change in the basicity of the ligand on the rate of reaction. The second-order rate constant k_2 increased in the following order for the different ligands used in the study: $P(OC_2H_5)_3$ < $P(OCH_2)_3CCH_3$ < $PO_3C_6H_9$. The basicity of these ligands toward BH_3 and $B(CH_3)_3$ increases in the same order.[13,14]

If 2,2'-dipyridyl (pK_a = 4.50) is replaced in the Mo complex by a stronger base, 4,4'-dimethyl-2,2'-dipyridyl (pK_a = 5.45), the result should be an increase in the formal negative charge on the Mo atom. Therefore if the reaction does proceed by a displacement mechanism (this would also be consistent with the dissociation mechanism), then the second-order rate constant for the reaction of $Mo(CO)_4(dipy)$ with L should be greater than the second-order rate constant for the reaction of $Mo(CO)_4(4,4'-dimethyl-dipy)$ with L. Using ligand concentrations of 0.262, 0.786, and 1.18 M, rate constants of 3.41×10^{-4}, 4.18×10^{-4}, and 5.00×10^{-4} sec.$^{-1}$, respectively, were found for the reaction of $Mo(CO)_4(4,4'-dimethyl-dipy)$ with $P(OCH_2)_3CCH_3$ at 47.9°. The first- and second-order rate constants are 2.94×10^{-4} sec.$^{-1}$ and 1.64×10^{-4} l./mole sec., respectively. If k_2 for this reaction is compared with k_2 for the corresponding $Mo(CO)_4$-(dipy) reaction (Table III) in 1,2-dichloroethane, it can be seen that k_2 does decrease as the basicity of the bidentate ligand is increased. It is also to be noted that k_1 for $Mo(CO)_4(4,4'-dimethyl-dipy)$ is about twice that for $Mo(CO)_4(dipy)$. This trend was observed for the analogous Cr complexes and discussed in detail in an earlier publication.[1]

(13) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, 1, 863 (1962).
(14) J. G. Verkade and C. W. Heitsch, *ibid.*, 2, 512 (1963).

$W(CO)_4(dipy)$ in its reactions with $PO_3C_6H_9$ and $P(OC_2H_5)_3$ also obeys a two-term rate law of the form given in eq. 3. The values of k_1 and k_2 at three different temperatures given in Table III show the same trends as for the reactions of $Mo(CO)_4(dipy)$, and the mechanisms corresponding to the two terms of the rate law are presumably the same as those discussed for the analogous Mo complex. Again k_2 increases with increasing basicity of L in the order $P(OC_2H_5)_3$ < $PO_3C_6H_9$.

Because W is a slightly larger atom than Mo, the displacement mechanism would predict that k_2 might be greater for the W complex than the Mo complex, if the Mo–CO and W–CO bond energies were the same. However, this is not immediately evident from the second-order activation energies since the $W(CO)_4$-(dipy) reactions have considerably higher second-order activation energies than do the corresponding $Mo(CO)_4$ dipy reactions in the same solvent. The higher activation energies for the W reactions may be accounted for by the presence of not only a stronger W–L bond as compared to the Mo case but also a stronger W–CO bond in the activated complex. The stronger W–CO bond may more than compensate for a stronger W–L bond, thus increasing the activation energy to a point where it is actually greater than the activation energies for the $Mo(CO)_4(dipy)$ reactions.

The activation energies of the first-order path are remarkably similar for the complexes of Cr, Mo, and W. They do not reflect trends in the M–CO bond strengths[15] of the hexacarbonyls of these metals. The differences in the rates of these reactions depend largely on differences in the entropies of activation.

(15) A. Foffani and S. Pignataro, *Z. physik. Chem.* (Frankfurt), 45, 79 (1965).

Electron-Transfer Reactions Involving Chelating Bridging Groups[1]

Ronald D. Butler[2] and Henry Taube

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received August 23, 1965

When α-hydroxy acids act as bridging groups in the reduction of carboxylatopentaamminecobalt(III) ions by Cr^{2+}, the specific rates are significantly higher than for previously reported systems involving simple adjacent attack. With glycolate as bridging group, the initial chromium(III) product is metastable and reverts to a species identical with the glycolatochromium(III) ion prepared by conventional methods; this evidence, together with the fact that the initial Cr(III) product has a higher extinction coefficient, indicates that the chromium is chelated by the bridging group in the activated complex. The rates of the oxidation–reduction reactions are independent of acid in the range 0.05 to 1.0 N H^+, and in each case the reaction is described by the rate law $-d(Co^{III})/dt = k(Co^{III})(Cr^{II})$. *When alkyl-substituted malonates are the ligands, the rate law is of the general form* $-d(Co^{III})/dt = k_1(Co^{III})(Cr^{II}) + k_2(Co^{III})\cdot(Cr^{II})/(H^+)$. *No acid-catalyzed path is observed for these reactions, in contrast to the case of the malonato complex, presumably because the inductive effect of the alkyl group makes the loss of the methylene hydrogen more difficult.*

