

# RECENT PROGRESS IN THE STUDY OF INNER-SPHERE ELECTRON TRANSFER REACTIONS

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## ABSTRACT

Progress made during the past ten years or so by the author's associates in studying inner-sphere electron transfer reactions is reviewed, emphasizing organic molecules as bridging groups. Evidence is outlined for reduction by remote attack in the reaction of chromous ion with isonicotinamidepentaamminecobalt(III) and with the analogous nicotinamide complex. That there be a conjugated bond system in a bridging group, even when there is a suitable remote polar group, is not a sufficient condition for effective mediation by the bridging group in electron transfer by remote attack. Moreover, conjugated bond systems are shown to exert effects even when they are not in the direct line of electron transfer, that is, when they are in pendent positions. The 'reducibility' of the bridging group appears to be important in determining its capacity to mediate in electron transfer between Cr(II) and Co(III).

In the systems referred to, with reducible bridging ligands, electron transfer is understood as taking place in a stepwise manner. As was anticipated by Halpern and Orgel, the symmetry properties of the donor, carrier and acceptor orbitals are important in determining rates and mechanisms. Thus the mechanism of electron transfer seems to be different when Ru(III), a  $\pi$  electron acceptor, rather than Cr(III) or Co(III), which are  $\sigma$  acceptors, is oxidant.

The electronic structures of the metal ions are important also in determining the lability of binuclear precursor and product complexes. A number of product binuclear complexes are mentioned containing both Ru(II) and Cr(III) bound to a bridging group, and evidence for an electromeric equilibrium in such systems is cited. The study of the binuclear complexes is an interesting subject in its own right, and the ion (XXI) (see text) is introduced as illustrating some of the issues relating to the interaction between metal ions which arise in considering binuclear species. Finally, some of the opportunities and problems facing those interested in the field are outlined.

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In a plenary lecture given a decade ago<sup>1</sup> during the Fifth International Conference on Coordination Chemistry, a subject which was then still very new, that of electron transfer between metal ions as mediated by organic ligands, was featured prominently. Much additional research on this topic has been done in the past ten years, and there have been basic changes in the way it is understood. The field seems to me to be important enough to have warranted the large expenditure of effort which has been devoted to it. Most of the research of my own group in the field of electron transfer reaction has been done on systems reacting by inner-sphere mechanisms, and concern with organic molecules as bridging ligands has been central to it. In reviewing

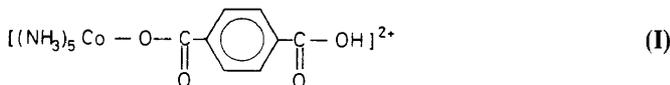
the progress we have made, or feel we have made in the broader field, I have chosen to begin by outlining the changes in outlook which have been brought about by a continuation of research on electron transfer reactions mediated by organic bridging groups.

Three aspects of the subject will be dealt with: remote attack, activation effects accompanying electron transfer and the mechanisms of electron transfer transport through conjugated bond systems. Of these, the first two were dealt with in some detail in the earlier lecture. In the interim, a number of experimental results pertaining to them have been revised. The new results are proving to be a sound foundation for the growth of knowledge in this field and for what appears to be a substantial advance in understanding the third aspect. This is by no means a claim to having arrived at full understanding of the mechanism of electron transport through organic molecules. But the views now held do seem to be sufficiently sound to guide the research being done in productive directions.

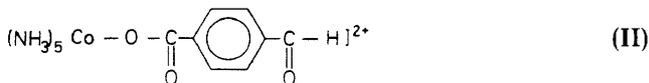
It will not be profitable in the course of this lecture to detail all the errors made in the early work—they are, in any case, and regrettably so, permanently recorded in the literature—but they will be mentioned when this is necessary for the purposes of the particular themes which will be developed. Before concluding this brief apology, it is perhaps worth mentioning that some of the effects reported in the early work seem to have been sound in principle and have manifested themselves in the course of research on different but related systems.

### REMOTE ATTACK

Since remote attack deals with the fundamental question of the geometry of the activated complex, this issue will be dealt with first. The term refers to a mechanism in which the reducing agent† attacks an oxidizing complex such as



at the remote polar group. When a mechanism of this kind operates for a large bridging group, the reducing agent in the activated complex is so remote from the oxidant that direct overlap of metal ion orbitals cannot provide a means for electron transport and the organic molecule can, therefore, be taken as mediating in the electron transfer process. Setting aside the earlier claims<sup>2</sup> of proof for remote attack in the reduction of molecules related to (I), we note that in the interim, proof of remote attack has been provided for small molecules<sup>3-5</sup> such as  $\text{CN}^-$  and  $\text{NCS}^-$  acting as bridging groups. It was strongly suggested for the reaction of



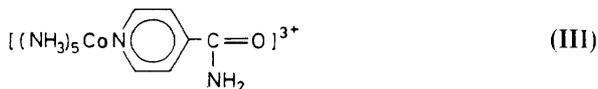
with chromous ion by the observation that in this case the ligand is not

† In most of the studies dealt with in the early part of the lecture, chromous ion is the reducing agent. In selecting it, advantage is taken of the fact that it is a powerful reducing agent and that it yields a substitution-inert product on being oxidized.

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trapped in the chromium(III) product, but is found free in solution after reaction<sup>2b</sup>. This is the result expected if chromous ion attacks the aldehydic carbonyl—note that a chromium(III)–aldehyde complex will aquate very rapidly. Experiments now in progress<sup>6</sup> show that a labile intermediate is formed in the reaction. This intermediate could be the aldehyde complex, thus bearing out the original claim of a remote attack mechanism for this reaction.

