

both wave lengths.⁹ The difference in slopes that is observed clearly shows that several collisions are required before the vibrationally excited molecule

(9) This statement does not take into account the change in the microscopic isomerization rate with increasing vibrational energy. However, calculations show that the observed difference in slopes cannot be wholly accounted for by such an effect alone, and that it is

loses enough energy to prevent it from participating in reaction 6.

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probably a combination of this effect and weak collisional interactions that actually exists.

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Factors Controlling the Rate of Electron Transfer. I. The Effect of Halogen Substitution in Organic Mediators¹

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A kinetic study has been made of the reduction by Cr^{++} , V^{++} or Eu^{++} of complex ions of the type $(\text{NH}_3)_5\text{Co}(\text{III})\text{L}$, where L is a halogen derivative of acetic, benzoic or fumaric acid. With the acetato and benzoato complexes, the rate of chromous ion reduction decreases as the size of the substituent increases. Changes in opposite directions in ΔS^\ddagger in chromous and vanadous reactions are interpreted in terms of substitution labilities of the reductants. Substitution of $-\text{CO}_2\text{H}$ in the 2-position of the ligand catalyzes reduction by V^{++} and Eu^{++} ; $-\text{OH}$ in the 2-position catalyzes reduction by Cr^{++} . The role of halogen substitution in fumaric acid is more complex, but can be related both to the size of the halogen and its electromeric effect. All three reductants react by inner-sphere (bridged) activated complexes.

Introduction

The chromous ion reduction of pentammine cobalt(III) complexes has recently been studied in some detail.³ Besides attack by the reductant at the carboxyl bound to the cobalt, attack at a remote $-\text{CO}_2\text{R}$ group with electron transfer through the (conjugated) ligand has been demonstrated. This paper reports the results of substituting halogen for hydrogen in the ligand: in the acetates and benzoates the carbon involved in halogenation is not a participant in the electron transfer path, while in the fumarates the halogen is attached to carbon situated between the cobalt center and the remote carboxyl. Although the rate of reaction is changed only slightly, there are striking alterations in the reaction paths for the reduction as the position of halogenation is varied.

Experimental

Chemicals. Compounds Used as Ligands.—The carboxylic acids used were the purest grade available from Distillation Products Industries or from the Fisher Scientific Co., except 4-cyanobenzoic acid and chloromaleic anhydride (The Aldrich Chemical Co.). Chlorofumaric acid was prepared from chloromaleic anhydride by heating with excess hydrochloric acid on a water-bath. To prepare bromo- and iodofumaric acids, the corresponding hydrogen halide and acetylenedicarboxylic acid were mixed in water, allowed to stand, dried and recrystallized. Dichloro- and dibromofumaric acid were prepared by the action of chlorine or bromine on an aqueous solution of acetylenedicarboxylic acid at 0°. Diiodofumaric acid was prepared by the method of Eichelberger.⁴

The method for preparation of the pentammine cobalt(III) complexes has been described elsewhere.³

Reductants.—Solutions containing chromic, europic or vanadyl perchlorate and perchloric acid were reduced over amalgamated zinc and stored under nitrogen until required. The stock solution of vanadyl perchlorate was prepared from vanadyl sulfate and barium perchlorate. Europic perchlorate solution was obtained by dissolving 99%

europium oxide (Allied Chemical Corporation, Trona brand, code 1012) in perchloric acid, filtering and diluting with water. The sodium perchlorate solution used to adjust the ionic strength of solutions to 1.0 was prepared by mixing equivalent amounts of A.R. sodium hydroxide and perchloric acid.

Kinetic Measurements.—The solutions of the pentammine cobalt(III) complexes and the reductants were either mixed by a stream of nitrogen, then transferred under nitrogen to the 10-cm. optical cells, or the complex solution was degassed directly in the cells (fitted with serum caps), and the reductant then added from a syringe. Both methods gave the same rate constants. The rate of reaction was studied by following the rate of disappearance of the 500 m μ absorption maximum of the cobalt complex. Three spectrophotometers were used in the course of this work: a Beckman DK1 recording spectrophotometer, a Beckman DK2 and a Perkin-Elmer 350. The method for analysis of the rate plots to yield specific rate constants has been described previously.³ Infrared spectra were measured on a Perkin-Elmer Infracord.

