

Bound and Unbound Radical Intermediates in Inorganic Electron-Transfer Reactions

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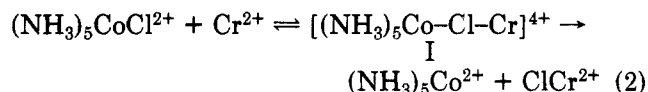
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Electron-transfer reactions involving changes of a single oxidation unit constitute an exceptionally broad subject.¹ Reactions of this type have been the subject of theoretical treatments, showing progressively increased refinement, for almost 3 decades.² Moreover, such reactions now figure prominently in such diverse research fields as gas-phase kinetics,^{3a} fast kinetics and pulse radiolysis,^{3b,c} solid-state conduction,⁴ biological energy transport,⁵ electrocatalysis,⁶ photochemical transformations,⁷ enzymology,⁸ organic reaction mechanisms,^{9a} and organic catalysis.^{9b}

Historically, the experimental backbone of this subject is based largely on the study of the reactions between metal ion centers in aqueous solution, an aspect in which interest continues to be lively.¹⁰ Work by Taube, Rich, and Myers in the early 1950s¹¹ established the two broad classes of electron-transfer reactions recognized today. In an *outer-sphere* transfer, an electron moves from reductant to oxidant with no chemical alteration of the primary coordination spheres, as in

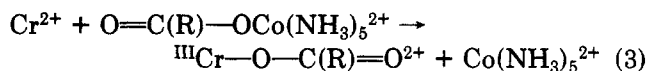


For an *inner-sphere* transfer, on the other hand, reaction occurs when one of the partners (usually the reductant) becomes attached to a ligand of the other partner, as in



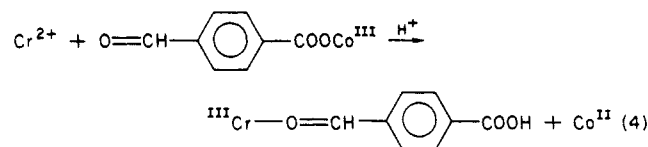
The binuclear intermediate, I, in the inner-sphere or bridged path (eq 2) is called the *precursor complex*, and the chloride is the *bridging* or *mediating group*. Although movement of the bridging group from oxidant to reductant was a useful diagnostic tool in the early work, it has not turned out to be a universal feature of the inner-sphere pathway.¹²

Taube further demonstrated, in 1955, that organic species (carboxylate anions) could act as inner-sphere mediators¹³



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It soon became evident that the bimolecular specific rates of reactions of type 3 generally fall within a remarkably narrow range (0.1-0.3 M⁻¹ s⁻¹),¹⁴ i.e., they were exceptionally insensitive to inductive, conjugative, and electrostatic effects (within group R) which usually affect organic reactivity. Substantial modifications in the rate law or accelerations could indeed be observed, but these, together with confirming evidence, pointed to fundamental mechanistic changes. Two such variants are (4)¹⁵ and (5).¹⁶



$$\text{rate} = (\text{Cr}^{2+})(\text{Co}^{\text{III}})(53 + 380[\text{H}^+])\text{M}^{-1} \text{s}^{-1}$$

(1) Many important aspects of electron transfer have been reviewed by: Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980. Coverage by this author extends through 1976.

(2) Representative examples of significant early and recent theoretical treatments are, respectively: (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* 1964, 15, 155. (b) Sutin, N. *Progr. Inorg. Chem.* 1983, 30, 441.

(3) (a) Ast, T.; Terwilliger, D. T.; Benyon, J. H.; Cooks, R. G. *J. Chem. Phys.* 1975, 62, 3855. (b) Hoffman, M. Z.; Whitburn, K. D. *J. Chem. Educ.* 1981, 58, 119. (c) Neta, P.; Behar, D. *J. Am. Chem. Soc.* 1980, 102, 4798.

(4) Clark, M. G.; DiSalvo, F. J.; Glass, A. M.; Peterson, G. E. *J. Chem. Phys.* 1973, 59, 6209.

(5) Raymond, K. N. *Adv. Chem. Ser.* 1977, No. 162, Chapters 7-19.

(6) (a) Ellis, C. D.; Gilbert, J. A.; Murphy, W. R.; Meyer, T. J. *J. Am. Chem. Soc.* 1983, 105, 4852. (b) Saveant, J.-M. *Acc. Chem. Res.* 1980, 13, 323.

(7) (a) Meyer, T. J. *Progr. Inorg. Chem.* 1983, 30, 389. (b) Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83.

(8) Walsh, C. *Annu. Rev. Biochem.* 1978, 47, 881.

(9) (a) Bunnett, *Acc. Chem. Res.* 1978, 11, 413. (b) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapters 2-17. Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* 1979, 101, 5593.

(10) For complementary detailed reviews, see: (a) Haim, H. *Progr. Inorg. Chem.* 1983, 30, 441. (b) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Progr. Inorg. Chem.* 1983, 30, 141. The first of these emphasizes historical background and experimental results; the second is more theoretically oriented.

(11) (a) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* 1983, 75, 4118. (b) Taube, H.; Myers, H. *J. Am. Chem. Soc.* 1954, 76, 2103.

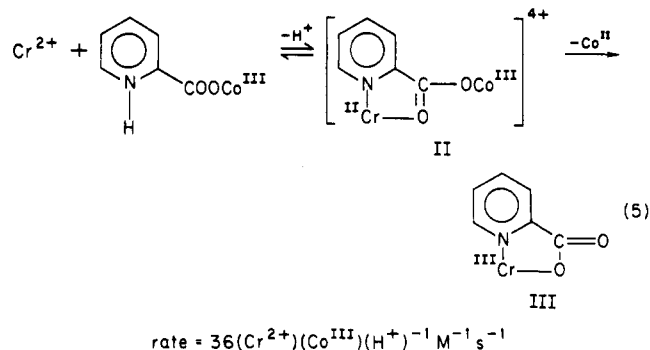
(12) See, for example: (a) Grossman, B.; Haim, A. *J. Am. Chem. Soc.* 1970, 92, 4835. (b) Seewald, D.; Sutin, N.; Watkins, K. O. *J. Am. Chem. Soc.* 1969, 91, 7307. (c) Movius, W. G.; Linck, R. G. *J. Am. Chem. Soc.* 1969, 91, 5394. In some instances, there is a significant delay between the act of electron transfer and the dissociation (of the so-called *successor* or *postcursor* complex) into products.

(13) Taube, H. *J. Am. Chem. Soc.* 1955, 77, 4481.

(14) Unless otherwise indicated, quoted specific rates refer to reactions at 25 °C, carried out at unit ionic strength ($\mu = 1.0$).

(15) Zanella, A.; Taube, H. *J. Am. Chem. Soc.* 1972, 94, 6403.

(16) (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* 1964, 86, 1318. (b) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* 1971, 93, 5661.



In (4), Cr²⁺ attacks the aldehyde group remote to, and conjugated with, COOCo^{III}. Reaction 5 yields a chelated Cr(III) product, III, which stems from a chelated precursor complex, II; the high rate here reflects, in part, a greater concentration of precursor than would intercede in the absence of chelation.