For complex organic ligands, the first convincing proof<sup>7</sup> of remote attack was obtained in the investigation of the reduction of



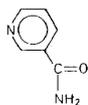
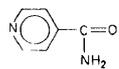
by chromous ion. It was concluded that the primary product of the reaction is



the constitution of (IV) having been established by its cation exchange behaviour, its visible absorption spectrum, and most convincingly, by the i.r. frequencies of the amide group as observed in deuterium oxide as solvent. Whenever proof of mechanism rests on intermediate product identification, the possibility of reorganization during reaction of a primary product must be taken into account. The reorganization in the present system is catalysed by chromous ion. It was separately studied and has been allowed for. The results obtained on this feature of the reaction are important in later context and will be cited when the mechanism of electron transfer is under discussion.

When (III) is the oxidant, species (IV) is the only significant primary

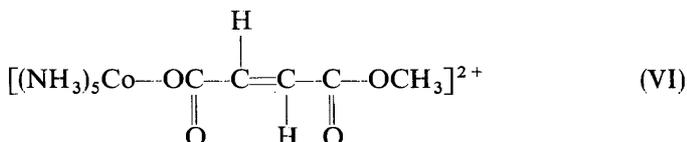
Table 1. Summary of kinetic data on the reduction by chromium(II) of pentaamminecobalt(III) complexes with pyridine and derivatives (medium at  $\mu = 1.0$ ,  $\text{LiClO}_4\text{--HClO}_4$ )

Ligand	Primary product	$k$ at 25° $\text{M}^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger$ $\text{kcal mole}^{-1}$	$\Delta S^\ddagger$ $\text{e.u.}$
	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	$4.0 \pm 0.1 \times 10^{-3}$	$9 \pm 2$	$39 \pm 7$
	$\left\{ \begin{array}{l} \text{Cr}(\text{H}_2\text{O})_6^{3+} \\ (\text{CrL})^{4+} \end{array} \right.$	$1.4 \pm 0.1 \times 10^{-2}$ $3.3 \pm 0.2 \times 10^{-2}$	$9 \pm 2$ $10 \pm 1$	$36 \pm 7$ $31 \pm 3$
	$\text{CrL}^{4+}$	17.4	$3.9 \pm 0.3$	$40 \pm 1$

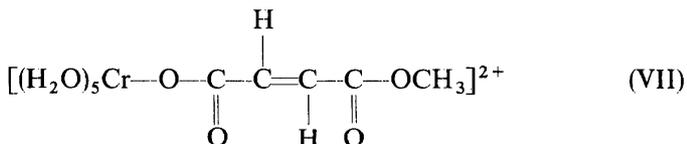
product which contains chromium(III), but when the analogous nicotinamidecobalt(III) complex (V) is the oxidant, hexaaquochromium(III) as well as the chromium(III) complex of nicotinamide analogous in constitution to (IV), is formed. On the basis of this evidence, we conclude that in the reduction of (III), a remote attack mechanism is by far the dominant process, but that in the reduction of (V), reaction takes place by two parallel paths. Of these, only the inner-sphere path definitely involves remote attack and the other, outer-sphere path leads to the production of hexaaquochromium(III). The foregoing qualitative conclusions are summarized in more quantitative form in *Table 1*.

#### Activation effects accompanying electron transfer

Of the 'activation effects' accompanying electron transfer between chromous ion and cobaltamine complexes which were reported earlier, the hydrolysis<sup>2</sup> of the ester in the reaction of

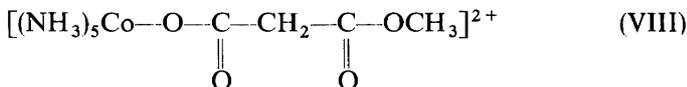


with chromous ion was of special significance as indicating a remote attack mechanism. A re-investigation<sup>5</sup> of the reaction failed to yield evidence of substantial ester hydrolysis, and showed (VII)



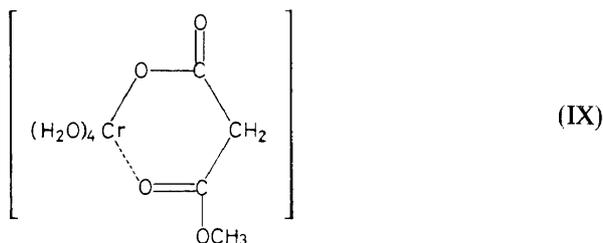
to be the major product of the reaction. The methylacetate complex of pentaamminecobalt(III) was prepared<sup>9</sup>, though not in pure form, and was found to react with water, not by ester hydrolysis, but by aquation. This suggests that even if an ester complex of chromium(III) were formed as a result of remote attack, it would not react by ester hydrolysis. In the reaction of chromous ion with (VI), when the steady-state concentration of the reducing agent is kept low, some free ligand together with hexaaquochromium(III) is produced<sup>8</sup>. This observation indicates that an ester complex is formed to some extent, and that this rearranges under the influence of chromous ion to (VII), or aquates to form free ligand.