Analysis of Complexes.—The nitrogen content of the pentammine cobalt complexes was determined by the modified Kjeldahl method of Horan and Eppig.⁵ Experiment showed that the reproducibility was better than 2%.

The perchlorate content of the complexes was determined by precipitation with tetraphenylarsonium chloride. The acid equivalent of each complex was determined by titration with standard base,³ using a Phillips 9400 pH meter equipped with an Ingold combination electrode (No. 404).

Reduction in O¹⁸-Enriched Water.—The succinate complex (1×10^{-4} mole) was dissolved in 10 cc. of enriched water (1.6% D₂O¹⁸; The Isomet Corporation); acid and water (total added = 0.5 cc.) were added to bring the $[\text{H}^+]$ to 0.2 or 0.6 M, then 1 cc. of 0.1 M vanadous ion was added. The solution was stirred with nitrogen for 30 minutes, extracted with ether for 4 hr. and the extract dried over anhydrous sodium sulfate for 24 hr. After removal of the ether by warming, the dried residue was dissolved in sodium carbonate solution, then acidified and re-extracted with ether. The product was analyzed for O¹⁸ content by the method of Anbar and Guttman.⁶

Results

1. Reactions Independent of Hydrogen Ion Concentration.—All these reactions obeyed the rate law

$$-d(\text{CoL}^{++})/dt = k(\text{CoL}^{++})(\text{reductant})$$

(5) H. A. Horan and H. J. Eppig, *ibid.*, **71**, 581 (1949).

(6) M. Anbar and S. Guttman, *Intern. J. Appl. Radiation and Isotopes*, **5**, 233 (1959).

(1) Presented in part at the Sixth International Conference on Coordination Chemistry, Detroit, Mich., August, 1961.

(2) Department of Chemistry, The University of Kansas, Lawrence, Kan.

(3) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).

(4) L. Eichelberger, *ibid.*, **48**, 1321 (1926).

where CoL^{++} represents the pentamminecobalt (III) complex. Rate measurements were made over a range of 25° , and the free energies, heats and entropies of activation were determined from the usual expressions

$$k(\text{specific rate constant}) = (kT/h)e^{\Delta F^\ddagger/RT}$$

$$= (kT/h)e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

The results for averaged k , ΔS^\ddagger and ΔH^\ddagger are listed in Tables I-III.

TABLE I
SPECIFIC RATE CONSTANTS AT 25° (L. MOLE $^{-1}$ SEC. $^{-1}$)
 $\mu = 1.0$, $\text{CoL}^{++} = 5 \times 10^{-4} M$

Complex	$k_{\text{Cr}^{++}}$	$k_{\text{V}^{++}}$	$k_{\text{Eu}^{++}}$
Acetato	0.18 ^a	0.43	0.18
Chloroacetato	.10	1.25	3.16
Cyanoacetato	.11	1.13	..
Dichloroacetato	.074	1.03	2.08
Benzoato	.14	0.52	0.24
<i>o</i> -Chlorobenzoato	.074	.57	.39
<i>o</i> -Iodobenzoato	.082	.90	.28
<i>o</i> -Phthalato	.075 ^a	1.01	2.16
<i>m</i> -Phthalato	.093 ^a	0.60	0.64
<i>p</i> -Chlorobenzoato	.21	.60	..
<i>p</i> -Iodobenzoato	..	.37	0.27
<i>p</i> -Hydroxybenzoato	.13	.53	..
<i>p</i> -Cyanobenzoato	.18	.88	..
<i>p</i> -Sulfobenzoato	.16 ^b

^a Ref. 3. ^b Ref. 8.

TABLE II
ENTROPIES OF ACTIVATION (CAL./MOLE DEGREE)

Complex	$\Delta S^\ddagger_{\text{Cr}^{++}}$	$\Delta S^\ddagger_{\text{V}^{++}}$	$\Delta S^\ddagger_{\text{Eu}^{++}}$
Acetato	-50 ^a	-41	-47
Chloroacetato	-37	-27	-25
Cyanoacetato	-49	-27	..
Dichloroacetato	-55	-26	-35
Benzoato	-46	-37	-40
<i>o</i> -Chlorobenzoato	-43	-24	-50
<i>o</i> -Iodobenzoato	-54	-5	-51
Salicylato	..	-27	..
<i>o</i> -Phthalato	-45 ^a	-24	-30
<i>m</i> -Phthalato	-56 ^a	-29	-33
<i>p</i> -Chlorobenzoato	-28	-33	..
<i>p</i> -Iodobenzoato	..	-30	..
<i>p</i> -Hydroxybenzoato	-30	-28	..
<i>p</i> -Cyanobenzoato	-37	-24	..
<i>p</i> -Sulfobenzoato	-34 ^b

^a Ref. 3. ^b Ref. 8.

