The Reaction between Chromous Ion and Acetylenedicarboxylic Acid. The Nature and Reactions of Intermediate Species[1]

Rudolph S. Bottei and William A. Joern[2]

Contribution from the Department of Chemistry and the Radiation Laboratory,[3] *University of Notre Dame, Notre Dame, Indiana.* *Received March 18, 1967*

Abstract: The reaction between chromous ion and acetylenedicarboxylic acid in dilute perchloric acid solution takes place in four consecutive steps, the final products being the hexaaquochromium(III) ion and fumaric acid: (1) $2Cr^{II} + HO_2CC{\equiv}CCO_2H \longrightarrow I\,(k_1)$; (2) $I + H^+ \longrightarrow II\,(k_2)$; (3) $II + H_2O \longrightarrow III + Cr^{III}\,(k_3)$; (4) $III + H_2O \longrightarrow HO_2CCH{=}CHCO_2H + Cr^{III}\,(k_4)$. Species I and II have 2:1 ratios of Cr(II) to acetylenedicarboxylic acid. Species III is a 1:1 Cr(III)–fumaric acid complex. The kinetic rate laws, including the hydrogen ion dependence, for all the steps are: (step 1) rate $= k_1[Cr(II)]^2[HO_2CC{\equiv}CCO_2H]/[H^+]$; (step 2) rate $= k_2K[H^+][I]/(1 + K[H^+])$; (step 3) rate $= \{k_3 + (k_3'/[H^+])\}[II]$; (step 4) rate $= \{k_4 + k_4'[H^+]\}[III]$. For step 2, $K \simeq 1.6$, $\Delta H^{\ddagger} = 14.8 \pm 3.0$ kcal/mole, and $\Delta S^{\ddagger} = -22.1 \pm 4.4$ eu. Infrared data indicate that there is strong interaction of the carboxyl groups with the chromium ions in all the intermediate species.

Certain acetylenes are reduced to the corresponding *trans*-olefins by chromous ion in aqueous solution or in mixed solvents.[4] Acetylenedicarboxylic acid, phenylpropiolic acid, propargyl alcohol, and 1-butyn-3-ol are reduced quite rapidly; phenylacetylene, 2-carboxydiphenylacetylene, and 2-butyn-1-ol are reduced less easily; and diphenylacetylene, 4-carboxydiphenylacetylene, and 2,5,5-trimethyl-3-hexyn-2-ol are relatively inert. Thus, the functional groups adjacent to the acetylenic carbons have a pronounced effect upon the ease of reduction.

Of interest in the reaction of chromous ion with acetylenedicarboxylic acid (referred to from now on as "Adca") is the formation of a red-brown color immediately after the reactants are mixed. With time, the color of the reaction mixture slowly changes to the blue-violet characteristic of chromium(III) species. This is in contrast to the chromous sulfate–propargyl alcohol reaction, in which the color changes from the sky blue of the aquated chromous ion to the light green of the $CrSO_4^+$ product upon mixing the reagents.[4] Apparently the presence of the carboxyl groups causes the former reaction to take place by a mechanism quite different from that of the latter.

It was thought that a careful study of the reaction between chromous ion and acetylenedicarboxylic acid would lead to a better understanding of the role of the functional groups adjacent to the acetylenic carbon atoms in these reductions.

Experimental Section

Water used in the experiments was distilled a second time from alkaline permanganate in an all-Pyrex still. Chromium(III) perchlorate was prepared from chromium trioxide and hydrogen peroxide (both Mallinckrodt AR) in perchloric acid (G.F. Smith, ACS) and recrystallized twice from water.[5] Chromous solutions were prepared from chromic perchlorate solutions by reduction with amalgamated zinc[6] or by electrolytic reduction[7] and stored in bottles fitted with serum caps. The prepurified nitrogen gas used in preparing and handling the chromous solutions was passed through two chromous sulfate solutions to remove traces of oxygen. The chromous solutions were dispensed with a gas-tight syringe, except in the continuous variation study, in which an apparatus described by Lingane and Pecsok[6] was used.

The total chromium content of the solutions was determined by oxidizing an aliquot in alkaline medium to the chromate species and comparing the absorbance at 372 mμ to that of a standard chromate solution.[8] To obtain the chromous ion concentration, an aliquot was injected into a degassed iron(III) sulfate solution, and the iron(II) produced was titrated with standard dichromate using *p*-diphenylaminesulfonic acid as the indicator.[9] The hydrogen ion concentration of the chromous solutions prepared electrolytically was determined by passing an air-oxidized aliquot through a Dowex 50 W-X8 ion-exchange resin in the acid form and titrating the acid eluted. Knowing the concentration of Cr(II) and Cr(III) in the solution, the hydrogen ion concentration was calculated from the relationship: moles of H^+ = moles of H^+ of eluent − 2[moles of Cr(II)] − 3[moles of Cr(III)].[10]

The monopotassium salt of acetylenedicarboxylic acid (Eastman White Label) was used without further purification. The free acid was prepared from the monopotassium salt by the method of Truce and Kruse.[11] Deuterium oxide (99.5%) was from Columbia Organic Chemicals Co., Inc. Solutions of sodium perchlorate were prepared by neutralizing perchloric acid with carbonate-free sodium hydroxide (Baker, ACS).

In the continuous variation experiment, a solution containing the acetylene was degassed for 30 min and the proper amount of chromous solution added. The absorbance of the solution (in a 1.00-cm cell) was then recorded on a Beckman DB spectrophotometer-Sargent SRL recorder unit.

To study the spectral changes *vs.* time at low pH, a solution of Adca and perchloric acid was degassed for 1 hr in a 4.00-cm cell, the chromous solution was injected, and the spectra were recorded.

For the ir study, a solution of chromous sulfate in deuteriosulfuric acid was prepared by the method of Lux and Illman,[12] using 99.999% chromium metal purchased from the Gallard-Schlesinger Chemical Mfg. Corp., New York, N. Y. The D_2SO_4 was obtained by reaction of sulfur trioxide with D_2O.[13] The proper amount of Adca was put in a vial fitted with a serum cap, a certain volume of D_2O added, and the resulting solution degassed for 20 min with prepurified nitrogen which was passed through concentrated

---

[1] (a) Presented in part before the Division of Physical Chemistry, 150th National Meeting of the American Chemical Society, Sept 1965, Abstracts, p V65; (b) taken from the Ph.D. Thesis of W. A. Joern, University of Notre Dame, Aug 1967; (c) part of this work done at Gannon College, Erie, Pa.

[2] The Monsanto Co., St. Louis, Mo.

[3] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-423.

[4] C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, **86**, 4358 (1964).

[5] A. L. Phipps and R. A. Plane, *ibid.*, **79**, 2458 (1957).