The mode of reaction with water of the ester complexes referred to in the preceding paragraph is interesting in the light of observations<sup>10</sup> which have been made on the stoichiometry of the reaction of

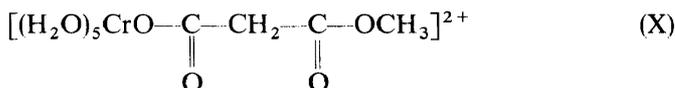


with chromous ion. Here substantial (55 per cent) ester hydrolysis does accompany the electron transfer reaction, and it is reasonable to suppose that this results from the formation of the intermediate

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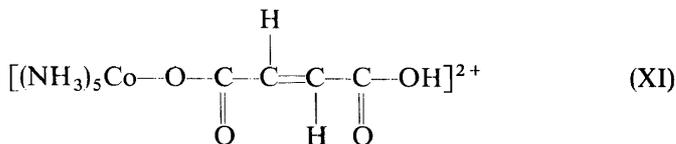


in the electron transfer reaction. Attack limited to the adjacent carboxyl group must also contribute substantially to the reaction, and this can account for the portion of the product which appears as



The difference in behaviour of the chelated ester complex and the monodentate complexes is reasonable in the light of experience with other systems. The metal to nitrogen bond in  $\text{Ni}(\text{NH}_3)_2^{2+}$  is broken more rapidly<sup>11</sup> than in  $\text{Ni}^{2+}$ ; thus, by analogy, the chelated ester complex understandably may survive ring opening by aquation long enough to undergo ester hydrolysis under the influence of chromium(III) acting as a Lewis acid. As expected on this interpretation, reduction of (VIII) by europium(II) or vanadium(II) does not<sup>10</sup> lead to ester hydrolysis. Even were intermediates analogous to (IX) formed in electron transfer, owing to the lability of europium(III) and vanadium(III), aquation rather than ester hydrolysis would be expected.

Another activation effect which was reported earlier<sup>12</sup> is the partial transformation of maleate to fumarate when

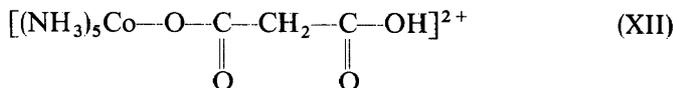


reacts with chromous ion. A re-investigation<sup>13</sup> of this reaction has failed to show evidence of fumaric acid being formed in yields even remotely approaching those reported earlier. In fact, the yields are so low that only an upper limit can be set, *ca.* one per cent conversion at 0.86M ( $\text{H}^+$ ) to be compared to *ca.* 40 per cent as previously reported. The re-investigation has produced a quite interesting result as byproduct, namely the discovery that substantial conversion of maleate to malate accompanies the aquation of the maleato-chromium(III) complex. Under the same conditions, there is virtually no hydration of free maleic acid. In the sense that electron transfer provides a means for forming the maleate complex efficiently, this can be considered as an activation effect accompanying electron transfer, but not in the direct sense of occurring in the act of electron transfer.

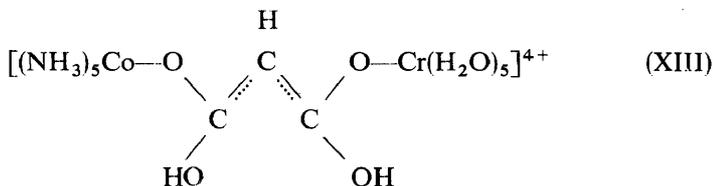
It should be noted that there is substantial conversion of maleate to fumarate<sup>14</sup> when maleate reacts with vanadium(II). The reaction takes place with incorporation of solvent hydrogen into the fumarate, as was

reported<sup>12</sup> for the fumarate claimed as product of the reaction with chromous ion. The mechanism of the reaction is not understood, but the earlier suggestion that the reducing agent transforms the organic molecule to a radical which then picks up a proton from the solvent still seems reasonable.

To conclude the discussion of activation effects, a phenomenon observed in the reaction of



with chromous ion will be mentioned. Malonate is the only saturated acid which, when acting as a bridging ligand in the cobalt(III)-chromium(III) reaction, shows a term first-order in the concentration of hydrogen ion in the rate law for the redox reaction. This term has been interpreted<sup>15</sup> as involving loss of a proton from the methylene group, and the interpretation is given some credibility if a radical ion mechanism for the reaction obtains. A process involving electron transfer to the ligand from the reducing agent would be greatly facilitated were malonate to assume the form



It may be suggested, therefore, that in tending to transfer an electron to the ligand, chromous ion promotes rearrangement of the malonate. The suggestion is offered in a very tentative way, and more study is needed to clarify the chemistry of this system.

The activation effects which have been described are believed to have their origin in two different features linked to the electron transfer act: that of placing as a Lewis acid a substitution-inert metal ion on a sensitive position in the ligand molecule, and the transfer of an electron from the reducing agent to the ligand, thereby affecting its reactivity. The latter involves an assumption about the mechanism of electron transport in these systems, and its mention will be taken as an introduction to the explicit discussion of this topic.

## MECHANISM OF ELECTRON TRANSPORT THROUGH CONJUGATED BOND

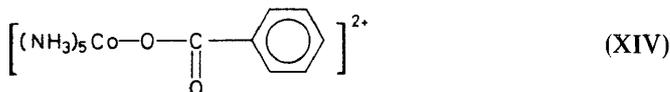
### Systems

Early in the history of the concern with mediation by organic molecules in electron transfer processes, it seemed reasonable, to the extent that electron transfer by remote attack could be viewed as being reasonable, that a conjugated bond system extending from a remote polar group such as  $-\text{CO}_2\text{H}$  to a carboxyl group bearing the metal ion oxidant would ensure facile electron transfer through the bridging molecule. Observations made during the last few years have shown this supposition to be incorrect; the

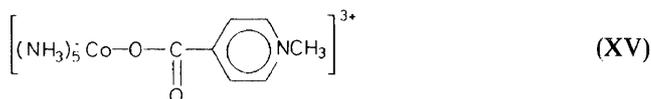
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conditions as stated are neither necessary nor sufficient for facile electron transport by an organic bridging group.

