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Electron Transfer. 46. Carbon–Carbon Bond Scission Resulting from Induced Electron Transfer

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The $(NH_3)_5Co^{III}$ complexes of the α-hydroxy acids lactic, mandelic, and benzilic acids react with Ce(IV) in perchlorate media, yielding Ce(III), carbon dioxide, and the carbonyl compound derived from decarboxylation and two-electron oxidation of the carboxyl ligand. In each case, Co(II) is formed in quantity equivalent to the (carboxylato)cobalt(III) reacting. The reactions are thus of the type $>C(OH)COOCo^{III} + Ce(IV) \rightarrow >C{=}O + CO_2 + Ce^{3+} + H^+ + Co^{2+}$ and feature internal electron transfer from Co(III), induced via attack by the one-electron oxidant Ce(IV) as well as breakage of a C–C bond. Rates are proportional to the concentration of a 1:1 Ce(IV)–Co(III) complex, the formation of which may be observed spectrophotometrically. In contrast to earlier examples of induced transfer, in which dual paths were observed for the radical–cation intermediate formed in the initital one-electron act, the present systems show no evidence for partition of intermediates, even when the Ce(IV):Co(III) ratio taken exceeds 20:1. Our results are thus consistent with a mechanism in which the acts of electron transfer from hydroxyl to Ce(IV), internal electron transfer to Co(III), and C–C fission are synchronous, or nearly so. Reactions of the same Co(III) complexes with Cr(V) or Cr(VI), both of which may undergo either one- or two-electron reduction, give only 20–30% yields of Co^{2+}.

Studies in the 1960s by Taube and co-workers[2] dealt with induced electron transfers, i.e., reactions in which a cobalt(III)-bound organic ligand suffered a net two-electron oxidation initiated through attack by an external one-electron oxidant, yielding a radical–cation intermediate. The latter could then rapidly undergo a second one-electron oxidation, resulting from intramolecular action by the Co(III) center. In all cases but one,[3a] reaction centers on the cobalt complex were separated by conjugated systems, and oxidation took place without alteration of the carbon skeleton of the ligand.

The present communication is concerned with additional induced electron transfers involving ligands in which no conjugated fragment separates the reaction centers. Each of these reactions entails breakage of a carbon–carbon bond. Our complexes are formally similar to the $(NH_3)_5Co^{III}$ derivative of oxalic acid, the oxidation of which was described in an early, and largely qualitative, report by Saffir.[3a]

Experimental Section

Materials. Ammonium cerium(IV) nitrate [Fisher Certified ACS grade. Anal. Calcd for $(NH_4)_2Ce(NO_3)_6$: Ce, 25.5. Found (ignition to CeO_2): Ce, 25.5] and carboxylic acids employed as ligands (Aldrich products) were used as received. The $(NH_3)_5Co^{III}$ complexes of lactic and benzilic acids were prepared as their perchlorates as described by Butler[4] and the corresponding derivatives of mandelic and phenylglyoxylic acids by the method of Fan.[5] Carbon–hydrogen (Galbraith Laboratories) and cobalt[6] analyses of the latter two complexes, which do not appear as yet to have been satisfactorily characterized, were in accord with the assigned structures. Sodium bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) was prepared by the method of Krumpolc and Roček.[7]

Rate Measurements. Rates of reactions of the Co(III) complexes were estimated from measurements of decreases in absorbance at 502 nm by using a Beckman 5260 recording spectrophotometer. Ionic strength was regulated by addition of known quantities of $HClO_4$ and $NaClO_4$. Oxidation rates were independent of acidity in the range 0.5–2.0 M H^+ when ionic strength was held constant. Reactions were accelerated by Mn^{2+} or Ag^+, strongly inhibited by oxalate, but unaffected by atmospheric oxygen or by addition of Ce^{3+}. With Ce^{IV} in excess, oxidations were first order in Co^{III} but showed kinetic saturation behavior (see below) with respect to Ce^{IV}. Rate measurements were generally run under pseudo-first-order conditions with $[Ce^{IV}]/[Co^{III}]$ greater than 5. Conversions were followed for at least 4 half-lives. Rate constants from successive half-life values within a single run agreed to within 6%, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction times. Specific rates obtained from replicate runs checked to better than 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Although the reactions of Ce(IV) with the parent carboxylic acids were not studied in detail, preliminary runs, monitored at 400 nm, indicated that these acids reacted 10^2–10^3 times as rapidly as their Co(III) complexes under comparable conditions, mandelic and benzilic acids being somewhat more reactive than lactic.