[6] J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

[7] R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

[8] R. J. Baltisberger and E. L. King, *ibid.*, **86**, 795 (1964).

[9] N. H. Furman, Ed., "Standard Methods of Chemical Analysis," Vol. 1, 6th ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1962, p 542.

[10] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

[11] W. E. Truce and R. B. Kruse, *ibid.*, **81**, 5372 (1959).

[12] H. Lux and G. Illman, *Chem. Ber.*, **91**, 2143 (1958).

[13] R. H. Herber, *Inorg. Syn.*, **7**, 155 (1963).

sulfuric acid before it entered the vial. The chromous solution was then injected, the vial shaken, and after 5 min the solution put into a liquid sample infrared cell (barium fluoride windows) having a path length of 0.05 mm. The spectra were obtained on a Perkin-Elmer 521 or Infracord spectrophotometer, with the reference cell containing D_2O. A sample of α,β-dideuteriofumaric acid was isolated from this reaction mixture by the procedure of Castro and Stephens[4] and recrystallized once from ether–petroleum ether (bp 40–70°) and once from water. The infrared spectra of the solid in KBr and the solution (D_2O) were quite similar to that of fumaric acid, except that the fumaric acid peaks at 2712, 2550, 1422, 1276, and 928 cm^{-1} (KBr) were shifted to 2695, 2570, 1417, 1257, and 916 cm^{-1}, respectively, in the deuterated compound. A strong peak at 1685 cm^{-1} was found in both compounds. The carboxylate bands of the organic acids were observed by adding NaOD to the solutions. The NaOD was prepared by allowing metallic sodium to react with D_2O.

To study the pH change during the reaction, solutions of Acda were prepared and degassed, and the pH was measured with glass–calomel electrodes using a Beckman expanded-scale pH meter. While the electrodes were still in the solution and with the nitrogen gas still flowing through the system, the stoichiometric amount of chromous solution was injected and the pH read after various time intervals.

The resin used for the ion-exchange studies, Dowex 50W-X8, was pretreated in the manner described by Thompson and Gordon.[14] The column was 1 cm in diameter and 10 cm long, and was kept at 4° during the elutions.

The polarographic studies were carried out using a Leeds and Northrup Type E or a Heath No. EUW-401 polarographic apparatus. Two- or three-electrode systems were employed, using a dropping mercury test electrode, a calomel reference electrode, and a platinum counter electrode. Sodium perchlorate or perchloric acid was used as the supporting electrolyte. The temperature was not controlled but was fairly constant at about 24°.

In the experiments designed to obtain the kinetics of formation of species I, a solution containing Adca and one containing sodium perchlorate and perchloric acid were degassed and added to a 1.00-cm cell fitted with a serum cap. The cap was left in the thermostated cell compartment of the spectrophotometer for 10–20 min, a thermostated Cr(II) solution injected, and the absorbance at 542 mμ recorded as a function of time.

The concentration of chromous ion could be calculated at any time from the relationships

$$A^{542} = \epsilon_c[\mathrm{C}] + \epsilon_{\mathrm{Cr(II)}}[\mathrm{Cr(II)}] \qquad \text{(a)}$$

$$[\mathrm{Cr(II)}]_0 = [\mathrm{Cr(II)}] + 2[\mathrm{C}] \qquad \text{(b)}$$

from which the following expression can be derived

$$[\mathrm{Cr(II)}] = \frac{(\epsilon_c[\mathrm{Cr(II)}]_0/2) - A^{542}}{\epsilon_c/2 - \epsilon_{\mathrm{Cr(II)}}}$$

where A^{542} is the absorbance of the solution at 542 mμ, C refers to a 2:1 chromous ion–Acda adduct,[15] ϵ_c and $\epsilon_{\mathrm{Cr(II)}}$ are the molar absorptivity indexes of the adduct and Cr(II), respectively, at 542 mμ, and $[\mathrm{Cr(II)}]_0$ is the initial concentration of the chromous ion.

In the reactions involving stoichiometric amounts of the reagents, the data were analyzed using the equation[16]

$$\frac{1}{[\mathrm{Cr(II)}]^2} - \frac{1}{[\mathrm{Cr(II)}]_0^2} = k_{\mathrm{obsd}}t$$

When nonstoichiometric ratios were used, the equation[17]

$$\frac{1}{2B_0 - A_0}\left(\frac{1}{A} - \frac{1}{A_0}\right) + \frac{2(2.303)}{(2B_0 - A_0)^2}\log\frac{B_0A}{A_0B} = k_{\mathrm{obsd}}t$$

was used, where A_0 and B_0 refer to the initial concentrations of chromous ion and Acda, respectively, and A and B refer to their concentrations at time t.

To study the reaction, I + H^+ → II (k_2), chromous solution was added to a degassed solution of Adca at high pH. The mixture was allowed to stand for 10 min to ensure quantitative formation of species I. Aliquots were then added to thermostated acid–salt solutions, and the resulting mixture was poured into 1.00-cm spectrophotometric cells. The cells were placed in the thermostated (17–30°) cell compartment of a Beckman DU-2 spectrophotometer, and the absorbance at 270 mμ was recorded at various time intervals. Plots of log $(A_t - A_\infty)/(A_0 - A_\infty)$ *vs.* time were linear to greater than 90% completion.

A similar technique was used to study the hydrolysis reactions of species II and species III. After forming species I at high pH, a reaction mixture was added to a thermostated acid–salt solution and the resulting solution poured into 1.00-cm spectrophotometric cells. After being in the thermostated (50.8°) cell compartment of the DU-2 for 20 min, reaction of species I to form species II was judged complete. The absorbance *vs.* time data at 538 mμ (the isosbestic point for the reaction of species I to form species II as measured on the DU-2) and at 570 mμ for the slow reactions of species II and III were recorded over a period of 2 days. The experimental absorbance values at 538 mμ were then plotted *vs.* time, a smooth curve was drawn through the points, and interpolated values of the absorbance were obtained at 100-min intervals. The data were then treated by a computer program designed for consecutive first-order reactions as illustrated in the text by Wiberg.[18] This program was modified for reactions of the type A → B + C (k_3) and B → C (k_4), which apply in the present case. The values of the molar absorptivity indexes at 538 mμ for species II, species III, and hexaaquochromium(III) ion which were used in the computer program are 56.7, 22.9, and 10.2 M^{-1} cm^{-1}, respectively. Initial estimates of k_3 were obtained from the data at the beginning of the reaction, when no appreciable amount of species III had formed. During the latter stages of the reaction, when a very small concentration of species II remained, the initial estimates of k_4 were made. Further details of the method can be found.[19]

Results

Visible–Ultraviolet Spectra. When a chromous perchlorate solution is added to a degassed aqueous solution of Adca at pH 2–3, a light yellow color is observed, which changes to red-brown after a few minutes. The visible–ultraviolet spectrum shows wavelength maxima at 272 mμ (ε 2720), 384 (158), and 488 (45.5).