Almost all organic bridges feature at least one unshared pair of nonbonding electrons (a *lead-in site*) for coordination to the reducing center, and, further, the donor atom at that site is unsaturated (this in contrast to the halide ion bridges operating in the prototype reactions). In addition to carboxylate anions (which coordinate to the reductant at the carbonyl oxygen),¹⁷ important lead-in groups are aldehyde, keto, ester, amide,^{18a} cyano,^{18b} and (particularly instructive) donor nitrogen in aromatic heterocyclic systems. Moreover, strong evidence has been presented^{18c} for redox bridging by cobalt(III)-bound methyl and ethyl groups in reactions of the alkyl derivatives of vitamin B₁₂ with Cr²⁺.

Virtually all of the early work, and many recent investigations as well, dealt with cobalt(III) complexes as oxidants (for these are generally prepared in a straightforward manner and retain their structure in solution) and with Cr²⁺ as a reductant (for the resulting Cr^{III} products likewise maintain their structural integrity). Subsequent studies have utilized Cr(III) and Ru(III) as oxidizing centers.

Reactions of Cr(III) complexes, which are less strongly oxidizing than those of Co(III) by about 2 V, have been less informative,^{19a} but reductions of Ru(III) complexes offer a feature of special interest. The electron which six-coordinate Ru(III) (t_{2g}⁵) accepts enters a metal-centered t_{2g} orbital, whereas with Co(III) (t_{2g}⁶) and Cr(III) (t_{2g}³), the incoming electron enters an e_g orbital. Since t_{2g} orbitals, but not e_g orbitals, enjoy symmetry-matching overlap with π-orbitals of unsaturated bridging groups, inner-sphere reductions of Ru(III) complexes generally proceed much more rapidly (by several powers of 10) than the corresponding reductions of Co(III) and Cr(III) derivatives.^{19b,c} At the same time, however, Ru(III) reductions fail to exhibit

(17) Scott, K. L.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* 1972, 1832.

(18) (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* 1968, 90, 1162. (b) Hua, L. H.-C.; Balahura, R.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1978, 17, 3692. Note that the bridging action of these groups is abrogated if the carbonyl function of the amide or the nitrile nitrogen is blocked off by coordination. (c) See, for example: Espenson, J. H.; Sellers, T. D., Jr. *J. Am. Chem. Soc.* 1974, 96, 94.

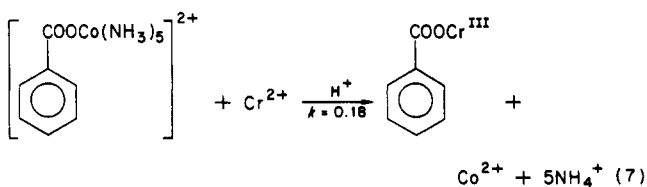
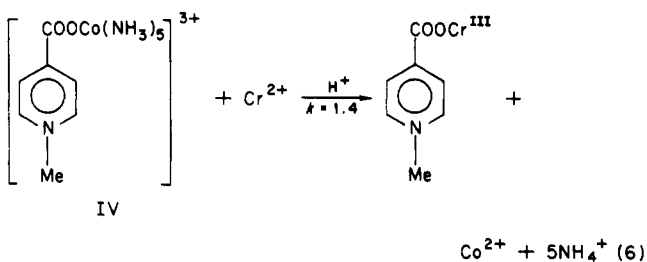
(19) (a) Liu, C.-L.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1978, 17, 1831. (b) Gaunder, R. G.; Taube, H. *Inorg. Chem.* 1970, 9, 2627. (c) Berrie, B. H.; Earley, J. E. *Inorg. Chem.* 1984, 23, 774. (d) Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* 1969, 91, 1968. (e) Baker, B. R.; Orhanovic, M.; Sutin, N. *J. Am. Chem. Soc.* 1967, 89, 722. (f) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* 1973, 95, 5539. (g) Wang, R. T.; Espenson, J. H. *J. Am. Chem. Soc.* 1971, 93, 380. (h) Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* 1963, 85, 2035.

the mechanistic feature of principal interest (see below) in this Account.

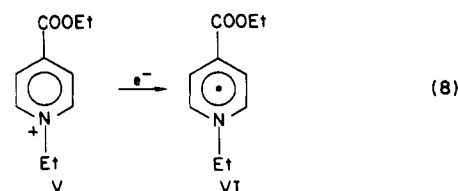
In addition to Cr²⁺, inner-sphere reactions of metal-centered reductants having formal potentials (*E*^o values) spanning a 1.4 V range have been examined. Reactions of the poorly reducing species, Fe²⁺ (+0.77 V) are often inconveniently sluggish, and the study of Cu⁺ (+0.17 V) is complicated by the tendency of this species to undergo disproportionation in aqueous solution.^{19d} Inner-sphere rates with V²⁺ (-0.42 V) and Ti³⁺ (+0.40 V) are limited by relatively slow coordination by these centers to the bridging site,^{19e,f} whereas those with the powerfully reducing U³⁺ (-0.63 V) fall in the range accessible only with stop-flow.^{19g} The reactions of Eu²⁺ (-0.38 V) resemble, to a remarkable degree, those of Cr²⁺ (-0.41 V), aside from the reluctance of the oxidation product, Eu(III) to remain bonded to the bridging ligand.

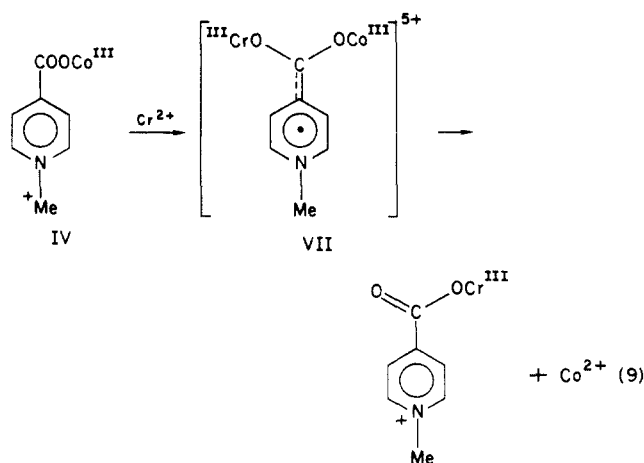
Radical-Cation Intervention: the Chemical Mechanism

Experiments reported in 1964 hinted at another mechanistic variation.^{16a} 4-Pyridinecarboxyl (NH₃)₅-Co^{III} complex of *N*-methylpyridine-4-carboxylic acid (IV) is reduced by Cr²⁺ 8 times as rapidly as the corresponding complex of benzoic acid



The difference in specific rates is a modest one, but it is in the "wrong" direction; for the tripositive ion, IV, must overcome a greater electrostatic barrier to reaction than the dipositive. Moreover, the effect could not be accounted for on the basis of any mechanism then recognized. At nearly the same time, however, Kosower and Poziomek^{19h} described the isolation of the pyridyl-related radical, VI, prepared by metal reduction of the pyridinium cation, V, which is closely related to the ligand in cobalt(III) complex IV. The latter report prompted the proposal that the reduction of complex IV entailed preliminary conversion to the metal-bound radical, VII, which then underwent internal electron transfer to Co^{III}, yielding the observed products





It was further suggested that the rate at which reaction 9 occurs is determined by the rate at which the ligand is reduced to radical-cation VII. Such a sequence is said to represent reduction by the *radical-cation mechanism* or the *chemical mechanism*.²⁰ In the present Account, we shall review the evidence for this mechanism, demonstrate its close similarity to the intermolecular analogue involving an external radical center, then indicate how these two variations pertain to two quite different topics of current interest.

