The two possible nonvertical transitions of *cis*-stilbene are indicated by wavy arrows and spectroscopic transitions by straight arrows in the figure. Excitation of *cis*-stilbene by low energy sensitizer triplets cannot involve the spectroscopic *cis* triplet because the sensitizers do not possess the requisite energy content and the processes do not have significant activation energies.[1]

We believe that production of nonspectroscopic states by energy transfer is a common process and a number of examples now have been observed in our Laboratory. Therefore, we should examine the details of the process which we are suggesting. It appears to us that reaction 1 and similar transfers in which acceptors are not promoted in accordance to the Franck–Condon principle have some of the characteristics of both thermal and spectroscopic processes but are identical with neither. The process is not spectroscopic since the restrictions imposed by the Franck–Condon principle are removed. On the other hand, the behavior is unlike that of common thermal reactions because the donor–acceptor system does not come to equilibrium with the surrounding medium. The electronic excitation energy of the sensitizer triplet is handed over to the acceptor and the latter then is released in a long-lived excited state.[2] Since the lifetime of the excited acceptor is long enough to allow it to encounter other solutes present in low concentration, we may be reasonably certain that energy transfer has not become a pure thermal process, *i.e.*, the excitation does not appear in the acceptor as vibrational excitation. If this were the case, vibrational relaxation should deactivate the molecule before it could move from its original solution site. Further evidence of the fact that the energy transfer does not merely involve vibrational excitation of the acceptor comes from consideration of the special role of *cis*-stilbene as an acceptor. The sensitized reactions have been carried on in benzene solution and measurements of quantum yields show that *cis*-stilbene is enormously more active as an energy acceptor (by at least a factor of 2500) than benzene. Even this estimate of the relative reactivities probably vastly underestimates the difference in reactivity since it treats the radiationless decay of species such as fluorenone triplets as though deactivation were entirely due to transfer of vibrational excitation to individual solvent molecules, a most unlikely circumstance.[3]

Even though the donor–acceptor complex does not become equilibrated with its surroundings, the over-all change may be effected by passage through many "internal equilibrium" states which effectively mix vibrational and electronic states of the donor–acceptor system. In other words, the electronic systems of the two components must interact and some vibrational motions of the two molecules must become strongly coupled. In this respect discussion of the configuration of the system at the time the energy is being transferred should resemble discussions of the transition states involved in ordinary thermal reactions.

Efficiencies in energy transfer involving nonvertical excitation of an acceptor are characteristically lower than corresponding transfers in which the sensitizer triplet has sufficient excitation to promote the acceptor to a spectroscopic state. However, if the acceptor is present in the solution in high concentration, the over-all quantum yields in a photoprocess may be very high. This merely reflects the fact that donor triplets may have sufficiently long lifetimes to allow them to undergo many collisions with potential acceptor molecules. Since the transfer rates typically fall below the diffusion controlled rates by one or more orders of magnitude, and since pairs of molecules remain nearest neighbors in solution for times of the order of 10^{-9} sec., it is evident that the time constants for the nonvertical excitation process must be of the order of 10^{-8} sec. or longer. In view of this fact, it is not surprising that considerable adjustment of nuclear positions may be coupled with the transfer of "electronic" energy.

It is interesting to speculate that similar considerations may be important in the description of other "slow" electronic processes such as radiationless decay of excited states, such as S_1 or T_1, to ground states. For example, we have suggested that stilbene triplets having transoid configurations may decay to give both *cis* and *trans* ground state molecules. It is very likely that if a molecule exists in several, closely-related, isomeric ground state configurations, excited states having the geometry of any of the ground states will explore all of the various ground state geometries in attempts to find suitable routes for radiationless deactivation. Such a pseudo-thermal behavior may be largely responsible for the fact that excitation of many molecules seems to be followed by decay to high energy isomers of the original substrate.

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Inner- and Outer-Sphere Mechanisms in the Oxidation of Pentacyanocobaltate(II) by Pentaamminecobalt(III) Complexes

Sir:

Only in a relatively few favorable cases has it been possible to establish unambiguously whether the mechanism of electron transfer between two metal complexes is of the inner- or outer-sphere type.[1,2] We report here studies on another such system which is of special interest, in that both types of mechanism appear to operate, the contribution of each being separately measurable. A particularly promising opportunity thereby is afforded for the systematic examination of the factors influencing the choice between these two mechanisms.

Our studies relate to the stoichiometry and kinetics of the $Co(CN)_5^{-3}$-catalyzed substitution of various pentaamminecobalt(III) complexes by CN^-, which apparently proceeds through an electron transfer mechanism. The products of substitution were identified spectrophotometrically and the kinetics, which are rapid, were measured with a stopped-flow apparatus.