The rate of reaction of the pentamminesuccinato or methyl-succinato complex with vanadous or europous ion is independent of hydrogen ion concentration but is much greater than when the reductant is chromous. Table IV shows the average values of k found as a function of temperature.

Titration of the solutions containing Co^{++} , Eu^{++} and the ligand immediately after reaction showed that acid was produced equivalent to the pentamminemethylsuccinato complex reduced. Further, ether extraction of these solutions when either Eu^{++} or V^{++} was the reductant yielded succinic acid, not the half-ester.

Experiments were repeated using enriched water (1.6% D_2O^{18}) and the resulting succinic acid analyzed for isotopic oxygen content. The results are

TABLE III
HEATS OF ACTIVATION (KCAL./MOLE)

Complex	$\Delta H^\ddagger_{\text{Cr}^{++}}$	$\Delta H^\ddagger_{\text{V}^{++}}$	$\Delta H^\ddagger_{\text{Eu}^{++}}$
Acetato	3.5 ^a	5.8	4.4
Chloroacetato	7.9	9.4	9.3
Cyanoacetato	4.0	9.4	..
Dichloroacetato	2.5	9.6	6.9
Benzoato	4.9	6.7	6.2
<i>o</i> -Chlorobenzoato	6.0	10.5	3.2
<i>o</i> -Iodobenzoato	2.8	15.8	3.3
Salicylato	..	9.3	..
<i>o</i> -Phthalato	5.1 ^a	10.2	8.2
<i>m</i> -Phthalato	2.6 ^a	9.0	7.9
<i>p</i> -Chlorobenzoato	10.0	8.0	..
<i>p</i> -Iodobenzoato	..	9.0	2.1
<i>p</i> -Hydroxybenzoato	9.6	9.3	..
<i>p</i> -Cyanobenzoato	7.5	10.2	..
<i>p</i> -Sulfobenzoato	8.3 ^b

^a Ref. 3. ^b Ref. 8.

TABLE IV
SPECIFIC RATE CONSTANTS FOR REACTION OF SUCCINATO AND METHYLSUCCINATO COMPLEXES (L. MOLE $^{-1}$ SEC. $^{-1}$, $\mu = 1.0$)

Complex	$k_{\text{Cr}^{++}}$	$k_{\text{V}^{++}}$	$k_{\text{Eu}^{++}}$	Temp., °C.
Succinato	0.27 ^a	0.89	2.6	25.0
	.17 ^a			14.1
		0.39		11.6
Methylsuccinato			1.85	17.0
	.17 ^a	1.0	2.5	25.0
		0.32		7.6

^a Ref. 3.

shown in Table V. The succinic acid from which the complexes were prepared gave $\text{O}^{18}/\text{O}^{16} = 0.004110$.

TABLE V
ISOTOPIC OXYGEN CONTENT OF SUCCINIC ACID

Co(III)- methylsuccinate, moles $\times 10^4$	V^{++} , moles $\times 10^4$	$[\text{H}^+]$, M	$\text{O}^{18}/\text{O}^{16}$
1.0	1.0	0.2	0.006906
4.0	4.0	.2	.008180
1.0	1.0	.6	.008034
3.9	3.9	.6	.006608

2. Reactions of Substituted Fumarate and Maleate Complexes.—The rate of reduction of cobalt(III) complexes containing fumaric acid or one of its halogen derivatives was usually dependent on the acid concentration. The form of the rate law found was

$$-d(\text{Co(III)L})/dt = [k_1 + k_2(\text{H}^+) + k_3/(\text{H}^+)](\text{Co(III)L})(\text{Red})$$

(with some complexes k_2 or k_3 was equal to zero). The specific rate constants found are listed in Tables VI and VII.

Table VIII summarizes the specific rate constants at 25° and lists ΔH^\ddagger and ΔS^\ddagger for reaction by the non-protonated path.