Introduction

The subject of electron transfer through organic bridging groups has been explored in considerable detail.[2-6]

(1) From a dissertation submitted by R. D. B. in partial fulfillment of the requirements for the Ph.D. degree, April 1964.
(2) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, 83, 1785 (1961).

(3) R. T. M. Fraser and H. Taube, *ibid.*, 83, 2239 (1961).
(4) R. T. M. Fraser and H. Taube, *ibid.*, 83, 2242 (1961).
(5) G. Svatos and H. Taube, *ibid.*, 83, 4172 (1961).
(6) R. T. M. Fraser, *ibid.*, 83, 4920 (1961).

The influence of conjugation, mobile bond order, steric factors, and the presence of various types of substituents have been studied, and in many cases the results have established the position of attack by the reductant. We report here evidence that chelation of Cr^{2+} by the ligand on Co(III) in the activated complex can and does affect the reaction rates and activation parameters.

Fraser and Taube[4] have suggested that conjugation effects are responsible for the comparatively high reaction rates of chromium(II) with maleato- and fumaratopentaamminecobalt(III) and that a chelating effect operates to bring about a higher rate in the case of the maleato isomer; indeed, their evidence for the induced isomerization of the maleato bridging group during electron transfer rests in part upon the assumption that maleate forms the chelated chromium(III) complex quantitatively, while fumarate can form only the monodentate. Svatos and Taube[5] suggest that chelation may be a significant factor in electron transfer through malonate. Both the maleato- and malonatochromium-(III) products have been isolated and identified as the chelates. However, the question of whether chelation actually occurs in the activated complex has not been fully resolved, since ring closure can conceivably occur as a rapid, independent step subsequent to the electron-transfer reaction itself. Recent experiments in this laboratory[7] have shown that the monodentate form of malonatochromium(III) ion does in fact undergo ring closure slowly, and since the Cr(III) product of the reaction of Cr^{2+} with the malonate complex is known to be the chelate, the results support the interpretation that chromous is chelated by malonate in the activated complex. In the experiments we are reporting here, we have established that in certain systems the bridging group does form a chelated structure with the reducing cation, and that this more favorable geometry leads to higher specific rates than are normally observed when only attack at the bound carboxyl can take place.

Experimental Section

Materials. Salts of the type $(NH_3)_5CoL(ClO_4)_2$, where L is the anion of an organic acid, were prepared by methods described previously.[2] Aquopentaamminecobalt(III) perchlorate (4.6 g., 0.01 mole) was dissolved in a minimum of hot water, a large excess (usually 0.10 to 0.20 mole) of the organic acid was added with stirring, and the pH of the solution was adjusted to 4–5 with reagent grade $NaHCO_3$. The mixture was heated for 2–3 hr. at 70° to effect conversion to the carboxylato complex. A stoichiometric amount of 60% $HClO_4$ was added and the product allowed to crystallize by slowly cooling first to room temperature, then in a refrigerator at 5°, and finally in an ice bath. The crystals were filtered, washed thoroughly with 1 N $HClO_4$, ethanol, and ether, and recrystallized twice from 1 N $HClO_4$. Final drying was done overnight in a vacuum oven at 50°.

Most of the samples prepared in this manner were obtained as good crystals in pure form. However, difficulties were encountered in the preparation of complexes of several substituted malonates. Attempts to synthesize the complexes of phenylmalonate, chloromalonate, bromomalonate, and benzalmalonate were unsuccessful, primarily for two reasons. First, the

