and kinetics of the radical reactions which occur in this system. It would also appear in order to reinvestigate certain aspects of the pulse radiolytic work in acidic solutions keeping in mind the fact that more than one radical is now known to be present.

Acknowledgment. We wish to thank Dr. B. H. J. Bielski of Brookhaven National Laboratory for drawing our attention to questions about the structure of the ascorbic acid radical and for many valuable discussions on this subject. We are indebted to Dr. B. M. Tolbert of the University of Colorado for furnishing the sample of ascorbic-*4-d*$_1$ acid and for his various suggestions. We also wish to thank Dr. W. L. Mock of Carnegie-Mellon University for many helpful discussions on the synthesis of α-hydroxytetronic acid and to thank Miss M. A. Schuler for her assistance in the preparation of this compound and Professors Y. Kirino and T. Kwan of the University of Tokyo for furnishing the final sample which allowed observation of the ^{13}C spectra of radical III.

Three-Electron Oxidations. II. The Chromium(VI) Oxidation of Oxalic Acid[1]

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Abstract: The chromic acid oxidation of oxalic acid ($H_2C_2O_4$) has been reinvestigated over a wide range of conditions. Oxalic acid is oxidized by chromium(VI) by two different mechanisms, each involving a different oxalic acid–chromic acid complex. The complete mechanism (Scheme III) leads to the rate law $v = [Cr_T][OxH_2]\{k_1h_0 + (kK_I \cdot K_{II}K_a^{OxH_2}[OxH_2])/(1 + h_0/K_a^{H_2CrO_4} + K_I[OxH_2]h_0 + K_IK_{II}'K_a^{OxH_2}[OxH_2]^2/h_0)\}$, where $[OxH_2]$ is the concentration of undissociated oxalic acid and $[Cr_T]$ the sum of the concentrations of all chromium(VI) species present. Kinetic evidence for the formation of a chromium(VI)–oxalic acid 1:1 and 1:2 complexes has been obtained and the equilibrium constants for their formation have been determined. The 1:1 complex exists as a neutral species and is most probably a cyclic anhydride. The 1:2 complex is stable as a dianion and exists most likely in an open chain form in which the usual coordination number of four for chromium(VI) is retained. The reactive intermediate in the second-order reaction is the monoanion of the 1:2 complex, $HO_2CCO_2CrO_3COCO_2^-$. It is proposed that this intermediate decomposes directly into $[Cr(H_2O)_6]^{3+}$, three molecules of CO_2 and a free radical $\cdot CO_2H$, in a one-step three-electron oxidation reaction. The formation of free-radical intermediates has been demonstrated. In the presence of an excess of acrylamide, the yield of carbon dioxide is reduced to a limiting value which is in agreement with the proposed mechanism. An unexpected exchange between $[Cr(H_2O)_6]^{3+}$ and oxalic acid under the reaction conditions has been observed.

In the first paper of this series[1] we reported what we believe to be the first documented case of a three-electron oxidation in organic chemistry.[2,3]

As organic substrates generally undergo at most a two-electron oxidation in a single step, a one-step three-electron reduction of an oxidant must involve more than one molecule of an organic substrate in the activated complex and the rate law will therefore be higher than first order in the total of organic compounds involved. In looking for further examples of three-electron oxidation reactions, we were therefore interested in those reactions for which a higher than first-order kinetic dependence in the substrate was reported. As chromium(VI) oxidation of oxalic acid is the prime example of such a reaction, we decided to investigate it in more detail.

The chromic acid oxidation of oxalic acid has been the subject of numerous studies.[4–13] According to Chakravarty and Ghosh,[8] the reaction is first order in hexavalent chromium, is second and third order in oxalic acid, and exhibits a too complex dependence on acidity to allow simple description in form of a rate law. Rao and Ayyar[9] reported similar results and proposed a mechanism involving chromium(VI) species with coordination numbers of six and eight. Chandra, Shukla, and Chatterji[10] reported a second-order dependence in oxalic acid and independence on the hydrogen ion concentration, but close examination of their data reveals a slightly higher order in oxalic acid and a noticeable acidity dependence. Bakore and Jain[11] were the first to notice that a much simpler rate dependence can be obtained if instead of the total oxalic acid concentration the concentrations of undissociated

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(1) Part I: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

(2) Haight earlier suggested a three-electron oxidation in an organic system involving chromium(VI) and hydrogen sulfite.[3]

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(9) G. G. Rao and R. V. V. Ayyar, *Z. Phys. Chem. (Leipzig)*, **236**, 17 (1967).

(10) S. Chandra, S. N. Shukla, and A. C. Chatterji, *J. Inorg. Nucl. Chem.*, **31**, 805 (1969).

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oxalic acid and of the monooxalate anion are calculated and considered separately. They suggested that chromic acid and oxalic acid form an intermediate, $HOCrO_2OCOCOOH$, which then reacts further with a monooxalate ion. Durham[12] reexamined Bakore and Jain's report and proposed that decomposition of a 1:1 and a 1:2 complex occurs at comparable rates leading to the rate law

$$v = (k[Ox^{2-}] + k'[Ox^{2-}]^2)[H^+]^3[CrO_4H^-]$$

However, the values of the rate constants reported by Durham differ greatly from those of Bakore and Jain.[11] The most recent investigation was carried out by Haight and coworkers[13] who determined quantitatively the different chromium(III) species formed in the reaction. These authors proposed a reaction mechanism consonant with the formation of the several chromium(III) complexes and with the absence of any evidence for the formation of free radical intermediates.[9,11,13] In order to avoid the necessity of postulating a free-radical intermediate, the proposed mechanism assumed that chromium(IV) formed in the rate-limiting step of the reaction disproportionates to chromium(III) and chromium(V) and is thus converted into a two-electron oxidant.

Many of the above investigations were carried out under insufficiently defined conditions and conclusions about rate laws and mechanisms were based on studies confined to narrow concentration ranges. Further, we were recently able to estimate that the equilibrium constant for the reaction $Cr(VI) + Cr(IV) \rightleftarrows 2Cr(V)$ has the value of about[14] 4×10^{-4}; the equilibrium is thus entirely on the left hand side which makes any mechanism[9] requiring the oxidation of chromium(IV) to chromium(V) very unlikely. We have also demonstrated[14] that chromium(IV) is an extremely reactive one-electron oxidant. We find it therefore difficult to accept that it could accumulate, in the presence of oxalic acid, to reach a sufficient concentration to make its bimolecular disproportionation an important step in the oxidation mechanism.[13] We therefore felt that a reinvestigation of the reaction mechanism of the chromic acid oxidation of oxalic acid was required.

Experimental Section

Materials. Oxalic acid (Mallinckrodt AR), acrylamide (Eastman-Kodak), mercuric chloride (Mallinckrodt AR), sodium dichromate (J. T. Baker, Reagent), and chromium nitrate (Fisher purified) were used without further purification. Perchloric acid solutions were prepared from 70% perchloric acid (B&A Reagent).

Acrylonitrile (Practical Grade) was distilled before using and the fraction boiling between 77 and 79° was collected.

Kinetic Measurements. A large excess (10- to 2000-fold) of oxalic acid was used for all kinetic measurements. The reactions were followed spectrophotometrically, using Cary 15 and Zeiss PMQII spectrophotometers equipped with thermostated cell holders. The rates were determined by following the decrease in the absorbance of chromium(VI) at 350 nm. Pseudo-first-order rate constants were calculated from the slopes of the plots of the logarithm of the absorbance *vs.* time. The reaction obeyed good first-order kinetics and the rate constants obtained from multiple determinations were within ±4% of each other.

