

Ester Hydrolysis in the Reaction of Methyl- and Ethylmalonatopentaamminecobalt(III) Complexes with Chromous Ion

D. H. Huchital and Henry Taube

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received July 28, 1965

An investigation has been made of the product distribution in the reaction of chromous ion with the methyl- and ethylmalonatopentaamminecobalt(III) complexes. Ester hydrolysis does accompany the oxidation-reduction reaction in each case. For the former complex, ca. 50% of the ligand appears as the chelated product, $[\text{Cr}(\text{O}_2\text{C})_2\text{-CH}_2]^+$, and for the latter, ca. 67%. The alcohol corresponding to the amount of chelated product formed is found free in solution. The remainder of the ligand appears as the ester malonato complex of Cr(III). Only a single term is observed in the rate law for the reaction, $-d(\text{complex})/dt = k(\text{complex})(\text{Cr}^{2+})$, where k for the methyl half-ester complex is $0.50 \text{ M}^{-1} \text{ sec}^{-1}$, and for the ethyl, $0.61 \text{ M}^{-1} \text{ sec}^{-1}$, both at 25° , 1 M H^+ , and $\mu = 2$. It is proposed that there are parallel paths for the reaction: one corresponding to simple adjacent attack leading to the monodentate half-ester complex and the other, to an intermediate in which both ends of the ligand are trapped in the coordination sphere of Cr(III). This intermediate then decomposes largely by ester hydrolysis, leaving the malonate group chelated. The interpretation is consistent with the fact that V^{2+} and Eu^{2+} as reducing agents do not induce hydrolysis, and that ester hydrolysis does not take place with the succinate half-ester complex for any of the three reducing agents, Cr^{2+} , V^{2+} , and Eu^{2+} .

Introduction

Svatos and Taube¹ have reported that in the reaction of chromous ion with the acid malonatopentaamminecobalt(III) the expected reaction paths which are zero and inverse first order in (H^+) appear, but they report evidence also for a path which is first order in (H^+) . While such a path is not unexpected for ligands featuring conjugated double bond systems,² it is unexpected for a saturated ligand such as the malonate group. The authors¹ suggested that the unusual path corresponds to loss from the ligand of a methylene proton, the resulting delocalized system of electrons making possible remote attack by the reducing agents. In view of the evidence which has been presented for ester hydrolysis accompanying electron transfer in a number of complexes^{3,4} having half-esters of conjugated dibasic acids as ligands, it seemed of interest to search for ester hydrolysis in the reaction of chromous ion with half-ester malonatopentaamminecobalt(III) complexes.

In this paper we describe the preparation of the ethyl and methyl half-ester complexes of malonatopentam-

minecobalt(III), the results of the study of the kinetics of the reaction of the complexes with chromous ion, and of the experiments designed to determine the identity of the products. Ester hydrolysis does accompany electron transfer, but by a chelating mechanism which involves trapping the ester end of the ligand in the Cr(III) product, rather than by the simple remote attack envisaged by Svatos and Taube.¹ It should be mentioned that while our work was in progress experiments performed here⁵ have raised serious doubts about the evidence obtained earlier for ester hydrolysis resulting from remote attack by the reducing agent.

The vanadous and europous ion reductions of the ester malonatopentaamminecobalt(III) complexes were also studied to learn whether ester hydrolysis is limited to the special case in which chromous ion is the reductant. No significant hydrolysis was observed to accompany electron transfer and, in light of these results, it was thought worthwhile to reinvestigate the reactions of vanadous and europous ions with methylsuccinatopentaamminecobalt(III) for which ester hydrolysis has been reported.⁶

Experimental Section

Reagents. The reducing agents were prepared as follows: chromium(II) and europium(II) either by electrolytic or by zinc-amalgam reduction of the corresponding M(III) perchlorates; V(II), by reduction of ammonium metavanadate in 1 M HClO_4 using zinc amalgam. The concentrations of the reducing agents were determined by bringing them to react with $(\text{NH}_3)_5\text{-CoCl}_3$ in acid solution, then measuring the Co(II) released as the chloro complex in 9.6 M HCl .

Methyl and ethyl hydrogen malonates were prepared using the method of Breslow, *et al.*⁷ Methyl hydrogen succinate was prepared following the procedure given in "Organic Syntheses."⁸

Pentaamminecobalt(III) complexes containing organic ester ligands were prepared using a modification of the method of Sebera and Taube.² The acid ester (0.1–0.15 mole) was dissolved in distilled water (usually 10 ml.), and the solution was brought to pH 4–5 with sodium carbonate. The resulting solution was added to a slurry of $[(\text{NH}_3)_5\text{CoOH}_2](\text{ClO}_4)_3$ (0.01 mole) and the mixture heated for 3.5–4 hr. at $65\text{--}75^\circ$. Crystals that precipitated upon cooling to 0° were filtered, and an equal volume of 8 M sodium perchlorate was added to

(5) J. Hurst and H. Taube, to be published.

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

(7) D. S. Breslow, E. Baumgarten, and C. R. Hauser, *ibid.*, **66**, 1287 (1944).