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

Table I. Elementary Analyses on Various Pentaamminecobalt(III) Perchlorates

Ligand		Co	Cl[a]	C	H	N
Benzylmalonate	C[b]	11.0	13.3	...	4.5	13.1
	O	12.0	12.9	...	4.6	13.6
Glycolate	C	14.1	17.0	5.8	4.3	16.8
	O	13.5	17.0	5.9	4.6	16.7
Lactate	C	...	16.4	8.3	4.7	16.2
	O	...	15.9	8.4	4.7	16.4
Benzilate	C	...	12.4	29.5	4.6	12.3
	O	...	11.9	28.1	4.6	11.5
d-Tartrate	C	12.0	14.4	9.8	4.1	14.2
	O	11.2	13.9	9.8	4.2	13.7
Ethoxyacetate	C	...	15.9	10.8	5.0	15.7
	O	...	14.5	11.0	5.3	15.4
Phenoxyacetate	C	...	14.4	19.5	4.5	14.2
	O	...	13.9	20.0	4.9	14.5
Pyruvate	C	13.7	16.5	8.4	4.2	16.3
	O	13.6	15.1	9.1	4.5	16.1

[a] Difficulty is often encountered with the chlorine analyses in these compounds, and the results are almost invariably too low. [b] C for calculated, O for observed.

conditions required for conversion to the cobaltic complexes were such that some decarboxylation took place and undesired products were formed.[8] Second, the products did not crystallize well, forming microcrystalline precipitates that were difficult to filter and recrystallize. In most cases, appreciable quantities of the parent organic acids were occluded in the products and could not be completely removed by recrystallization and washing with organic solvents.

Good samples as judged by homogeneity of the product, and in many cases by analysis (Table I), were obtained with malonate, dimethylmalonate, ethylmalonate, glycolate, lactate, methyllactate, benzilate, methoxyacetate, ethoxyacetate, phenoxyacetate, pyruvate, and d-tartrate. Complexes with β-hydroxy acids as ligands could not be prepared because of their marked tendency to form lactones and polymeric species. The synthesis of malatopentaamminecobalt(III) ion led to the formation of two isomers, as expected, since coordination can occur with the hydroxyl group either α or β to the bound carboxyl. Fortuitously, repeated crystallization of this material led to the separation of two fractions which were kinetically different and which were assigned structures on the basis of their different reactivities toward Cr^{2+}. A kinetically homogeneous preparation of the isomer which reacted more slowly was obtained; the sample comprised predominantly of the other isomer contained about 10% of the "slower" form. Fraser[9] has also reported two forms of the malato complex but did not succeed in separating them completely. For complexes used in this study and not mentioned in Table I, cobalt analyses were performed and extinction coefficients measured. If these agreed reasonably well with the expected values and if the preparations were nicely crystalline, the complexes were taken as being sufficiently pure.

Chromous ion was prepared by reducing standard stock solutions of chromic perchlorate with amalgamated zinc under an atmosphere of purified nitrogen. Freshly prepared samples of Cr^{2+} in standard $HClO_4$

(8) E. Gelles, *J. Am. Chem. Soc.*, 75, 6199 (1953).
(9) R. T. M. Fraser, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 187–195.

were used for each set of experiments. The chromous generator consisted of a 25-ml., two-neck flask fitted with rubber serum-bottle stoppers. Purified N_2 was introduced by means of a stainless steel hypodermic needle, and a second needle served as a vent. Samples of the air-sensitive reagent were withdrawn and transferred with ordinary hypodermic syringes (Becton–Dickinson). The syringes were calibrated and found to be sufficiently accurate to allow reliable volumetric transfers, as well as air-tight so that no detectable atmospheric oxidation of the chromous occurred. No difficulty was encountered with respect to contamination by the stainless steel needles; with the malonato and ethylmalonato systems, a number of experiments were done in all-glass apparatus without using syringes, and the results agreed with those obtained by the syringe techniques.

Standard solutions of sodium and lithium perchlorates were prepared by treating weighed samples of the respective primary standard carbonates with a slight excess of 60% $HClO_4$. After effervescence had ceased, the solutions were heated to remove CO_2 and diluted to volume with distilled water. Excess acid was determined by titration with standard 0.1 N NaOH.

Organic acids were obtained from Eastman Organic Chemicals, K and K Laboratories, and Matheson Coleman and Bell. They were used as received, except for those malonate derivatives that were available only as the diethyl esters. The esters were treated with a stoichiometric amount of sodium hydroxide in methanol and refluxed until saponification was complete. The sodium salts, which are insoluble in methanol, were filtered, washed thoroughly with methanol, and dried *in vacuo*. The free acids were not isolated, rather the sodium salts were used directly for the preparation of the cobalt complexes.