Correlation of Ligand Attachment with Rate.—Because an unsymmetrical dibasic ligand may be attached to the cobalt by either of the carboxyl groups, two different complexes will result on heating the pentammineaquocobalt perchlorate with

TABLE VI

SUMMARY OF SPECIFIC RATE CONSTANTS FOR PENTAMMINE-FUMARATOCOBALT(III) COMPLEXES AND CHROMOUS ION
 $(\text{NH}_3)_5\text{Co(III)L} = 5 \times 10^{-4} M$, $\mu = 1.0$, $\text{Cr}^{++} = 2 \times 10^{-2} M$

Complex	(H ⁺)	Temp., °C.	k_f^a , 1. m. ⁻¹ sec. ⁻¹	k_s , 1. m. ⁻¹ sec. ⁻¹
Chlorofumarate	0.1	20.2	1.37	0.47
	.2		1.40	.046
	.4		1.78	.27
	.6		1.95	.29
	1.0		2.50	.35
	0.1	35	..	2.3
Dichlorofumarate	.2		..	1.4
	.4		..	1.1
	.6		..	1.1
	.1	24.0	1.57	None
	.15		1.03	
	.2		1.01	
Bromofumarate	.6		0.92	
	.1	25.2	1.45	0.43
	.2		1.10	.30
	.4		0.85	.20
	.6		0.80	.13
	.1	35.0	2.4	..
Dibromofumarate	.2		1.9	.52
	.4		1.6	.37
	.6		1.6	.22
	.2	24.0	0.13	None
	.4		.13	
	.1	15.0	.078	
Iodofumarate	.6		.077	
	.1	16.5	.66	..
	.2		.60	..
	.4		.59	..
	.6		.58	..
	.1	25.2	1.08	..
Diiodofumarate	.2		1.00	0.33
	.4		0.95	.24
	.6		0.82	.10
	.1	33.5	1.60	..
	.2		1.30	..
	.4		1.15	..
Dichlorofumarate	.6		1.10	..
	.1	15.0	0.061	None
	.4		.062	
	.2	24.0	.090	
Chloromaleate	.6		.089	
	.1	24.9	18	0.89
	.2		19	.86
	.4		23	.54
			28	.60

^a k_f and k_s in this and the following table are the specific rate constants for the fast and the slow reactions, respectively.

malic acid or the halogenofumaric acids, and it is found that these complexes react at different rates with the reductants. It is important to determine which complex reacts faster: in the case of the pentamminemalato ions, this is not difficult because a comparison may be made with the rate of reduction of pentamminesuccinatocobalt(III) complex on the one hand and pentamminelactatocobalt(III) on the other (Table IX). For the halogenofumarates the assignment is not as straightforward. However, in the case of the chlorofuma-

TABLE VII

SUMMARY OF SPECIFIC RATE CONSTANTS FOR PENTAMMINE-FUMARATOCOBALT(III) COMPLEXES AND VANADOUS ION
 $(\text{NH}_3)_5\text{Co(III)L} = 5 \times 10^{-4} M$, $\mu = 1.0$, $\text{V}^{++} = 2 \times 10^{-2} M$

Complex	(H ⁺)	Temp., °C.	k_f , 1. m. ⁻¹ sec. ⁻¹	k_s , 1. m. ⁻¹ sec. ⁻¹
Fumarate	0.1	25.0	0.70	None
	.2		1.72	
	.6		4.6	
Chlorofumarate	.1	22.6	0.74	0.06
	.2		.77	.07
	.4		.95	.08
	.6		1.07	.09
	1.0		2.0	..
	0.1	35.0	1.9	..
Bromofumarate	.2		2.6	..
	.1	25.2	0.86	..
	.2		.77	..
	.4		.83	..
	.6		1.0	..
	.1	35.0	2.8	..
Dibromofumarate	.4		1.9	..
	.6		2.2	..
	.1	25.2	1.03	..
	.2		0.87	..
	.4		.57	..
	.6		.58	..
Iodofumarate	.1	35.0	1.2	None
	.2		1.1	
	.4		0.68	
	.6		0.68	
	.1	25.2	1.25	..
	.2		0.95	..
Diiodofumarate	.4		.86	..
	.6		.85	..
	.1	35.0	3.4	..
	.2		2.6	..
	.4		2.4	..
	.6		2.6	..
Chloromaleate	.1	25.2	0.84	None
	.2		.70	
	.4		.52	
	.6		.46	
	.1	35.0	2.0	
	.2		1.60	
			1.1	
			..	1.95

