	$3 \times 10^{-8}$	18	-16	8
(v) <sup>d</sup> $trans-Cr(C_2O_4)_2^- + Cr^{2+} \rightarrow cis-Cr(C_2O_4)_2^- + Cr^{2+}$	0.11	12	-23	15
(vi) <sup>f</sup> $cis-Cr(C_2O_4)_2^- + H^+ \rightarrow Cr(C_2O_4)^+ + HC_2O_4^-$	$2 \times 10^{-6}$	24	-5	29
(vii) <sup>f</sup> $cis-Cr(C_2O_4)_2^- + H^+ + Cr^{2+} \rightarrow Cr(C_2O_4)^+ + HC_2O_4^- + Cr^{2+}$	0.04	12	-24	This work
(viii) <sup>g</sup> $Cr(C_2O_4)_3^{3-} + H^+ \rightarrow Cr(C_2O_4)_2^- + HC_2O_4^-$	$4 \times 10^{-5}$	23	-2	5
(ix) <sup>c</sup> $Cr(C_2O_4)_3^{3-} + Cr^{2+} \rightarrow Cr(C_2O_4)_2^- + Cr^{2+} + C_2O_4^{2-}$	0.13	8	-35	15

<sup>a</sup> Ligand water molecules not included. <sup>b</sup>  $[H^+] = 1.0 M$ . Rate law is of the form such that  $k = k_1 + k_2/[H^+]$ . <sup>c</sup> Independent of  $[H^+]$  above 0.02 M. <sup>d</sup>  $[H^+] = 0.016 M$ . Acid dependence unknown. <sup>e</sup> Result of single experiment. <sup>f</sup>  $[H^+] = 1.0 M$ . Rate is first order in  $[H^+]$ . <sup>g</sup>  $[H^+] = 1.0 M$ . Rate law is of the form such that  $k = k_1[H^+] + k_2[H^+]^2$ .

Considering now the results summarized in Table IV, a number of instructive comparisons can be made. First, one notes the large difference in rate between ligand-water-bridged electron transfer between chromium(II) and chromium(III) as compared to oxalate-bridged systems (*cf.* entry (i) with (ii) and (iii)). It is also seen that the rates are very similar whether one or two oxalate groups are available for the bridging (entries (ii) and (iii)), supporting our concept of the similar doubly chelated reactive intermediate for both of the reactions we have studied. Further, the large increase in rate in changing from ligand water as the probable bridging group to oxalate (a factor of about 300, as seen by comparing entries (i) and (ii)) parallels similar though more marked contrasts found in other systems. Thus, the  $Co(NH_3)_5C_2O_4^+-Cr_{aq}^{2+}$  reaction, with a rate constant<sup>16</sup> of  $4.6 \times 10^4 M^{-1} \text{ sec}^{-1}$  at 25°, is nearly  $10^5$  times as rapid as the corresponding reduction of the aquopentaamminecobaltic species (rate constant of  $0.6 M^{-1} \text{ sec}^{-1}$ ).<sup>35</sup> The acid-catalyzed isomerization and aquation reactions (entries (iv), (vi), and (viii)) are seen to be in each case several orders of magnitude slower than the corresponding  $Cr_{aq}^{2+}$ -catalyzed processes. This metal ion catalysis is no doubt a function of the efficiency of the oxalato-mediated electron transfer as noted in entries (ii) and (iii). However, a portion of the catalytic effect can possibly be ascribed to the general ion-pairing effect already noted for the isomerization reactions by other investigators,<sup>36</sup> who report, for example, second-order rate constants for catalysis by  $Ca_{aq}^{2+}$ ,  $Zn_{aq}^{2+}$ , and  $Cu_{aq}^{2+}$  at 25°, pH 3, and  $I = 1.0 M$  of 0.006, 0.021, and  $0.047 M^{-1} \text{ sec}^{-1}$ , respectively, only the first of which is very much smaller than the rate constant noted in entry (v). It is sig-

(35) A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **81**, 1288 (1959).

(36) H. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).

nificant that all the  $Cr_{aq}^{2+}$ -catalyzed reactions have much more negative entropies of activation than do those catalyzed by  $H^+$  or the other metal ions, indicative of the specific geometric requirement of the activated complex proposed for the  $Cr_{aq}^{2+}$  systems.

Finally, some comment should be made concerning the contrasting effect of acidity in entry (vii) as compared to (ii) and (ix). A related contrast has been previously noted in the reductions of *cis*- and *trans*- $Co(NH_3)_4(N_3)_2^+$  ions by  $Fe_{aq}^{2+}$  ion.<sup>37</sup> Here, the *cis* reaction is not acid catalyzed, and both  $N_3$  groups are transferred to the  $Fe^{2+}$  ion, but with the *trans* species, acid catalysis is observed and only one  $N_3$  group is transferred, possibly assisted by the protonation of the  $N_3$  group opposite to the one forming the bridge. A similar situation is proposed in our explanation of the acid catalysis of the  $Cr(C_2O_4)_2(H_2O)_2^- - Cr_{aq}^{2+}$  reaction above. Why a corresponding effect is not observable<sup>15</sup> in the  $Cr(C_2O_4)_3^{3-} - Cr_{aq}^{2+}$  aquation is not clear, but it may be related to the much more complete ion pairing to be expected in the latter case, where the (3-)(2+) ion pairs would be expected to have association constants of as high as  $10^8$  or more.<sup>30</sup> This could greatly facilitate the formation of the highly symmetrical transition state (note the large negative entropy of activation in the case of (ix)) and eliminate any necessity for assistance to the process by protonation of a non-bridging oxalate group.

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(37) A. Haim, *J. Amer. Chem. Soc.*, **85**, 1016 (1963).