Experimental Methods. All spectrophotometric measurements were made on a Cary Model 14 recording spectrophotometer. An external constant-temperature bath with a circulating pump served to maintain the temperature of the cell compartment constant to within 0.1°.

All reagents except the reductant were first measured into a 50-mm. cylindrical spectrophotometer cell having two openings. The openings were sealed with rubber serum-bottle stoppers and the solutions thoroughly degassed with purified nitrogen, in the manner described above for the chromous reagent. After waiting for the system to reach the desired temperature, a measured aliquot of standard Cr^{2+} was injected; the cell was shaken to ensure thorough mixing and rapidly transferred to the spectrophotometer. A stopwatch was started simultaneously with the addition of the reductant to note zero time. The spectrophotometer controls were set to record the decrease in absorbance of the Co(III) species as a function of time; the wave length was selected so that the absorbance due to the cobaltic ion was at a maximum, *viz.*, 350 mμ (ϵ ~60) or 503 mμ (ϵ ~73).

Second-order specific rates were computed by means of the equation

$$\log \frac{aA_t + (b-a)A_0 - bA_\infty}{a(A_t - A_\infty)} = \frac{b-a}{2.303}kt + \log \frac{b}{a}$$

where a = initial concentration of Co(III), b = initial

concentration of Cr(II), and A_0, A_t, A_∞ = absorbance at times $t = 0$, t, and ∞, respectively. The rate constant k was determined graphically from a plot of the function on the left-hand side against time.

When the rates were low ($k \leqslant 0.10$ F^{-1} sec.$^{-1}$), it was found convenient to use a large excess of reductant (for most purposes a 20-fold excess of chromous was sufficient) and the system treated as for a first-order reaction. All plots of the rate data were taken to be satisfactory if they were linear over approximately 90% consumption of the deficient reactant.

Identification of Reaction Products. In all of the reactions studied, transfer of the bridging ligand from cobalt to chromium was observed, and the substitution-inert carboxylatochromium(III) ions were identified by means of their absorption spectra. For comparison, authentic samples of a number of the CrL^{2+} species were prepared by the method of Hamm, *et al.*[10] Equimolar amounts of $Cr(H_2O_6)^{3+}$ and organic acid were heated at 90° for 3–4 hr. in 0.1 N HClO$_4$ and the products separated by ion exchange. Ions of charge +1 were eluted readily from a Dowex 50W-X12 column while +2 ions were removed by 1 N acid; unreacted chromic ion was held back strongly. The complexes were characterized spectrophotometrically; the reported extinction coefficients were calculated on the basis of the chromium concentration, which was determined colorimetrically as chromate.

Results

Spectra of Reactants and Products. The absorption spectra of all the $(NH_3)_5CoL^{2+}$ ions studied were found to be remarkably similar. The values listed in Table II demonstrate the near constancy of their spectrophotometric properties. All have maxima at or near 503 mμ, with extinction coefficients close to 73. In most cases maxima were also observed at 350 mμ, and the corresponding extinction coefficients were in the range 58 to 62; where no value of ϵ is given, the ligand itself absorbs in the 350-mμ region and the spectrum exhibited either a shoulder or a continuous increase of extinction into the ultraviolet.

Table II. Spectrophotometric Properties of Carboxylatopentaamminecobalt(III) Ions, $(NH_3)_5CoL^{2+}$

Ligand	$\epsilon_{503\ m\mu}$	$\epsilon_{350\ m\mu}$
Malonate	73.1	58.0
Ethylmalonate	73.5	58.6
Benzylmalonate	73.0	61.1
Glycolate	73.0	59.8
Lactate	73.0	62.1
Methyllactate	72.6	...
Benzilate	72.5	...
d-Tartrate	73.4	61.0
Ethoxyacetate	72.6	60.2
Phenoxyacetate	72.6	...

A wider range of spectral properties was observed for the complex ions of chromium(III). Values listed in Table III for these ions were taken from three sources: the published data of Hamm, *et al.*[10]; measurements on samples we prepared from $Cr(H_2O)_6^{3+}$ and the respective organic acids and isolated by ion exchange; and the spectra of the reduction products of $(NH_3)_5$-