Product Analysis. Carbon Dioxide. The yield of carbon dioxide was determined manometrically in a Warburg apparatus[15] using "Fast Green F.C.F." dissolved in ethyl lactate as the manometric fluid. In a typical experiment oxalic acid (1.0 ml, 0.266 *M*), perchloric acid (0.8 ml, 6.08 *M*), and distilled water (0.20 ml) were mixed in a Warburg reaction flask kept at 25°, the mixture was saturated with carbon dioxide, and a sodium dichromate solution (0.010 ml, 0.517 *M*) was injected through the side arm fitted with a serum cap. The evolution of carbon dioxide was recorded until a constant pressure was reached (*ca.* 2 hr). The results were corrected for the volume of liquid injected.

Chromium(III). The chromium(III) species in the product were separated following the method of Haight and coworkers,[13] using Dowex 50W-X8 as the cation-exchange resin and Dowex 2-X8 as the anion-exchange resin. After separation, the chromium(III) species were oxidized to chromium(VI) by alkaline hydrogen peroxide[16] and their concentrations determined spectrophotometrically from their absorbances at 370 nm.

Evidence for the Formation of Free Radicals. A. With Acrylamide. A solution of sodium dichromate (5 ml, 0.534 *M*) was added to a solution containing oxalic acid (20 mmol) and acrylamide (5.2 g), a total volume 30 ml. When the color of chromium(VI) disappeared the mixture was diluted with 100 ml of methanol which led to the precipitation of a white polymer. Larger amounts of polymers were formed when the same experiment was carried out in the presence of sodium hydrogen oxalate (0.5 mmol). On the other hand, no polymers were found in the presence of perchloric acid (1.0 *M*). Control experiments showed that no polymerization of acrylamide takes place under the experimental conditions with either chromic acid or oxalic acid alone.

B. With Acrylonitrile. A solution of sodium dichromate (5.0 ml, 0.534 *M*) was added to a mixture of oxalic acid (25 mmol), sodium hydrogen oxalate (0.5 mmol), and acrylonitrile (2.5 g) in a volume of 32.5 ml. The reaction was allowed to go to completion as judged from the change in color of the solution and then diluted with 100 ml of methanol; a white precipitate of a polymer appeared slowly. The blank experiment in absence of oxalic acid or sodium dichromate did not show the formation of any such precipitate. No polymer formation was observed in the absence of sodium hydrogen oxalate or in the presence of perchloric acid. The inability to detect free radicals in acidic solutions is in agreement with previously reported results.[9,11,13]

C. With Mercuric Chloride. Sodium dichromate solution (1.0 ml, 0.517 *M*) was added to a mixture of oxalic acid (1.6 mmol), sodium hydrogen oxalate (0.5 mmol), and mercuric chloride (1.2 g) in a volume of 35 ml. A white precipitate of mercurous chloride appeared as the oxidation reaction proceeded. Blank experiments performed in the absence of oxalic acid or dichromate did not show the formation of any mercurous chloride. No precipitate formation could be observed when the oxidation was carried out without the addition of sodium hydrogen oxalate or in an acidified solution (29.3 mmol perchloric acid), confirming earlier reports that no radical induced reduction of mercuric chloride could be observed in acid solutions.[9,11]

Results

Kinetics of the Chromic Acid Oxidation. Figure 1 gives an example of the kinetic curves from which pseudo-first-order rate constants for the oxidation were determined. The initial deviation from linearity is due to the formation of a chromium(V) intermediate, a reaction which is discussed in detail in another paper from this laboratory.[17] As the chromium(V) concentration reaches a steady state within a short period of time, the rate of the chromium(VI) reaction can be determined from the linear part of the curve.[17]

Figure 2 and Tables I and II give the result of a study of the chromic acid oxidation of oxalic acid over a concentration range of almost three orders of magnitude. Because of the high dependence of oxidation rates on the oxalic acid concentration, the studies had to be carried out under two different sets of conditions. The oxidations at low concentrations were studied at 60° in 2.43 *M* perchloric acid (Table I, curve A in Figure 2) whereas the studies at higher concentrations were car-

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Table I. Chromic Acid Oxidation of Oxalic Acid in 2.43 *M* Perchloric Acid

$[OxH_2]_T$,[a] *M*	$[OxH_2]$,[b] *M*	Chromium(VI), *M*	*T*, °C	k_{exptl}, sec^{-1}	$10^2k_{exptl}/[OxH_2]$	$k_{exptl}/[OxH_2]^2$
1.06×10^{-3}	1.06×10^{-3}	5.30×10^{-5}	60	2.99×10^{-5}	2.82	26.6
2.66×10^{-3}	2.66×10^{-3}	1.06×10^{-4}	60	5.68×10^{-5}	2.14	8.04
5.32×10^{-3}	5.32×10^{-3}	1.06×10^{-4}	60	1.24×10^{-4}	2.33	4.37
1.06×10^{-2}	1.06×10^{-2}	2.12×10^{-4}	60	2.51×10^{-4}	2.37	2.24
2.66×10^{-2}	2.66×10^{-2}	2.12×10^{-4}	60	1.12×10^{-3}	4.21	1.58
5.32×10^{-2}	5.32×10^{-2}	2.12×10^{-4}	60	3.96×10^{-3}	7.44	1.39
1.33×10^{-1}	1.27×10^{-1}	2.12×10^{-4}	60	1.57×10^{-2}	11.80	0.97
5.32×10^{-3}	5.32×10^{-3}	1.06×10^{-4}	25	1.20×10^{-5}	0.23	0.43

[a] $[OxH_2]_T$ = total concentration of oxalic acid. [b] $[OxH_2]$ = concentration of undissociated oxalic acid.

Table II. Chromic Acid Oxidation of Oxalic Acid in 0.097 *M* Perchloric Acid at 25°, Chromium(VI) = 4.24×10^{-4} *M*

$[OxH_2]_T$,[a] *M*	$[OxH_2]$,[b] *M*	k_{exptl}, sec^{-1}	$10^3k_{exptl}/[OxH_2]$	$k_{exptl}/[OxH_2]^2$	k_{calcd}, sec^{-1}
1.31×10^{-2}	8.0×10^{-3}	1.73×10^{-5}	2.16	0.270	1.76×10^{-5}
2.38×10^{-2}	1.50×10^{-2}	5.41×10^{-5}	3.61	0.240	6.04×10^{-5}
4.76×10^{-2}	3.10×10^{-2}	2.47×10^{-4}	7.94	0.256	2.74×10^{-4}
9.52×10^{-2}	6.50×10^{-2}	9.85×10^{-4}	14.80	0.227	1.00×10^{-3}
1.31×10^{-1}	9.10×10^{-2}	1.82×10^{-3}	19.78	0.217	1.80×10^{-3}
2.62×10^{-1}	1.93×10^{-1}	6.80×10^{-3}	35.21	0.182	6.30×10^{-3}
3.92×10^{-1}	2.99×10^{-1}	1.20×10^{-2}	42.00	0.140	1.15×10^{-2}
4.76×10^{-1}	3.62×10^{-1}	1.50×10^{-2}	40.01	0.110	1.46×10^{-2}
5.23×10^{-1}	4.09×10^{-1}	1.72×10^{-2}	44.4	0.108	1.69×10^{-2}
5.61×10^{-1}	4.41×10^{-1}	1.80×10^{-2}	41.2	0.093	1.83×10^{-2}
6.54×10^{-1}	5.21×10^{-1}	2.20×10^{-2}	41.0	0.078	2.18×10^{-2}
7.48×10^{-1}	6.02×10^{-1}	2.50×10^{-2}	41.8	0.069	2.50×10^{-2}
8.41×10^{-1}	6.82×10^{-1}	2.88×10^{-2}	42.2	0.061	2.78×10^{-2}
9.16×10^{-1}	7.49×10^{-1}	3.20×10^{-2}	42.7	0.057	3.01×10^{-2}

[a] $[OxH_2]_T$ = total concentration of oxalic acid. [b] $[OxH_2]$ = concentration of undissociated oxalic acid.