rates, for example, examination of the rate plots shows that the ratio of fast reacting complex to slow is 2:1. Accordingly, 3×10^{-4} mole of the mixture of the two cobalt chlorofumarate complexes was dissolved in the least amount of 0.6 M perchloric acid, 1 cc. of 0.1 M vanadous perchlorate solution added (*i.e.*, equal to half the amount of the faster ion) and the mixture stirred by passing nitrogen through it for twenty minutes. The solution was then treated with a twofold excess of concentrated hydrochloric acid and ether and ethyl alcohol added to precipitate the cobalt(III) complex. Table X shows the relative peak heights for the carbonyl absorption found in the chlorofumarate mixture (Nujol mull) before treatment with V⁺² (sample 1) and after recovery (sample 2). The carbonyl absorption frequencies for chlorofumaric acid under the same conditions are also shown.

TABLE VIII
RATE DATA AT 25°

Complex	Reductant	Spec. rate constants, ^b sec. ⁻¹	ΔH^\ddagger , kcal./mole	ΔS^\ddagger , e.u.
Chlorofumarato (fast)	Cr ⁺⁺	1.25 + 1.2(H ⁺) ^a		
	V ⁺⁺	0.75 + 1.7(H ⁺)	8.7	-30
Chlorofumarato (slow)	Cr ⁺⁺	.09 + 0.5(H ⁺) + 0.08/(H ⁺)	6.4	-47
	V ⁺⁺	.06 + 0.05(H ⁺)		
Bromofumarato (fast)	Cr ⁺⁺	.70 + 0.08/(H ⁺)	11.9	-24
	V ⁺⁺	.43 + .87(H ⁺) + .18/(H ⁺)	8.3	-32
Bromofumarato (slow)	Cr ⁺⁺	.10 + .04/(H ⁺)	11.0	-26
Iodofumarato (fast)	Cr ⁺⁺	.89 + .02/(H ⁺)	6.0	-39
	V ⁺⁺	.56 + .3(H ⁺) + .07/(H ⁺)	8.0	-33
Iodofumarato (slow)	Cr ⁺⁺	.10 + .045/(H ⁺)		
Dichlorofumarato	Cr ⁺⁺	.19 + .9(H ⁺) + .13/(H ⁺)		
Dibromofumarato	Cr ⁺⁺	.14	9.1	-32
	V ⁺⁺	.23 + .35(H ⁺) + .08/(H ⁺)	8.1	-34
Diiodofumarato	Cr ⁺⁺	.10	6.5	-42
	V ⁺⁺	.39 + .06/(H ⁺)		

^a 20.2°. ^b From $-d(\text{CoL}^{++})/dt = [k_1 + k_2(\text{H}^+) + k_3/(\text{H}^+)](\text{CoL}^{++})(\text{Red})$.

In the case of the pentammine complexes, the frequency observed must be that of the remote free carboxyl, not the carbonyl group bonded to the cobalt ($\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O}^- \end{array}$, 1600 cm.⁻¹, 1400 cm.⁻¹). Thus the complex which reacts at a faster rate with Cr⁺⁺ or V⁺⁺ is $[(\text{NH}_3)_5 \text{CoO}_2\text{C}-\text{CH}=\text{CClCO}_2\text{H}]^{++}$.

TABLE IX
AVERAGE SPECIFIC RATE CONSTANTS FOR HYDROXY ACID COMPLEXES (L. MOLE⁻¹ SEC.⁻¹, $\mu = 1.0$)

Complex	$k_{\text{Cr}^{++}}$	$k_{\text{V}^{++}}$	[H ⁺], M	Temp., °C.
Succinato	0.17			
Malato (slow)	0.17			19.0
		0.15		22.0
Malato (fast)		2.4		22.0
	1.2		0.65	19.0
	1.3		.40	19.0
	2.1		.20	19.0
	2.7		.10	19.0
Lactato		0.58		24.8
	0.98		.65	24.8
	2.2		.20	24.8
Salicylato		0.64		29.3
	0.08		.60	17.0
	.09		.20	17.0
	.12		.15	17.0
	.15		.10	17.0