The data from a continuous variation experiment at high pH are plotted in Figure 1. The results indicate that the stoichiometric ratio of reactants is 2 moles of chromous ion to 1 mole of Adca. The same result is evident from the potentiometric titration of Adca with standard chromous chloride.[20]

In another experiment, an aliquot of a reaction mixture (2.03×10^{-2} M Cr(II), 1.12×10^{-2} M Adca) at pH 2–3 was withdrawn 2 min after mixing and tested for the presence of unreacted Cr(II). Only 6% of the Cr(II) originally present was detected.

In a solution of pH 2–3, the wavelength maxima at 384 and 488 mμ decrease over a period of about 10 hr to final values of 402 mμ (ε 64) and 516 mμ (ε 34), and the color becomes a light red-violet. During this change, an isosbestic point is observed at 542 mμ (ε 30). These results indicate that an initial adduct (I) is formed from chromous ion and Adca (maxima at 384 and 488 mμ), and this in turn reacts further to form a second species (II) (maxima at 402 and 516 mμ).

The behavior of the system at low pH ($[H^+] = 0.4$ M) is quite different. In this case, the color immediately

---

(14) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).

(15) More exactly, *C* refers to the sum of the concentrations of two species, one formed from the other. However, since 542 mμ is an isosbestic point of the two species, the sum is essentially a measure of how much of the initial 2:1 adduct has been formed.

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 14.

(17) Reference 16, pp 20–21.

(18) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 181–185.

(19) W. A. Joern, Ph.D. Thesis, University of Notre Dame, Aug 1967, pp 17–22.

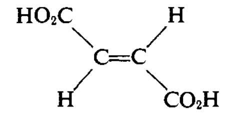
(20) R. S. Bottei and N. H. Furman, *Anal. Chem.*, **27**, 1183 (1955).

after mixing is blue and changes to yellow after about 5 min. The dark red-brown color is not observed. The initial spectrum shows wavelength maxima close to 384 and 488 mμ, as well as the Cr(II) peak at about 700 mμ, but the absorbancies at the peaks are quite low. After a short time the maxima shift toward the red and the absorbancies increase, until after about 10 hr the spectrum is identical with that of species II.

If the solution containing species II is heated at 65°, the maxima slowly shift and the absorbancies decrease. At a hydrogen ion concentration of 0.25 *M*, there seems to be a relatively fast change to a spectrum having wavelength maxima at about 410 mμ (ϵ 25) and 568 mμ (ϵ 22), and the color of the solution becomes violet. After 24 hr at 65°, the spectrum was identical with that of the hexaaquochromium(III) ion. Polarographic analysis of this solution resulted in $E_{1/2}$ and i_d values identical with those of a synthetic mixture of $Cr(H_2O)_6^{+3}$ and fumaric acid at the same concentrations.

pH Change during Reaction. On the basis of the continuous variation study, the potentiometric titration study,[20] and the fact that 94% of the expected amount (no other organic products are found) of fumaric acid can be isolated from the reaction mixture,[4] the stoichiometry of the over-all reaction can be written as

$$2Cr^{II} + HO_2CC{\equiv}CCO_2H + 2H^+ = 2Cr^{III} +$$



Since the over-all reaction consumes hydrogen ions, the pH of a reaction mixture was followed as a function of time. To a solution of Adca was added enough Cr(II) solution so that the final concentrations were 0.010 *M* Cr(II), 0.0050 *M* Acda, and 0.010 *M* $HClO_4$. The pH immediately after mixing was 1.93; 15 min later, still 1.93; 5 hr later, 2.04; and after 20 hr, 2.19. The pH of a "blank" solution of 0.010 *M* Cr(II) in 0.010 *M* $HClO_4$ was 1.95. These results indicate that hydrogen ion is not consumed during the initial reaction, but rather during the change from species I to species II, and perhaps during subsequent reactions of species II.

Ion-Exchange Studies. When a reaction mixture of Cr(II) and Adca is put on a Dowex 50 W-X8 column 5 min after mixing and eluted with 0.50 *M* $HClO_4$, a small amount (about 2.5% of the total chromium present in the reaction mixture) of a red-pink colored species is found, having wavelength maxima at about 396 mμ (ϵ 90) and about 502 mμ (ϵ 70).

Elution with 3.0 *M* $HClO_4$ produces red-violet colored fractions containing the majority of the chromium and having maxima at 402 mμ (ϵ 64) and 516 mμ (ϵ 34). The shape of the spectra of all the 3.0 *M* $HClO_4$ fractions was essentially the same. These fractions apparently contain species II. About 15% of the total chromium remained on the column, even after elution with 70% $HClO_4$.

Certain fractions of both the 0.50 *M* and the 3.0 *M* eluents were heated at 65° overnight and analyzed for fumaric acid by comparing the absorbance at 208 mμ to a standard fumaric acid solution of similar acidity. The total chromium content of the eluents was determined by oxidation to chromate.[8] The 0.50 *M* eluent indicated a Cr/fumaric acid ratio of 0.9,[21] while the ratio for the 3.0 *M* eluents was 2.2.

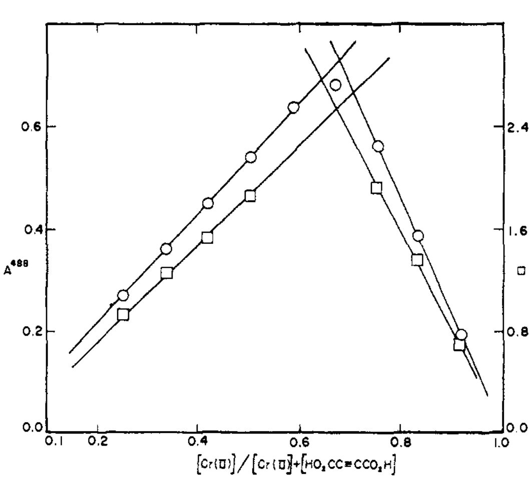


Figure 1. Continuous variation plots for reaction mixtures of Cr(II) and acetylenedicarboxylic acid: (○) *A* at 488 mμ; (□) *A* at 384 mμ; $[H^+] = 0.001$ *M*.

In another experiment, an amount of $Cr(H_2O)_6^{+3}$ was added to the reaction mixture before elution. The initial fractions of the 3.0 *M* eluents were rich in $Cr(H_2O)_6^{+3}$, whereas the latter fractions contained mostly species II, showing that $Cr(H_2O)_6^{+3}$ is eluted faster than species II.