Estimation of Reaction Products. Cobalt(II) was estimated in reaction mixtures having excess Ce^{IV} by diluting 10-fold with concentrated HCl, allowing evolution of Cl_2 to cease, and then measuring the absorbance of Co^{II} at 692 nm ($\epsilon = 560$).[6] Treatment of the Co(III) complexes with $Tl(ClO_4)_3$ did not yield detectable quantities of Co^{2+}. For reaction mixtures having Co^{III} in excess, the quantity of Co(III) consumed was calculated from the observed decrease in absorbance at 502 nm, by using the measured extinction coefficients for the Co(III) complexes (approximately 80 in each case[4]), taking that for Co^{2+} as 4.0, and assuming other species to contribute negligibly at that wavelength. Benzaldehyde (from the reaction of the mandelato complex) was estimated by reducing excess Ce^{IV}, if present, with a measured quantity of Fe(II), SO_3^{2-}, or N_2H_4, diluting 100- to 500-fold with water, and then measuring the absorbance at 250 nm ($\epsilon = 11\,400$).[8] A similar sequence was used to estimate benzophenone ($\epsilon_{257} = 18\,500$) from reaction of the benzilato complex. Suitable "blank" measurements allowed corrections to be made for absorbance by the unreacted cobalt(III) complex (if present) and by Fe^{3+}. Because of the volatility of acetaldehyde, the ease with which it undergoes oxidation, and its relatively low molar absorbtivity, no attempt was made to estimate this compound from the reaction of the lactato complex. Carbon dioxide was estimated by carrying out reactions on a 0.03-mmol scale in a closed system using an excess of Ce(IV), heating at 55 °C for 4 h, passing the vapors through aqueous $Ba(OH)_2$, and then drying and weighing the $BaCO_3$ formed. With this procedure, it was found that 0.030 mmol of the mandelato complex yielded 0.024 mmol of CO_2, whereas the corresponding recoveries for the lactato and benzilato complexes were 0.025 and 0.030 mmol.

Results and Discussion

Representative kinetic data, pertaining to the cerium(IV) oxidation of the $(NH_3)_5Co^{III}$ complex of mandelic acid (II),

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(2) (a) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **82**, 4152 (1960). (b) R. Robson and H. Taube, *ibid.*, **89**, 6787 (1967). (c) J. E. French and H. Taube, *ibid.*, **91**, 6951 (1969). (d) For a review of early work, see H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, 1970, pp 73–97.

(3) (a) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960). (b) For a related study, see J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).

(4) R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965).

(5) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).

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

(7) M. Krumpolc and J. Roček, *J. Am. Chem. Soc.*, **101**, 3206 (1979).

(8) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, p 18.

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Table I. Kinetic Data for the Reaction of (Mandelato)pentaamminecobalt(III) with Cerium(IV)[a]

$[\mathrm{Ce^{IV}}]_{\mathrm{total}}$, M	$[(\mathrm{Ce^{IV}})_{\mathrm{monomeric}}]$, M	$[\mathrm{H^+}]$, M	10^3k_1, $\mathrm{s^{-1}}$ [b]
0.0103		0.50[c]	3.2
0.0103		1.00[d]	3.1
0.0103		2.00	3.4
0.0040	0.0031[k]	1.00[e]	1.90
0.0060	0.0042	1.00	2.5
0.0103	0.0062	1.00	2.6
0.021	0.0100	1.00	2.8
0.041	0.0156	1.00	3.1
0.0037	0.0026[l]	0.50[f]	1.16
0.0049	0.0032	0.50	1.38
0.0061	0.0038	0.50	1.52
0.0103	0.0054	0.50	1.99
0.021	0.0088	0.50	2.3
0.041	0.0132	0.50	2.4
0.0061		4.0[g]	7.7
0.031		4.0	7.2
0.0103		1.0[h]	3.0
0.0103		4.0[i]	9.2
0.0103		4.0[j]	12.6