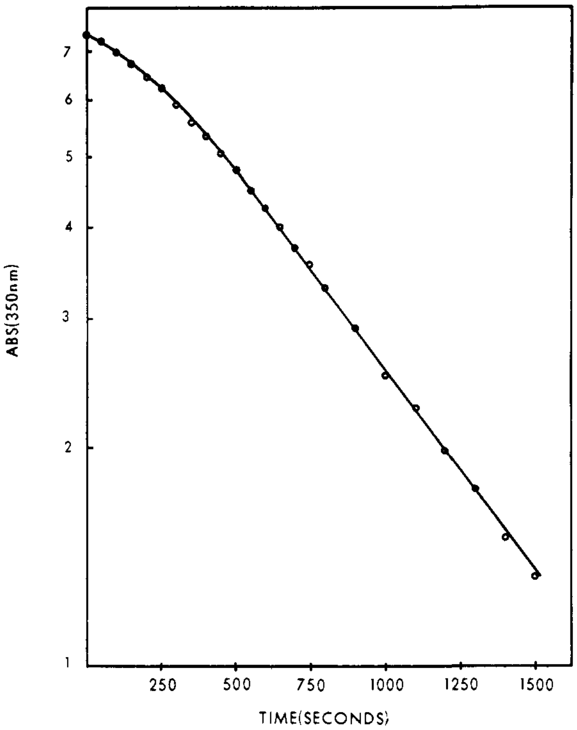

Figure 1. Time dependence of ln absorption at 350 nm at 25°: oxalic acid, 0.102 *M*; $HClO_4$, 0.252 *M*; chromium(VI), 7.3×10^{-3} *M*.

ried out at 25° and in 0.097 *M* perchloric acid (Table II, curve B in Figure 2).

From the inspection of the data it is clear that the kinetics of the oxidation undergo two changes. The reaction is first order in oxalic acid at very low concentrations, second order at intermediate concentrations, and again of apparent first order at high substrate concentrations, suggesting that the oxidation proceeds by at least two distinct mechanisms.

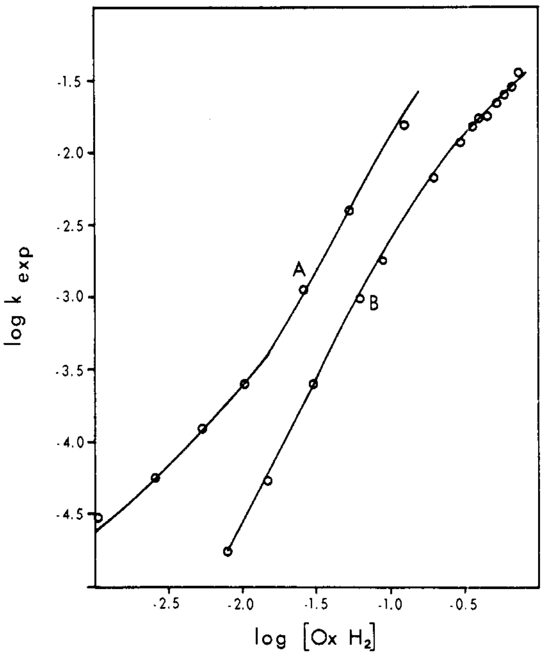

Figure 2. Effect of concentration on the rate of chromic acid oxidation of oxalic acid: (A) $HClO_4$ = 2.43 *M*; *T* = 60°; (B) $HClO_4$ = 0.097 *M*, *T* = 25°.

First-Order Oxidation of Oxalic Acid. Table III shows the acidity dependence of the chromic acid oxidation of oxalic acid in the region in which the reaction is essentially first order in oxalic acid. The

Table III. Effect of Acidity at Low Oxalic Acid Concentrations[a] at 60°

Perchloric acid, M	H_0	10^5k_{exptl}, sec^{-1}	$H_0 + \log k_{\mathrm{exptl}}$
0.314	−0.10	1.68	−4.87
0.628	−0.32	3.01	−4.84
1.26	−0.69	6.30	−4.89
2.43	−1.01	12.4	−4.92

[a] Conditions: oxalic acid, 5.35×10^{-3} M; ionic strength, 2.51 M.

simplest rate law describing the reaction over the region of concentrations used is given in eq 1 where OxH_2

$$v = k_1[OxH_2][Cr_T]h_0 \quad (1)$$

stands for undissociated oxalic acid and Cr_T for the total concentration of chromium(VI).

Second-Order Oxidation of Oxalic Acid. At intermediate oxalic acid concentrations from about 10^{-2} to 10^{-1} M, the reaction is second order in oxalic acid with the first-order term becoming negligibly small.

The first five lines of Table IV give the results at the acidity dependence of the oxidation rates in the second-order region. The experimental pseudo-first-order rate constants (column 5) has the highest value in about 0.3 M perchloric acid and decreases with both an increase and a decrease in acidity.

Table IV. Effect of Acidity at Intermediate and High Oxalic Acid Concentrations (Chromium(VI) = 4.24×10^{-4} M, Ionic Strength = 2.51 M)

$[OxH_2]_T$,[a] M	$HClO_4$, M	$-H_0$[20]	$[OxH_2]$,[b] M	10^2k_{exptl}, sec^{-1}	$10k_{\mathrm{exptl}}/[OxH_2]^2$	$10^2k_{\mathrm{exptl}}/[OxH_2]$	$10k_{\mathrm{exptl}}\cdot[Cr(VI)]/[OxH_2]^2\cdot[HCrO_4^-]$[c]	$10^2k_{\mathrm{exptl}}\cdot[Cr(VI)]/[OxH_2]\cdot[HCrO_4^-]$[c]
0.107	0.063	−0.68	0.064	0.121	3.00		0.315	
0.107	0.314	0.10	0.096	0.220	2.44		0.318	
0.107	0.628	0.32	0.102	0.210	2.06		0.308	
0.107	1.26	0.69	0.106	0.139	1.26		0.273	
0.107	2.51	1.01	0.107	0.098	0.89		0.305	
0.566	0.018	−1.10	0.323	1.78		5.68		0.058
0.566	0.063	−0.68	0.440	2.04		5.36		0.056
0.566	0.314	0.10	0.540	2.17		4.20		0.055
0.566	0.628	0.32	0.550	2.10		3.92		0.059
0.566	1.26	0.69	0.559	1.41		2.55		0.055
0.566	1.94	0.88	0.561	1.08		1.94		0.054

[a] $[OxH_2]_T$ = total concentration of oxalic acid. [b] $[OxH_2]$ = concentration of undissociated oxalic acid. [c] $[Cr(VI)] = [H_2CrO_4] + [HCrO_4^-]$.