(10) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).
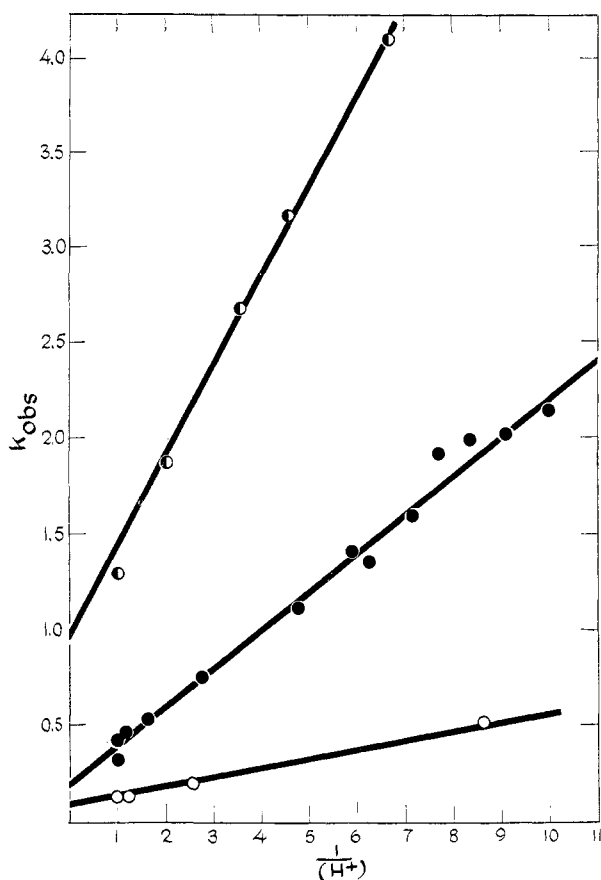
Figure 1. The effect of acidity on the rate of reduction by Cr^{2+} of substituted malonatopentaamminecobalt(III) ions: ◑, phenylmalonate; ●, ethylmalonate; ○, dimethylmalonate.

CoL^{2+} by Cr^{2+} taken immediately after reaction. The values reported by Laswick and Plane[11] for $Cr(H_2O)_6{}^{3+}$ are included for comparison.

Table III. Spectrometric Properties of Aquo- and Carboxylatochromium(III) Ions

Ligand	λ, mμ	ε	λ, mμ	ε
Water[a]	408	15.6	574	13.4
Acetate[b]	406	20.7	568	21.6
Malonate[b]	415	27.2	560	32.4
Malonate[c]	415	25.3	560	31.2
Ethylmalonate[c]	418	25.1	562	29.7
Glycolate[b]	409	23.6	569	21.8
Glycolate[c]	411	30.9	569	24.5
Glycolate[d]	411	39.3	569	30.3
Lactate[b]	409	31.2	563	25.7
Lactate[d]	411	45.0	570	40.1
d-Tartrate[b]	416	36.6	555	33.4

[a] Data of Laswick and Plane.[11] [b] Calculated values of Hamm, et al.[10] [c] Authentic sample prepared by method of Hamm, et al.,[10] and isolated by ion exchange. [d] Initial product of oxidation-reduction reaction between Cr^{2+} and the respective pentaamminecobalt(III) complex.

Substituted Malonates as Bridging Groups. Svatos and Taube[5] reported that the reduction of malonatopentaamminecobalt(III) ion by chromium(II) is described by a three-term rate law

$$\text{rate} = (Co^{III})(Cr^{II})[k_1 + k_2/(H)^+ + k_3(H^+)] \quad (1)$$

At 25° and $\mu = 1.0$, the values reported for the specific

(11) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, 81, 3564 (1959).

Table IV. Summary of Rate Data for the Reactions of Cr^{2+} and Substituted Malonatopentaamminecobalt(III) Ions

Ligand	Temp., °C.	k_1, F^{-1} sec.$^{-1}$	k_2, sec.$^{-1}$
Ethylmalonate[a]	14.7	...	0.09
	25.0	0.18	0.20
	35.6	0.25	0.40
Benzylmalonate	25.0	0.99	0.46
Dimethylmalonate	25.0	0.070	0.050

[a] For the k_1 path, $\Delta H^* = 5.3$ kcal., $\Delta S^* = -44$ e.u.; for the k_2 path, the parameters are 11.7 kcal. and -23 e.u., respectively. We consider the values of ΔH^* reported to be accurate to within 1.5 kcal.; the corresponding accuracy in ΔS^* is 5 e.u.