[a] Reactions were carried out at 25 °C with $\mathrm{Ce^{IV}}$ in excess. $[\mathrm{Co^{III}}]_0$ was 0.0013 M throughout. [b] The pseudo-first-order specific rate, k_1, is $d \ln [\mathrm{Co^{III}}]/dt$. [c] $[\mathrm{HClO_4}] = 0.5$ M; $[\mathrm{NaClO_4}] = 1.5$ M. [d] $[\mathrm{HClO_4}] = [\mathrm{NaClO_4}] = 1.0$ M. [e] $[\mathrm{HClO_4}] = 1.0$ M; no $\mathrm{NaClO_4}$ added. [f] $[\mathrm{HClO_4}] = 0.5$ M; no $\mathrm{NaClO_4}$ added. [g] $[\mathrm{HClO_4}] = 4.0$ M. [h] $[\mathrm{Ce^{III}}] = 0.032$ M. [i] $[\mathrm{Ag^+}] = 0.0080$ M. [j] $[\mathrm{Ag^+}] = 0.032$ M. [k] Calculated by using the dimerization constant 50 $\mathrm{M^{-1}}$ for Ce(IV) in 1.0 M $\mathrm{HClO_4}$ reported by Heidt and Smith.[10a] [l] Calculated by using a dimerization constant 80 $\mathrm{M^{-1}}$ in 0.5 M $\mathrm{HClO_4}$ extrapolated from the data of King and Pandow.[10b]

appear in Table I. The reaction is first order in cobalt(III) and, as expected, proceeds more rapidly at the greater ionic strengths. Rates are independent of acidity within the range 0.5–2.0 M $\mathrm{H^+}$, in accord with the kinetic data of French,[2c] which indicated that $\mathrm{Ce^{IV}}$ is present very largely at a single protonation level (probably $\mathrm{CeOH^{3+}}$) in these media, but in disagreement with conclusions derived from the earlier spectrophotometric study of Hardwick and Robertson.[9]

Rates increase with increases in $[\mathrm{Ce^{IV}}]$ at low concentrations of the latter but approach limiting values at high concentrations. Kinetic saturation of this type indicates that the reaction rate is proportional to the concentration of a $\mathrm{Ce^{IV}}$–$\mathrm{Co^{III}}$ complex which is partially dissociated at low $[\mathrm{Ce^{IV}}]$. A further complication is partial dimerization of $\mathrm{Ce^{IV}}$ in these systems, but reported values[10] of dimerization constants at various $\mathrm{HClO_4}$ concentrations allow us to calculate the concentration of the $(\mathrm{Ce^{IV}})_{\mathrm{monomer}}$ in each solution. If the formation of 1:1 (two-metal center) complex involving monomeric $\mathrm{Ce^{IV}}$ is assumed and the dimer is taken to be inactive, this picture corresponds to rate law 1, where k_{lim} is the limiting specific

$$\text{rate} = \frac{k_{\mathrm{lim}}[\mathrm{Co^{III}}][(\mathrm{Ce^{IV}})_{\mathrm{monomer}}]}{K^{-1} + [(\mathrm{Ce^{IV}})_{\mathrm{monomer}}]} \qquad (1)$$

rate, observed at very high $[\mathrm{Ce^{IV}}]/[\mathrm{Co^{III}}]$ ratios, and K is the association constant of the cerium–cobalt complex.

Table II. Cerium(IV) Complexes with (Carboxylato)pentaamminecobalt(III) Derivatives

Co(III) derivative	λ_{max}, nm (ϵ)	$10^{-2}K$, $\mathrm{M^{-1}}$ [a]	10^3k_{lim}, $\mathrm{s^{-1}}$ [b]
$\mathrm{CH_3C(OH)HCOOCo(NH_3)_5{}^{2+}}$ (I)	488 (800)	0.36	2.7
$\mathrm{C_6H_5C(OH)HCOOCo(NH_3)_5{}^{2+}}$ (II)	486 (228)	4.0, 1.84[c]	3.6, 3.7[c]
$\mathrm{(C_6H_5)_2C(OH)COOCo(NH_3)_5{}^{2+}}$ (III)	481 (162)	4.9	1.07