This type of defense, a pH profile with a maximum, is characteristic of reactions in which two acid–base equilibria are taking place. In this reaction the processes responsible for the observed acidity dependence are the dissociations of oxalic acid

$$OxH_2 \rightleftharpoons OxH^- + H^+ \quad K_a^{OxH_2} = 0.059^{18} \quad (2)$$

and of chromic acid

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \quad (3)$$

Column 6 in Table IV gives the values obtained by dividing the experimental rate constants by the squares of the concentrations of undissociated oxalic acid. The new values decrease steadily with increasing acidity.

The dependence of the rate constant on acidity is removed in column 8 in which the values of column 6 have been divided by the factor

$$\frac{[HCrO_4^-]}{[Cr(VI)]} = \frac{K_a^{H_2CrO_4}}{K_a^{H_2CrO_4} + h_0} \quad (4)$$

where $[Cr(VI)] = [H_2CrO_4] + [HCrO_4^-]$, $K_a^{H_2CrO_4} = 4.2$ is the first dissociation constant[19] of H_2CrO_4, and h_0 is the acidity function.[20]

The rate law for the second-order oxidation of oxalic acid thus can be expressed by eq 5

$$v = k_5[OxH_2]^2[HCrO_4^-] \quad (5)$$

which is equivalent to

$$v = k_6[OxH_2][H_2CrO_4][OxH^-] \quad (6)$$

where $k_6 = k_5K_a^{H_2CrO_4}/K_a^{OxH_2}$.

The second half of Table IV gives the acidity dependence for the oxidation at high oxalic acid concentrations and concentrations where the reaction again becomes first order in oxalic acid. The experimental rate constants show the same pattern with a maximum in 0.3 M perchloric acid. Acidity independent values again are obtained by correcting for the changes in the concentrations of undissociated oxalic acid (column 7) and of the acid chromate anion (column 9).

At high oxalic acid concentrations the rate law therefore assumes the form of eq 7

$$v = k_2'[OxH_2][HCrO_4^-] = k_7'[OxH^-][H_2CrO_4] \quad (7)$$

where $k_7' = k_7K_a^{H_2CrO_4}/K_a^{OxH}$.

Complex Formation. The apparent decrease in the order in oxalic acid at high oxalic acid concentrations (Table II, Figure 2) is typical for a reaction in which an intermediate complex between reagent and substrate is formed.

The discussion which will follow will serve to demonstrate that the reaction given in Scheme I represents the simplest mechanistic scheme which can account for the experimental results. In this scheme OxH_2 stands for the undissociated oxalic acid, OxH^- for the hydrogen oxalate anion, C_1 for the chromic acid 1:1 complex and C_2H^- and C_2^{2-} for the mono- and dianion of the 1:2 complex.

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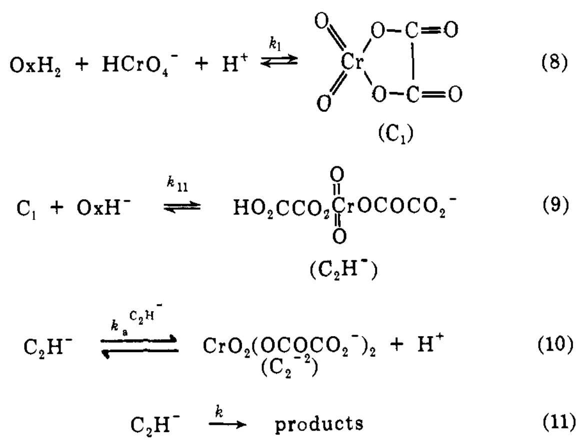
(18) "Handbook of Chemistry and Physics," 51st ed, The Chemical Rubber Co., Cleveland, Ohio, 1970–1971. The value was not corrected for changes in ionic strength. This obviously introduces a certain error in the numeric values given in this paper, but does not affect any of the conclusions which have been reached concerning the mechanism of the reaction.

(19) J. Y. Tong, *Inorg. Chem.*, 3, 1804 (1964).

(20) B. C. Challis and J. H. Ridd, *J. Chem. Soc.*, 5208 (1962).

Scheme I



Assuming that oxalic acid is present in large excess, the concentrations of the intermediates of Scheme I can be expressed by eq 12 and 13.

$$[C_I] = K_I[OxH_2][HCrO_4^-][H^+] \quad (12)$$

$$[C_2H^-] = K_{II}[C_I][OxH^-] = K_IK_{II}[OxH_2][OxH^-][HCrO_4^-][H^+] = [C_2^{2-}][H^+]/K_a^{C_2H^-} \quad (13)$$

Taking into account the oxalic acid–monooxalate anion equilibrium (eq 2) and substituting K_{II}' for $K_{II}K_a^{C_2H^-}$ one obtains eq 14 and 15.

$$[C_2H^-] = K_IK_{II}K_a^{OxH_2}[OxH_2]^2[HCrO_4^-] \quad (14)$$

$$[C_2^{2-}] = K_IK_{II}'K_a^{OxH_2}[OxH_2]^2[HCrO_4^-]/[H^+] \quad (15)$$

Assuming that C_2H^- is a rather strong acid and is therefore present only in very small amounts, the total concentration of chromium(VI) can be expressed as

$$[Cr_T] = [HCrO_4^-] + [H_2CrO_4] + [C_I] + [C_2^{2-}] \quad (16)$$

From eq 4, 12, 15, and 16 one can obtain the equation

$$[Cr_T] = [HCrO_4^-](1 + [H^+]/K_a^{H_2CrO_4} + K_I[OxH_2][H^+] + K_IK_{II}'K_a^{OxH_2}[OxH_2]^2/[H^+]) \quad (17)$$

According to Scheme I the rate law of the oxidation is

$$\text{rate} = k[C_2H^-] = k_{exptl}[Cr_T] \quad (18)$$

From eq 14, 17, and 18, eq 19 and 20 can be obtained.

$$k_{exptl} = \frac{kK_IK_{II}K_a^{OxH_2}[OxH_2]^2}{1 + [H^+]/K_a^{H_2CrO_4} + K_I[OxH_2][H^+] + K_IK_{II}'K_a^{OxH_2}[OxH_2]^2/[H^+]} \quad (19)$$

$$\frac{[OxH_2]}{k_{exptl}} = \frac{1 + [H^+]/K_a^{H_2CrO_4}}{kK_IK_{II}K_a^{OxH_2}}\frac{1}{[OxH_2]} + \frac{[H^+]}{kK_{II}K_a^{OxH_2}} + \frac{K_{II}'[OxH_2]}{kK_{II}[H^+]} \quad (20)$$

The last term of eq 16 reflects the accumulation of the 1:2 complex, C_2^{2-}, which becomes significant only at very high concentrations of oxalic acid. Therefore, this term can be neglected at moderate concentrations and the simplified expression (21) is then obtained.