Table V. Rate Data for the Reactions of Cr^{2+} and α-Hydroxy Acid Complexes of Pentaamminecobalt(III) at $\mu = 1.0$. ((H^+) Varied for Each Complex; Data Reported for 1 $M H^+$)

Ligand	Temp., °C.	k,[a] F^{-1} sec.$^{-1}$	ΔH^*, kcal.	ΔS^*, e.u.
Glycolate	6.1[b]	1.10	9.0	-26
	14.7[b]	1.91		
	25.0[b]	3.06		
	36.0[b]	5.64		
Lactate	25.0[c]	6.65		
Methyllactate	14.7	6.70	9.1	-24
	25.0[d]	11.5		
	36.2	20.3		
Benzilate	11.9	0.98	9.7	-25
	25.0[e]	1.93		
	36.2	3.65		
α-Malate	25.0[f]	$2.7 + 0.3/(H^+)$		

[a] Values reported were measured in $HClO_4$ or $HClO_4$–$LiClO_4$ media with total $(ClO_4^-) = 1.0 F$; rates in $HClO_4$–$NaClO_4$ media were acid dependent and slightly lower when extrapolated to zero acid. [b] (H^+) varied over the range 0.1 to 1.00 M to test rate law. [c] (H^+) varied over range 0.05 to 0.98 M. [d] (H^+) varied over range 0.05 to 1.00 M. [e] (H^+) varied over range 0.07 to 1.00 M. [f] (H^+) varied over range 0.10 to 0.99 M.

rates are $k_1 = 0.34 \ F^{-1}$ sec.$^{-1}$, $k_2 = 1.08$ sec.$^{-1}$, and $k_3 = 0.94 \ F^{-1}$ sec.$^{-2}$. A re-examination of this system by us gave results that are in substantial agreement; from our experiments, $k_1 = 0.29 \ F^{-1}$ sec.$^{-1}$, $k_2 = 1.24$ sec.$^{-1}$, and $k_3 = 1.00 \ F^{-2}$ sec.$^{-2}$. Little deviation from these parameters was observed when the ionic strength was increased to as high as 4.0 F by the addition of perchloric acid.

Analogous complexes, in which the hetero ligands are malonates having alkyl substituents on the central carbon atom, exhibit somewhat different kinetic behavior. Here the respective rate laws contain only two terms, the path linear in hydrogen ion being absent.

$$\text{rate} = k_1(Co^{III})(Cr^{II}) + k_2(Co^{III})(Cr^{II})/(H^+) \quad (2)$$

Figure 1 shows the rate data on the reaction of Cr^{2+}(aq) with substituted malonatopentaamminecobalt(III) ions at 25°. The individual specific rates for the three complexes are summarized in Table IV and the values found for the enthalpy and entropy of activation in the reaction of the ethylmalonato complex are recorded.

Hydroxy and Alkoxy Acids as Bridging Groups. In Tables V–VII are listed values describing the kinetic behavior of a number of complexes in which the bridging ligands contain OH or OR groups in the position α to the bound carboxyl. In our preliminary experiments on some of the hydroxy acid (glycolate and lactate) complexes, we noted an apparent dependence

Table VI. Rate Data for the Reactions of Cr^{2+} and α-Alkoxy Acid Complexes of Pentaamminecobalt(III) at $\mu = 1.0$

Ligand	Temp., °C.	$k,^a F^{-1}$ sec.$^{-1}$	ΔH^*, kcal.	ΔS^*, e.u.
Methoxyacetate	19.6°	0.285 ± 0.009	11.3	-23
	30.1	0.57 ± 0.03		
	40.0	1.030 ± 0.014		
Ethoxyacetate	25.0	0.41 ± 0.02		
Phenoxyacetate	25.0	0.148 ± 0.006		

^{a} Values reported were measured in $HClO_4$–$NaClO_4$ media with total $(ClO_4^-) = 1.0 F$ and were independent of acid concentration over the range 0.11 to 1.00 M for methoxyacetate, 0.08 to 1.00 for ethoxyacetate, and 0.13 to 1.00 for phenoxyacetate.