[a] Formation constant for the Ce(IV)–Co(III) complex, obtained as the intercept:slope ratio of plots of $1/k_{\mathrm{obsd}}$ vs. $1/[(\mathrm{Ce^{IV}})_{\mathrm{monomer}}]$. Values refer to reaction in 1.0 M $\mathrm{HClO_4}$ unless otherwise indicated. [b] Limiting specific rate for consumption of Ce(IV) and Co(III), obtained as intercepts of plots of $1/k_{\mathrm{obsd}}$ vs. $1/[(\mathrm{Ce^{IV}})_{\mathrm{monomer}}]$ (see text). [c] Values for reaction in 0.5 M $\mathrm{HClO_4}$.

In such cases, both the limiting rate and the formation constant may be evaluated from a plot of $1/k_{\mathrm{obsd}}$ $(= [\mathrm{Co^{III}}]/\text{rate})$ vs. $1/[(\mathrm{Ce^{IV}})_{\mathrm{monomer}}]$. Plots so constructed are closely linear for reactions of the lactato (I), mandelato (II), and benzilato (III) complexes and lead to limiting specific rates (as intercepts) and association constants (as ratios of intercept to slope) listed in Table II. As anticipated, the formation constant, pertaining to a reaction between a 2+ and a 3+ ion ($\mathrm{CeOH^{3+}}$), increases markedly with ionic strength. Indeed, the formation of the cerium(IV)–mandelato complex is so nearly complete in 4 M $\mathrm{HClO_4}$ that the reaction rate in this medium is seen to be nearly independent of Ce(IV), provided that the latter is taken in excess. The visible absorption maximum for each of these complexes doubtlessly arises from overlap of the usual (carboxylato)pentaamminecobalt(III) peak at 502 nm[6] with the thick tail of the alcohol-bound Ce(IV) peak near 255 nm, which has been observed in a number of cobalt-free systems.[11] The association constants calculated are almost 10^2 as great as that reported by Ardon[12] for the $\mathrm{Ce^{IV}}$–ethanol complex, suggesting that the $\mathrm{Ce^{IV}}$–$\mathrm{Co^{III}}$ complexes in the present study derive a measure of extra stabilization through chelation.

Although the present experiments indicate the formation of a cerium–cobalt complex in each system, they do not demand that it intervene in the redox sequence, for our kinetic data are equally consistent with reaction between monomeric cerium(IV) and (carboxylato)cobalt(III) in mobile equilibrium with the binuclear species. However, the detailed nature of the redox process points to attack by $\mathrm{Ce^{IV}}$ on the OH group in the early stages of reaction. The binuclear complex is then a very reasonable intermediate.

The yields of products from a number of representative oxidations are listed in Table III. The mandelato complex (II) gives, aside from $\mathrm{CO_2}$, benzaldehyde as the sole identified organic product. This may be considered to result from a combination of a two-electron oxidation and decarboxylation of the participating ligand. The benzilato complex (III) yields benzophenone, which may be taken to arise in an analogous fashion. Since the aldehyde is consumed by Ce(IV) at a significant rate,[13] its formation would be expected to complicate those mandelato studies carried out with Ce(IV) in excess. This difficulty does not intrude with the benzilato reactions in which the quantity of benzophenone formed is found to be equivalent to the cobalt(III) complex taken. In the mandelato reaction, the moles of benzaldehyde detected fall, as anticipated, well below the moles of Co(III) taken when Ce(IV) is in excess but are equivalent to Ce(IV) consumed (and to Co(III) consumed) when the carboxylato complex is in excess.

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(9) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

(10) (a) L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, **70**, 2476 (1948); (b) E. L. King and M. L. Pandow, *ibid.*, **74**, 1966 (1952).

(11) See, for example: (a) V. K. Grover and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **31**, 1403 (1969); (b) V. K. Grover, S. K. Mishra, and Y. K. Gupta, *Ind. J. Chem.*, **8**, 247 (1970).

(12) M. Ardon, *J. Chem. Soc.*, 1811 (1952).