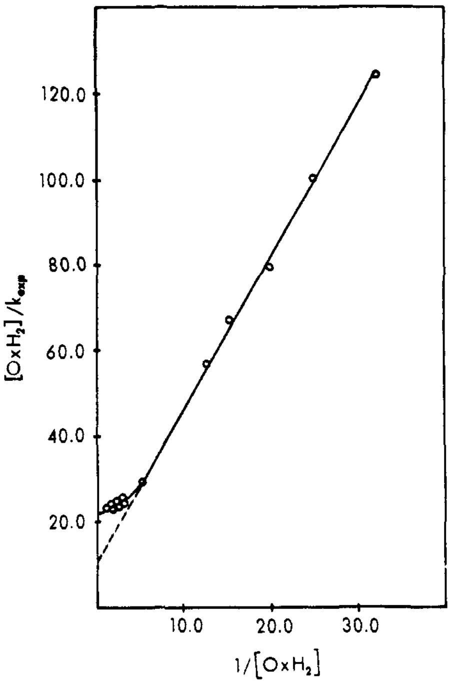


Figure 3. Determination of equilibrium constants for the chromic acid–oxalic acid complex from rate data at 25°, HClO$_4$, 0.097 *M*.

$$\frac{[OxH_2]}{k_{exptl}} = \frac{1 + [H^+]/K_a^{H_2CrO_4}}{kK_IK_{II}K_a^{OxH_2}}\frac{1}{[OxH_2]} + \frac{[H^+]}{kK_{II}K_a^{OxH_2}} \quad (21)$$

A plot of $[OxH_2]/k_{exptl}$ *vs.* $1/[OxH_2]$ for experiments using moderate concentrations of oxalic acid thus should give a straight line with a slope, *S*, and intercept, *I*, defined by eq 22 and 23. The value of the product

$$S = (1 + [H^+]/K_a^{H_2CrO_4})/kK_IK_{II}K_a^{OxH_2} \quad (22)$$

$$I = [H^+]/kK_{II}K_a^{OxH_2} \quad (23)$$

kK_{II} can be obtained from eq 23 and the value of the equilibrium constant K_I for the formation of the 1:1 complex C_I from expression 24.

$$K_I = \frac{I([H^+] + K_a^{H_2CrO_4})}{S[H^+]K_a^{H_2CrO_4}} \quad (24)$$

The value of the equilibrium constant K_{II}' for the reaction

$$C_I + OxH^- \rightleftharpoons C_2^{2-} + H^+ \quad (25)$$

can be obtained by rearranging eq 20 into eq 26.

$$K_{II}' = \frac{kK_{II}[H^+]}{k_{exptl}} - \frac{[H^+](1 + [H^+]/K_a^{H_2CrO_4})}{K_IK_a^{OxH_2}[OxH_2]^2} - \frac{[H^+]^2}{K_a^{OxH_2}[OxH_2]} \quad (26)$$

Figure 3 gives an example of a plot of $[OxH_2]/k_{exptl}$ against $1/[OxH_2]$, using the data in Table II. The good straight line dependence obtained at lower oxalic acid concentrations serves as evidence for the formation of an oxalic acid–chromic acid complex. From the plot (Figure 3) the values of $kK_{II} = 0.76\ M^{-1}\ sec^{-1}$, $K_I = 9.5\ M^{-2}$, and an average value of $K_{II}' = 0.20$ (Table

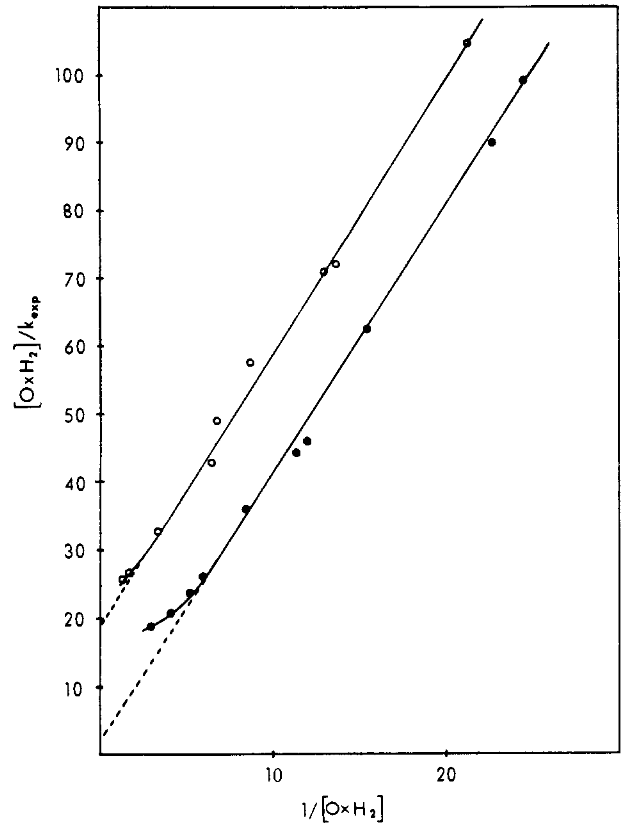


Figure 4. Effect of acidity on the equilibrium constants for the chromic acid–oxalic acid complex at 25°, ionic strength = 0.63 *M*: open circles, $HClO_4$ = 0.628 *M*; closed circles, $HClO_4$ = 0.063 *M*.

Table V. Determination of the Value of K_{II}' from Data in Table II[a]

$[OxH_2]$, *M*	10^2k_{exptl}, sec^{-1}	K_{II}'
0.031	0.0247	0.17
0.065	0.0985	0.25
0.091	0.182	0.19
0.299	1.20	0.16
0.362	1.50	0.18
0.409	1.72	0.21
0.441	1.80	0.23
0.521	2.20	0.21
0.602	2.50	0.22
0.682	2.88	0.20
0.749	3.20	0.18

[a] Average K_{II}' = 0.20 ± 0.027.

V) using eq 22, 24, and 26, respectively, were determined. The calculated rate constants, k_{calcd}, given in the last column of Table II were obtained from eq 15 using these values and show a very satisfactory agreement with the experimental data.

It should be noted that K_{II}' defines the equilibrium between the monooxalato and dioxalato complexes at a given acidity and oxalic acid concentration (eq 25). If the dioxalato complex was formed only in a very small amount, the value of K_{II}' would be low and the third term of eq 20 would approach zero leading to the same limiting form 21 derived earlier for intermediate oxalic acid concentrations. Equation 21 thus represents the type of relationship which would be expected for a mechanism involving the accumulation of only the 1:1 intermediate. It was the nonlinearity of plots of $[OxH_2]/k_{exptl}$ *vs.* $1/[OxH_2]$ (Figures 3 and 4) which made it necessary to postulate that a second intermediate becomes kinetically significant in high enough concentrations of oxalic acid.

In order to determine the effect of acidity on the various equilibrium and rate constants, we determined the effect of the concentration of oxalic acid on the observed reaction rate at a number of different acidities at constant ionic strength. Two examples of these sets of measurements are given in Figure 4. It was the result of this study which lead us to conclude that the 1:1 complex must be accumulated as a neutral species (C_I), the 1:2 complex[21] as the dianion (C_2^{2-}), but that the species actually reacting in the rate-limiting step is the monoanion (C_2H^-) as shown in Scheme I. Only these assumptions permitted us to define constants, the value of which did not vary with acidity. All other mechanistic schemes which were tried led to acid-dependent equilibrium and/or rate constants.[22] Thus the constancy of the values given in Table VI over a 20-fold range of acidities serves to support the assumptions included in Scheme I and in rate law 19 for the second-order oxidation path.