Two distinct types of substitution behavior, differing both in stoichiometry and kinetics, were observed, depending on the nature of the ligand X in the pentaamminecobalt(III) complex, $Co(NH_3)_5X$. For X = Cl^-, N_3^-, NCS^-, and OH^-, the stoichiometry of the substitution reaction was found to be (as previously

(2) The long lifetime of the triplet produced by nonvertical excitation of *cis*-stilbene is evidenced by its ability to enter into reversible energy exchange with certain sensitizers and to be quenched to *trans*-stilbene by low concentrations ($<10^{-2}$ M) of azulene.[1]

(3) The theories of Robinson and Frosch[4] and Gouterman[5] both indicate that an important feature of radiationless deactivation of excited states is direct transfer of energy into solvent phonon bands.
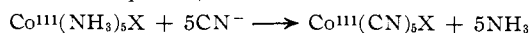
(4) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).

(5) M. Gouterman, *ibid.*, **36**, 2846 (1962).

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(2) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

reported by Adamson[3] for the corresponding bromo and iodo complexes)

$$Co^{III}(NH_3)_5X + 5CN^- \longrightarrow Co^{III}(CN)_5X + 5NH_3$$

and the rate law, $k_i[Co^{III}(NH_3)_5X][Co(CN)_5^{3-}]$. We conclude that the substitution in these cases proceeds by the mechanism originally proposed by Adamson,[3] involving *inner-sphere* electron transfer between $Co^{II}(CN)_5^{3-}$ and $Co^{III}(NH_3)_5X$ through the bridged intermediate $[(CN)_5Co^{II}-X-Co^{III}(NH_3)_5]$, and that the observed rate constant, k_i, (values of which are listed in Table I), refers to this step.

TABLE I
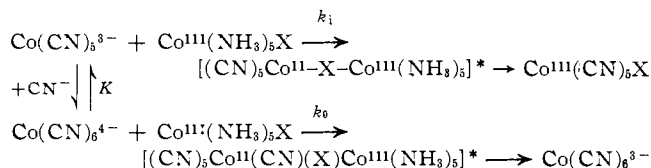
RATE CONSTANTS AT 25°; $\mu = 0.2^a$

X	k_1, M^{-1} sec.$^{-1}$	k'_0, M^{-2} sec.$^{-1}$
Cl$^-$	$\sim 5 \times 10^7$	...
N$_3^-$	1.6×10^6	$(<8 \times 10^5)^b$
NCS^{-c}	1.1×10^6	$(<5 \times 10^5)^b$
OH$^-$	9.3×10^4	$(<5 \times 10^4)^b$
F$^-$	1.8×10^3	1.7×10^4
NH$_3$	$(<4 \times 10^2)^b$	8×10^4
SO$_4^{2-}$	$(<3 \times 10^2)^b$	4×10^4
OAc$^-$	$(<1 \times 10^2)^b$	1.1×10^4
Fumarate^{2-}	$(<1 \times 10^2)^b$	1.2×10^4
Oxalate^{2-}	$(<1 \times 10^2)^b$	1.0×10^4
Maleate^{2-}	$(<1 \times 10^2)^b$	7.5×10^3
Succinate^{2-}	$(<50)^b$	6×10^3
CO$_3^{2-}$	...	$\sim 1 \times 10^3$
PO$_4^{3-}$	$(<1)^b$	5.2×10^2

^{a} The pH was generally adjusted by addition of 0.005 M NaOH. In a few cases the pH was varied without effect on the rate. ^{b} Upper limit based on absence of detectable contribution from this path. ^{c} The spectrum of the product of this reaction was consistent with the data reported by Haim and Wilmarth (*Inorg. Chem.*, 1, 573 (1962)) for the product of the reaction of SCN$^-$ with Co(CN)$_5$OH$_2^{3-}$. It is not established whether the species in question is Co(CN)$_5$NCS^{3-} or Co(CN)$_5$SCN^{3-}.

For a number of other pentaamminecobalt(III) complexes, including those in which X = PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, NH$_3$, OAc$^-$, and various other carboxylates, the substitution, while still catalyzed by Co(CN)$_5^{3-}$, was found to follow a quite different course, the stoichiometry being

$$Co^{III}(NH_3)_5X + 6CN^- \longrightarrow Co(CN)_6^{3-} + 5NH_3 + X$$
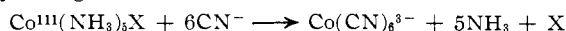
and the rate law, $k'_0[Co^{III}(NH_3)_5X][Co(CN)_5^{3-}][CN^-]$. We conclude that the reaction in these cases proceeds through an *outer-sphere* electron transfer between $Co^{II}(CN)_6^{4-}$ (presumed to co-exist in equilibrium with $Co(CN)_5^{3-}$) and $Co^{III}(NH_3)_5X$, *i.e.*

$$Co(CN)_5^{3-} + Co^{III}(NH_3)_5X \xrightarrow{k_i}$$
$$[(CN)_5Co^{II}-X-Co^{III}(NH_3)_5]^* \to Co^{III}(CN)_5X$$
$$+CN^- \Big\updownarrow K$$
$$Co(CN)_6^{4-} + Co^{III}(NH_3)_5X \xrightarrow{k_0}$$
$$[(CN)_5Co^{II}(CN)(X)Co^{III}(NH_3)_5]^* \longrightarrow Co(CN)_6^{3-}$$