(13) In preliminary experiments with $[\mathrm{Ce^{IV}}]_{\mathrm{total}} = 4 \times 10^{-4}$ M and [PhCHO] $= 4.4 \times 10^{-3}$ M, we find the reduction of Ce(IV) to be a pseudo-first-order process with specific rate 0.015 $\mathrm{s^{-1}}$ (1 M $\mathrm{HClO_4}$, 25 °C). Note, however, that the reactivity of Ce(IV) in the presence of excess (carboxylato)cobalt(III) in the present study is very much less than that in cobalt-free systems since the major portion of Ce(IV) has been shown to be tied up in the Ce–Co complexes formed.

Table III. Products from Reaction of Cerium(IV) with Carboxylato Derivatives of $(NH_3)_5Co^{III}$ [a]

$(NH_3)_5Co^{III}$ complex	$[Co^{III}]_0$, mM	$[Ce^{IV}]_0$, mM	$[(Co^{III})_{consumed}]$, mM	$[Co^{2+}]$, mM (%)[h]	[C=O product], mM (%)[h]
mandelato (II)	2.8	10.3		2.7 (97)	
	1.39	10.3		1.38 (99)	
	16.0	2.7	2.9		
	7.0	2.7	2.9		
	7.0	2.2	2.6	2.2 (100)	
	6.5	2.1			2.0[b] (95)
	0.90	4.0			0.67 (75)
	1.04	10.3			0.66 (63)
	2.3	0.80	0.72	0.71 (89)	
	1.39[c]	6.1		1.40 (101)	
	1.39[c]	31		1.35 (97)	
	2.8[c]	10.3		2.7 (96)	
lactato (I)	1.40	10.3		1.36 (97)	
	0.94	6.0		0.89 (95)	
	2.3	0.75	0.69	0.69 (92)	
benzilato (III)	1.05	10.3		1.03 (98)	
	1.52	0.80	0.83		
	2.0	1.60	1.45	1.43 (89)	
	1.72	4.0			1.60[d] (92)
	2.3	10.3			2.2 (96)
phenylglyoxylato[e]	0.90	4.0		0.39 (43)	
mandelato + 4.9 mM Cr(V)[f]	9.8			1.10 (22)	
mandelato + 7.9 mM Cr(VI)[g]	1.84			0.50 (27)	

[a] Reactions were carried out at 25 °C in 1.0 M $HClO_4$ unless otherwise noted. [b] Benzaldehyde. [c] Reaction medium was 4 M $HClO_4$. [d] Benzophenone. [e] $C_6H_5C(=O)COOCo(NH_3)_5^{2+}$. [f] Oxidant was bis(2-hydroxy-2-ethylbutyrato)oxochromate(V).[7] Reaction was carried out at pH 4.5 with [EDTA] = 2.0×10^{-4} M. The cobalt(II) formed was estimated by the method of R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950), as modified by Robson.[2b] [g] Oxidant was $K_2Cr_2O_7$. [h] Yield calculated on the basis of reagent taken in deficiency.

The most striking facet of this study is that, with all three complexes, Co^{2+} is formed in quantity equivalent to the (carboxylato)cobalt(III) reacting, whether the reaction is carried out with Ce(IV) or with Co(III) in excess. Indeed, this equivalency persists even when the Ce:Co ratio chosen exceeds 20:1. The primary reaction may then be represented by eq 2.

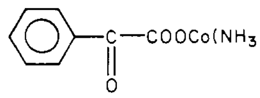
$$>C(OH)COOCo^{III} + Ce^{4+} \rightarrow >C{=}O + CO_2 + Ce^{3+} + Co^{2+} + H^+ \quad (2)$$

The fragmentation of the ligand is thus of the same type as that reported for free α-hydroxy acids when oxidized with Ce^{4+} in acidic media.[11,14] In the latter cobalt-free systems, however, both acts of electron transfer involve Ce(IV) ions which, neither at the beginning nor at the end of the net reaction, are coordinated to the reductant, whereas in the present systems one act of electron transfer requires a cobalt(III) center that remains bound to the substrate until this transfer has occurred. Put another way, one electron comprising the C–C bond ultimately broken moves toward an electron-deficient center resulting from action of Ce(IV), whereas the other electron of this pair moves internally in the direction of Co(III).