TABLE X
CARBONYL FREQUENCIES FOR CHLOROFUMARIC ACID AND COMPLEXES

Compound	$\nu_{\text{C=O}}$, cm. ⁻¹	Rel. peak height	Assignment
HO ₂ CCH=CClCO ₂ H	1720	..	In HO ₂ CCCl=
(= HL)	1690	..	In HO ₂ CCH=
(NH ₃) ₅ CoL ⁺⁺	1715	0.88	In HO ₂ CCCl=
(sample 1)	1690	1.0	In HO ₂ CCH=
(NH ₃) ₅ CoL ⁺⁺	1715	0.44	In HO ₂ CCCl=
(sample 2)	1690	1.0	In HO ₂ CCH=

Discussion

1. The reduction by Cr⁺⁺ of the cobalt(III) complexes listed in Table I takes place through at-

tack by chromous ion at the carboxyl group adjacent to the cobalt. Remote attack with subsequent electron transfer through the ligand is not found even with terminal groups such as —SO₂OH, —OH or —C≡N.

The free energy of activation for the reduction by Cr⁺⁺ at 25° lies in the range 18.4–19.1 kcal./mole. It appears to increase slightly with alpha or *ortho* substitution (acetate 18.5, chloroacetate 18.7, *o*-chlorobenzoate 19.1) thus lowering the rate, but to decrease very slightly with *para* substitution (benzoate 18.7, *p*-chlorobenzoate 18.4 kcal./mole). Over-all, the effect of the substituents appears to be small, changing the specific rate constant by a factor of only three. When the reductant is vanadous ion, any substitution appears to lower ΔF^\ddagger (18.1 to 17.3 kcal./mole) and a similar, though larger, change is found with europous ion (18.5 to 16.8 kcal./mole). Zwickel and Taube⁷ have compared the rates of reaction of some cobalt(III) complexes with chromous and vanadous ions and with chromous trisdipyridyl. From the similarity of rate constants they suggest that vanadous ion reacts through an outer sphere activated complex (as Cr(dipyridyl)₃⁺⁺ does), not a bridged activated complex. A comparison of rates listed in this present work suggests that if a carboxyl group is available, reduction by vanadous or europous ion may proceed through bridged complexes. Other evidence in support of this view has been found: the reduction of pentamminemethylfumaratocobalt(III) ion with Cr⁺⁺ aq., V⁺⁺ aq., or Eu⁺⁺ aq. occurs with accompanying ester hydrolysis, but this is not the case when the reductant is chromous or vanadous trisdipyridyl ion.⁸

The free energy of activation, ΔF^\ddagger , may be written as $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, and while it is found that substitution in the ligand has only a small effect on ΔF^\ddagger , this is not so for ΔH^\ddagger or ΔS^\ddagger . Large changes (in opposite directions) occur in both. The line best fitting the experimental points is given by

$$\beta = \alpha\Delta H^\ddagger - T\Delta S^\ddagger$$

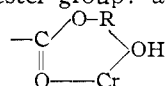
(7) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(8) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

where for chromous ion, $\alpha = 0.94$, $\beta = 18.0$ kcal./mole, for vanadous or europous, $\alpha = 0.97$, $\beta = 17.5$ kcal./mole. Plots of ΔH^\ddagger have been used⁹ as criteria for the absence of reduction by remote attack, non-protonated path: deviations are found with complexes such as fumarato or phenylfumarato where other methods¹³ have definitely established reaction by this path.

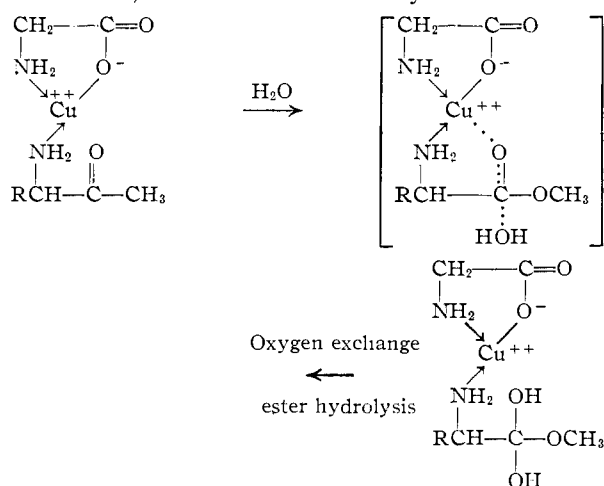
Considering the changes in ΔS^\ddagger [when chromous ion is the reductant, replacement of an *ortho* hydrogen by chlorine or iodine makes ΔS^\ddagger much more negative; when vanadous ion is reductant, ΔS^\ddagger becomes much less negative (-37 , -24 , -5 e.u.)], a similar, though smaller, trend in opposite directions is found in the acetates and the *para* substituted benzoates. As the size of the substituent increases, ΔS^\ddagger usually becomes more negative when the reductant is chromous ion and less negative when the reductant is vanadous. In the cobalt(III)-chromous system, the result of the electron transfer is the formation of one substitution-inert Cr(III) complex from the inert Co(III); in the cobalt(III)-vanadous system, the change is from the substitution-inert Co(III) complex to the labile V(III). Because of the requirement¹⁰ that the six groups be in place about Cr(II) before electron transfer, the trend toward more negative ΔS^\ddagger with increasing size of substituent is to be expected. There are no such stringent requirements when vanadous is the reductant; the activated complex can involve looser bonds.