When the reaction mixture was allowed to stand for 2 days before treatment, a greater amount (two- or threefold) of the species with maxima at 396 and 502 mμ was eluted by the 0.50 *M* $HClO_4$. Elution by 3.0 *M* $HClO_4$ indicated the presence of $Cr(H_2O)_6^{+3}$ (or a species having similar wavelength maxima) in the earlier fractions, but the latter fractions become more concentrated in species II.

After standing for 4 days, there was a negligible amount of chromium in the 0.50 *M* fractions, and the 3.0 *M* eluents had spectra similar to that of $Cr(H_2O)_6^{+3}$.

Polarographic Studies. It was found in reaction mixtures of Cr(II) and Adca that some waves were fairly sharp and easy to interpret, but waves at more negative potentials, presumably due to reduction of chromium, were difficult to analyze. Nevertheless, some useful data were obtained.

The reactants were mixed at high pH to facilitate the quantitative formation of the initial adduct; then aliquots were pipeted into solutions of perchloric acid after standing various amounts of time. The results are summarized in Table I.

It was found that the potential of the first wave (at −0.71 v) was dependent on hydrogen ion concentration: at $[H^+] = 0.50$ and 0.01 *M*, the wave appeared at −0.81 and −1.04 v, respectively. The potential of the wave due to $Cr(H_2O)_6^{+3}$ in 3.0 *M* $HClO_4$ is −0.89 v.

Infrared Studies. Solutions studied by infrared techniques were 20 times more concentrated than those of the other experiments in this paper, and chromous sulfate solutions were used rather than chromous perchlorate. Listed in Table II are the peaks for D_2O solutions of α,β-dideuteriofumaric acid, Adca, and the

---

[21] This fraction may contain a Cr(III)-maleic acid chelate, which would explain the Cr/organic acid ratio, the high absorptivity indexes, and the low charge (Cr(III) complexes with a +1 charge are eluted easily with 0.5 *M* perchloric acid). However, no further studies of the species in this fraction have been attempted.

Table I. Polarographic Study[a]

Run	Time after mixing, min	$E_{1/2}$, v	i_d, μa	$E_{1/2}$, v	i_d, μa	$E_{1/2}$, v	i_d, μa
No. 1	1	−0.71	6.6			−0.98	5.3
(No. 1b)	. .[b]	−0.71	6.4	−0.88	2.5	−0.98	3.0
No. 2	30	−0.71	8.4			−0.98	2.5

[a] $[Cr(II)] = 1.5 \times 10^{-3}$ *M*; $[Adca] = 7.5 \times 10^{-4}$ *M*; $[H^+] = 3.0$ *M*; $T = 24°$. [b] Reaction mixture no. 1 after standing 170 min.

Table II. Infrared Spectra

α,β-Dideuteriofumaric acid (~0.06 *M*)			Acetylenedicarboxylic acid (0.18 *M*)			Reaction mixture[a]		
ν, cm⁻¹	Assignment	Ref	ν, cm⁻¹	Assignment	Ref	After 10 min	After 24 hr	After 1 month
1696 (s)	$-CO_2D$	*b*	1697 (s)	$-CO_2D$			1696 (s)	1696 (s)
1614 (w)	C=C	*b*	1614 (s)			1664 (b)	Gone	
			1589 (s)			1601 (s)	1601 (s)	Gone
1570 (s)	$-CO_2^-$ (as)	*b*				1566 (s)	Gone	
1560 (s)						1534 (s)	Gone	
			1449 (w)			1479 (s)	1479 (s)	Gone
1374 (s)	$-CO_2^-$ (sym)	*b*				1405 (s)	1405 (s)	Gone
			1349 (s)	$-CO_2D$	*d*			
1344 (s)	C—O and O—H	*c*					1344 (b)	1344 (b)
			1336 (s)					
						1314 (b)	Gone	

[a] $[Cr(II)] = 0.32$ *M*; $[Adca] = 0.16$ *M*; $[D^+] = 0.32$ *M*. [b] D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, 550 (1964). [c] T. Takenishi, *Nippon Kagaku Zasshi*, **82,** 319 (1961). [d] D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (London), **A216,** 247 (1953).

reaction mixture at various times after mixing (the reactants were mixed at high pH to ensure quantitative formation of the initial 2:1 adduct, and the proper amount of D_2SO_4 was added after 5 min). Peaks observed in "blank" solutions of chromic sulfate in D_2O are omitted.

Kinetic Studies. A kinetic analysis of the absorbance increase at 542 mμ *vs.* time data indicated that a third-order rate law was obeyed for the reaction: $2Cr^{II}$ + Adca → species I (k_1). Rate plots were linear to at least 90% completion. Results of experiments designed to test the order of reaction are listed in Table III.

Table III. k_{obsd} at Different Initial Concentrations of Cr(II) and $HO_2CC{\equiv}CCO_2H$ for the Formation of Species I[a]

[Cr(II)], $M \times 10^2$	[Adca], $M \times 10^2$	k_{obsd}, M^{-2} sec⁻¹	[Cr(II)]/[Adca]
0.972	0.486	24.4	2.00
0.972	0.486	26.1	2.00
4.70	0.486	23.6	9.70
0.972	1.949	21.1	0.50
1.949	1.949	24.0	1.00
1.949	0.975	24.6	2.00
0.972	7.776	21.4	0.125
4.70	0.235	19.1	20.0

[a] $[H^+] = 0.33$ *M*, adjusted with perchloric acid; $\mu = 0.50$ *M*, adjusted with sodium perchlorate; $T = 29.6°$; $\lambda = 542$ mμ.

The products of $[H^+]k_{obsd}$ at various hydrogen ion concentrations are listed in Table IV.

The rate constants at three temperatures and various acidities are plotted against the reciprocal of the $[H^+]$ in Figure 2. The effect of ionic strength upon the rate constants is shown in Figure 3.

Kinetic data were obtained for the reaction of species I with hydrogen ion to form species II. The effect of temperature, hydrogen ion concentration, and ionic strength upon the observed rate constants is shown in Table V. A plot of $1/k_{obsd}$ *vs.* $1/[H^+]$ at three temperatures is shown in Figure 4. The rate constants at various hydrogen ion concentrations obtained from the computer analysis of the data for the hydrolysis reactions of species II and species III are listed in Table VI. The values of k_{obsd} for the hydrolysis of species II are plotted *vs.* $1/[H^+]$ in Figure 5, and Figure 6 shows the values of k_{obsd} for the reaction of species III plotted *vs.* $[H^+]$.