Although our reactions are related to several described by earlier workers[2,3b] in that electron transfer to Co(III) is induced by the initial transfer (in the opposite direction) to Ce(IV), there are dissimilarities as well. Most obviously, the organic substrates used by Fraser,[2a] Robson,[2b] and French[2c] were chosen to allow interaction between the two electron-transfer sites through conjugated units (benzene or pyridine rings) whereas such interaction is not possible with our ligands. Moreover, earlier substrates featured C–H bonds at or near the site of external attack whereas the benzilato complex (III) which, among our substrates, reacts in the most straightforward fashion, has only a C–O–H sequence. The latter difference is informative, for it rules out intervention of radicals of the type $>\dot{C}{-}OH$ between the act of electron transfer to Ce(IV) and the induced transfer to Co(II) in this series, although analogous intermediates were favorably considered for earlier electron-transfer sequences.[2b,c] Here, electron transfer to Ce(IV) must involve the hydroxyl oxygen in the case of the benzilato reaction and, by implication, for the mandelato and lactato reactions as well.

Partition of a proposed radical intermediate between two competing paths was an important facet of past studies,[2b,c,3b] for such a partition constitutes evidence that such an intermediate enjoys an independent existence. In a number of instances, dual pathways were reported, with the Co^{2+}-forming reaction accompanying an alternative process in which the ligand suffered a two-electron change, leaving the coordinated cobalt(III) untouched. Although such a divergence may be interpreted as a competition in which the initial radical intermediate may undergo either internal electron transfer or external oxidative attack, consideration of such systems was generally complicated by the possibility of two different radical intermediates from a single ligand. In the present study, we find no indication of duality of reaction paths. Some variation in ratios of reaction products has been noted, but this may be accounted for by a secondary reaction, the oxidation of the product aldehyde by Ce(IV). In particular, the conversions of Co(III) to Co^{2+} in the mandelato oxidations are seen to be virtually quantitative, even under conditions most favorable to external oxidative attack, i.e., when Ce(IV) is in large excess.

Note also that the two-electron oxidation product of the mandelato complex, the phenylglyoxylato derivative, IV, is



IV

ruled out as an intermediate in the principal mandelato oxidation sequence. Although this complex is consumed under our conditions, reaction is, in large part, by aquation at the

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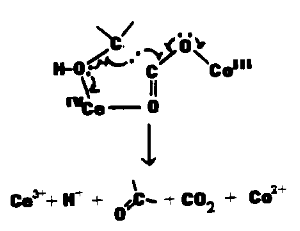
(14) See, for example: (a) B. Krishna and K. C. Tewari, *J. Chem. Soc.*, 3097 (1961); (b) A. McAuley and C. H. Brubaker, Jr., *ibid.*, 961 (1966); (c) T. J. Kemp and W. A. Waters, *ibid.*, 1192 (1962). For descriptions of closely related reactions, see: (d) P. M. Nave and W. S. Trahanowski, *J. Am. Chem. Soc.*, **90**, 4756 (1968); (e) J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956).

Scheme I



Co(III) center, and less than half has been found to be converted to Co^{2+} (Table III).

If it is assumed that electron transfer from the hydroxyl group to Ce(IV) occurs by an inner-sphere path, the lactato, mandelato, and benzilato reactions should proceed through intermediates having compositions and structures corresponding to the Ce(IV)–Co(III) complexes detected spectrophotometrically (Table II). It further appears that the breakage of the C–C bond and the electron transfer to Co(III) are concerted, for without the former there is no reasonable mode by which the effects of alteration at the Ce(IV)–O site may be transmitted to Co(III). Moreover, our experiments give no hint that other species intervene between formation of the Ce(IV)–Co(III) complex and the induced electron transfer to Co(III), being thus consistent with a mechanism in which C–C fragmentation and the two acts of electron transfer to the metal ion centers are synchronous, or very nearly so. This is represented by Scheme I.