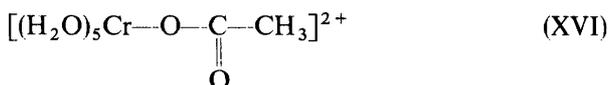
That the conditions outlined are not necessary is suggested by the comparison of the rate of reduction of



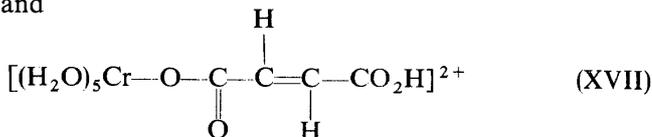
( $k = 0.15 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>16</sup> and



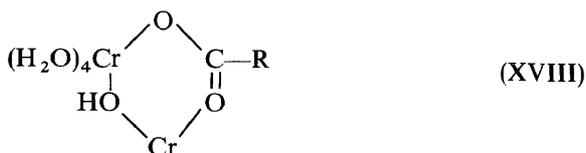
( $k = 1.4 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>17</sup>. In both cases adjacent attack occurs, and thus steric effects for the two complexes are likely identical. Despite the higher positive charge on (XV), it is reduced by chromous ion nine times more rapidly than (XIV). The comparison is all the more remarkable because the group causing the difference in rate is not in the direct line of electron transfer, but is pendent to the conjugated bond system of the carboxyl group. A similar effect, but now greatly enhanced, is shown in comparing the rates of electron transfer between chromous ion and



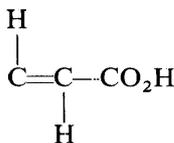
on the one hand<sup>18</sup> and



on the other<sup>19</sup> [as measured in each case by the rate of chromium exchange between chromous ion and the chromium(III) complex]. The rate law in question for the present comparison is  $k[\text{Cr}^{2+}][\text{Cr}(\text{III})]/[\text{H}^+]$  and there are reasons to believe that it corresponds to an activated complex of the geometry

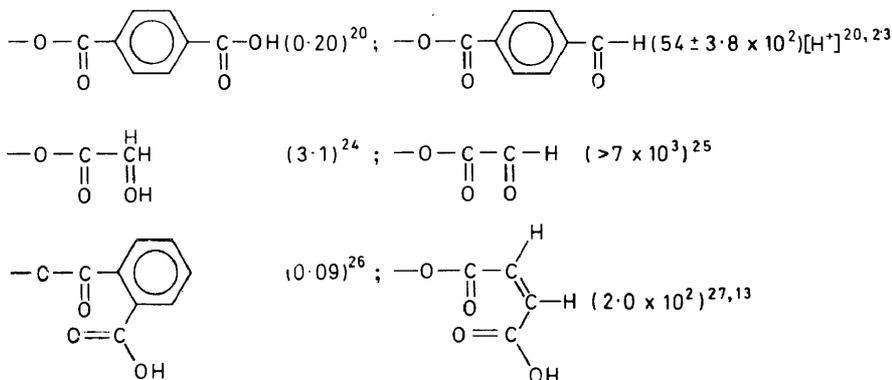


The specific rate  $k$  is *ca.* 1000 times greater when R is



than when it is  $\text{CH}_3$ . Here again, the group affecting the rate of electron transfer is pendent to the bridging function.

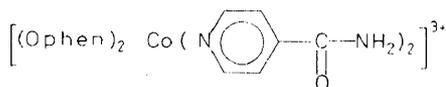
That the conditions as stated are not sufficient was convincingly demonstrated by Gould<sup>20</sup> in correcting an early tentative value for the rate of reduction by chromous ion of (I). In contrast to the earlier result, Gould found that (I) is not reduced significantly more rapidly than is the benzoate complex. Complex (I), it should be noted, has a suitable remote polar group and a conjugated bond system connecting remote and adjacent positions. It has been suggested<sup>17, 21, 22</sup> that 'reducibility'—probably better, the accessibility of the lowest unoccupied orbital—of a ligand of the type under discussion is an important factor in determining how effective it is in mediating electron transfer between chromous ion and  $(\text{NH}_3)_5\text{Co(III)}$ . The importance of this factor is indicated by the results quoted in the paragraphs just preceding, and is borne out also by the three comparisons which follow. The ligands comprising each pair are chosen so that within a pair factors such as chelating or steric effects do not significantly favour the second member in terms of rate of reduction. The pairs are:



Each ligand is complexed to  $(\text{NH}_3)_5\text{Co(III)}$ , and the reducing agent is chromous ion.

In considering the mechanism of electron transfer<sup>28, 29</sup>, it seems important in the first approximation to distinguish resonance transfer, in which the electron passes directly from reducing agent to oxidizing agent by a 'tunneling' process, from a stepwise process in which the mediating ligand is first reduced (oxidized) and then passes the electron (electron hole) on to the oxidizing (reducing) metal ion. The first kind of mechanism will be referred to as 'resonance', and the second as 'stepwise' transfer. The qualitative correlation of reducibility with rate is compatible with either mechanism. The stepwise (or chemical)<sup>28</sup> mechanism is, however, strongly favoured by some rate comparisons which involve isonicotinamide as a bridging group.