By its nature, the radical-cation mechanism requires the presence of an oxidant-bound ligand which itself is reducible. 4-Pyridinecarbonyl (isonicotinoyl) groups figure prominently both in prototype and in recent examples, and associated with these is a most informative feature. If the carbonyl function is moved to the 3- or β -position on the pyridine ring (converting the group to nicotinoyl), evidence for radical intervention disappears.^{16a} The difference is certainly related to the much greater ease with which isonicotinoyl derivatives undergo one-electron reduction.²¹ Typically, the $1e^-$ reduction potential of isonicotinamide is recorded^{21b} as -0.78 V (25 °C, pH 7), whereas that for the 3-isomer, nicotinamide, is -1.20 V. This marked difference is doubtless a conjugative effect; in valence-bond language, structures in which the unpaired electron is situated on the pyridine nitrogen may contribute to the isonicotinoyl (γ) radical but not to the nicotinoyl (β).

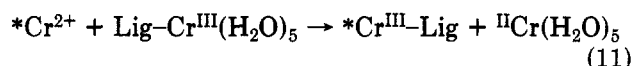
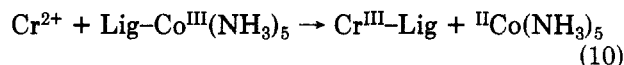
An important question pertaining to this mechanism is as follows: "Of the two reducible sites on the oxidant (the metal center and the participating aromatic ligand), the metal center, when uncoordinated, generally features a more favorable reduction potential than does the free ligand. Why, then, does attack occur preferentially at the ligand?" It has long been recognized^{2a} that the rate of electron transfer depends not only on thermodynamic driving force, but also how drastically the reactant species must be reorganized during the act of electron transfer. The extent of reorganization is

(20) (a) The term "chemical mechanism" is used to differentiate such electron transfer from those mediated by nonreducible bridges, in which direct interaction ("resonance transfer") between metal centers is thought to occur. For detailed arguments against the chemical mechanism in inner-sphere reactions mediated by halide and acetate, see: Taube, H.; Gould, E. S. *Acc. Chem. Res.* 1969, 2, 321. (b) Closely related reactions of cobalt(III) complexes, in which the radical-cation intermediate is generated by oxidation rather than reduction, were earlier described by: Saffir, P.; Taube, H. *J. Am. Chem. Soc.* 1960, 82, 13 and by Candlin, J. P.; Halpern, J. *Am. Chem. Soc.* 1963, 85, 2518.

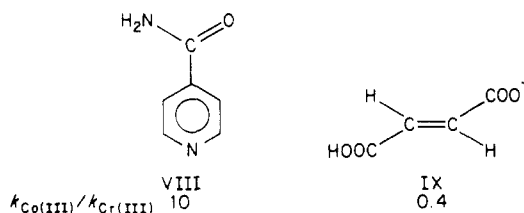
(21) See for example: (a) Cohen, H.; Meyerstein, D. *Isr. J. Chem.* 1974, 12, 1049. (b) Bruhlmann, U.; Hayon, E. *J. Am. Chem. Soc.* 1974, 96, 6169.

reflected in the rates for electron exchange (self-exchange) at the redox sites. Reduction of, say, a trivalent to a divalent metal ion generally entails considerable lengthening of the metal-to-ligand bonds and modification of the secondary hydration sphere. In contrast, when an aromatic species accepts an electron, the geometry of the reduced quasiaromatic product often closely resembles that of the reductant, the effects of the added electron being dispersed over the entire cyclic system. As a result, in the absence of complicating factors, electron transfers between metal centers are slower (often much slower) than those between a metal ion and an aromatic species, and these are, in turn, slower than transfers between an aromatic oxidant and an aromatic reductant.

In the chemical mechanism, the rapidity of internal electron transfer complicates detection of the radical-cation intermediate. However, several items of indirect evidence lent early support to the mechanism. The most typical are based upon the argument that when specific rates are determined by the rate of reduction of the ligand, they should be relatively insensitive to the identity of the oxidizing center. Compare for example, reactions of type 10 with those of type 11²²



When the bridging ligand is not reducible (e.g., F^- or OH^-), the $\text{Cr}^{\text{II}}-\text{Co}^{\text{III}}$ reaction, (10), is found to be 10^6 – 10^8 times as rapid as the $\text{Cr}^{\text{II}}-\text{Cr}^{\text{III}}$ reaction, (11), a reflection mainly of the highly positive oxidation potential associated with Co^{III} . However, with isonicotinamide (VIII) or fumarate (IX) as mediating ligand, this ratio plummets to near unity, implying that ligand reduction is now setting the pace.^{10a,18a,23}



A more subtle clue arose from a comparison of reduction rates, again using Cr^{2+} , of $\text{Lig}-\text{Co}^{\text{III}}(\text{NH}_3)_5$ complexes with rates for the corresponding isotopically substituted $\text{Lig}-\text{Co}^{\text{III}}(\text{ND}_3)_5$ derivatives.²⁴ When the "sixth" ligand, "Lig", is nonreducible, the kinetic isotope effect, $k_{\text{H}}/k_{\text{D}}$ (for 15 D atoms per molecule) falls between 1.40 and 1.60, suggesting that the ammonia hydrogens, which are hydrogen-bonded to water molecules in the secondary coordination sphere of the oxidant, can influence the ease with which $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ can displace those water molecules and approach close enough to allow effective electron transfer. In contrast, however, when the sixth ligand is reducible (e.g., VIII or IX), the

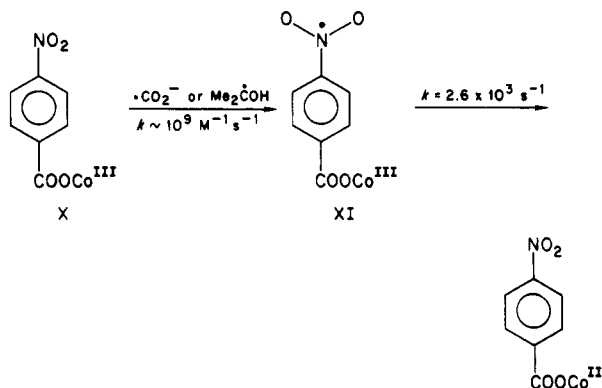
(22) As indicated, reactions of type 11 must generally be monitored with labeled chromium. An exceptional case involves 4-pyridinecarboxamide, 4-PyCONH₂, as the mediating ligand. Here, Cr(III) is bound to the amide oxygen in the reactant, but to the ring nitrogen in the product.

(23) Diaz, H.; Taube, H. *Inorg. Chem.* 1970, 9, 1304.

(24) Itzkowitz, M. M.; Nordmeyer, F. *Inorg. Chem.* 1975, 14, 2124.

