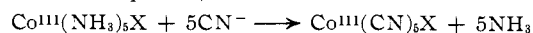


reported by Adamson⁸ for the corresponding bromo and iodo complexes)



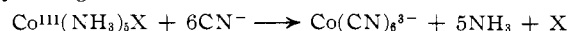
and the rate law, $k_i[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}]$. We conclude that the substitution in these cases proceeds by the mechanism originally proposed by Adamson,³ involving *inner-sphere* electron transfer between $\text{Co}^{\text{II}}(\text{CN})_5^{3-}$ and $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ through the bridged intermediate $[(\text{CN})_5\text{Co}^{\text{II}}\text{-X-Co}^{\text{III}}(\text{NH}_3)_5]$, 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°; $\mu = 0.2^a$

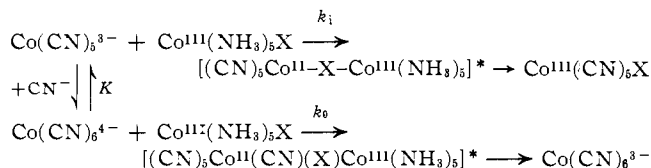
X	$k_i, M^{-1} \text{sec}^{-1}$	$k'_0, M^{-2} \text{sec}^{-1}$
Cl ⁻	$\sim 5 \times 10^7$...
N ₃ ⁻	1.6×10^6	$(< 8 \times 10^6)^b$
NCS ⁻	1.1×10^6	$(< 5 \times 10^6)^b$
OH ⁻	9.3×10^4	$(< 5 \times 10^4)^b$
F ⁻	1.8×10^3	1.7×10^4
NH ₃	$(< 4 \times 10^2)^b$	8×10^4
SO ₄ ²⁻	$(< 3 \times 10^2)^b$	4×10^4
OAc ⁻	$(< 1 \times 10^2)^b$	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 $\text{Co}(\text{CN})_5\text{OH}_2^{3-}$. It is not established whether the species in question is $\text{Co}(\text{CN})_5\text{NCS}^{3-}$ or $\text{Co}(\text{CN})_5\text{SCN}^{3-}$.

For a number of other pentaamminecobalt(III) complexes, including those in which X = PO₄³⁻, CO₃²⁻, SO₄²⁻, NH₃, OAc⁻, and various other carboxylates, the substitution, while still catalyzed by $\text{Co}(\text{CN})_5^{3-}$, was found to follow a quite different course, the stoichiometry being



and the rate law, $k'_0[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_6^{3-}][\text{CN}^-]$. We conclude that the reaction in these cases proceeds through an *outer-sphere* electron transfer between $\text{Co}^{\text{II}}(\text{CN})_6^{4-}$ (presumed to co-exist in equilibrium with $\text{Co}(\text{CN})_5^{3-}$) and $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$, *i.e.*



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 $\text{Co}(\text{CN})_5^{3-} + \text{CN}^- \rightleftharpoons \text{Co}(\text{CN})_6^{4-}$) 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 $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ 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 $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$.

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 $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ deviates significantly, appears to be for k'_0 to increase, in the expected direction, with increasing positive charge of $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ from $5 \times 10^2 M^{-2} \text{sec}^{-1}$ for $\text{Co}(\text{NH}_3)_5\text{PO}_4$ to $8 \times 10^4 M^{-2} \text{sec}^{-1}$ for $\text{Co}(\text{NH}_3)_6^{3+}$. 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, $\text{Co}^{\text{III}}(\text{CN})_5\text{X}$.

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(4) Alfred P. Sloan Research Fellow.