Table IV. The Product of $k_{obsd}[H^+]$ for the Formation of Species I[a]

	k_{obsd}, M^{-2} sec⁻¹		
$[H^+]$, *M*	22.4°	29.6°	36.4°
0.10		8.20	
0.14	5.01	8.21	11.8
0.20	4.90	8.70	12.9
0.25		8.62	
0.33	6.10	8.64	12.7
0.50	4.97	8.05	11.5
0.70		9.30	
1.00	5.90	8.42	11.4
1.40		8.05	
	5.38 ± 0.50	8.47 ± 0.33	12.02 ± 0.58

[a] $[Cr(II)] = 9.67 \times 10^{-3}$ *M*; $[Adca] = 4.84 \times 10^{-3}$ *M*; $\mu = 1.43$ *M*, adjusted with sodium perchlorate.

Discussion

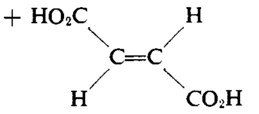
Over-all Reaction. The results indicate that the over-all reaction occurs in four steps (eq 1–4). Evi-

$$2Cr^{II} + HO_2CC{\equiv}CCO_2H \xrightarrow{k_1} I \tag{1}$$

$$I + xH^+ \xrightarrow{k_2} II \tag{2}$$

$$II + H_2O \xrightarrow{k_3} III + Cr^{III} \tag{3}$$

$$III + H_2O \xrightarrow{k_4} Cr^{III} +$$



(4)

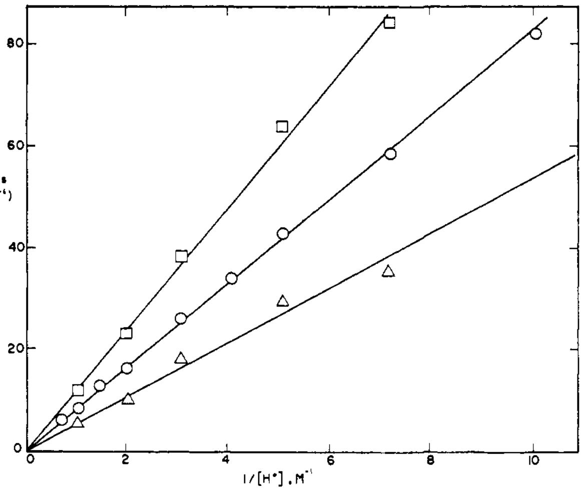


Figure 2. Observed rate constants at different temperatures for reaction of Cr(II) (9.67 × 10^{-3} *M*) and acetylenedicarboxylic acid (4.84 × 10^{-3} *M*) plotted *vs.* $1/[H^+]$: μ = 1.43 *M;* (□) at 36.4°; (○) at 29.6°; (△) at 22.2°. From absorbance *vs.* time data at 542 mμ.

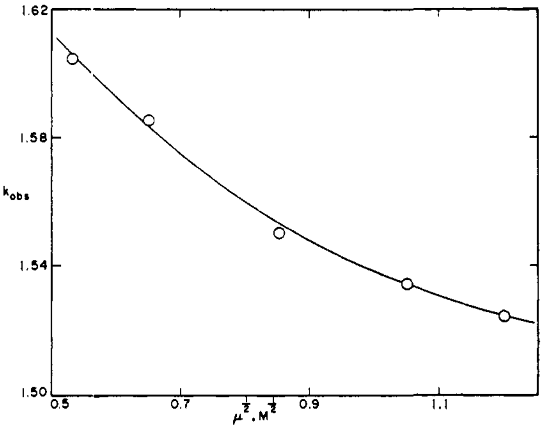


Figure 3. Logarithm of the observed rate constant for the reaction of Cr(II) (9.67 × 10^{-3} *M*) and acetylenedicarboxylic acid (4.84 × 10^{-3} *M*) plotted *vs.* the square root of the ionic strength; *T* = 29.6°; $[H^+]$ = 0.25 *M*. From absorbance *vs.* time data at 542 mμ.

dence that species I is a 2:1 rather than a 1:1 adduct comes from the fact that essentially all of the Cr(II) has reacted after about 2 min of reaction at high pH (it requires about 10 hr for species II to be formed from species I under the same conditions). Also, the visible spectrum shows no peak at 700 mμ, the Cr(II) maximum, and no discontinuity at 560–580 mμ, where Cr(III) species would absorb.

That species II also has a 2:1 ratio, rather than being a 1:1 species with an equimolar amount of Cr(III) present, is indicated by the lack of a polarographic wave due to $Cr(H_2O)_6^{+3}$ in the reaction mixture and the fact that the spectra of all the 3.0 *M* $HClO_4$ eluents in the ion-exchange study were identical and had a 2:1 chromium–fumaric acid ratio. If $Cr(H_2O)_6^{+3}$ were present, it would have been eluted faster than species II, and the spectra of the earlier fractions would have been different from those of the latter. That hydrogen ion is consumed in step 2 is deduced from the pH *vs.* time study.

The assumption that species II is a 2:1 complex leads to the necessity of a two-step mechanism to reach the final products. The fact that the kinetic data for the hydrolysis of species II and III fit a consecutive reaction scheme is evidence, then, for steps 3 and 4.

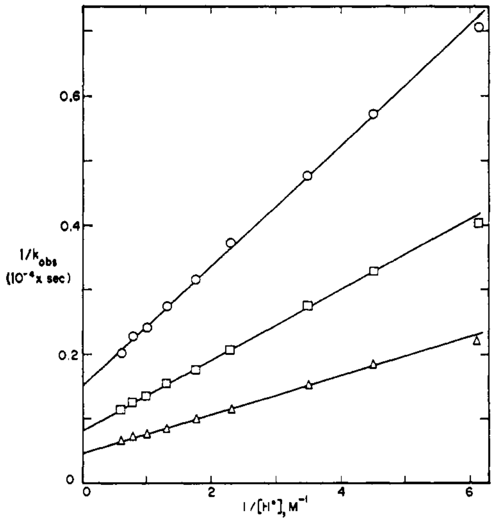


Figure 4. The reciprocal of the observed rate constants at three temperatures for the reaction of species I (1.24 × 10^{-4} *M*) with hydrogen ion plotted *vs.* $1/[H^+]$; μ = 1.7 *M*. From absorbance *vs.* time data at 270 mμ; (○) at 17.2°; (□) at 23.6°; (△) at 30.2°.