Table VI. Effect of Hydrogen Ion Concentration on K_I, K_{II}', and kK_{II} at 25°, Ionic Strength = 0.63 *M*

H^+, *M*	K_I, M^{-2}	K_{II}'	kK_{II}, M^{-1} sec^{-1}
0.031	6.7	0.92	0.94
0.063	7.1	0.88	0.79
0.126	7.4	0.83	0.86
0.251	7.7	1.01	0.75
0.502	7.7	0.83	0.90
0.628	8.4	0.82	0.89

It will be noted that the values for the equilibrium constants K_I obtained at the earlier discussed measurements in 0.097 *M* perchloric acid were considerably higher than the values given in Table VI. The first value was obtained in a series of measurements in which the ionic strength varied from about 0.1 to about 0.25, whereas the latter experiments were carried out at an ionic strength of 0.63. As the equilibrium constant K_I represents the formation of a neutral complex from a cation, an anion, and a neutral molecule (eq 8), the decrease of the equilibrium constant with increasing ionic strength is in agreement with the proposed mechanistic scheme. On the other hand, the equilibrium constant K_{II}' represents a reaction in which a negatively charged species reacts to form a doubly negatively charged complex and a proton (eq 25). This reaction therefore should be favored by increasing the ionic strength, as was indeed observed.

Complete Rate Law. The complete rate law, valid over the whole range of concentrations which were investigated and which therefore includes both the first-order and second-order oxidation of oxalic acid, can be summarized in eq 27 where the values of the rate

---

[21] Even by qualitative inspection it can be noted that the accumulation of the 1:2 complex which causes the deviation from straight line behavior at high oxalic acid concentration is much more extensive at low acidity.

[22] *E.g.*, if one assumes, as we originally did, that the intermediate which is accumulated is the monoanion C_2H^- one obtains equilibrium constants the values of which increase linearly with the reciprocal of the hydrogen ion concentration.

$$v = [\mathrm{Cr_T}][\mathrm{OxH_2}]\left(k_1h_0 + \frac{kK_\mathrm{I}K_\mathrm{II}K_\mathrm{a}{}^{\mathrm{OxH_2}}[\mathrm{OxH_2}]}{1 + h_0/K_\mathrm{a}{}^{\mathrm{H_2CrO_4}} + K_\mathrm{I}[\mathrm{OxH_2}]h_0 + K_\mathrm{I}K_\mathrm{II}{}'K_\mathrm{a}{}^{\mathrm{OxH_2}}[\mathrm{OxH_2}]^2/h_0}\right) \qquad (27)$$

constants and equilibrium constants at 25° are the following: at ionic strength = 2.51 M, $k_1 = 9.0 \times 10^{-4}\ M^2\ \mathrm{sec}^{-1}$, and at ionic strength = 0.63 M, $kK_\mathrm{II} = 0.85\ M^{-1}\ \mathrm{sec}^{-1}$, $K_\mathrm{I} = 7.5\ M^{-2}$, $K_\mathrm{II}' = 0.88$. At 60° and 2.51 M ionic strength $k_1 = 9.0 \times 10^{-3}\ M^2\ \mathrm{sec}^{-1}$. As the rate law is valid even at rather high acidities, h_0 is used instead of $[\mathrm{H}^+]$.

Reaction Products. Free Radicals. Earlier investigators have been unsuccessful in detecting the presence of free radicals during the chromic acid oxidation of oxalic acid.[9,11,13] As the formation of free radicals is required by the three-electron oxidation mechanism which we suspected could provide the clue to the understanding of this complex reaction, we decided to reinvestigate this aspect of the reaction and test again for the presence of free-radical intermediates despite previous failures by other groups.

We were indeed able to obtain positive evidence for the formation of free radicals using three different tests: the initiations of polymerization of acrylamide and of acrylonitrile and the reduction of mercuric chloride. In order to obtain positive reactions indicating the presence of free-radical intermediates, the reaction had to be carried out at low acidities, either in the absence of mineral acid or, preferably, in solutions in which the acidity was lowered by the presence of small amounts of sodium hydrogen oxalate.

The reason why free radicals can be detected in less acidic media but not in solutions of higher acidity lies probably in the fact that of the three reactions, 28–30,

$$\mathrm{R}\cdot + \mathrm{Cr(VI)} \longrightarrow \text{product} \qquad (28)$$

$$\mathrm{R}\cdot + \text{monomer} \longrightarrow \text{polymer} \qquad (29)$$

$$\mathrm{R}\cdot + \mathrm{HgCl_2} \longrightarrow \mathrm{RCl} + \mathrm{HgCl_2} \qquad (30)$$

only the first reaction is expected to be acid catalyzed. Increasing acidity thus will favor oxidation of the free radical over the other reactions which form the basis of the tests used for their detection. The failure to recognize this dependence on the acidity of the reaction medium helps to understand why earlier attempts to demonstrate free-radical formation were unsuccessful.

Carbon Dioxide. In the absence of other substrates, oxalic acid undergoes a quantitative oxidation to carbon dioxide following the stoichiometry of eq 31.

$$3\mathrm{H_2C_2O_4} + 2\mathrm{Cr(VI)} = 6\mathrm{CO_2} + 2\mathrm{Cr(III)} \qquad (31)$$

If the oxidation is carried out in the presence of free-radical scavengers like acrylamide, the formation of free-radical intermediates is indicated by the formation of polymers. In order to determine whether the formation of free radicals may represent only a minor side reaction or whether it plays an important part in the mechanism of the reaction, we investigated the effect of the concentration of an added free-radical scavenger on the yield of carbon dioxide formed in the oxidation. The results given in Table VII and in Figure 5 show that the yield of carbon dioxide is reduced in the presence of acrylamide and further that a limiting value is reached when the yield of carbon dioxide is reduced to five-sixths of the stoichiometric amount.

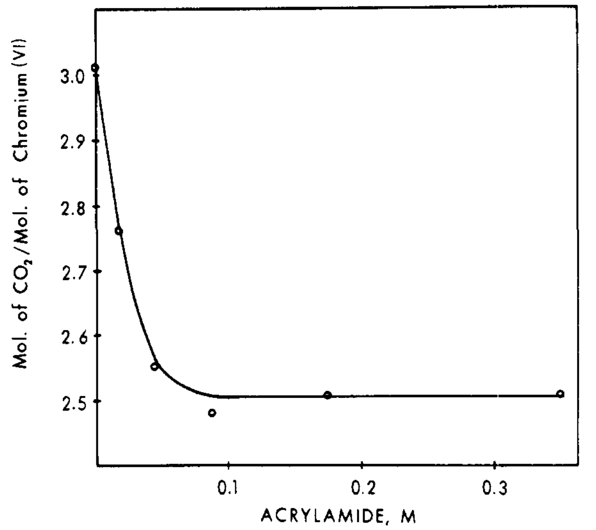


Figure 5. Effect of acrylamide on the yield of carbon dioxide: oxalic acid, 0.133 M; chromium(VI), 5.17×10^{-3} M; no mineral acid added.

Table VII. Yield of Carbon Dioxide in the Chromic Acid Oxidation of Oxalic Acid[a]

Acrylamide, M	Mol of CO_2/ mol of Cr(VI)[b]	Acrylamide, M	Mol of CO_2/ mol of Cr(VI)[b]
0.00	3.01	0.0870	2.48
0.0174	2.76	0.174	2.51
0.0435	2.55	0.348	2.51

[a] Chromium(VI) = 5.17×10^{-3} M, oxalic acid = 0.133 M, and no mineral acid added. [b] These results are averages of several experiments; the differences between the values were less than 4% of each other.