(8) J. Cason, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 169.

(1) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

(2) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(3) D. K. Sebera, R. T. M. Fraser, and H. Taube, *ibid.*, **81**, 2906 (1959).

(4) R. T. M. Fraser, *ibid.*, **83**, 564 (1961).

the filtrate which was then kept for several hours at -5° (note: perchloric acid was not used as it catalyzes the hydrolysis of the ester group, yielding the acid complex). The complexes were recrystallized from warm water (40°) precipitating the product as described above. *Anal.* Calcd. for $[(\text{NH}_3)_5\text{CoL}](\text{ClO}_4)_2$ (a) $\text{L} = -\text{O}_2\text{CCH}_2\text{CO}_2\text{CH}_3$: C, 10.4; H, 4.38; N, 15.2; Co, 15.4. Found: C, 10.2; H, 4.42; N, 15.0; Co, 14.7. (b) Calcd. for $\text{L} = -\text{O}_2\text{CCH}_2\text{CO}_2\text{C}_2\text{H}_5$: C, 12.7; H, 4.68; N, 14.8; Co, 15.0. Found: C, 12.2; H, 4.70; N, 14.2; Co, 14.3. (c) Calcd. for $\text{L} = -\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$: C, 12.7; H, 4.68; N, 14.8; Co, 15.0. Found: C, 12.5; H, 4.53; N, 14.86; Co, 14.63. The content of acid, as either the aquo or acido complexes, was less than 3% in all preparations.

Spectrophotometric Measurement of Reaction Rates. The reactions were performed under pseudo-first-order or second-order conditions. The reaction vessels were either 1- or 2-cm. quartz absorption cells with narrow openings. All reagents except chromous ion, and in some cases, acid, were added to the cell which was then fitted with a serum cap. After degassing cell and contents with nitrogen, acid and chromous ion were added using hypodermic syringes. All spectrophotometric studies were made using a Cary Model 14 recording spectrophotometer. The temperature of the reaction mixture for kinetic runs was maintained to $\pm 0.2^\circ$ using a Forma-Temp Jr. refrigerated thermostat.

Determination of Product Distributions. For the chromium(II) reductions of methyl- and ethylmalonatepentaamminecobalt(III) perchlorates (hereafter to be designated as the methyl or ethyl ester complex), one or more of three methods was used to determine the product distribution. The methods were spectrophotometric, ion exchange, and a determination of free alcohol released upon electron transfer. In most experiments the concentrations of the reactants were adjusted so that Co(III) remained in about 5% excess at the completion of the reaction.

It may be worth mentioning explicitly that the following changes in the product complexes are very slow on the time scale of the analytical methods: dissociation of the organic ligand, chelation of the monodentate malonate form, and chelation of half-ester complexes. The half-time for chelation of the monodentate malonate complex is 3×10^4 sec. or longer under our conditions, and for the half-ester complex is much longer still. The agreement between the methods of analysis, for example, the spectrophotometric one which takes only a short time and does not disturb the system, and the ion-exchange method, which takes a much longer time and may disturb the system, further bears out the assertions we have made earlier in this paragraph.

In the spectrophotometric method the spectrum of the reaction mixture was taken after approximately ten half-lives for the oxidation-reduction reaction had elapsed. The apparent extinction coefficients of the chromium(III) products were calculated after correction for the absorbancies of other species. It was assumed at first and later shown to be so by ion exchange, that two products were formed, one the malonatochromium(III) chelate and the other a monodentate chromium(III) species. Ion-exchange methods provided the true extinction coefficients of these two species (*cf.* Table I) which, together with the apparent extinction

coefficients determined above, permitted calculation of the per cent chelate and monodentate species.

The extinction coefficients of the chromium(III) products and related chromium(III) complexes are listed in Table I. The values for the extinction coefficients at the two maxima were determined on samples prepared following one or more of three methods. The first method involved heating the free ligand acid (0.80 M) with chromium(III) perchlorate (0.02 M) in HClO_4 at 90° for 10 hr. and separating the chromium(III) complex by ion exchange (see below). This method could not be used to prepare the ester complexes as hydrolysis of the ester group occurred at the elevated temperatures. In the second method a chromous ion solution was added to a solution containing Pb(II), the free organic acid, and HClO_4 , the chromium(III) products being separated by ion exchange. This method proved useful in preparing the complexes with the organic acid anions as ligands. When malonate is the ligand, the dominant form of the complexed chromium(III) is the chelate, but some of the monodentate form is also present.⁹ It was not used in an effort to prepare the chromium complexes of the half-esters. In the third method use was made of the pentaamminecobalt(III)-chromium(II) reaction, separating the products as described below.

Table I. Spectrophotometric Properties of Aquo- and Carboxylatochromium(III) Complexes

Ligand	λ ,	ϵ	λ ,	ϵ
	$m\mu$		$m\mu$	
Water ^a	574	13.4	408	15.6
Malonate (chelate)	559	31.4	415	26.1
		(32.4) ^b		(27.2)
Acetate	568	24.0	411	22.2
		(21.6)		(20.7)
Methylmalonate (monodentate)	567	23.9	412	22.0
Malonate (monodentate) ^c	568	25.6	412	23.4

^a Data of J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959), for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. ^b Values in parentheses are those reported by R. E. Hamm, *et al.*, *ibid.*, **80**, 4469 (1958). ^c Reference 9.