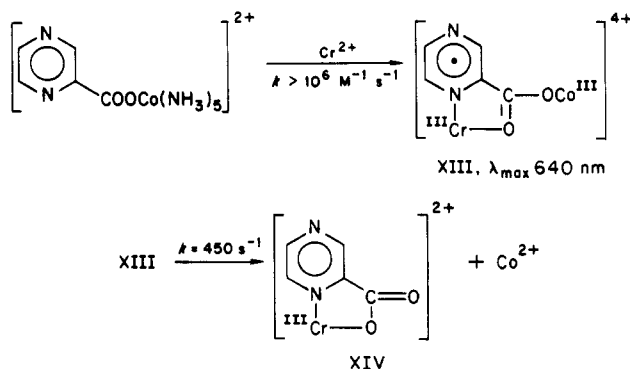
ratio k_H/k_D falls to near 1.1, indicating that the rate of reaction is no longer governed by an event directly involving the Co(III) center.

When the ligand is a particularly strong oxidant ($E_0 > 0.00$ V), the radical-cation intermediate can sometimes be detected, and its disappearance monitored. In a classic example, involving the $(\text{NH}_3)_5\text{Co}^{\text{III}}$ complex of *p*-nitrobenzoic acid (X), reducing agents were the radicals $\cdot\text{CO}_2^-$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, rather than a second metal ion center.²⁵ The cobalt(III)-bound nitro radical, XI, was detected as a strongly absorbing species ($\epsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 310 nm) which decays unimolecularly



($k = 2.6 \times 10^3 \text{ s}^{-1}$ at 25 °C) to the corresponding cobalt(II) product.

A quite different system features the pyrazine ring, one of the most easily reducible of the simple heterocyclic units. The Cr^{2+} reduction of the Co^{III} complex of pyrazinecarboxylic acid (XII) is initiated by the very quick formation of a radical cation, the ESR spectrum of which has been recorded in a rapid flow apparatus.²⁶ This species also undergoes unimolecular decay ($k = 4.5 \times 10^2 \text{ s}^{-1}$ in 0.12 M HClO_4)²⁷ to yield the chromium(III) chelate XIV. Hence, the intermediate may be assigned the radical-cation structure XIII. A number



(25) (a) Hoffmann, M. Z.; Simic, M. *J. Am. Chem. Soc.* 1972, 94, 1757. (b) Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *J. Am. Chem. Soc.* 1977, 99, 2166. In this work, the organic radicals used as reductants were generated by pulse radiolysis of aqueous solutions of N_2O . The primary radiolytic product, e_{aq}^- , reacts rapidly with N_2O , yielding N_2 , OH^- , and OH^\cdot , the latter of which reacts, in turn, with added formate or 2-propanol to form, respectively, $\cdot\text{CO}_2^-$ and $\text{Me}_2\dot{\text{C}}\text{OH}$. Note that complex X is one of several nitro species studied in detail by these workers.

(26) Spiecker, H.; Wieghardt, K. *Inorg. Chem.* 1977, 16, 1290.

(27) Gould, E. S., unpublished experiments. This specific rate, which falls very near the limit measurable by conventional stop-flow, and the lower limit for formation of XIII, supersede values reported previously (Gould, E. S. *J. Am. Chem. Soc.* 1972, 94, 4360), that now appear to apply instead to the secondary reaction of Cr(III) complex XIV with excess Cr^{2+} .

of additional Cr(III)-bound pyrazine radicals have subsequently been prepared.²⁸ These "pyrazine greens" vary greatly in their stability, but each exhibits strong absorption near 640 nm.

Under what conditions would the radical-cation mechanism be expected to assume importance? First, the potential of reductant must lie close enough to that of the aromatic ligand to allow generation of at least a small quantity of the radical. Since this mechanism is not observed if the gap between these potentials exceeds 300 mV, we may infer that extent of ligand-to-radical conversion must exceed about 10^{-5} . Secondly, competing accelerating effects (e.g., chelation) must not overshadow reaction through the radical intermediate, and any outer-sphere component must also be negligible. Moreover, it is reemphasized that the symmetry character of the π -orbitals accommodating the migrating electron in the radical must not match that of the acceptor orbitals of the oxidant. Thus, the chemical mechanism would not be expected to occur in reductions of coordinated low-spin ruthenium(III), for which the acceptor (t_{2g}) orbital has π -, rather than σ -type symmetry. Although the early examples of this mechanism involved substitution-labile metal center reductants, this is not a necessary feature, for the initial act of electron transfer to the ligand may be outer-sphere, as is the case with Hoffmann's nitrobenzoato oxidant, X.

Since conversion to the radical in the initial step need proceed only to a small extent, one may ask whether this step can be reversed, whether, for example, a reduction by Eu^{2+} via the chemical mechanism may be retarded by addition of excess Eu^{3+} . Although this is, in principle, possible, it has not yet been observed in systems involving bound radicals (although, as we shall see, it is an important facet of the intermolecular analogue of this mechanism). The implication here is that bimolecular reversal of the initial reduction of the ligand does not compete successfully with unimolecular internal electron transfer from radical to the oxidizing center.

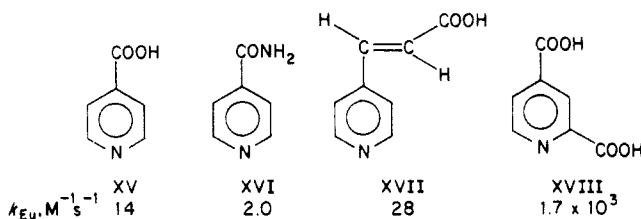
Role of External Aromatic Radicals

In the instances of radical-cation intervention considered thus far, the reducible function is bound to, and lies in conjugation with, the oxidizing center. However, a host of redox systems have now been examined, each with a reducible aromatic species present but not coordinated to either metal center, in which the aromatic nevertheless markedly affects the primary reaction.²⁹ For example, the rates of the very sluggish outer-sphere reactions of Eu^{2+} with $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ can be increased by several powers of 10 by addition of 4-pyridinecarboxylic acid (XV) at the 10^{-3} M level, although the reaction products remain unchanged. Additional pyridine derivatives exhibit analogous catalytic action, with isonicotinamide (XVI) somewhat less effective than the parent acid, 4-pyridineacrylic acid

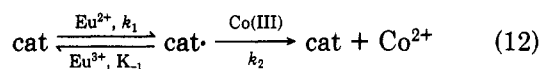
(28) (a) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1978, 17, 326. (b) Dunne, T. G.; Hurst, J. K. *Inorg. Chem.* 1980, 19, 1152. (c) Swartz, J.; Anson, F. C. *Inorg. Chem.* 1981, 20, 2250.

(29) (a) Norris, C.; Nordmeyer, F. *J. Am. Chem. Soc.* 1971, 93, 4044. (b) Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* 1977, 99, 1073. (c) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* 1977, 16, 1942.

(XVII) more effective, and 2,4-pyridinecarboxylic acid (XVIII) very effective indeed. (The k_{Eu} values accompanying the formulas refer to the specific rates of $1e^-$ reduction by Eu^{2+} at 25 °C in 1 M $HClO_4$ which, as indicated below, may determine catalytic potency.) Very nearly all such catalysts have unsaturated functions lying in the 4-position of the ring; again, the corresponding 3-substituted pyridines are virtually without effect.