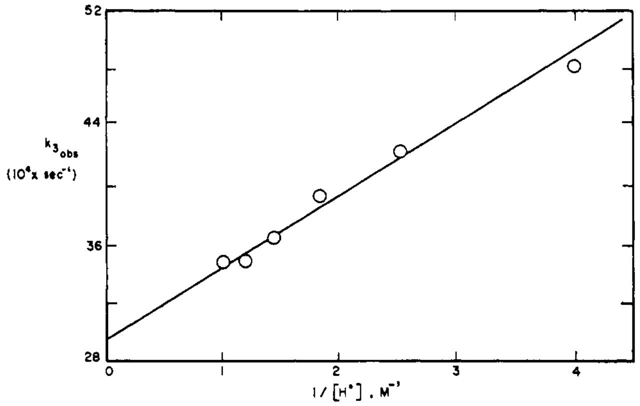


Figure 5. Observed rate constants for the hydrolysis of species II (7.67 × 10^{-3} *M*) plotted *vs.* $1/[H^+]$; *T* = 50.8°; μ = 1.0 *M*. From absorbance *vs.* time data at 538 mμ.

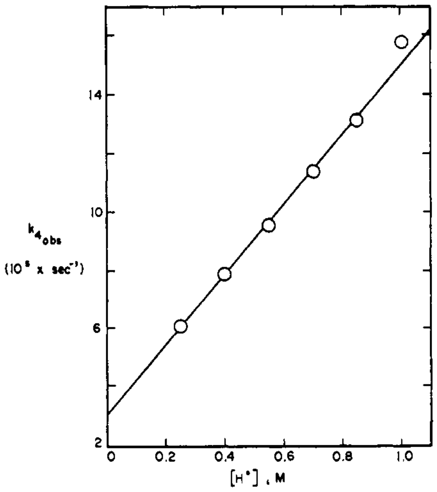


Figure 6. Observed rate constants for the hydrolysis of species III (7.67 × 10^{-3} *M*) plotted *vs.* $[H^+]$; *T* = 50.8°; μ = 1.0 *M*. From absorbance *vs.* time data at 538 mμ.

Table V. k_{obsd} for the Reaction of Species I as a Function of Acidity, Temperature, and Ionic Strength[a]

[H+], M	μ,[b] M	T, °C	k_{obsd}, 10^4 sec^{-1}
1.68	1.7	17.2	4.95
1.30	1.7	17.2	4.38
1.01	1.7	17.2	4.09
0.769	1.7	17.2	3.65
0.576	1.7	17.2	3.17
0.432	1.7	17.2	2.68
0.288	1.7	17.2	2.09
0.221	1.7	17.2	1.75
0.163	1.7	17.2	1.42
1.68	1.7	23.6	8.70
1.30	1.7	23.6	8.10
1.01	1.7	23.6	7.38
0.769	1.7	23.6	6.51
0.576	1.7	23.6	5.76
0.432	1.7	23.6	4.85
0.288	1.7	23.6	3.63
0.221	1.7	23.6	3.04
0.163	1.7	23.6	2.47
1.68	1.7	30.2	15.8
1.30	1.7	30.2	13.9
1.01	1.7	30.2	13.3
0.769	1.7	30.2	12.0
0.576	1.7	30.2	10.2
0.432	1.7	30.2	8.95
0.288	1.7	30.2	6.65
0.221	1.7	30.2	5.46
0.163	1.7	30.2	4.58
0.40	0.40	25.6	4.50
0.40	0.55	25.6	4.64
0.40	0.70	25.6	4.67
0.40	0.85	25.6	4.58

[a] [Cr(II)] = 2.43×10^{-4} *M*; [Adca] = 1.24×10^{-4} *M*. [b] Adjusted with sodium perchlorate.

Table VI. k_{obsd} at Various Hydrogen Ion Concentrations for the Hydrolysis Reactions of Species II and Species III[a]

[H+], M	k_{obsd}, 10^{-6} sec^{-1} Species II	 Species III
1.00	34.8[b]	15.8[b]
0.85	34.8	13.1
0.70	36.4	11.4
0.55	39.5	9.48
0.40	42.5	7.82
0.25	48.2	6.03

[a] [Cr(II)] = 1.53×10^{-2} *M*; [Adca] = 7.67×10^{-3} *M*; *T* = 50.8°; μ = 1.0 *M*, adjusted with sodium perchlorate. [b] These are averages of 15–17 experimental values of absorbance *vs.* time. The standard deviations from the computer program were 1–3% of the listed values.

The polarographic study can be interpreted in terms of the suggested reaction scheme. The waves at −0.98 and −0.71 v could be due to species I and species II, respectively. Comparing run no. 1 and 2, the data show that species I would decrease and species II would increase with the amount of time the mixture stands at pH 2–3. Comparing run no. 1 after 170 min (run no. lb) to the initial results, it can be argued that the decrease in i_d at −0.98 v is caused by the reaction of species I to form species II, and the new wave at −0.88 v is due to species III, $Cr(H_2O)_6^{+3}$, or both, formed by the hydrolysis of species II. The constancy of the i_d at −0.71 v would then be explained by assuming that the concentration of species II is simultaneously being increased by the former reaction and decreased by the latter.

Infrared Data. Evidence that the carboxyl groups of Adca are participating in some type of bonding with chromium is found in the infrared spectra of the reaction mixtures. None of the free carboxyl bands of Adca or fumaric acid is observed immediately after mixing. Since the conversion of species I to species II is quite rapid in acidic solution (at [H+] = 0.5*M*, a solution of 0.01 *M* Cr(II) was converted to species II after 20 min), it is probable that most of the chromium was in the form of species II when the first ir spectrum was recorded. Thus, all the observed peaks may be characteristic of species II.

The presence of so many peaks in the carboxyl region suggests that each carboxyl group of species II may be in a different environment. Indeed, the peaks can be divided into two groups. One group, at 1664, 1566, 1534, and 1314 cm^{-1}, gradually disappears from the spectrum after about 24 hr; the other, at 1601, 1479, and 1405 cm^{-1}, is lost much more slowly. The bands at 1601 and 1405 cm^{-1} indicate a $-CO_2^-$ group coordinated to chromium, since Fraser[22] reports that bands at 1600 and 1400 cm^{-1} are due to a $-CO_2^-$ group coordinated to cobalt in a chlorofumaratopentaamminecobalt(III) ion. Ferraro[23] suggests that in metal salts of carboxylic acids the carbonyl band of the free acid is lost, and two bands due to the asymmetric stretch and symmetric stretch of the carboxylate group appear at 1550–1610 and 1300–1400 cm^{-1}, respectively. It is possible that the bands at 1566 and 1534 cm^{-1} and that at 1314 cm^{-1} are due to the asymmetric and symmetric stretch, respectively, of a $-CO_2^-$ group of Adca, shifted to lower wavenumbers because of some interaction with chromium.

Thus, the disappearance after 1 day of the peaks at 1664, 1566, 1536, and 1314 cm^{-1}, together with the appearance of the free carbonyl bands at 1696 and 1344 cm^{-1} (found in the fumaric acid spectrum), would correspond to the hydrolysis of species II to species III, the latter having one carboxyl group bound to a chromium ion and the other group free. The slow disappearance of the peaks at 1601, 1479, and 1405 cm^{-1} would correspond to the slow hydrolysis of species III.