All three methods showed that when malonic acid was the ligand most of the chromium(III) product was chelated. The evidence is based on the fact that the complex was readily eluted from the ion-exchange column by 0.2 M NaClO_4 , thus implying that the complex has a +1 charge. The acetatochromic complex of charge +2 was retained by the column with eluent as concentrated as 0.45 M in NaClO_4 . Furthermore, the monodentate malonatochromic complex prepared in these laboratories has been shown⁹ to have extinction coefficients similar to those reported in Table I for the acetato and methylmalonato complexes.

The ion-exchange analyses of product distributions were performed using Bio-Rad AG 50W-X8, 50-100 mesh analytical grade exchange resin which was converted to the sodium form before use. Ion-exchange separations were carried out as follows. An aliquot of the reaction mixture was diluted with distilled water to reduce the ionic strength to *ca.* 0.2 F. This solution

(9) D. H. Huchital and H. Taube, to be published.

was then slowly passed through the ion-exchange column and the column washed with a solution of 0.20 *M* in NaClO₄ and 0.05 *M* in HClO₄ until all ions of charge +1 were eluted (usually four-to-five column volumes). The resulting effluent was diluted to a known volume and subjected to spectrophotometric and total chromium analyses.

As subsequent eluents 0.45 *M* NaClO₄-0.05 *M* HClO₄ and 0.70 *M* NaClO₄-0.05 *M* HClO₄ solutions were used; the latter elutes some Co⁺²(aq) product along with the Cr(III) product of charge +2.

Methanol (or ethanol) was recovered from the reaction mixture by distillation at reduced pressure. The method used to determine the free alcohol in the distillate was a slight modification of that reported by Bessot and Scemama.¹⁰ The procedure was checked using J. T. Baker spectrophotometric methanol and absolute ethanol.

Results

Kinetics. Kinetic data for the reduction of methyl- and ethylmalonatopentaamminecobalt(III) ions by chromium(II) are summarized in Table II. The course of the reaction was followed at 351 μ , the wave length at which the cobalt(III) complex is at maximum absorbance (ϵ 57) while that of the products is much smaller (e.g., $\epsilon_{\text{Co(II)}}$ 0.50, $\epsilon_{\text{Cr(III)}}$ \sim 3.5). Reactions were run in which either Co(III) was in small excess, Cr(II) was in large excess, or both reactants were at the same concentration. The rate law was thus shown to be

$$\text{rate} = k_0[\text{Co(III)}][\text{Cr(II)}]$$

where k_0 can be expressed as $k_1 + k_2(\text{H}^+)$. The variation of k_0 with (H^+) , however, does not mean that the rate law has an acid-dependent path; the variation of rate with (HClO_4) disappears when LiClO₄ is used in place of NaClO₄ as the supporting electrolyte.

Table II. Specific Rate Constants and Kinetic Parameters for the Reduction of Methyl- and Ethylmalonatopentaamminecobalt(III) Ions by Chromium(II)

Ligand	Specific rate, $M^{-1} \text{ sec.}^{-1}$	ΔH^* , kcal. mole ⁻¹	ΔS^* , e.u.
Methyl malonate (-O ₂ CCH ₂ CO ₂ CH ₃)	0.50 ^a	10.1	-26
Ethyl malonate (-O ₂ CCH ₂ CO ₂ C ₂ H ₅)	0.41 + 0.09 (H ⁺) ^c 0.67 ^b 0.50 + 0.11 (H ⁺) ^c 0.38 + 0.11 (H ⁺) ^d	9.6	-27.5

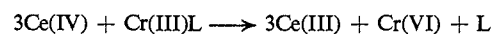
^a 25°, H⁺ = 1.0 *M*, μ = 2 *M* (NaClO₄). ^b 25°, H⁺ = 1.54 *M*, μ = 2 *M* (NaClO₄). ^c Apparent acid increase in NaClO₄-HClO₄ media; μ = ca. 2 *M*. ^d Apparent acid increase in NaClO₄-HClO₄ media; μ = ca. 1 *M*.

The data on the change in specific rate with temperature are summarized herewith. For these experiments, $(\text{Co(III)})_0 \sim 7 \times 10^{-3}$ *M*, $(\text{Cr}^{2+})_0 \sim 3 \times 10^{-3}$ *M*, μ = 2.0 (NaClO₄). For the methyl ester complex, (HClO_4) = 1.0 *M* and for the ethyl ester, 1.5 *M*. The specific

rates for the methyl ester complex at the temperatures 16.0, 7.3, 25.0, and 35.5° were 0.29 (3), 0.176 (1), 0.50 (3), 0.93 (3), and for the ethyl ester complex at 7.0, 16.8, 25.0, and 38.3° were 0.228 (2), 0.44 (2), 0.67 (2), and 1.37 (1). The numbers in parentheses represent the number of experiments done for each entry.