Chromium(III). Table VIII summarizes the composition of the chromium(III) compounds obtained in the chromic acid oxidation of oxalic acid. The first line of the table shows that about 50% of chromium is formed in the hexaaquochromium form but that substantial amounts of the monooxalato, dioxalato, and trioxalato complexes are also produced. These results are in essential agreement with those obtained earlier by Haight and coworkers.[13]

If one accepted the assumption that chromium(III) compounds once formed are stable toward ligand exchange and thus in effect present a "fossilized image" of the transition state of the reaction by which chromium(III) was first formed, then one would have to conclude that the simplest mechanism to account for the reduction of chromium(VI) to chromium(III) by oxalic acid must involve a set of chromium–oxalic acid complexes containing up to four molecules of oxalic acid per atom of chromium. This was essentially the conclusion reached by previous investigators.[13] Our control experiment carried out in the presence of added $\mathrm{Cr(H_2O)_6}^{3+}$, however, demonstrated convincingly that chromium(III) exhibits a surprising ability to exchange ligands. The yields of all complexes are considerably higher than calculated on the assumption that no exchange would take place. It should be noted that the ability to incorporate oxalic acid is obviously greatly enhanced by the presence of chromium(VI) and possibly other valence states of chromium during the reac-

Table VIII. Yields of Chromium(III) Complexes in the Chromic Acid Oxidation of Oxalic Acid

Initial concentrations, *M*				Products, %				
OxH_2	$HClO_4$	Cr(VI)	$[Cr(H_2O)_6]^{3+}$		$[Cr(H_2O)_6]^{3+}$	$[Cr(C_2O_4)]^+$	$[Cr(C_2O_4)_2]^-$	$[Cr(C_2O_4)_3]^{3-}$
0.166	0.097	0.0166	0.0		55.8	20.4	18.0	5.0
0.166	0.097	0.0166	0.0236	Calcd[a]	82.9	9.1	5.0	3.0
				Obsd	69.0	15.0	13.0	4.0
0.406	0.251	0.0414	0.0		48.9	23.7	18.3	8.8
0.406	0.251	0.0414	0.0525	Calcd[a]	77.1	10.6	8.2	4.1
				Obsd	63.2	17.1	13.3	6.3
0.406	0.251	0.0	0.0525	Calcd[a]	100.0	0.0	0.0	0.0
				Obsd	92.8	4.0	2.1	1.0

[a] Calculated for the assumption that no incorporation of oxalic acid into the added $Cr(H_2O)_6{}^{3+}$ ions would take place.

tion. The results reported on the last line of Table VIII show that relatively little exchange takes place when $Cr(H_2O)_6{}^{3+}$ is treated with oxalic acid in the absence of chromium(VI).

It should be noted that although extensive exchange with the added chromium(III) took place under the reaction conditions, the composition of the chromium(III) compounds isolated after the reaction in the two experiments is not identical. Thus, a full equilibrium with the added chromium(III) is obviously not reached, and the higher degree of incorporation of oxalic acid into the chromium(III) form in the oxidation reaction must indicate that the reduction of at least one oxalic acid-containing complex is indeed involved. However, due to the extensive exchange taking place, this information is only qualitative and unfortunately does not permit a more detailed insight into the reaction.

The reason for the incorporation of oxalic acid into the added chromium(III) can be understood on the basis of Altman and King's[23] work on the exchange reaction between chromium(III) and chromium(VI). These authors found that the chromium(III) and chromium(VI) exchange involves a rapid reversible reaction between chromium(VI) and chromium(III) leading to chromium(IV) and chromium(V) which in the exchange reaction is then followed by a rate-limiting reaction between chromium(V) and chromium(III). We believe that the rapid reaction between chromium(III) and chromium(VI)

$$\mathrm{Cr(III)} + \mathrm{Cr(VI)} \overset{\text{fast}}{\rightleftarrows} \mathrm{Cr(IV)} + \mathrm{Cr(V)}$$

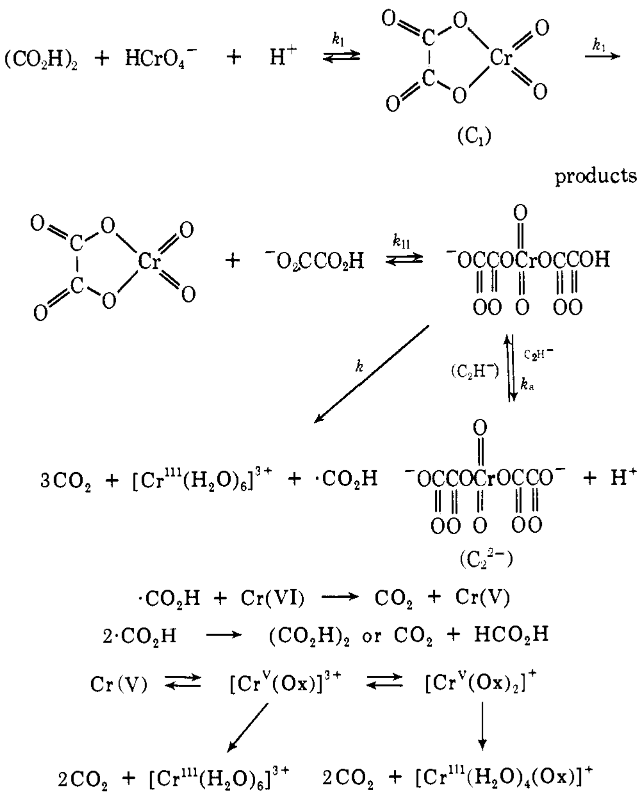
is the clue to the understanding of the facile oxalic acid incorporation by a process indicated in Scheme II.

Scheme II

$$\begin{tikzcd}
{[\mathrm{Cr^{III}(H_2O)_6}]^{3+} + \mathrm{Cr^{VI}}} \arrow[r, leftrightarrows] & {[\mathrm{Cr^{IV}(H_2O)_6}]^{4+} + \mathrm{Cr^{V}}} \\
{[\mathrm{Cr^{IV}(H_2O)_6}]^{4+} + \mathrm{OxH_2}} \arrow[r, rightleftarrows] & {[\mathrm{Cr^{IV}(H_2O)_4(Ox)}]^{2+} + 2\mathrm{H^+}} \arrow[d, shift right, "\mathrm{Cr^{V}}"'] \\
 & {[\mathrm{Cr^{III}(H_2O)_4(Ox)}]^{+}} \arrow[u, shift right, "\mathrm{Cr^{VI}}"'] \\
{[\mathrm{Cr^{IV}(H_2O)_4(Ox)}]^{2+} + \mathrm{OxH_2}} \arrow[r, rightleftarrows] & {[\mathrm{Cr^{IV}(H_2O)_2(Ox)_2}] + 2\mathrm{H^+}} \arrow[d, shift right, "\mathrm{Cr^{V}}"'] \\
 & {[\mathrm{Cr^{III}(H_2O)(Ox)_2}]^{-}} \arrow[u, shift right, "\mathrm{Cr^{VI}}"'] \\
{[\mathrm{Cr^{IV}(H_2O)_2(Ox)_2}] + \mathrm{OxH_2}} \arrow[r, rightleftarrows] & {[\mathrm{Cr^{IV}(Ox)_3}]^{2-} + 2\mathrm{H^+}} \arrow[d, shift right, "\mathrm{Cr^{V}}"'] \\
 & {[\mathrm{Cr^{III}(Ox)_3}]^{3-}} \arrow[u, shift right, "\mathrm{Cr^{IV}}"']
\end{tikzcd}$$