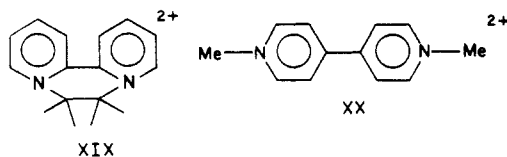
The structural features common to the catalysts, the chemical nature of the reactants, and the observed inhibition by added Eu^{3+} point to a catalytic path proceeding through a pyridine-derived radical ($cat\cdot$), formed at small steady-state concentrations, which reacts with the oxidant, $Co(III)$. And that is not all; a number of such radicals have been generated by pulse radiolysis^{21a} and shown to react very rapidly with cobalt(III) compounds which are devoid of bridging ligands. The catalytic sequence, which is consistent with the observed rate law 13^{29a,b}, is then:



$$rate = \frac{k_1 k_2 (Co^{III})(Eu^{2+})(cat)}{k_{-1}(Eu^{3+}) + k_2(Co^{III})} \quad (13)$$

When $Co(III)$ is in large excess and no Eu^{3+} is added, the specific rate of the overall conversion approaches k_1 , pertaining to the $1e^-$ reduction of the catalyst to its radical, ($cat\cdot$). With Eu^{2+} in excess and Eu^{3+} present in large amount, catalytic potency is determined largely by the ratio k_1/k_{-1} which, in turn, reflects ΔE_0 for the initial step. Analogous behavior has been observed for reductions by $V(II)$,^{29c} $U(III)$,³⁰ and, with modification, $Cr(II)$.³¹

The initial reduction step in the overall sequence with catalysts XV–XVIII is mainly inner-sphere, with attack by Eu^{2+} at the donor carbonyl function. With the catalysts “diquat” (XIX) and methylviologen (XX), which are devoid of lead-in groups, this step must be outer-sphere, and is sluggish. Aromatics of the latter

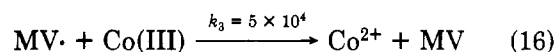
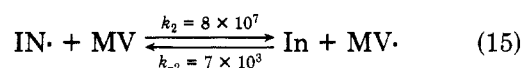
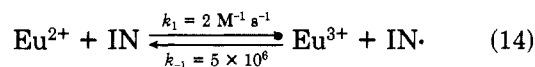


type, if taken in conjunction with suitable carbonyl-containing catalysts and used under the correct con-

(30) Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1978, 17, 3689.

(31) Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* 1978, 17, 1142. The modification, in the case of $Cr(II)$ reductions, reflects the substitution-inert character of $Cr(III)$ centers. In the initial act of reduction of the catalyst, $Cr(III)$ remains bound to the radical ($Cr^{III}cat\cdot$). The final step then yields a $Cr(III)$ -bound catalyst molecule.

ditions, have been found to exhibit *catalytic synergism*, i.e., catalytic effectiveness exceeding the sum of the individual catalyses.³² Typically, the reduction of 10^{-3} M $Co(en)_3^{3+}$ by 0.2 M Eu^{2+} (25 °C, 1 M $HClO_4$) is accelerated 230-fold by 0.0127 M isonicotinamide (XVI), 780-fold by 5×10^{-4} M methylviologen (XX), but 8400-fold by a combination of the two catalysts. The enhanced effectiveness of the two catalysts in tandem arises because the radical from methylviologen ($MV\cdot$, $E^\circ -0.52$ V), which attains the greater steady-state concentration, is generated by Eu^{2+} at a lower specific rate ($k_{Eu} = 0.7$) than the radical from isonicotinamide ($IN\cdot$, -0.66 V, $k_{Eu} = 2.0$). The principal catalytic sequence is then:



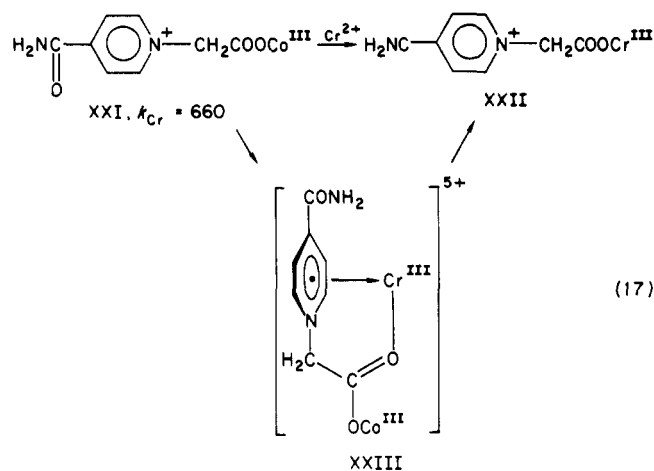
In effect, isonicotinamide, the more rapidly reacting (inner-sphere) catalyst, catalyzes the formation of $MV\cdot$, the predominant species reacting with $Co(III)$. By kinetic treatment of favorable cases,^{32b} it has been found possible to estimate specific rates for all five rate constants (three forward, two reverse) in sequence 14–16. Values indicated in this sequence refer to reduction of $Co(en)_3^{3+}$ at pH 4.6. The thermodynamically favored electron transfer between the $IN\cdot$ radical and methylviologen is, as expected, considerably more rapid than the other steps. Note that this sequence constitutes a *four-member electron-transport chain*, analogous to, but much simpler than, those found in biosystems.³³

Complex XXI represents an initial attempt to design an intramolecular analogue of external catalytic systems. It was anticipated that preliminary attack by a reductant should occur at the activated pyridine center, followed by rapid electron transfer to $Co(III)$. This oxidant differs from those used in early studies (e.g., IX, X, and XII) in that the two centers are blocked off by an “insulating” CH_2 group, presumably precluding conjugative interaction between the centers. Reduction of this “internally insulated oxidant”, using Cr^{2+} , proceeds at a very much enhanced rate ($k_{Cr} = 660$),³⁴ and this must be attributed to the activated pyridine ring, for if the activating 4- $CONH_2$ group is moved to the 3-position, or if it is removed altogether, acceleration disappears (k_{Cr} drops below 0.06 in both cases). The primary product from the rapid reaction is the carboxyl-bound $(H_2O)_5Cr^{III}$ complex, XXII. Hence chro-

(32) (a) Fanchiang, Y.-T.; Gould, E. S. *J. Am. Chem. Soc.* 1977, 99, 5226. (b) Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1978, 17, 1138. A reviewer suggests that at very low concentrations of $Co(III)$, eq 14 and 15 are in equilibrium and the added catalytic action of isonicotinamide should disappear. However, we emphasize that in the presence of $Co(III)$, the concentrations of both radical $IN\cdot$ and $MV\cdot$ fall far below the equilibrium values. Moreover, no evidence for the attrition of synergism at low $[Co(en)_3^{3+}]$ was obtained experimentally.

(33) See, for example: (a) Ohnishi, T. *Biochem. Biophys. Acta* 1973, 301, 105. (b) King, T. E.; Klug, M., Eds. “Electron and Coupled Energy Transfer in Biological Systems”; Dekker: New York, 1972. (c) Chapman, S. K.; Davies, D. M.; Vuik, C. P. J.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* 1983, 868. (d) Beoku-Betts, D.; Chapman, S. K.; Knox, C. V.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* 1983, 1150.

(34) Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* 1979, 18, 1289.