Table VII. Rate Data for the Reactions of Cr^{+2} and Miscellaneous Carboxylatopentaamminecobalt(III) Ions at 25°

Ligand	μ	k, F^{-1} sec.$^{-1}$
d-Tartrate^a	1.0	$1.49 + 0.06/(H^+)$
α-Malate^b	1.0	$2.7 + 0.30/(H^+)$
β-Malate^c	1.0	$0.36 + 0.03/(H^+)$
Pyruvate^d	0.10	$>2 \times 10^3$
Formate	1.0 (H^+)	~ 7

^{a} Rate law tested over an acid range from 0.07 to 1.03 M for d-tartrate, 0.10 to 0.99 M for α-malate, and 0.30 to 1.00 M for β-malate. ^{b} In ref. 9 the specific rate as a function of (H^+) is given as $0.80 + 0.23/(H^+)$ at 19°. ^{c} In ref. 9 the specific rate at 19° and $\mu = 1.0$, but unspecified acidity, is given as 0.17. ^{d} Reaction rate too high to measure precisely by our present methods or to determine the order with respect to acid.

of the rate on acid concentration, indicating a path first order in (H^+). Thus, when $NaClO_4$ is used as the background electrolyte to maintain constant ionic strength, replacement of $NaClO_4$ by an equivalent amount of $HClO_4$ leads to an increase in the specific rate, and the values observed in 1 N $HClO_4$ are some 10–25% higher than those found by extrapolating to zero acid. However, when $LiClO_4$ is used as the electrolyte, the rates are independent of acid and, within experimental error, the same as those obtained in 1 N acid. Thus the observed variations in the $NaClO_4$ media can be ascribed to changes in the activities of the reacting species and of the activated complex rather than being a manifestation of a (H^+)-dependent path.

There is a discrepancy between the values found by us for the lactate complex and those reported by Fraser.[9] Where Fraser reports a rather low reaction rate and a path inverse in hydrogen ion, we find that the reduction of the lactato complex proceeds at an unusually high rate, and we were unable to observe an inverse-hydrogen path even when the concentration of (H^+) was at the lowest possible level, which was 0.05 N in these experiments. The reasons for this disagreement are not immediately apparent. It should be noted that the materials used in the present study gave good analyses and that the specific rate we report for the lactato reaction is consistent with those observed for reactions involving related hydroxy acids.

When glycolatopentaamminecobalt(III) ion is reduced by chromous ion, the spectrophotometric evidence indicates that the glycolatochromium(III) species formed initially is distinctly different from that prepared directly from $Cr(H_2O)_6{}^{3+}$ and glycolic acid (see Table III). The apparent extinction coefficients at 411 and 569 mμ are almost 25% higher than expected, but slowly decrease to the predicted values in a first-

order process with a half-time of 22 ± 2 hr.; this rate is independent of (H^+) and does not appear to be complicated by the competing aquation reaction.

Table VII lists rate data for several related reactions. The assignment of structures to the two isomeric malatopentaamminecobalt(III) complexes was made on the basis of their comparative reactivities toward Cr^{2+}. The rate corresponding to the acid-independent path for one of the isomers is $k_1 = 2.7\ F^{-1}$ sec.$^{-1}$, which is in the same range as those for most of the α-hydroxy acid complexes studied; therefore, it was assumed that this species is the isomer having the hydroxyl group in the position α to the coordinated carboxyl, while the less reactive material ($k_1 = 0.36\ F^{-1}$ sec.$^{-1}$) was concluded to be β isomer. The stoichiometry of the oxidation–reduction reaction involving pyruvate was studied with Co(III) in excess, Cr^{2+} being added to Co(II), and the results show that one Co^{2+}(aq) is produced for each Cr^{2+} reacting, and the reaction under the conditions specified proceeds without reduction of the bridging group. The value for the reduction of formatopentaamminecobalt(III) is tentative but has been confirmed by subsequent experiments.[7]

Discussion

The results obtained for the reduction of the α-hydroxy complexes of pentaamminecobalt(III) taken in total seem to provide proof of chelation of Cr^{2+} by the hetero ligand on the oxidizing agent. The rate of reduction of any complex of this kind which we have examined is considerably in excess of that of the acetato complex, for example. If the inductive effect of the electronegative group were responsible for the rate increase, then the chloroacetato complex should be reduced at a greater rate than the acetato complex, but its rate of reduction is actually somewhat lower ($k^{12} = 0.10\ M^{-1}$ sec.$^{-1}$ compared[3] to 0.18 M^{-1} sec.$^{-1}$ for acetato). The chelate ring making use of an α-hydroxy group is expected to be more stable than one making use of an α-chloro group, and chelation of the reducing agent by the α-hydroxy ligands does therefore afford a reasonable explanation of the rate differences. It also explains the rate increase observed for the series of complexes containing glycolate, lactate, and methyllactate as ligands (the specific rates at 25° are 3.1, 6.7, and 11.8 M^{-1} sec.$^{-1}$, respectively) because the OH group is expected to become more basic with substitution of H on the α carbon by CH_3.