Despite evidence that the two oxidizing centers operate in concert, coordinated Co(III) does not facilitate attack by Ce(IV), for the uncomplexed hydroxy acids are found to react 10^2–10^3 times as rapidly as their $(NH_3)_5Co^{III}$ derivatives under comparable conditions. This is, in substantial part, an electrostatic effect, analogous to that described for the Ce(IV) reaction of cobalt(III)-bound oxalate.[3a] When, however, the two reaction centers are separated by a more extended system of bonds, i.e., by an aromatic ring, rates at which the ligand and its Co(III) complex are attacked become similar.[2b,c]

Finally, it is of interest that, although both Cr(V) and Cr(VI) react readily with the mandelato complex, yields of Co^{2+} are only 20–30%. This is in accord with the ability of these oxidants to undergo either one- or two-electron reduction and suggests that the latter mode is predominant with both oxidation states under our conditions. Treatment with thallium(III), which ordinarily functions solely as a two-electron oxidant, yields no detectable Co^{2+}.[15]

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Registry No. I, 34464-03-4; II, 73543-61-0; III, 47253-58-7; $C_6H_5C(O)COOCo(NH_3)_5^{2+}$, 49861-82-7; Ce^{4+}, 16065-90-0; bis(2-hydroxy-2-ethylbutyrato)oxochromate(V), 75476-70-9; $K_2Cr_2O_7$, 7778-50-9; benzaldehyde, 100-52-7; benzophenone, 119-61-9; Co^{2+}, 22541-53-3; CO_2, 124-38-9; Ce^{3+}, 18923-26-7.

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(15) An analogous instance of induced electron transfer involving the action of Fe(III) on complexes of Cr(III), yielding Fe^{2+} and Cr^{2+}, has been described by J. J. Espenson and A. Bakac, *J. Am. Chem. Soc.*, **102**, 2488 (1980).

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Electron Transfer. 47. Deteriorative Processes in Electron-Transfer Catalysis[1]

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Europium(II) reductions of (pyridine)pentaamminecobalt(III), $py(NH_3)_5Co^{III}$, in the presence of the very powerful catalysts derived from 2,4-pyridinedicarboxylic acid yield kinetic plots showing marked departures from those exponential curves expected if the concentration of catalyst were to remain constant throughout a run. The observed behavior has been shown to correspond to a superposition, onto the primary catalyzed reaction, of two deteriorative processes, both involving the radical intermediate cat·, which results from one-electron reduction of the catalyst. The first of these is a bimolecular disproportionation of the radical; the second is a reaction with an additional Eu^{2+} ion, yielding an unreactive dihydro derivative, $catH_2$. Consideration of the kinetic data, in conjunction with estimated formal potentials of the catalysts, allows calculation of specific rates for the attrition reactions for the several catalysts. Rate constants for disproportionation of the radicals derived from the 2,4 diacid and its methyl ester exceed 10^8 M^{-1} s^{-1}; i.e., the values are slightly below the diffusion-controlled limit for bimolecular reactions. Specific rates for "overreduction" of the radicals by reaction with Eu^{2+} fall in the range 70–400 M^{-1} s^{-1}, about one-tenth the rates for one-electron reductions of the parent aromatics. N-Methylation of the 2,4 diacid greatly improves its catalytic recycling properties without affecting its activity in the medium employed, for this alteration retards attrition by overreduction sixfold and reduces disproportionation to an undetectable level. N-Methylation of the dimethyl ester of this acid yields compound V, which is found to be the most active electron-transfer catalyst of this type thus far prepared. Under conditions of use, however, it suffers deterioration unusually rapidly.

Catalysis of electron-transfer reactions by unbound aromatics has been shown to proceed by preliminary reduction of the catalyst to a radical intermediate, cat·, which then reacts with the oxidant.[2] Earlier reports dealing with this type of catalysis pointed out that such catalysts may deteriorate with use.[2,3] It was further found that degrees of deterioration among different catalysts may vary widely, and evidence was presented[4] that catalytic attrition occurs when the radical

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(2) See, for example: (a) C. Norris and F. Nordmeyer, *J. Am. Chem. Soc.*, **93**, 4044 (1971); (b) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *ibid.*, **99**, 1073 (1977).

(3) (a) J. R. Barber, Jr., and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 4045 (1971); (b) M. R. Loar, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, **17**, 3689 (1978).

(4) C. A. Radlowski, P.-W. Chum, L. Hua, J. Heh, and E. S. Gould, *Inorg. Chem.*, **19**, 401 (1980).

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