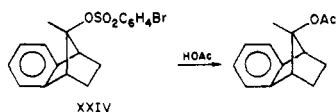


mium must be carboxyl bound just after the act of electron transfer (for Cr^{III} cannot shift sites rapidly); yet it must also interact with the pyridine ring. We have suggested, with perhaps some hesitation, the intervention of an intermediate of type XXIII, in which $Cr(III)$ "sees" both the carbonyl group of $COOCr^{III}$ and the ring. Such dual interaction is, in a formal sense, analogous to *homoaromatic interactions* in organic systems,³⁵ in which a saturated carbon intervenes between an aromatic activating group and the reaction center. Note that the enhancement of k_{Cr} observed with oxidant XXI far exceeds those for complexes IV and VIII, in which conjugation is unbroken. The effect, however, suffers severe attenuation as the insulating fragment is lengthened; with insulation by $(CH_2)_3$ rather than by CH_2 , k_{Cr} falls to only 1.9.

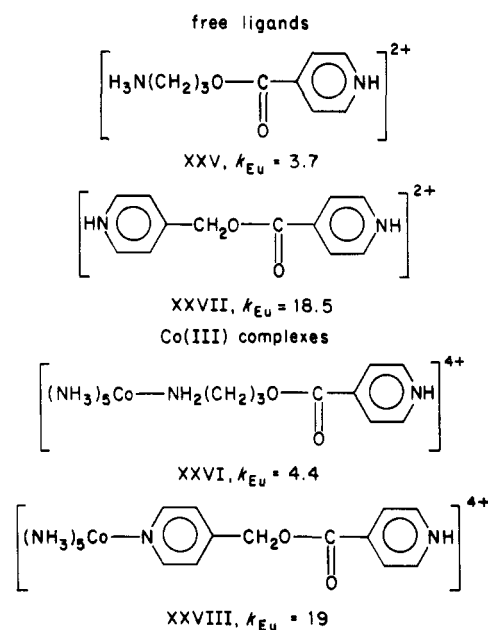
Data from catalytic experiments bear directly on our consideration of the radical-cation or chemical mechanism, for we now have at hand specific rates for 1-electron reduction of the free ligand, which may then be compared with rates for the coordinated ligand. Thus Eu^{2+} rates for free ligands XXV and XXVII have been found³⁶ to correspond almost exactly to rates for reduction of the respective $(NH_3)_5Co^{III}$ complexes, XXVI and XXVIII to Co^{2+} , thus providing us with particularly clear-cut examples of electron transfers between metal centers which proceed at rates determined by ligand reduction.

At this point, we may comment on the role that conjugation assumes in promoting the chemical mechanism. In virtually all instances, the acceptor ligand features a conjugated function, and if a pyridine-carboxylate or related species is involved, the ring nitrogen must lie in conjugation with the carbonyl unit, (i.e., the carbonyl must be situated at the 4- or 2-position, but not at the 3-position). It is to be emphasized, however, that the oxidizing metal center need not be included in the conjugated system, for rapid internal

(35) See, for example: Story, P. R.; Clark, B. C., Jr. in "Carbocation Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1972; Vol. 3, Chapter 23. Typically, homoaromatic interaction is thought to occur in the reaction of sulfonate ester XXIV with acetic acid, which proceeds 6×10^6 times as rapidly as the reaction of the corresponding ester with the fused benzene ring removed (Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* 1960, 82, 1240).



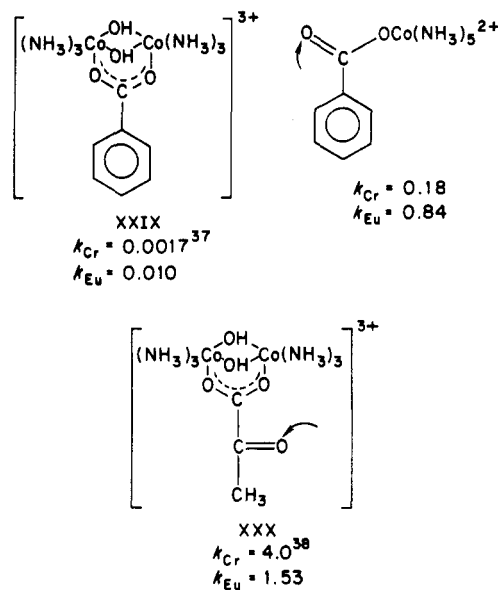
(36) Goli, U. B.; Gould, E. S. *Inorg. Chem.* 1984, 23, 221.



electron transfer from the radical can occur through space.

Recent Glimpses

Carboxylato-bridged dimeric cobalt(III) complexes of type XXIX differ from the more familiar monomeric carboxylato oxidants in that the $C=O$ group, the "lead-in site" for inner-sphere reductions, has been blocked off by coordination to a second $Co(III)$ center.



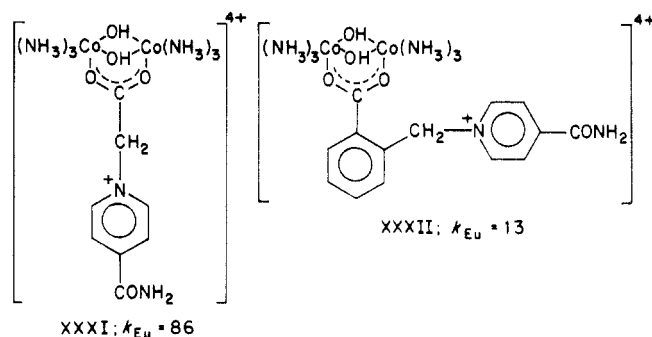
Reductions of the dimeric oxidants must therefore proceed by a sluggish outer-sphere path unless a remote lead-in group is incorporated in the bridging ligand (as in the μ -pyruvato complex, XXX) or a reducible function is appended which will permit more rapid reduc-

(37) Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* 1974, 651.

(38) Srinivasan, V. S.; Singh, A. N.; Wieghardt, K.; Rajasekar, N.; Gould, E. S. *Inorg. Chem.* 1982, 21, 2532. Arguments are presented here that the reduction of the "first" $Co(III)$ is much slower than subsequent processes and that the specific rates indicated apply to this first reductive step.

(39) Srinivasan, V. S.; Rajasekar, N.; Singh, A. N.; Radlowski, C. A.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* 1982, 21, 2824.

tion via internal catalysis. Of several known dimeric complexes of the latter type, two (XXXI and XXXII)³⁹ are shown. On both, the catalytically active center is the isonicotinoyl group. Rate enhancements for Eu^{2+} ,



while not as spectacular as some of those observed for monomeric Co(III) oxidants, are substantial and, once again, disappear when the CONH_2 function is shifted to the 3-position on the pyridine ring. In both of these, the site of initial attack lies distant from both Co(III) centers and is conjugated with neither of them. Hence, we are seeing reactions requiring considerable through-space interaction between the generated radical center and the ultimate electron acceptor.