The rate at which chromous ion reacts with (III) is only ten times faster<sup>7b</sup> than the rate at which it reacts with the corresponding complex with  $(\text{H}_2\text{O})_5\text{Cr}$  in place of  $(\text{NH}_3)_5\text{Co}$ , despite the enormously greater driving force for the reaction with (III). With simple, non-reducible bridging groups such as  $\text{F}^-$ ,  $\text{OH}^-$  or  $\text{OAc}^-$ , the complexes of  $(\text{NH}_3)_5\text{Co(III)}$  react at least  $10^4$  more rapidly than do those of  $(\text{H}_2\text{O})_5\text{Cr(III)}$ . Experiments have been done also<sup>30</sup> with

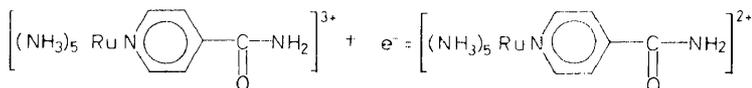


as oxidant. These are complicated by rather rapid redistribution reactions involving the chromium(III) complexes initially produced, but an analysis of the initial rate data points to a rate of reduction per ligand unit, approximately one half that observed for (III). The insensitivity of the rates to the nature of the acceptor centre points to a mechanism in which electron transfer from chromous ion to ligand is (almost) rate-determining, and this is tantamount to invoking the stepwise process.

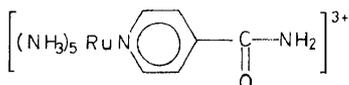
### Electronic structure and mechanism of electron transfer

The conclusions about the mechanism of electron transport through conjugated bond systems reached in the preceding section are offered only as applying to systems which were under discussion and not as necessarily applying regardless of the identity of the metal ion centres. The stepwise mechanism seems reasonable for chromous ion reacting with cobalt(III) and chromium(III) complexes when the symmetries of the donor, acceptor and carrier orbitals are taken into account<sup>29</sup>. In the cases under discussion, the metal ion centred orbitals are of  $\sigma$  symmetry, while the low-lying, unoccupied orbitals of the ligand are of  $\pi$  symmetry. It is not surprising, therefore, that the symmetry mismatch which the description implies is circumvented in stepwise fashion—a special distortion around the chromium(II)–ligand bond leading to orbital overlap and electron transfer and then, in due course, another special distortion at the cobalt(III)–ligand bond bringing about eventual transfer to the oxidizing metal centre. In adopting this line of thought, there is no difficulty in supposing that for the special distortions at the two remote bond positions to occur simultaneously as independent events is highly improbable and, in the absence of a basis for making quantitative estimates, it is not difficult further to suppose that such a coincidence of events is less probable than the stepwise mechanism which is proposed. The success of the stepwise process as outlined does depend on the reducing agent being powerful enough to transfer an electron to the ligand, and this mechanism may well be replaced by resonance transfer when the reducing agent is much weaker.

The interpretation of the observations made with cobalt(III) and chromium(III) as acceptor centres leads naturally to enquiring whether a change to a  $\pi$  electron acceptor will lead to a change in mechanism. It was considerations of this kind that first directed our attention to the study of redox reactions of ruthenium amines<sup>31</sup>. Ruthenium(III) has a low-spin  $d^5$  electronic structure, and in being reduced to ruthenium(II), accepts a non-bonding  $\pi$  electron. In comparing the rate of reduction of a cobalt(III) complex with that of ruthenium(III), the relative driving forces for the two reactions need to be taken into account. The redox potential for the couple

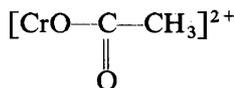


has been measured by standard electrochemical means, and the formal value of  $E^0$  is found to be<sup>32</sup> 0.44 V ( $\mu = 1.0, 24 \pm 1^\circ$ ). That of the corresponding cobalt(III) couple is much harder to determine. The overall reaction in the reduction of the cobalt(III) complex produces the aquocobalt(II) ion, and the driving force for this overall process is not relevant to the reduction by chromous ion where, in the primary act, the Co—NH<sub>3</sub> bonds probably remain intact<sup>33</sup>. The value of  $E^0$  for the reduction to the amminecobalt(II) complex is needed, and this is not accurately known. It is probably not less positive<sup>34</sup> than 0.30 V, and thus the driving force for the reduction of the cobalt(III) complex is, at most, only a little less than that for the ruthenium complex. The specific rate for the reduction of



by chromous ion at 25° and  $\mu = 0.1$  is  $3.9 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ <sup>32</sup> [to be compared to  $17.6$ <sup>7b</sup> for the cobalt(III) complex at 25° and  $\mu = 1.0$ ], under the same conditions the specific rate for the reduction of *cis*-diisonicotinamidetetraammineruthenium(III) is  $7 \times 10^6$ <sup>32</sup>. The significant point to be made is this: when chromium(III) and cobalt(III) are compared as acceptor centres, despite the large difference in driving force for the reactions, the rates of reduction through isonicotinamide as ligand are nearly the same, but when ruthenium(III) is included in the comparison, the rate of reduction is now greatly enhanced and, moreover, is sensitive to slight changes introduced at the ruthenium atom. The behaviour can be understood on the basis that of the three metal ions, only ruthenium(III) has the acceptor orbital of appropriate symmetry to overlap that of the ligand. When the electron is lost from chromous ion in the case of a ruthenium complex, it at once enters the final acceptor orbital. Thus resonance transfer rather than stepwise transfer is being invoked here.