The bands at 1664 and 1479 cm^{-1} have not been identified. They may be due to a type of metal–acetylene or metal–olefin interaction. A band at 1700 cm^{-1} has been found in complexes containing rhenium–,[24] platinum–,[25] and mercury–acetylene[26] bonds. Metal–olefin bands have been reported in the 1500-cm^{-1} region.[27]

Mechanism of Step 1. The dependence of the rate constants upon the reciprocal of the hydrogen ion concentration can be explained by a mechanism involving an equilibrium step which produces hydrogen ions prior to the rate-determining step. This reaction is not $Cr_{aq}^{+2} \rightleftharpoons CrOH^+ + H^+$, for it has been found that the reduction of propargyl alcohol with Cr(II) is not significantly acid dependent.[4] It appears then that the dis-

---

[22] R. T. M. Fraser, *J. Am. Chem. Soc.*, **84**, 3436 (1962).

[23] J. R. Ferraro, *J. Chem. Educ.*, **38**, 201 (1961).

[24] R. Colton, R. Levitus, and G. Wilkinson, *Nature*, **186**, 233 (1960).

[25] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[26] W. L. Budde and R. E. Dessy, *J. Am. Chem. Soc.*, **85**, 3964 (1963).

[27] (a) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, pp 376–379; (b) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

sociation of Adca would be the step that produces hydrogen ions.

The third-order rate law for the disappearance of Cr(II) can be explained by a mechanism similar to that proposed by Castro for Cr(II)-acetylene[4] and -olefin[28] reductions. The acid dissociation reaction

$$HO_2CC{\equiv}CCO_2H \overset{K_\alpha}{\rightleftharpoons} H^+ + HO_2CC{\equiv}CCO_2^- \qquad (5)$$

would be followed by the formation of a 1:1 Cr(II)-acetylene complex,[29] which is a reversible reaction, K_π being small.

$$Cr^{II} + HO_2CC{\equiv}CCO_2^- \overset{K_\pi}{\rightleftharpoons} [Cr{\cdot}HO_2CC{\equiv}CCO_2^-] \qquad (6)$$

The rate-determining step is the reaction of another chromous ion with the 1:1 complex to form a 2:1 adduct.

$$Cr^{II} + [Cr{\cdot}HO_2CC{\equiv}CCO_2^-] \xrightarrow{k_1} [Cr_2{\cdot}HO_2CC{\equiv}CCO_2^-] \qquad (7)$$

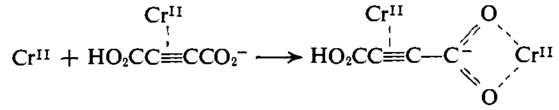
The complete rate law would then take the form[30]

$$\text{rate} = \frac{k_1K_\alpha K_\pi}{[H^+]}[Cr(II)]^2[HO_2CC{\equiv}CCO_2H]$$

accounting for the order of reaction and the inverse hydrogen ion dependence.

To explain the inverse hydrogen ion dependence of the Cr(II) reduction of certain pentaamminecobalt(III)-dicarboxylic acid complexes, Gould and Taube[31] include a term in the rate law which represents reaction of the chromous ion with the complex species having the remote carboxyl group in the ionized form. The rate constant for this pathway is about 10^3 times that for reaction with the un-ionized carboxyl group. The authors suggest that chelation of the reductant, and not merely the effect of the negative charge on the carboxylate group, is the reason for the increased rate.

In the present case, it may be that the rate-determining step involves the attack of the second chromous ion upon a carboxylate group and not upon the triple bond.



$$Cr^{II} + HO_2C\overset{Cr^{II}}{C}{\equiv}CCO_2^- \longrightarrow HO_2C\overset{Cr^{II}}{C}{\equiv}C{-}C\overset{O}{\underset{O}{{}^-}}Cr^{II}$$

The electron would then be transferred to the unsaturated bond through a system of conjugation in the organic molecule (a process similar to that suggested by Taube and coworkers for the reduction of the pentaamminecobalt(III) fumarate complexes and shown more conclusively for the pentaamminecobalt(III) nicotinamide and isonicotinamide complexes[32]). Such a process would involve coordination of the attacking Cr(II) ion with a carboxylate oxygen, and the inverse dependence upon hydrogen ion concentration would be explained. Indeed, the presence of the bands at 1601 and 1405 cm^{-1} in the ir spectrum of the reaction mixture strongly suggests coordination.

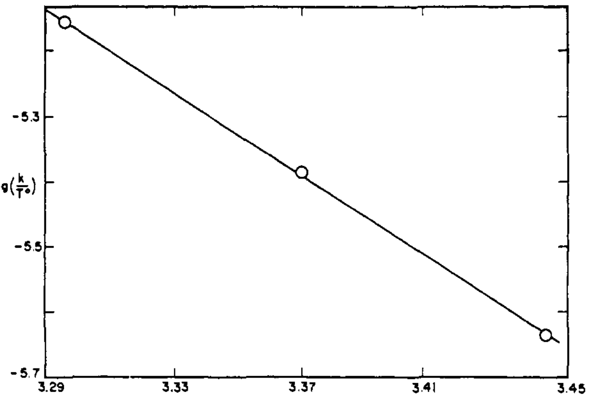


Figure 7. The logarithm of $k/T°$ for the reaction of species I (1.24×10^{-4} *M*) with hydrogen ion plotted *vs.* $1/T°$; $\mu = 1.7$ *M*. From absorbance *vs.* time data at 270 mμ.

Numerical values of the equilibrium constant K_π at various temperatures will have to be obtained before the activation parameters of reaction 7 can be calculated. Perhaps one of the recent techniques for measuring the rates of very fast reactions could be used to study the equilibrium reaction 6 before a significant amount of reaction 7 has occurred. The interpretation of the ionic strength effect must also wait, since changes in ionic strength could possibly affect any of the reactions 5–7.

Mechanism of Step 2. The pH study indicates that hydrogen ion is consumed during the reaction of species I to form species II. The complete rate law for this step can be derived by an "ion-pair" mechanism[33]

$$I + H^+ \overset{K}{\rightleftharpoons} I{-}H^+$$

$$I{-}H^+ \xrightarrow{k} II$$

If K is not small, the rate law becomes

$$\text{rate} = k_{obsd}[I] = \frac{kK[H^+][I]}{1 + K[H^+]}$$

Taking the reciprocal of k_{obsd}

$$1/k_{obsd} = 1/kK[H^+] + 1/k$$

From the slopes and intercepts of Figure 4, the values of k and K can be obtained. A plot of log ($k/T°$) *vs.* $1/T°$ is shown in Figure 7. The values of k, K, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are listed in Table VII.