Tripositive uranium, U^{3+} , is a powerful $1e^-$ reductant ($E^\circ = -0.69 \text{ V}$) which exhibits electron-transfer patterns remarkably similar to those of Cr^{2+} and Eu^{2+} , although specific rates are about 10^3 – 10^4 as rapid.⁴⁰ Recent comparisons,³⁶ involving substituted aminohydrin complexes, tell us that this reagent too may operate through the radical-cation mechanism. In the absence of activation (oxidants XXXIII and XXXIV) specific rates (k_{U} values) are seen to lie well below $100 \text{ M}^{-1} \text{ s}^{-1}$. Acylation of the remote hydroxyl with the 4-pyridine-carbonyl function (XXXV and XXXVI) boosts rates to 10^4 (the known³⁰ value of $1e^-$ reduction of uncomplexed 4-PyCOOH by U^{3+}), but, once more, the 3-carboxyl unit (XXXVII and XXXVIII) is ineffective. Extension of the chemical mechanism to U^{3+} is not a trivial matter, for there is the possibility that with such a strong reductant at hand, reduction of the radical center to an inactive dihydropyridyl species may compete with electron transfer to Co(III). Although such complications have been observed in other systems,⁴¹ their intrusion is evidently not important here. Note that evidence for the radical-cation mechanism has not yet been reported for reactions of the weaker reductants, Cu^I ($E^\circ = +0.17 \text{ V}$) and $\text{Ru}(\text{NH}_3)_6^{2+}$ ($E^\circ = +0.214 \text{ V}$).⁴²

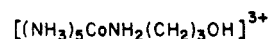
Until 1982, virtually all strongly supported examples of the chemical mechanism involved heterocyclic systems or nitro species. The question remained, "Can this mechanism be demonstrated to apply to carbocyclic or acyclic systems as well?" If we consider ligands that undergo one-electron reduction readily, the pyruvate group, $\text{CH}_3\text{C}(=\text{O})\text{COO}^-$, comes to mind.⁴³ This has

(40) (a) Wang, R. T.; Espenson, J. H. *J. Am. Chem. Soc.* 1971, 93, 380. (b) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* 1978, 17, 330.

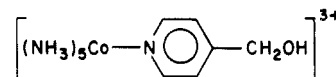
(41) See, for example: Singh, A. N.; Radlowski, C. A.; Reed, J. W.; Krishnamurthy, V. V.; Gould, E. S. *Inorg. Chem.* 1981, 20, 211.

(42) Endicott, J. F.; Taube, H. *Inorg. Chem.* 1965, 4, 437.

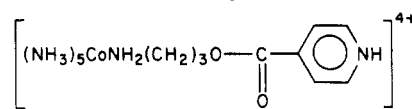
(43) Fleury, M. B.; Moiroux, J.; Fleury, D.; Dufresne, J.-C. *J. Electroanal. Chem.* 1977, 91, 365. Reduction potentials (1e, pH 0 vs. NHE) reported by these workers are -0.268 V for pyruvic acid and $+0.002 \text{ V}$ for phenylglyoxylic acid.



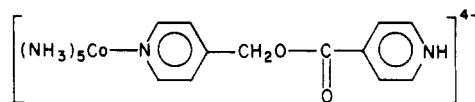
XXXIII: $k_{\text{U}} = 3.5$



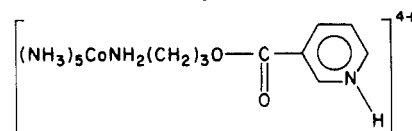
XXXIV: $k_{\text{U}} = 60$



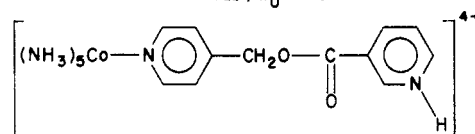
XXXV: $k_{\text{U}} = 1.2 \times 10^4$



XXXVI: $k_{\text{U}} = 4.5 \times 10^4$

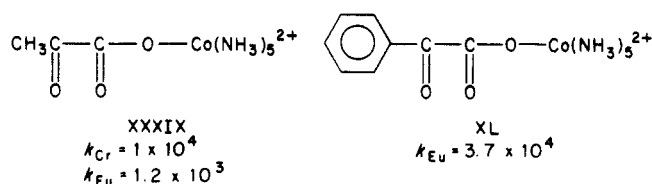


XXXVII: $k_{\text{U}} = 5.3$

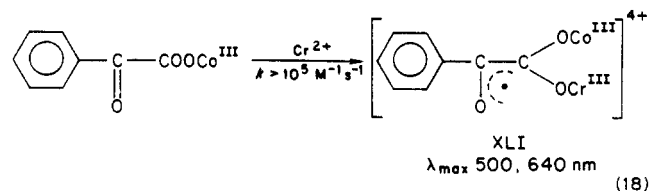


XXXVIII: $k_{\text{U}} = 150$

been long known to be an unusually effective bridging group (XXXIX),⁴⁴ but examinations of pyruvate-mediated reductions of Co(III) by $\text{Cr}(\text{II})$,^{44,45a} $\text{Eu}(\text{II})$,^{45b} and $\text{Ti}(\text{III})$ ^{45c} have not detected the expected radical-cation intermediate, either because it reacts too rapidly or because it absorbs too weakly (or both).



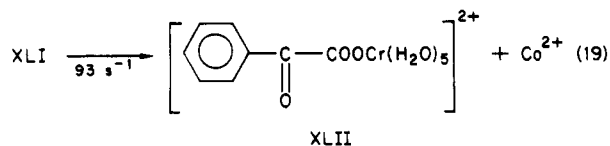
Phenylglyoxylate, $\text{PhC}(=\text{O})\text{COO}^-$, however, is an even more potent inner-sphere mediator than pyruvate^{45b,c} and is still more easily reduced.⁴³ Recent kinetic profiles⁴⁶ for Cr^{2+} reductions of both the monomeric (XL) and the dimeric bridged (XLIII) phenylglyoxylate complexes demonstrate the intervention of strongly absorbing intermediates similar to that observed in the pyrazine system XII. The intermediate XLI in the monomeric reduction is formed too rapidly for measurement by stop-flow spectrophotometry, but its unimolecular decay (19) may be followed.



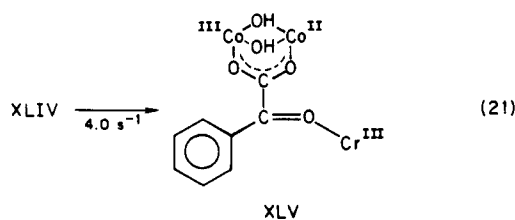
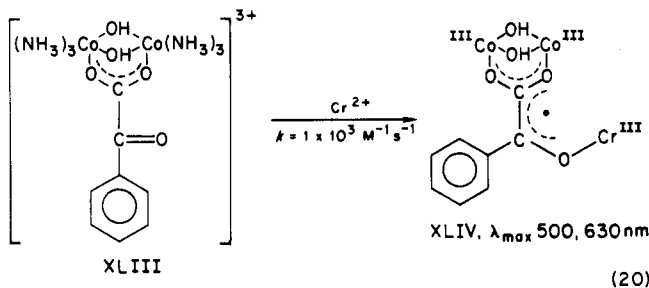
(44) Price, H. J.; Taube, H. *Inorg. Chem.* 1968, 7, 1.

(45) (a) Gould, E. S. *J. Am. Chem. Soc.* 1974, 96, 2373. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* 1974, 13, 2639. (c) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* 1983, 22, 1103.

(46) Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* 1984, 23, 2181.