The significance of the symmetry classification of the metal ion orbitals to the mechanism of electron transfer is borne out by other comparisons. The ratio of rates of reduction by chromous ion of  $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3]^{2+}$ <sup>16</sup> compared to  $(\text{NH}_3)_5\text{CoOH}^{2+}$ <sup>25</sup> is  $2 \times 10^{-7}$ ; when the same comparison is made for the corresponding ruthenium(III) complexes, the rate ratio is found<sup>36</sup> to be  $0.8 \times 10^{-2}$ . Relative to OH<sup>-</sup>, acetate is a much better electron mediator on ruthenium(III) than it is on cobalt(III). This can be ascribed to the matching symmetry of the acceptor orbital on the metal ion and the lowest lying, unoccupied orbital on the ligand. In effect, the electron hole is more effectively transferred to the carboxylate when the acceptor orbital has  $\pi$  symmetry than when it has  $\sigma$  symmetry. A similar explanation probably applies to the greater reactivity<sup>18</sup> of



toward vanadium(II), compared to chromium(II). Here the rate ratio exceeds  $2 \times 10^4$ , despite the fact that vanadous ion is a weaker reducing agent than is chromous. The former ion, it should be noted, yields an electron from an orbital of  $\pi$  symmetry, the latter from an orbital of  $\sigma$  symmetry.

### Binuclear intermediates

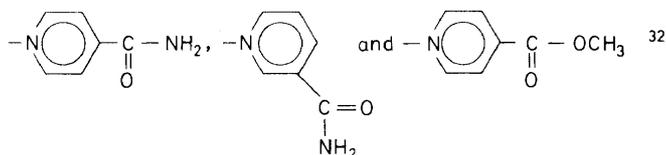
The group transfer observed when chromous ion reacts with most cobalt(III) complexes requires the activated complexes for reaction to be binuclear (this description implies that a primary bond system extends from one metal ion to the other). Indirect arguments<sup>37</sup>, which are by no means compelling, have been presented as suggesting that in fact a binuclear intermediate in labile equilibrium with reactants precedes the electron transfer act. Such precursor complexes have not been observed directly; this is hardly surprising because in most instances the affinity for chromous ion of the bridging ligand which is carried by oxidizing metal ion is expected to be small. Product binuclear complexes (binuclear intermediates formed on electron transfer) have also not been observed directly in chromium(II)–cobalt(III) reactions; again, this is not surprising because the electron added to cobalt(III) when it is reduced is antibonding, and thus the bond between the bridging ligand and the cobalt(II) resulting from electron transfer is expected to be very labile. Indirect evidence<sup>38</sup> based on the variation of rate with acidity, following arguments of the kind which have been advanced by Newton<sup>39</sup> and co-workers for some reactions of actinide ions, for a binuclear precursor complex in the reactions of [*trans*-Co(*trans*[14]diene(OH<sub>2</sub>)<sub>2</sub>)]<sup>3+</sup> and [*trans*-Co(tet *a*)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup>†] has been advanced by Litelpo and Endicott<sup>38</sup>. But though exceptions can arise, as illustrated by the last example, both precursor and product binuclear complexes for the electron structure type under discussion, for reasons already given, are expected usually to be unstable and labile.

When the oxidizing agent is a low-spin  $\pi$  electron acceptor, and with a suitable reducing agent, there is little difficulty in detecting binuclear intermediates as products of the electron transfer act. Thus the formation of a transient green colour in the product of the reaction of chromium(II) with IrCl<sub>6</sub><sup>2-</sup> was attributed in an early study<sup>40</sup> to the formation of the species CrIrCl<sub>6</sub>. This system has since been investigated thoroughly<sup>41</sup>, and the suggestion that CrIrCl<sub>6</sub> is formed as an intermediate has been confirmed. The more recent study shows, however, that only a portion of the reaction produces the binuclear intermediate, and the remainder produces Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> together with IrCl<sub>6</sub><sup>3-</sup>. Even prior to the recent work on Cr<sup>2+</sup> and IrCl<sub>6</sub><sup>2-</sup>, a binuclear product complex was well characterized<sup>42</sup> for the reaction of Co(CN)<sub>5</sub><sup>3-</sup> with Fe(CN)<sub>6</sub><sup>3-</sup>.

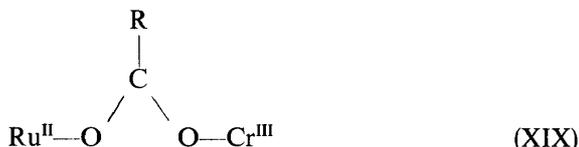
Binuclear intermediate products are produced the reactions of amminetuthenium(III) complexes with chromous ions. When the ruthenium(III) carries a suitable ligand, the chromium(III)–ligand bond formed on electron transfer is slow to undergo substitution. Usually, substitution at the product ruthenium centre (*d*<sup>6</sup>, low-spin) is sufficiently slow so that the

† 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively.

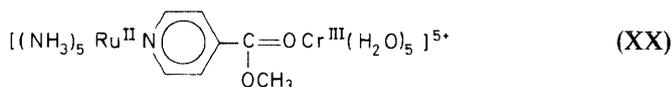
binuclear product persists, making its detection feasible. Binuclear intermediates have been observed for the pentaammine series<sup>36</sup> with  $\text{OH}^-$ ,  $\text{HCO}_2^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{C}_6\text{H}_5\text{CO}_2^-$ ,



as ligands. With oxygen as the lead-in atom, pentaammineruthenium(II) is fairly labile, and the ligand is lost from it on the time scale of a fraction of a second. The intercomparison<sup>36</sup> of the rates of aquation of the binuclear intermediates of this class leads to the conclusion that they have the structure