The best evidence for chelation was provided by an examination of the product of the reaction of the glycolato complex with Cr^{2+}. A chromic complex is formed as a result of the reaction which is metastable and which has a higher extinction coefficient than that of the final or stable form. The fact that the initial species is metastable indicates that it must have arisen before Cr^{2+} was oxidized to Cr^{3+}. It seems reasonable to suppose that in all the other reactions with Cr^{2+}(aq) of complexes of the α-hydroxy series, chelation by the ligand of Cr^{2+} also takes place. In each case there will, of course, also be a reaction path corresponding to simple adjacent attack, but if the specific rate for this reaction is at about its usual value, 0.2 M^{-1} sec.$^{-1}$, only a small fraction of the ligand will be present after reaction in the nonchelate form, which is the expected

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form of the Cr(III) product resulting from simple adjacent attack.

The rate enhancement for α-methoxyacetate or α-ethoxyacetate over acetate as ligand is considerably less than it is for the α-hydroxy complexes. This is consistent with the fact that complexing of dipositive metal ions by alcohols[13,14] is less strong than it is for water. The phenoxyacetato complex is reduced at a rate ($k = 0.15$) which suggests only simple adjacent attack by Cr^{2+}. The result for the phenoxyacetate complex also seems quite reasonable when the inductive effects of CH_3 or C_2H_5 and C_6H_5 are compared.

The six-membered ring which would result from chelation by β-hydroxyl, as in the case of β-malate, is apparently less stable than the five-membered rings which we have been considering. It should be noted also that the magnitude of the acid-independent term for malonate as ligand (0.34 from the earlier work,[5] 0.29 from the present) indicates that the contribution to the total rate by the chelate path is much less than it is for α-hydroxy ligands. Experiments with the malonate half-esters as ligands suggest 0.20 ± 0.05 as the specific rate for simple adjacent attack in the malonate system.[7]

Our experiments with substituted malonates as ligands confirm the observations made by Svatos and Taube: substitution of hydrogen at the methylene group of malonate by alkyl groups suppresses the term in the rate law which is first order in (H^+). This behavior is consistent with the view that dissociation of a proton from the methylene position accompanies attack by Cr^{2+} for the path corresponding to the term in the rate law which shows a first-order dependence on (H^+), but it by no means proves that this is the case. In fact, we must consider the possibility that the term in question is not real but is the result of a peculiar salt effect. Though this possibility is rendered unlikely by the fact that closely related complexes do not show the term in question, we feel that an effort to develop the term by investigating other derivatives, for example, those in which a methylene hydrogen is replaced by a halogen, should be made. Our own efforts in this direction did not meet with success, but we by no means exhausted the possibilities which are open for the preparations.

To what extent can the chelation effects which have been described be understood simply as improving the opportunity for Cr^{2+} to associate with the adjacent carboxyl by providing a binding site nearby which can cooperate with the adjacent carboxyl? Even with the simpler ligands such as glycolate and lactate, it is difficult to understand the effects on this simple basis. Our experiments show that the chelate form for glycolate bound to Cr(III) is not more stable than the monodentate, and a similar relationship probably obtains for the dipositive chromium ion. A second factor which may operate is that the reactivity of the Cr^{2+} is increased, perhaps because of the change in symmetry of the electric fields exerted by the ligands. When pyruvate is the ligand, an additional factor may well enter. The stability of the chelate ring with the α-carbonyl group is not likely to be much greater than with the α-hydroxy, and both groups form five-membered rings, yet the pyruvate complex reacts many times more rapidly than the glycolate or lactate. The high reactivity of the pyruvate complex can perhaps be linked to the fact that pyruvate is fairly readily reducible. The ready reducibility of the pyruvate complex and of pyruvate itself are both probably manifestations of the existence of a low-lying vacant orbital for the pyruvate structure. Whether the orbital functions in a resonance-transfer mechanism or whether as giving rise to a true radical-ion mechanism[15,16] is at present not known.

The high rate observed for the formate complex is quite surprising and is not understood by us even qualitatively. Does it point to a strong steric effect for CH_3 of acetate compared to H of formate or does it imply an electronic difference between the two ligands? The comparisons between dichloroacetate and acetate suggest that the steric effects are not great (0.074^9 vs. 0.18^2); on the other hand, it is also difficult to understand why there should be a significant electronic difference between the two ligands, acetate and formate.

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