Product Distributions. The results for the per cent chelated malonatetraaquo chromium(III) product obtained upon reduction of the methyl- and ethylmalonatopentaamminecobalt(III) complexes by chromium(II) are summarized in Tables III and IV. It is interesting to note the following. (1) No change in the product distribution for either the methyl or ethyl ester was observed over acidities ranging from 0.2 to 2.0 *M* at a constant ionic strength (2.0). (2) For the methyl ester, the results at high acid concentrations ($(\text{H}^+) = 3.5$ *M*) are essentially the same as those at low acid ($(\text{H}^+) = 0.2$ -2.0 *M*). (3) For the methyl ester, the same results are obtained using syringes or an all-glass system to transfer the reagents (no tests of this nature were run using the ethyl ester). (4) The product distribution is unaffected by zinc ions (*i.e.*, for some of the experiments the Cr²⁺ was prepared electrolytically). (5) The results of the product distribution analyses for the Cr²⁺ reduction of the methyl ester show no significant change with temperature. No temperature studies were made with the ethyl ester complex.

The results in Table III reveal only that the product formed upon reduction is approximately 50% chelated malonatochromium(III) and 50% free alcohol but do not reveal how the remaining alcohol is bound. A set of experiments was therefore done to distinguish between the following distributions of methanol in the chromium(III) products: (1) 50% malonatochromium(III) chelate containing methanol (50%) bound in the first coordination sphere of the chromium and 50% malonatochromium(III) monodentate acid with 50% free methanol; (2) 50% malonatochromium(III) chelate with free methanol (50%) in solution and (a) 50% methylmalonatochromium(III) or (b) 50% monodentate malonatochromium(III) containing methanol bound to the Cr(III). The experiments were done as follows. To a solution containing 0.125 mmole of the methyl ester complex, an equivalent amount of chromous ion was added and the reaction allowed to go to completion. An aliquot was removed and analyzed for methanol by the method already described. The results for two runs showed 49 and 45% free methanol. To a second aliquot a solution containing 3 mmole of Ce(IV) for each mmole of Cr(III) was added. The reaction



is nearly instantaneous in ClO₄⁻ media.¹¹ Directly after reaction the free methanol in the solution was recovered, the analyses showing 46% free methanol present in both runs. A blank experiment proved that Ce(IV) in the presence of Cr(III) would not induce hydrolysis of the free ester. Further, the oxidation of malonic acid by Ce(IV) is slower than the oxidation of Cr(III), requiring 10 min. to go to completion in 4 *M* HClO₄¹² (note: the final concentration of HClO₄ after Ce(IV) addition is ca. 2 *M*).

(11) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

(12) D. A. Skoog and D. A. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1963, pp. 454-456.

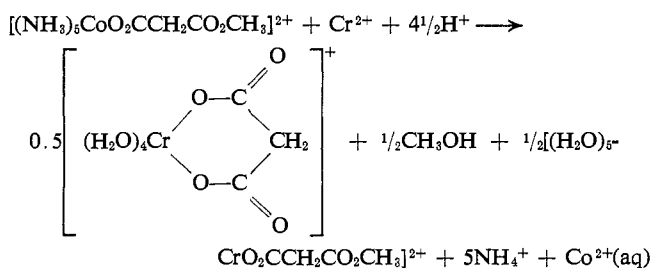
(10) L. Bessot and M. Scemama, *Compt. rend.*, **250**, 3897 (1960).

Table III. Product Distributions in the Reduction of Methyl- and Ethylmalonatopentaamminecobalt(III) Ions by Chromium(II)^a

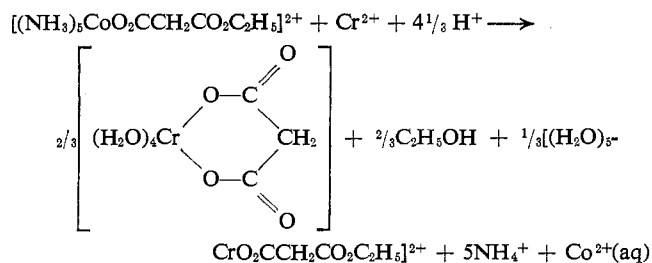
Method of analysis	Methyl ester			No. of expt.	Ethyl ester			No. of expt.
	(H ⁺)	μ	% chelated Cr(III)-malonate complex ^b		(H ⁺)	μ	% chelated Cr(III)-malonate complex ^b	
Ion exchange	1	2	55 ± 2	12	1	2	67 ± 2	6
	0.2	0.53	30-35	3	0.15	1.2	64	1
	0.2	2.3	57 ± 1	2	0.80	1.6	67	1
	2	2.3	55 ± 2	3	0.12	2.1	66	2
	3.5	4.0	52 ^c	1	1.9	2.1	68	2
Spectrophotometric	1	2	54 ± 4	10	1	2	64 ± 2	6
	0.1	1.1	47 ^d	1				
	1	1.1	47	1				
	3.5	4.0	55	1				
			57	1				
Alcohol determination	1	2	50 ± 3	22	1	2	66 ± 1	12
	0.2	0.53	30	1	3.5	4.0	60	1
	3.5	4.0	50	1			55	1
			55 ^c	1				
			49 (0°)	2				

^a (Co(III)) = ca. 1.1 × (Cr(II)), (Cr(II)) = ca. 0.010-0.015 M, 24 ± 2°. ^b For alcohol determination, quoted numbers refer to free alcohol. ^c All-glass apparatus. ^d (Cr(II)) = 0.050 M, (Co(III)) = 0.010 M.