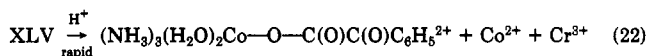
With the dimer XLIII both the formation (20) and unimolecular decay (21) of the intermediate XLIV may be monitored.⁴⁷ The spectral characteristics of this



intermediate (λ_{max} 500 nm ($\epsilon = 1.1 \times 10^3$), 630 nm ($\epsilon = 7 \times 10^2$)), are similar to those of the species intervening in the monomeric system, but both the growth and decay of the radical ion intermediate XLIV proceed at a more leisurely pace. In the dimer, XLIII, the carboxyl group is "tied up" by coordination to the second Co(III); attack by Cr^{2+} therefore occurs at the keto group of the ligand. The rapidity of sequence (18–19), involving the monomeric oxidant, as compared to (20–21), is in accord with earlier rate comparisons,³⁸ which indicate that in cases such as this the unblocked carboxyl is superior to the keto function as a lead-in group.

It is appropriate to ask whether electron-transfer reactions involving bound or unbound radicals have pertinence outside of the inorganic chemist's laboratory. Despite early speculation to the contrary,⁴⁸ there is serious doubt as to the wide applicability of the chemical mechanism, as we have described it, to biosystems, for these lack the strongly reducing species, Cr^{II} , Eu^{II} , and U^{III} , presumably needed for the initial step. On the other hand, the intervention of unbound aromatic radicals is of considerable significance in nature, not only the chemistry of excited states, but also in the transformations involving flavins, which are among the most versatile of the oxidation coenzymes. As shown for the most familiar member of the species, riboflavin,

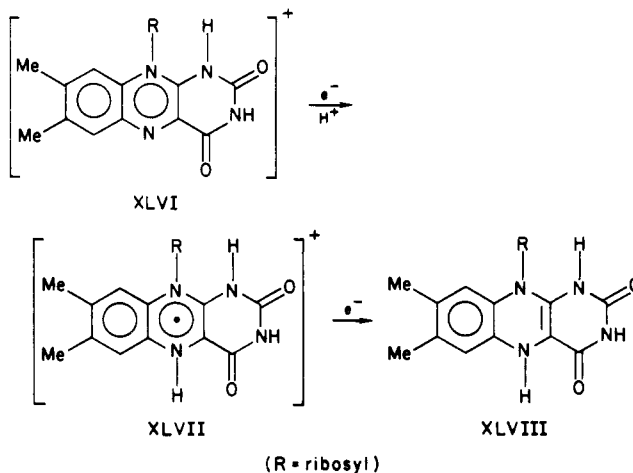
(47) Although it is not essential to the present story, one may inquire as to the fate of the Co(III)–Co(II) species, XLV, in this system. The subsequent collapse of XLV (reaction 22),³⁸ to $\text{Co}(\text{H}_2\text{O})_6^{2+}$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$,



and a monomeric Co(III) complex of the parent keto acid is expected to be very rapid in view of the extremely substitution-labile character of the Co(II) center. The departure of the keto-bound Cr(III) from XLV (by acid-catalyzed carbon–oxygen bond breakage) may also be taken to be rapid; see, for example: Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* 1976, 16, 1929.

(48) See, for example: LaMar, G. N.; Del Gaudio, J. *Adv. Chem. Ser.* 1977, No. 162, 207.

XLVI, flavins in acid solution may undergo both one- and two-electron reductions, yielding, respectively, radical (semiquinone) (XLVII) and dihydro (XLVIII) species. It has been shown⁴⁹ that both the radical and



dihydro derivatives of flavins reduce a variety of metal centers (Fe^{III} , Tl^{III} , Cu^{II} , Co^{III} , Hg^{II} , VO^{2+} , UO_2^{2+}) readily, generally by outer-sphere paths. Such reductions occur with both $1e^-$ and $2e^-$ metal oxidants, and reactions occur not only with hydrated metal ions but also with the complexes of a variety of ligands (halogens, carboxylate groups, amides, and N-bound heterocycles). The ease with which flavins participate in both $1e^-$ and $2e^-$ transactions is of unusual importance, for it leads to their ability to mediate between electron-transfer processes and the even-electron processes characterizing metabolic conversions.⁵⁰ It therefore appears that extension of electron-transfer studies to include systems featuring both flavin derivatives and metal centers in biologically related environments, e.g., metalloproteins and metalloporphyrins, will be especially informative.

Complexes undergoing reduction via bound radical intermediates have recently taken on added interest, for they may be considered to be homogeneous models of chemically modified electrodes which feature, in addition to a metal oxide or carbon surface, a chemically bound electron-transfer species.⁵¹ Among such redox-active coatings are nitro aromatics⁵² (analogous to the ligand in X), viologens⁵³ (closely related to XX), quinones,⁵⁴ and a number of reducible heterocyclic units.⁵⁵ Since the formal potential of the electron-transfer species lies close to that of the analogous unbound redox-active compound, the variety of surface treatments available permits a wide range of potentials for such modified electrodes. Just as the reducible ligand in monomeric systems catalyzes electron exchange between metal centers, so also may the redox-

(49) (a) Singh, A. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1982, 21, 1232. (b) Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* 1982, 21, 1236.

(50) See, for example: (a) Hemmerich, P. *Adv. Chem. Ser.* 1977, No. 162, 312. (b) Suckling, C. J. *Chem. Soc. Rev.* 1984, 13, 113.

(51) For recent reviews see: (a) Murray, R. W. *Acc. Chem. Res.* 1980, 13, 135. (b) Zak, J.; Kuwana, T. *J. Electroanal. Chem.* 1983, 150, 654.

(52) (a) Van De Mark, M. R.; Miller, L. L. *J. Am. Chem. Soc.* 1978, 100, 3223. (b) Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* 1977, 78, 195.

(53) Tse, D. C. S.; Kuwana, T.; Royer, G. P. *J. Electroanal. Chem.* 1979, 98, 345.

(54) Brown, A. P.; Anson, F. C. *Anal. Chem.* 1977, 49, 1589.

(55) See, for example: Roullier, L.; Lavivon, E. *J. Anal. Chem.* 1984, 162, 77.

active species catalyze electrolytic oxidation or reduction of a dissolved substrate that might react with difficulty (or at a higher potential) with the untreated electrode. Typically, viologen-bonded carbon electrodes have been used in the electrolytic reduction of water to H_2 ,⁵⁶ quinone-bonded carbon electrodes perform well in the oxidation of ascorbic acid,⁵⁷ and nitro-aromatic-bound platinum electrodes have been featured in the electrolytic reduction of dissolved CCl_4 .^{52a}

Concluding Remarks

We have examined representative evidence for radical

(56) Malpas, R. E.; Mayers, F. R.; Osborne, A. G. *J. Electroanal. Chem.* **1983**, *153*, 97.

(57) Cenas, N.; Rozgaite, J.; Pocius, A.; Kulys, J. *J. Electroanal. Chem.* **1983**, *154*, 121.

intervention in electron-transfer reactions. The evidence for these reactions has been strengthened and the scope of such reaction types greatly expanded by consideration of unbound, as well as bound, radical intermediates. The mechanistic ideas developed for these reactions are broadly applicable to current research areas which extend far beyond those simple complexes that furnished the early hints that such mechanisms might operate.

I am indebted to the donors of the Petroleum Research Fund (which is administered by the American Chemical Society) and to the National Science Foundation for continued support of the work on which much of this Account is based.