Mechanism. A mechanism which accounts for all experimental data in the chromic acid oxidation of oxalic acid is given in Scheme III. The first step

Scheme III



consists in a reversible formation of a neutral complex. While we have no evidence to support the proposed cyclic structure, such a structure provides a good rationalization as to why complex formations seem to be much more favored with oxalic acid which can act as a bidentate ligand than with monocarboxylic acid. Further, the cyclic structure is also in agreement with the neutral nature of the species. An open-chain oxalyl chromic acid would be a strong acid which would almost certainly lose either one or two protons. We assume that the first-order reaction observed at very low concentrations of oxalic acid involves the rate-limiting oxidative decomposition of this complex yielding carbon dioxide and probably a chromium(IV) species. As the purpose of the present study was primarily to investigate the second-order term of the reaction as a potential three-electron oxidation, no attempt was made to obtain more data for the first-order reaction. Thus, no more definitive and detailed discussion of this step can be offered at this time.

As a second step of the second-order reaction we envision the formation of a dioxalato complex. Unlike the monooxalato complex, the dioxalato complex seems

(23) C. Altman and E. L. King, *J. Amer. Chem. Soc.*, **83**, 2825 (1961).

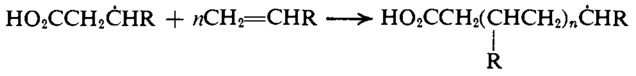
to be stable only in the form of dianion. It seems therefore more likely that the dioxalato complex has the structure of an open chain complex in which chromium(VI) retains its usual coordination number of four.

The nature of the rate law indicates that although the dianion is the predominant form in which the 1:2 complex is present, the kinetically active reaction intermediate is the monoanion. We believe that this monoanion in the rate-limiting step decomposes to yield a hexaaquochromium(III) ion, three molecules of carbon dioxide, and a $\cdot CO_2H$ radical. We are thus assuming that the rate-limiting step of the reaction consists of the one-step three-electron oxidation. The three-electron oxidation provides an attractive explanation for the obvious preference of oxalic acid to react *via* the 1:2 complex. This mechanism provides a route by which the formation of the highly unstable chromium(IV) intermediate can be avoided. The three-electron oxidation leads to the direct formation of three molecules of carbon dioxide and one relatively stable free radical.[24] It correctly predicts that at least 50% of chromium is formed originally in the form of $[Cr(H_2O)_6]^{3+}$.

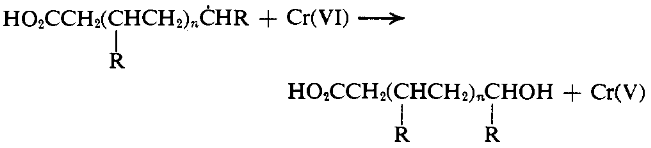
In the absence of a free-radical scavenger, the $\cdot CO_2H$ radical will react with a chromium(VI) species to yield carbon dioxide and a chromium(V) compound which then can react further with one or more molecules of oxalic acid. The observation that a larger amount of oxalato chromium(III) than would be expected from a simple equilibriation is formed seems to indicate that chromium(V) forms a complex with more than one oxalic acid molecule prior to the oxidation step. Besides undergoing oxidation, some $\cdot CO_2H$ radicals probably react in a bimolecular reaction to recombine to oxalic acid, or to disproportionate to carbon dioxide and formic acid. This reaction is necessary to explain the observed initial rate of chromium(III) formation[25] and is in agreement with the earlier observation[26] that free radicals undergo bimolecular dimerization and/or disproportionation reactions even in the presence of chromic acid.

In the presence of a free-radical scavenger, the reaction will be modified as

$$\cdot CO_2H + CH_2{=}CHR \longrightarrow HO_2CCH_2\dot{C}HR$$



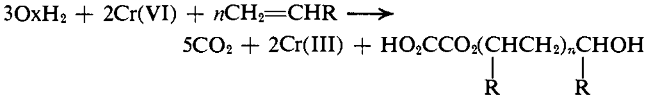
$$HO_2CCH_2\dot{C}HR + nCH_2{=}CHR \longrightarrow HO_2CCH_2(\underset{\displaystyle R}{\underset{|}{C}}HCH_2)_n\dot{C}HR$$



$$HO_2CCH_2(\underset{\displaystyle R}{\underset{|}{C}}HCH_2)_n\dot{C}HR + Cr(VI) \longrightarrow HO_2CCH_2(\underset{\displaystyle R}{\underset{|}{C}}HCH_2)_n\underset{\displaystyle R}{\underset{|}{C}}HOH + Cr(V)$$

$$Cr(V) + OxH_2 \longrightarrow Cr(III) + 2CO_2$$

The stoichiometry of the reaction then will be



$$3OxH_2 + 2Cr(VI) + nCH_2{=}CHR \longrightarrow 5CO_2 + 2Cr(III) + HO_2CCO_2(\underset{\displaystyle R}{\underset{|}{C}}HCH_2)_n\underset{\displaystyle R}{\underset{|}{C}}HOH$$

Thus, in the presence of a sufficient excess of a free-radical scavenger to trap all $\cdot CO_2H$ radicals, the yield of carbon dioxide should be reduced from six molecules to five molecules per two molecules of chromic acid, which is in exact agreement with our results.

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[24] *Cf.*, Part I of this series for a more detailed discussion and references.

[25] *Cf.* ref 17 for a more detailed discussion.

[26] M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

Activation of Aromatic Carbon–Hydrogen Bonds by Transition Metal Complexes. II.[1] Substituted Benzenes

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Abstract: Competitive exchange between D_2 and aromatics is catalyzed by polyhydride transition metal complexes. The relative rates of exchange of mono- and disubstituted benzenes increase in the order $p\text{-}(CH_3)_2 < CH_3 \sim OCH_3 < H < CF_3 \sim F < p\text{-}F_2$ for the $NbH_3(C_5H_5)_2$, $[NbH(C_5H_5)(\mu\text{-}C_5H_4)]_2$, and $IrH_5[(CH_3)_3P]_2$ catalyzed reactions. Except for *p*-xylene, only slight differences in rates were observed with $TaH_3(C_5H_5)_2$ and $TaH_3(C_5H_4CH_3)_2$. Differences in rates of the various positions were observed with the largest effect due to steric hindrance by the substituents. A mechanism involving a series of alternating reductive–elimination and oxidative–addition steps is proposed.

In recent years it has been recognized that transition metal complexes can catalytically activate aromatic C–H bonds.[2] Synthetic applications of this effect have included the selective ortho chlorination of azobenzene[3] and the ortho deuteration of triphenylphosphine.[4] These reactions seem to involve intramolecular attack on an aryl C–H bond of a coordinated ligand.

Relatively few intermolecular reactions of this sort have been observed. The reported examples include

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[1] Part I in this series is considered to be: E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).

[2] G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

[3] D. R. Fahey, *J. Organometal. Chem.*, **27**, 283 (1971).

[4] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).