The expectations on the basis of the possible distributions presented above are: (A) if the product distribution is that specified in (1) or (2b) above, then, upon addition of Ce(IV), 100% recovery of free alcohol would be expected; (B) if the product distribution is that stated in (2a) above, we would expect 50% free alcohol to be recovered after addition of Ce(IV). The results show the distribution of products to be that specified in (2a), namely, the products are the chelated malonatochromium(III) complex and free methanol, and the half-ester monodentate complex. Thus, the approximate stoichiometry of the reaction of methylmalonatopentaamminecobalt(III) perchlorate with chromous ion under the conditions used is



Similar experiments done with the products formed by reducing the ethyl ester complex with chromium(II) show that the monodentate product that is formed in approximately 35% yield is the ester complex, with the approximate stoichiometry for the reduction under the conditions used being



Vanadous and Europous Ions as Reducing Agents. To learn whether reducing agents besides Cr²⁺ (which is special, *vide infra*) cause ester hydrolysis, the reaction was repeated using V²⁺ and Eu²⁺ solutions. It should be remembered that Cr²⁺ is unique among the pure aquo ions in that it is substitution-labile in the reduced state, but the product formed upon its oxidation is very slow to undergo substitution. Thus, ester hydrolysis is not unexpected in the chromous ion reduction of organic ester cobalt(III) complexes if the ester group is

Table IV. Product Distribution at Various Temperatures in the Reduction of Methylmalonatopentaamminecobalt(III) by Chromium(II)^a

Method of analysis	Temp., °C.	% chelated Cr(III)-malonate complex ^b	No. of expt.
Ion exchange	24	55 ± 2	12
	15	52	1
	35	54	1
Spectrophotometric	24	55 ± 4	10
	15	54, 57	2
	35	46, 50	2
Methanol determination	Ca. 82	58	1
	24	50 ± 3	22
	0	48	1
	15	43	1
	35	44	1

^a (Co(III)) = ca. 1.1 × (Cr(II)), (Cr(II)) = ca. 0.010-0.015 M, (H⁺) = 1.0 ± 0.1 M, μ = 1 M. ^b For methanol determination, quoted numbers refer to free alcohol.

trapped in the first coordination sphere of the Cr(III) product. It was of interest to investigate vanadous and europous ions as reducing agents, for here the substitution lability of the products makes it unlikely that ester hydrolysis would take place after electron transfer, even if the ester group were trapped in the first coordination spheres on reaction.

Since the V(III) and Eu(III) products are substitution labile, neither the spectrophotometric nor the ion-exchange method could be used and the determination of extent of ester hydrolysis rested solely on the alcohol analyses. The results for the kinetics of the reduction of the methyl malonate complex, and for the alcohol analyses after electron transfer for the methyl and ethyl malonate complexes are listed in Table V. The results show that no ester hydrolysis accompanies the electron-transfer reaction when V^{2+} or Eu^{2+} are the reducing agents. Substantial ester hydrolysis is recorded in the experiments using V^{2+} as reductant. However, it is observed to a similar extent in the blank experiment using $(NH_3)_5CoOH_2^{3+}$ and the free half-ester with V^{2+} , so we must conclude that there is very little if any hydrolysis in the reaction of V^{2+} with the half-ester Co(III) complex.

Table V. Summary of Kinetic Results and the Alcohol Analyses for the Reduction of Methyl- and Ethylmalonatopentaamminecobalt(III) Ions by Vanadium(II) and Europium(II)^a

Ligand	Reductant	Specific rate, ^b $M^{-1} \text{ sec.}^{-1}$	% free alcohol ^{c,d}
Methyl malonate	V^{2+}	6.1	20.0, 18.4
	Eu^{2+}	14.0	Ca. 2
$KO_2CCH_2CO_2CH_3$	None		18.0
	^e		17.3
$[(NH_3)_5CoO_2CCH_2CO_2CH_3]^{2+}$	None		5.5
	V^{2+}		9.0
$KO_2CCH_2CO_2C_2H_5$	None		18.2
$[(NH_3)_5CoO_2CCH_2CO_2CH_3]^{2+}$	None		10

^a 25°, $(H^+) = 1.0 M$, $\mu = 2 M$. ^b Specific rates are good to $\pm 10-15\%$; $(Co(III)) = 0.0075 M$, $(V(II))$ and $(Eu(II)) = 0.0270 M$. ^c For alcohol determination runs, $(Co(III)) = 0.015$, $(V(II))$ and $(Eu(II)) = 0.013-0.014 M$. Reaction products distilled after 5 min. ^d Free esters and Co(III) complexes are kept ca. 40 min. in 1.0 M $HClO_4$ before distilling. ^e In presence of reaction product of $(NH_3)_5CoOH_2^{3+}$ and V^{2+} .