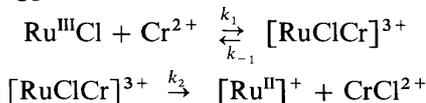
and this answers, at least for a ruthenium(III) carboxylate complex, the question of the position of attack by chromous ion. For the binuclear intermediates formed with  $\text{N}^{\text{II}}$  as the lead-in atom, the bond to ruthenium(II) is much more resistant to aquation<sup>43</sup> and, for the particular systems mentioned, the chromium(III)  $\text{O}=\text{C}$  bond, rather than the ruthenium-nitrogen bond, is broken on aquation. These intermediates show a strong charge transfer absorption<sup>43</sup> in the visible, attributable to the transition:  $t_{2g}$  (ruthenium)  $\rightarrow \pi^*$  (ligand); the absorption is extremely sensitive to changes on the ligand and is useful in studying the rate of loss of chromium(III) from the binuclear complex. Especially interesting is the aquation study of the binuclear complex formed when the ligand has the ester group in the 4 position. The resulting intermediate (XX) aquates according to the rate law



$d[\text{Cr}(\text{H}_2\text{O})_6^{3+}]/dt = [\text{Int}] (36.5 \pm 1 \times 10^{-3} + 2.24 \pm 0.08 \times 10^{-3}/[\text{H}^+])$  (at  $25^\circ$ ,  $\mu = 1.0$ , units M and sec) and in harmony with results already discussed, it releases the ester group without hydrolysis.

With  $\text{Cl}^-$  as the bridging group, analysis of the kinetic data<sup>36</sup> shows that an intermediate of finite life is formed, but the intermediate has not been as completely characterized as in the systems already described. An intermediate of considerably longer life is reported<sup>44</sup> as arising in the reaction of chromous ion with chloropentaquoruthenium(III). Of the intermediates which are

(or are believed to be) bridged by chloride, the most interesting one is that encountered<sup>45</sup> in the reaction of chromous ion with *cis*-dichlorotetraammine-ruthenium(III). As the concentration of chromous ion is increased at constant concentration of the oxidant, the rate does not increase proportionately, but a saturation value is reached at high chromous ion concentration. The kinetic behaviour suggests the mechanism



In the binuclear intermediates discussed thus far for ruthenium(III)-chromium(III) reactions, and in this one as well, the appropriate designation of oxidation state is likely ruthenium(II)-chromium(III), chromous ion being a much stronger reducing agent than is ruthenium(II). But to be compatible with the data, the mechanism requires the  $k_{-1}$  step to occur with Cr-Cl bond cleavage, and the data moreover require  $k_{-1}$  to be unexpectedly large for substitution on chromium(III). These requirements can be met without difficulty if it be supposed that electromeric forms of the intermediate are in equilibrium



Though the ruthenium(III)-chromium(II) state is expected to be in much lower concentration than the ruthenium(II)-chromium(III) state, it can offer an effective path for Cr-Cl bond cleavage owing to the extraordinarily great lability<sup>46</sup> of aquochromium(II).

### Comment on reactions involving outer-sphere activated complexes

The emphasis in this article has been on reactions proceeding by inner-sphere mechanisms, and, in fact even more narrowly, on reactions of chromous ion as reducing agent. Though this reducing agent shows a strong preference for reaction by an inner-sphere mechanism, several instances of outer-sphere reaction mechanisms have been referred to. In the reaction of chromous ion with nicotinamidepentaamminecobalt(III), only 70 per cent of the reaction leads to the chromium(III)amide complex as product<sup>7b</sup>. The remainder of the reaction produces hexaaquochromium(III), and this portion has been described as proceeding by an outer-sphere mechanism. But simply classifying the minor reaction path as 'outer-sphere' is by no means satisfactory, because important features of the structure of the activated complex remain to be specified. Thus, even granting that reducing agent and oxidizing agent approach closely in the activated complex, we would like to know whether the electron passes from chromous ion to cobalt(III) through the ammonia ligands, or whether special use is made of the heteroligand. The rate comparisons which follow suggest that the heteroligand may play a very specific role in reaction by an outer-sphere activated complex. As is shown by the data in *Table 1*, the specific rate for the reaction of chromous ion with the nicotinamidepentaamminecobalt(III) ion by the outer-sphere path is  $1.4 \times 10^{-3} \text{M}^{-1} \text{sec}^{-1}$ , and by the inner-sphere path it is 2.4 times

larger. Both reactions are very much more rapid<sup>32</sup> when nicotinamidepentaammineruthenium(III) is the oxidant ( $k$  for the outer-sphere path now is  $0.6 \times 10^4$ ) but the rate ratio for the two paths is almost unaltered (it is now 2.8). If the outer-sphere reaction were at the metal ion, without special intervention of the ligand, it would seem a remarkable coincidence that the rate ratios are unaltered. However, if both paths involve attack at the ligand—the inner-sphere path at the oxygen of the ligand, and the so-called outer-sphere path at the  $\pi$  system of the ligand—the insensitivity of the rate ratio to change in the metal ion can be understood, because now the ratio can reasonably be expected to be a property only of the ligand.

The suggestion as to the mechanism of the outer-sphere component of the reaction is, at this stage, highly speculative, and is offered as indicating a need for further research rather than as representing a firm conclusion.

### GENERAL COMMENTS

In reviewing work on electron transfer reactions which has been done by my research group during the last few years, I have made no effort to be complete even within the narrow confines of this assignment, let alone attempting to be complete for the field in general. I have purposely avoided taking on a broader assignment, not only because I despair of dealing with it effectively in the space of one hour, but also because this task has been very satisfactorily handled in a rather recent review<sup>47</sup>. There are, however, some important aspects of the subject of electron transfer reactions, closely related to those which I have discussed, which have not been pursued within my group but have been studied by others. Without attempting a complete and extensive review, a brief acknowledgement of some of these contributions seems to me to be very much in order.