The observed third-order rate constant, k'_0, for the second path is thus related to the rate constant of the outer-sphere electron transfer step through $k'_0 = k_0K$, where K (the equilibrium constant of the step Co(CN)$_5^{3-}$ + CN$^- \rightleftharpoons$ Co(CN)$_6^{4-}$) is not known but is estimated to lie within the limits 10^{-1} to 10^{-4} M^{-1}. Values of k'_0 are listed in Table I.

The case of Co(NH$_3$)$_5$F^{2+} is of special interest in that both paths are observed and either can be made to predominate by varying the concentration of CN$^-$. Preliminary observations suggest that this is also the case for Co(NH$_3$)$_5$NO$_3^{2+}$.

The pattern of results in Table I suggests that the outer-sphere mechanism operates quite generally, with a

(3) A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4260 (1956).

rate constant which shows only a relatively small dependence on the nature of X. The general trend, from which only Co(NH$_3$)$_5$SO$_4^+$ deviates significantly, appears to be for k'_0 to increase, in the expected direction, with increasing positive charge of $Co^{III}(NH_3)_5X$ from 5 $\times 10^2$ M^{-2} sec.$^{-1}$ for Co(NH$_3$)$_5$PO$_4$ to 8 $\times 10^4$ M^{-2} sec.$^{-1}$ for Co(NH$_3$)$_6^{3+}$. Failure to observe a contribution from the outer-sphere path is attributable to intervention of the alternative inner-sphere path, k_i exhibiting, as expected, a much more marked dependence on X. The detailed significance of this dependence remains to be established and further studies toward this end are in progress. Among other things, it would be of interest to determine to what extent the variation of k_i reflects that of the over-all free energy of reaction by the inner-sphere path, due to differences in the stability of the product complex, $Co^{III}(CN)_5X$.

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## Oxidation of Formatopentaamminecobalt(III) by Permanganate: Evidence for a Two-Step Mechanism

Sir:

Studies on the oxidation of oxalatopentaamminecobalt(III)[1] and p-aldehydobenzoatopentaaminecobalt-(III)[2] have revealed the interesting feature that oxidation of the organic ligand by two-electron oxidants (*e.g.*, Cl$_2$) results in retention of the oxidation state of the Co(III) center, whereas oxidation by one-electron oxidants (*e.g.*, Ce(IV)) is accompanied by reduction of the Co(III) to Co^{2+}. The latter observation gives rise to the question, which could not be resolved in these cases, as to whether reduction of the Co(III) center takes place simultaneously with that of the external oxidant or whether the reaction proceeds through a sequence of two one-electron steps with the formation of a radical ion intermediate (*e.g.*, $Co^{III} \cdot C_2O_4^-$) of finite lifetime. This question also arises in connection with many other multi-equivalent oxidation–reduction reactions.[3]

We report here some observations on the permanganate oxidation of formatopentaamminecobalt(III), a system closely related to those cited above, in which this question has been resolved and the operation of a stepwise mechanism and existence of a radical ion intermediate clearly demonstrated. The results also have a bearing on the mechanism of the oxidation of the formate ion itself.[4,5]

The results of measurements on the kinetics and stoichiometry of the reaction are summarized in Table I and are characterized by the following features.

1. The reaction proceeds according to the rate law, $-d[(NH_3)_5Co \cdot OCHO^{2+}]/dt = k[(NH_3)_5Co \cdot OCHO^{2+}] \cdot [MnO_4^-]$, k being substantially independent of the concentrations of reactants and of H$^+$.

2. The over-all reaction stoichiometry can be represented as a mixture of the following stoichiometries, in varying proportions

$$(NH_3)_5Co \cdot OCHO^{2+} + \frac{1}{3}MnO_4^- \longrightarrow CO_2 + Co^{2+} + \frac{1}{3}MnO_2$$
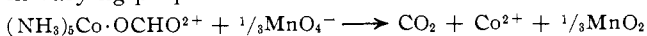
(1) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(2) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960).

(3) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

(4) S. M. Taylor and J. Halpern, *J. Am. Chem. Soc.*, **81**, 2933 (1959), and unpublished results.

(5) K. B. Wiberg and R. Stewart, *ibid.*, **78**, 1214 (1956).