The Reduction of Methylsuccinatopentaamminecobalt(III) Ions by Chromous, Vanadous, and Europous Ions. The reduction of the methyl succinate ester complex of $(NH_3)_5Co(III)$ by Cr^{2+} , V^{2+} , and Eu^{2+} has been studied by Sebera and Taube² and by Fraser.⁶ On the basis of results obtained on titrating the acid in the reaction mixtures after completion of the oxidation-reduction reaction, and because on extraction with ether the free organic acid rather than the half-ester was recovered from the reaction mixture, Fraser concluded that ester hydrolysis accompanies the reduction of the methyl succinate complex by V^{2+} and Eu^{2+} . It is expected that hydrolysis will be greater when a more stable chelate ring can be formed; the six-membered ring with the malonate is expected to be more stable than the seven-membered ring with the succinate. Since when the malonate half-ester is the ligand no significant hydrolysis was found to accompany electron transfer when V^{2+} or Eu^{2+} were the reductants, it was considered worthwhile to check Fraser's results.

The results on the kinetics of reduction by Cr^{2+} , V^{2+} , and Eu^{2+} and of the alcohol analyses are shown in Table VI. The experiments done with Cr^{2+} as reduc-

tant require little comment. The alcohol analysis results are in agreement with titration data² indicating that the ester does not undergo much hydrolysis in the electron-transfer process. However, an additional experiment was run in which Ce(IV) was added to the reaction mixture ($Co(III) = 0.0136 M$, $Cr(II) = 0.0124 M$, $(H^+) = 0.9 M$, $\mu = 1.2$) before distillation. The results, 8.5% methanol recovered as compared with 5.4% in the Ce(IV)-free blank, prove that little, if any, hydrolysis occurs in the chromous ion reduction of the methylsuccinate complex.

Table VI. Summary of Kinetic Results and the Alcohol Analyses for the Reduction of Methylsuccinatopentaamminecobalt(III) Ions by Chromium(II), Vanadium(II), and Europium(II) Ions^a

Reducing agent	Specific rate, $M^{-1} \text{ sec.}^{-1}$	% free alcohol
Cr^{2+}	0.165 ^b	7.4, 5.4
V^{2+}	$1.16 \pm 0.04^{c,e}$	2.2, 3.4 ^f
		0.0 ($H^+ = 0.2$, $\mu = 1.0 M$)
Eu^{2+}	$2.30^{d,e}$	2.0, 2.3 ^f
		4.7 ($H^+ = 1.0$, $\mu = 1.1 M$)

^a 25°, $(H^+) = 1.0 M$, $\mu = 2 M$. ^b Data from Sebera and Taube,² $\mu = 1.0 M$. ^c $(Co(III)) = 0.0078$, $(V(II)) = 0.0451 M$, $(H^+) = 0.14-0.93 M$, $\mu = 1.1-1.2 M$. ^d $(Co(III)) = 0.0075$, $(Eu(II)) = 0.0268 M$, $(H^+) = 1.0 M$, $\mu = 1.2 M$. ^e Data from Fraser: V(II) reduction, $k = 1.0 M^{-1} \text{ sec.}^{-1}$; Eu(II) reduction, $k = 2.5 M^{-1} \text{ sec.}^{-1}$. ^f Reaction mixture distilled within 10 min. after mixing.

There is a serious discrepancy between the results of this work and the published data of Fraser on the V^{2+} and Eu^{2+} reduction of the methyl succinate complex. The results of the alcohol analyses clearly show that no significant amount of free alcohol is produced upon completion of the reaction. Any possibility of bound alcohol can be ruled out by the known substitution lability of the products. Fraser's results may be in error for two reasons: (a) the apparent acid produced equivalent to the cobalt(III) complex reduced may be due to the water coordinated to the vanadium(III)-aquo complex (note the pK of $V(H_2O)_6^{3+}$ at 25° and $\mu = 0$ is 2.91³), and (b) the conditions used for the ether extractions⁵ may have effected the hydrolysis of the ester.

Discussion

The three kinds of analytical procedures used, all of which are mild enough so they do not themselves induce ester hydrolysis, yielded results which agree in showing that ester hydrolysis does accompany the reaction of the ethylmalonatopentaamminecobalt(III) complex with chromous ion. The two chromium-containing products are the chelated malonate complex, and the non-chelated complex with unhydrolyzed malonic methyl half-ester; the alcohol formed on hydrolysis is not bound to Cr(III) but is found free in the solution.