Carboxyl Group Catalysis.—The fairly close similarity in ΔF^\ddagger for reactions of Cr^{++} , V^{++} and Eu^{++} does not hold when the substituent in the *o*-position is $-\text{CO}_2\text{R}$, and even when the carboxyl group is removed to a β -position (as in succinic acid), vanadous and europous ions reduce the cobalt(III) complex much more rapidly. The ratio of specific rate constants $k(o\text{-phthalato})/k(\text{benzoato})$ is 0.5 for Cr^{++} reduction, but 1.95 for V^{++} and 9 for Eu^{++} reduction. With the succinato or methylsuccinato complexes, the ratio $k(\text{Me/succinato})/k(\text{acetato})$ is 1.0 for Cr^{++} , but 2.3 for V^{++} and 14 for Eu^{++} . The rate of this reduction by V^{++} or Eu^{++} is independent of the acid concentration of the solutions, and isotope experiments show carboxyl oxygen exchange up to an equivalent of 0.6 atom, in contrast to the 0.02 atom found in the reaction of the methylfumarato complex where remote attack and electron transfer through the ligand may occur.¹¹ Libby¹⁰ has discussed the alkyl-oxygen fission in terms of the stereochemistry of the (remote) ester group: a six-membered ring

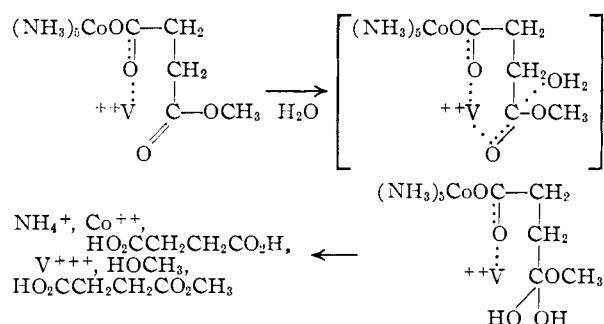
may be formed  with subsequent

capture of the R carbonium ion by the covalently bonded water. In the present case, attack is not at the remote carboxyl, but the adjacent; any hydrolysis of the remote ester group can be

regarded as metal-catalyzed. The second carboxyl group made available may coordinate and reduce further the repulsion of the positive charges of the metals. The ester hydrolysis is probably similar to that found in α -aminoesters induced by metal ions, where the reaction may be written as¹²



In the present work, the reaction may be written as



The effect is not observed when Cr^{++} aq. is reductant.³

Hydroxy Group Catalysis.—With alpha or *ortho* hydroxy substitution, adjacent attack occurs with all three reductants, but the rate law for chromous ion shows, in addition, a term inverse in hydrogen ion concentration. This catalysis is found only when the hydroxy group is alpha or *ortho* to the carboxyl bound to the cobalt: only one of the isomeric malato complexes ($[(\text{NH}_3)_5\text{CoO}_2\text{CCH}(\text{OH})\text{CH}_2\text{CO}_2\text{H}]^{++}$ and $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CH}(\text{OH})\text{CO}_2\text{H}]^{++}$) shows the effect; the other behaves in a similar way to the succinato or acetato complexes. Since the effect is found in complexes of monocarboxylic acids (lactic acid, for example), the acid-inverse term in the rate law must correspond to removal of a proton from the hydroxy group; the resulting chelation could again decrease the repulsion of charge on the metal centers.