The contributions include those of Sutin<sup>48</sup> and Newton<sup>49</sup> in extending the classification of mechanism based on the detection of intermediate products to labile metal centres, of Halpern<sup>50</sup> in developing the chemistry of  $\text{Co}(\text{CN})_5^{3-}$  as a reducing agent (this, like chromous ion, tends to react by group capture), of Haim<sup>51</sup> and Hunt<sup>52</sup> in exploring non-bridging ligand effects, of Linck<sup>53</sup>. Haim<sup>54</sup>, Endicott<sup>55</sup>, in attempting to systematize the data on ligand effects, of Espenson<sup>56</sup> in exploring the chemistry of  $\text{Cu}^+$  (this, like chromous ion, is a  $\sigma$  electron donor), of King<sup>57</sup> in demonstrating the doubly bridged activated complex, of Basolo *et al.*<sup>58</sup> in showing that bridging groups play a role also in  $2e^-$  redox reactions of metal ions. Each of these contributions, and others of equal significance which have not been cited, have enlarged the research horizons of the field. In closing, I wish to mention some of the opportunities for the future opened up by the work described which especially interest me at this juncture.

High in the list of priorities are experiments with a reducing agent which is a  $\pi$  electron donor. While vanadium(II) meets this criterion, substitution is so slow that the rate of reaction by inner-sphere paths is severely limited<sup>59</sup>. Substitution on iron(II) takes place much more rapidly<sup>60</sup>, but the aquo ion is not a strong enough reducing agent to act on the pentaammineruthenium(III) complexes. It can, however, be made reactive enough by adding ligands such as EDTA, which stabilize iron(III) over iron(II). By using a  $\pi$  electron donor as well as a  $\pi$  electron acceptor, it is possible that electron mediation

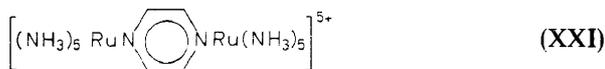
by even poorly 'conducting' organic molecules can be realized. A major problem in studying such bridging molecules is that of limiting the rate of outer-sphere reduction of the rutheniumammine(III) complexes. An important specific task here is to design and synthesize bulky polydentate complexing groups which, in combining with the metal ion, severely limit close approach by the reducing agent.

The systematic investigation of the effectiveness of organic groups as mediators as a function of their structure is clearly called for at this stage, both for the reactions believed to occur by the stepwise process, and for those which appear to react by resonance transfer. Steric interactions are of interest in this connection (what, for example, will be the effect of an alkyl group adjacent to the amide when isonicotinamide acts as a bridging group?), as are variations in the length of the mediating groups and in its reducibility. The search needs to be made for electron conduction along molecules not conjugated in the orthodox sense as, for example, across hydrogen bonds. In considering 'reducibility' as a factor involved in the effectiveness of a molecule as an electron mediator, it is important to develop a means of measuring the energy involved in transferring an electron from some common source to the different kinds of organic molecules which are of interest as bridging groups. For certain of the ligands, this can probably be done by measuring the energy of the charge transfer process<sup>43</sup>  $t_{2g} \rightarrow \pi^*$  when the ligands are in combination with suitable metal ions.

The conclusion that a stepwise mechanism operates for some reactions of chromium(II) with cobaltammines is by no means definite, and further work is needed to settle the issue. Of greatest significance would be the direct detection by some physicochemical method of the radical ion intermediates proposed. An attempt<sup>61</sup> was made to use e.s.r. for this purpose in the reaction of chromous ion with maleatopentaamminecobalt(III), but it led to no definite conclusions. It is certainly worth while trying this direct approach again in another system of this kind. Perhaps equally convincing would be chemical evidence for such intermediates. The fact that *cis-trans* isomerization is not efficient when maleate acts as a bridging group cannot be taken as evidence that a radical ion intermediate is not involved, and a continued search for effects of this kind in related systems seems worth while. Short of the direct approaches mentioned, there is clearly a need also for less direct tests of mechanism, among them the study already mentioned, of the pattern of reactivity when the reducing agent is made so weak that reduction of the bridging group cannot reasonably be invoked.

Finally, mention is made of some of the opportunities which can be exploited in studying binuclear bridged complexes. The purely preparative aspect of this work is itself of considerable interest. The kinetic stability of complexes such as (XIX) can be greatly enhanced by oxidizing Ru(II) to Ru(III), and the resulting species can probably be characterized by ion exchange techniques. The electromeric equilibrium of the kind proposed for the binuclear product complex postulated by Movius and Linck<sup>45</sup> has important implications for the reactivity not only of ground state species, but also of those excited by the absorption of light. The binuclear species pose the interesting problem of assignment of oxidation states. For the Ru(II)-Cr(III) intermediate (XIX) the absorption spectrum strongly supports the

assignment made. When the transferring electron is antibonding for at least one of the metal ion centres, there is little likelihood that in the stable state, the electron will be strongly delocalized over both centres. Even for the case<sup>62</sup>



arguments have been presented for preferring the assignment Ru(II)–Ru(III) rather than Ru(2.5)–Ru(2.5). Binuclear complexes of this type have interesting properties, giving rise as they do to what appears to be intervalency absorption<sup>63</sup>, and make feasible the systematic study of the coupling of the metal ion orbitals by the bridging group. The interaction can be extended as in



and the change in electronic behaviour as a function of the number of metal ion centres can also be studied systematically.

The workers in the field of electron transfer reactions are increasing in number, and in looking to the results of their efforts, I confidently expect the progress in the next decade to exceed by far that made in the past decade.

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