The kinetics of the reaction differ distinctly from those observed with the acid malonate complex; in the present case only the term in the rate law which is zero order in (H^+) is observed. The distribution of Cr(III) between

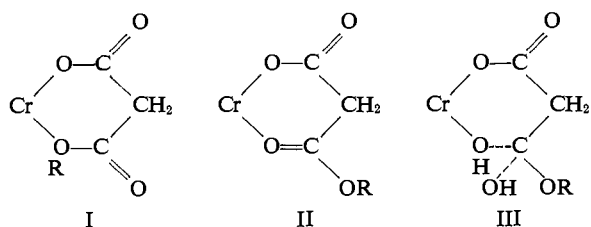
(13) J. P. Hunt, "Metal Ions in Aqueous Solution," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 50.

the two products is independent of the acidity over a wide range and furthermore appears to be independent of the temperature.

In view of kinetic results which have been cited, the formation of the chelate product and free alcohol can be understood if the reducing agent is chelated by the ligand before electron transfer to the cobalt center takes place. On electron transfer, both ends of the malonate group are trapped in the coordination sphere of Cr(III), and, because Cr(III) complexes are slow to undergo substitution, it is not altogether astonishing that ester hydrolysis, rather than Cr(III)-O bond rupture occurs. The interpretation is consistent with the finding that Cr²⁺, but not V²⁺ or Eu²⁺, induces ester hydrolysis in the reduction reaction.

It is important to know whether the entire reaction proceeds by way of an intermediate of the kind which has been described, which then reacts partly by Cr-O bond rupture and partly by ester hydrolysis, or whether there are parallel paths, one leading to the nonchelated product without hydrolysis and the other to the chelated product with hydrolysis. At the very least it can be asserted that the latter situation must account for part of the reaction, for it is known that attack by Cr²⁺ at the carboxyl associated to Co(III) takes place at a specific rate of about 0.2 M⁻¹ sec.⁻¹, and there is no way for reaction by this path to be denied to the system. No matter how rapidly reaction by other paths take place, reaction by simple adjacent attack must take place at a finite specific rate, of the order of 0.2 M⁻¹ sec.⁻¹. In fact, a plausible interpretation of the data is given if we assume that the methylmalonato-chromium(III) complex arises as a result of simple adjacent attack only, and hydrolysis occurs by the chelation path only. If this interpretation is accepted, using the known product distribution, the specific rate for adjacent attack is calculated to lie in the range 0.19-0.24 M⁻¹ sec.⁻¹ for the methyl half-ester complex. This is a very reasonable result in comparison to the rate of the chromous-succinate half-ester complex reaction. Some rupture of the chelate ester intermediate at the Cr-O position may occur, but it is unlikely to be more than 20% or so, because a larger contribution would assign to the reaction by simple adjacent attack a specific rate which is too low. It is a little surprising (but not impossible) that the activation energies for the reactions by the parallel paths are so nearly alike.

The nature of the intermediate which is formed by the chelate path is not known from the present work. There are three reasonable possibilities. Whatever



the nature of the intermediate, it is quite labile because no changes in the spectrum of the product were observed immediately after the oxidation-reduction reac-

tion was over, except for the very slow changes ascribable to ester hydrolysis and subsequent formation of the chelate species. Oxygen tracer experiments would help to narrow the field of possibilities. If we assume that structure I describes the intermediate, to explain the fact that alcohol is formed free in the solution, we would need to invoke R-O bond rupture on hydrolysis; intermediates II and III can lead to the observed products by either C-O or O-R bond rupture. If, as seems likely, C-O bond scission occurs, it will be worth trying to learn if substitution by something other than H₂O on carbon can be induced by electron transfer.

It is interesting and may be significant that the acid malonato but not the alkyl malonato complex features the path which is first order in (H⁺). The significance of this observation is not clear to us. It may be that the path in question is not real in the case of the acid malonate complex, but that the rate acceleration at high acid is a result of some specific salt effect. This, however, is quite unlikely because the path disappears when the half-ester complex reacts and when one of the methylene hydrogens is replaced by an alkyl group.^{1,14} The original interpretation of this path as corresponding to remote attack is set aside¹⁵ by the experiments which we have done on the behavior of the monodentate acid-malonatochromium(III) complex. Chelation must be assumed in the activated complex for this path. The difference between the acid malonate and the methylmalonatocobalt(III) complexes may stem from the fact that a proton is lost from the remote carboxyl on chelation in the case of the former complex and no corresponding reaction is possible in the latter. The significance of the apparent acid dependent term for the acid malonato complex will probably not be made obvious until further work is done.

The behavior of the succinato half-ester complex in relation to that of the malonate is easily understandable in terms of the ideas we have advanced. The chelate ring is expected to be less stable for the succinate ligand than it is for the malonate, and this is in accord with the observation that the rate at which chromous reacts with the succinato complex is no greater than that to be expected for simple adjacent attack, and that very little, if any, ester hydrolysis takes place in the reaction.

The kind of direct proof of mechanism which can be advanced for reactions of Cr²⁺ is unfortunately difficult if not impossible for Eu²⁺ and V²⁺. The fact that the methyl malonate-cobalt(III) complex reacts more rapidly with these reducing agents than does the methyl succinate does suggest, however, that the possibility of chelation is being exploited in the reactions of the former complex, and this presumably means that an inner-sphere mechanism operates. Even if this conclusion is accepted, it does not mean that when chelation does not occur, reaction takes place by an inner-sphere mechanism. The ions Eu²⁺ and V²⁺ may not show the strong preference for one mechanism over another which is exhibited by Cr²⁺; there is, in fact, good evidence that both Eu²⁺ and V²⁺ react with (NH₃)₅CoH₂O³⁺ by outer-sphere mechanisms.¹⁶

Acknowledgments. The authors wish to thank the

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(15) D. H. Huchital and H. Taube, to be published.