2. Substituted Fumarate Complexes.—If the ligand is not symmetric about the double bond, then two different complexes can be obtained, and experimentally two different rates of reaction are found when the mixture is reduced with chromous or vanadous ion. The range of temperatures over which the measurements can be made is

(9) "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, ed., The Macmillan Co., New York, N. Y., 1961, p. 293, Figs. 1, 2.

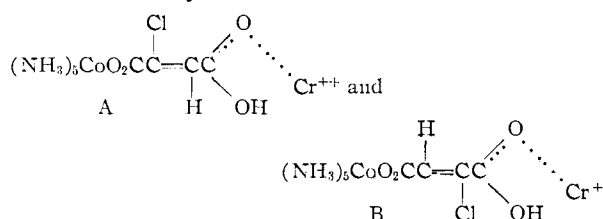
(10) W. F. Libby, Natl. Acad. Sci., Autumn Meeting, October-November, 1961, California.

(11) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **81**, 5000 (1959).

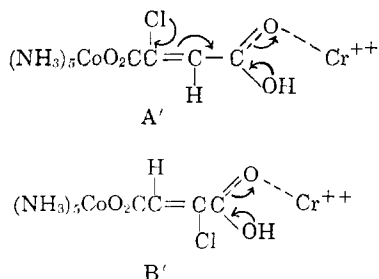
(12) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957).

limited, since at low temperatures the rate of reduction of the ligand becomes faster than the rate of reduction of the complex, while at higher temperature the rate of complex reduction becomes too fast to measure. The infrared study shows that the complexes which react faster with the reducing agent are $[(\text{NH}_3)_5\text{CoO}_2\text{C}-\text{CH}=\text{C}(\text{Hal})\text{CO}_2\text{H}]^{++}$. With chromous ion, the rate of the reaction by the acid-independent path is greater than the rate of reaction of the pentammineacetato complex, implying at least some electron transfer by remote attack.¹³ This is in contrast to the acid-independent term in the rate law for the slower reaction of the isomeric complexes: the specific rate constants are almost identical with those for the corresponding halogenoacetato complexes, and ΔH^\ddagger and ΔS^\ddagger both fit the α, β -equation.

The transition states for remote attack in the two isomers may be written as



The difference in rates may be related back to the + Electromeric effect¹⁴ of the halogens, + E_{Cl} , + E_{Br} , + E_{I} . In A, the halogen (here chlorine) is conjugated with the remote carbonyl oxygen; any increase in the double bond character of the Cl-C bond (A') will be at the expense of conjugation between the chromous and cobalt(III) centers. Thus, while increasing the possibility of bonding



(13) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 564 (1961).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 88.

between O and Cr, the possibility of electron transfer decreases, whereas the chlorine in B is not conjugated with the carbonyl oxygen, and consequently cannot influence the rate in the same way (B'). The size of the substituent, however, is just as important here as in the case of the substituted acetato and benzoato complexes: as the size increases, the term in the rate law relating to remote attack with electron transfer by the protonated path becomes negligible in relation to the adjacent attack, probably not because of any intrinsic loss of conjugated system, but rather because of greater differences in times required for rearrangement of the ligand into a configuration suitable for electron transfer. This is possibly also the reason for the non-appearance of the acid-dependent term in the rate laws of the dibromo- and diiodofumarato complexes with chromous ion. The effect is not limited to derivatives of fumaric acid: for the chloromaleato mixture

$$\begin{aligned}
 -d(\text{CoL}^{++})/dt &= [17 + 20(\text{H}^+)](\text{CoL}^{++})(\text{Cr}^{++}) \quad (\text{fast}) \\
 &= [0.12 + 0.07/(\text{H}^+) + \\
 &\quad 0.6(\text{H}^+)](\text{CoL}^{++})(\text{Cr}^{++}) \quad (\text{slow})
 \end{aligned}$$

Reduction by vanadous ion never occurs by remote attack on the non-protonated ligand, even with the fumarato complex (at 25°, $-d(\text{CoL}^{++})/dt = [0.3 + 7.1(\text{H}^+)](\text{CoL}^{++})(\text{V}^{++})$). This absence of a remote attack, acid-independent term has been noted before in the reactions of vanadous ion with phthalate and carboxynaphthalene complexes.¹⁵ Because the bonding requirements (and consequently, the orientation of the ligand) are not as stringent as for chromous ion, the remote attack protonated path persists even in the reduction of the dibromo- and iodofumarato complexes.

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(15) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 4920 (1961).