The observed value of K is typical of ion-pair complexes. The fact that changes in the ionic strength of

---

(28) C. E. Castro, R. D. Stephens, and S. Moje, *J. Am. Chem. Soc.*, **88**, 4964 (1966).

(29) There is some spectral evidence for the initial formation of a π complex in the Cr(II)–propargyl alcohol reduction. The authors find that, immediately after the reagents are mixed, the absorbance at 408 mμ (near the ultraviolet, where π complexes typically show strong absorption) increases very fast and reaches a plateau (A = 0.95 for $[Cr(II)]_0 = 0.048$ *M*, $[HC{\equiv}CCH_2OH]_0 = 1.40$ *M*, $[H^+] = 0.5$ *M*) after 20 sec. The absorbance then slowly increases to a maximum of 1.40 after 45 min, falls to 1.08 after 135 min and after 18 hr is 0.85. In contrast, the absorbance at 574 mμ slowly increases with time to a final value of 0.69 after 18 hr, and an isosbestic point is observed at 640 mμ probably due to the formation of $Cr(H_2O)_6^{+3}$ from Cr_{aq}^{+2}).

(30) It is also possible that the acid-dissociation step occurs after the formation of the π complex, *i.e.*

$$Cr^{II} + HO_2CC{\equiv}CCO_2H \overset{K_\pi'}{\rightleftharpoons} [Cr{\cdot}HO_2CC{\equiv}CCO_2H] \qquad (5a)$$

$$[Cr{\cdot}HO_2CC{\equiv}CCO_2H] \overset{K_\alpha'}{\rightleftharpoons} H^+ + [Cr{\cdot}HO_2CC{\equiv}CCO_2^-] \qquad (6a)$$

The rate law then would include different values for K_α and K_π. However, it is impossible to distinguish kinetically between these two sequences.

(31) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(32) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961); F. R. Nordmeyer and H. Taube, *ibid.*, **88**, 4295 (1966).

(33) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 149.

Table VII. Values of k, K, and the Activation Parameters for the Reaction of Species I with Hydrogen Ion at Three Temperatures

T, °C	$1/k$, 10^4 sec	k, 10^{-4} sec^{-1}	K, M^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
17.2	0.150	6.67	1.61		
23.6	0.082	12.2	1.51	14.8 ± 3.0	−22.1 ± 4.4
30.2	0.047	21.3	1.57		

the medium have no effect upon the rate constant is consistent with the proposed mechanism.

Mechanism of Step 3. The hydrolysis of species III follows the rate law

$$\text{rate} = \{2.95 \times 10^{-5} + 4.95 \times 10^{-6}[H^+]^{-1}\}[II]$$

(units in sec^{-1} and M^{-1}). This indicates that the reaction proceeds by two pathways, one (8) independent of, and the other (9, 10) dependent upon the reciprocal of, the hydrogen ion concentration.

$$II + H_2O \xrightarrow{k_3} III + Cr^{III} \qquad (8)$$

$$[RCr(H_2O)_5{}^{n}] \xrightleftharpoons{K_3} [RCr(OH)(H_2O)_4{}^{n-1}]\ (II') + H^+ \qquad (9)$$

$$II' + H_2O \xrightarrow{k_3'} III + Cr(OH)(H_2O)_5{}^{+2} \qquad (10)$$

For the second pathway, $k_3'K_3 = 4.95 \times 10^{-6}\ M^{-1}$ sec^{-1}. Assuming that K_3 is of the order of 10^{-4},[34] the value of k_3' is 10^3 times larger than k_3. This can be explained by the "labilizing" effect of the OH ligand, as observed in substitution reactions of Co(III) complexes.[35]

Mechanism of Step 4. The hydrolysis of species III follows the rate law

$$\text{rate} = \{3.10 \times 10^{-6} + 1.20 \times 10^{-5}[H^+]\}[III]$$

(units in sec^{-1} and M). Acid-independent (11) and acid-dependent (12, 13) reaction pathways are indicated.

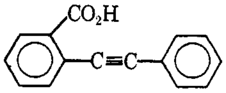
$$\underset{\text{III}}{\text{Cr–fumarate complex]}} + H_2O \xrightarrow{k_4} \text{fumarate ion} + Cr^{III} \qquad (11)$$

$$III + H^+ \xrightleftharpoons{K_4} III \cdot H^+ \qquad (12)$$

$$III\ H^+ + H_2O \xrightarrow{k_4'} \text{fumaric acid} + Cr^{III} \qquad (13)$$

A similar hydrogen ion dependence has been found in the hydrolysis of Cr(III)–oxalato complexes.[36]

Comparison with the Chromous Reduction of Propargyl Alcohol. Under similar conditions, the reaction of chromous ion with propargyl alcohol and the first step in the reaction of chromous ion with acetylenedicarboxylic acid both follow the same third-order rate law. It is assumed that the actual electron transfer occurs during this step. The rate of this reaction is much greater (~6 × 10^3) for the monoanion of acetylenedicarboxylic acid than it is for the alcohol,[37] indicating that the carboxylate group facilitates the electron transfer. Of interest would be studies of the chromous reduction of

$HC{\equiv}CCO_2H$, $HO_2CCH_2C{\equiv}CCO_2H$,  , etc.

which would further the understanding of the role of the carboxyl group in these reductions. The study of $HC{\equiv}CCO_2H$ has been started.

Acknowledgments. The authors wish to thank Charles McEachern of the University of Notre Dame and the Monsanto Information Services Department for computer results, Dr. R. H. Becker of Gannon College for help in the interpretation of the ir data, and Dr. G. M. Harris of State University of New York at Buffalo for suggestions concerning some of the kinetic data. The award of a Radiation Laboratory Research Assistantship and a NASA Traineeship to W. A. J. is gratefully acknowledged.

---

(34) J. E. Earley and R. D. Cannon, "Transition Metal Chemistry," Vol. 1, Marcel-Dekker, Inc., New York, N. Y., 1965, pp 70, 71.

(35) J. Lewis and R. G. Wilkins, ref 34, p 115.

(36) K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

(37) $k_{\text{obsd(acid)}} = kK_{\pi}K_a/[H^+]$; $k_{\text{obsd(alcohol)}} = k'K_{\pi}'$. Assuming that $K_{\pi} \simeq K_{\pi}'$, $k/k' \simeq 11(0.5)/(1.3 \times 10^{-2})(7 \times 10^{-2})$. The value of $k_{\text{obsd(acid)}}$ at 0.5 M [H$^+$] from this paper; that of $k_{\text{obsd(alcohol)}}$ from ref 4; value of K_a from M. Charton, *J. Org. Chem.*, **26**, 735 (1961), and checked potentiometrically in this laboratory.