(16) P. Dodel and H. Taube, *Z. Physik. Chem. (Frankfurt)*, 44, 92 (1965); H. Dieble, P. Dodel, and H. Taube, to be published.

donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for support of this research.

Funds to purchase the spectrophotometer were made available by the National Science Foundation under Grant No. 22611.

Solubility of Uranyl Fluoride in Hydrofluoric Acid-Nitric Acid Solutions at 25°¹

Leslie M. Ferris

Contribution from the Chemical Technology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee. Received July 9, 1965

At 25° the solubility of UO_2F_2 in hydrofluoric acid solutions decreased from 4.82 to 0.15 M (60.1 to 3.5 wt. % UO_3) as the HF concentration increased from 0 to 28.4 M (0 to 47.4 wt. %). The equilibrium solid phase in this concentration range was $UO_2F_2 \cdot 2H_2O$. In HF- HNO_3 solutions the solubility decreased regularly with increasing hydrofluoric and nitric acid concentrations, but no change in equilibrium solid phase ($UO_2F_2 \cdot 2H_2O$) was noted.

Introduction

Studies of phase equilibria in the system UO_3 -HF- H_2O at 20 to 25° have been made previously,^{2,3} but no similar investigations in the system UO_3 -HF- HNO_3 - H_2O appear to have been made. In the present study, phase relationships in a portion of the system UO_3 -HF- H_2O at 25° were reinvestigated and some studies were made in the system UO_3 -HF- HNO_3 - H_2O .

Experimental Section

Uranyl fluoride was prepared by the reaction of UO_3 with hydrogen fluoride at about 300°. Anal. Calcd. for UO_2F_2 : U, 77.3; F, 12.3. Found: U, 75.7; F, 11.4; H_2O , 0.87. The X-ray diffraction pattern of the uranyl fluoride was identical with that reported by Zachariassen⁴; however, the low F:U atom ratio (1.88) suggests the presence of some unreacted UO_3 . All solutions were prepared from reagent grade acids and distilled water.

Excess UO_2F_2 was added to a series of hydrofluoric acid solutions varying in initial HF concentration from 0 to 28 M and to HF- HNO_3 solutions (4.68, 9.45, and 14.6 M HNO_3) that had HF concentrations as high as 9.3 M. Each sample was equilibrated at 25° for at least 10 days, although periodic analyses showed that equilibrium was reached in 4 days or less. After equilibration, samples of the saturated solutions

were obtained by centrifugation at 25° for density measurement and chemical analysis. Wet residues were drained as free of liquid as possible before dissolution in water and analysis.

Uranium was determined by Coulometric titration,⁵

Table I. Solubility of UO_2F_2 in HF- HNO_3 Solutions at 25°

Sample	Density, g./ml.	Concentration, M		
		HF ^a	HNO_3	U
1	2.2969	0.0	0.0	4.82
2	1.6879	1.42	0.0	2.45
3	1.5494	3.56	0.0	1.88
4	1.5029	5.34	0.0	1.69
5	1.4715	6.99	0.0	1.54
6	1.432	9.57	0.0	1.34
7	1.375	12.7	0.0	1.08
8	1.357	13.7	0.0	0.972
9	1.327	15.9	0.0	0.814
10	1.277	17.9	0.0	0.607
11	1.225	21.9	0.0	0.343
12	1.2103	28.4	0.0	0.149
13	1.4525	0.0 ^b	4.65	1.14
14	1.2315	1.86	4.74	0.248
15	1.2151	4.21	4.66	0.149
16	1.2165	5.88	4.74	0.113
17	1.2201	7.71	4.64	0.091
18	1.2264	9.32	4.66	0.075
			Av. 4.68	
19	1.3795	0.0	9.51	0.385
20	1.3009	1.73	9.25	0.056
21	1.3098	4.05	9.30	0.029
22	1.3080	5.63	9.33	0.025
23	1.3210	7.80	9.72	0.019
24	1.3259	9.02	9.62	0.018
			Av. 9.45	
25	1.4610	0.0	14.2	0.305
26	1.3947	1.58	14.4	0.029
27	1.4023	3.66	15.0	0.011
28	1.4018	5.62	14.7	0.0082
29	1.4070	7.88	14.9	0.0051
			Av. 14.6	

^a Defined as the total F concentration minus twice the uranium concentration. ^b HF concentration tabulated as 0 although the F:U atom ratio by analysis was only 1.79.

(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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(5) W. D. Shults, "Uranium, Automatic Controlled Potential Coulometric Titration Method," Method No. 1 219225 and 9 00719225 (1-29-60), ORNL Master Analytical Manual, TID-7015, 1961, Suppl. 3.