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RECEIVED JUNE 21, 1963

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

Sir:

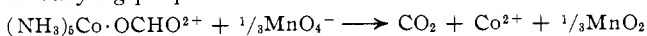
Studies on the oxidation of oxalatopentaamminecobalt(III)¹ and *p*-aldehydobenzoatopentaamminecobalt(III)² have revealed the interesting feature that oxidation of the organic ligand by two-electron oxidants (*e.g.*, Cl₂) results in retention of the oxidation state of the Co(III) center, whereas oxidation by one-electron oxidants (*e.g.*, Ce(IV)) is accompanied by reduction of the Co(III) to Co²⁺. 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.*, $\text{Co}^{\text{III}}\cdot\text{C}_2\text{O}_4^-$) 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, $-d[(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}]/dt = k[(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}][\text{MnO}_4^-]$, 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



(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).

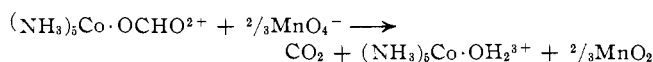
(4) S. M. Taylor and J. Halpern, *J. Am. Chem. Soc.*, **81**, 2933 (1959); and unpublished results.

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

TABLE I
 RATE CONSTANTS FOR THE OXIDATION OF $(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$ BY MnO_4^- ($\mu = 1.0$)^a

Temp., °C.	$[(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}\cdot(\text{ClO}_4)_2] \times 10^4, M$	$[\text{KMnO}_4] \times 10^2, M$	$[\text{HClO}_4], M$	$k \times 10^2, M^{-1} \text{sec}^{-1}$	$[(\text{NH}_3)_5\text{Co}\cdot\text{OH}_2^{3+}]/[\text{Co}^{2+}]$
0.1	1.5	1.5	0.1	2.54	...
.1	1.5	4.8	.1	2.55	...
.1	6.0	4.8	.1	2.64	...
.1	3.0	1.0	.1	...	3.5 (3.5) ^b
.1	3.0	2.0	.1	...	6.6 (6.4) ^b
.1	3.0	4.0	.1	...	10.5 (11.2) ^b
.1	3.0	5.0	.1	2.55 (0.232) ^b	14.5
.1	3.0	10	.1	...	29 (25) ^b
.1	3.0	4.8	1.0	2.17	...
14.8	3.0	4.8	0.1	9.25	...
20.0	3.0	4.8	.1	14.5	...
25.0	3.0	4.8	.1	21.3	...

^a Adjusted with NaClO_4 . ^b Using $(\text{NH}_3)_5\text{Co}\cdot\text{OCDO}^{2+}$ in place of $(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$

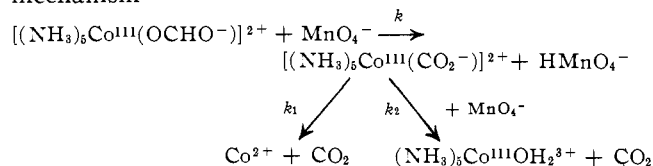


The ratio of unreduced to reduced cobalt was found to depend on the concentration of MnO_4^- according to

$$[(\text{NH}_3)_5\text{Co}\cdot\text{OH}_2^{3+}]/[\text{Co}^{2+}] = 3 \times 10^2 [\text{MnO}_4^-] \quad (1)$$

3. Substitution of $(\text{NH}_3)_5\text{Co}\cdot\text{OCDO}^{2+}$ for $(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$ reduced the rate by a factor of 10.5 but the stoichiometry of the reaction was substantially unchanged.

These observations provide strong support for the mechanism



in which Co^{2+} and $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{OH}_2^{3+}$ arise through competitive reactions of a common intermediate of finite lifetime, formed by an initial rate-determining one-electron oxidation step. The large deuterium kinetic isotope effect and the observation that the reaction stoichiometry is unaffected by this isotopic substitution further suggest that this initial one-electron oxidation is effected by abstraction of an H atom. Equation 1 yields $k_2/k_1 = 3 \times 10^2 M^{-1}$.

The permanganate oxidation of formic acid itself in aqueous solution has previously been found⁴ to proceed according to the rate law

$$-d[\text{HCOOH}]/dt = k_{\text{HCOOH}}[\text{HCOOH}][\text{MnO}_4^-] + k_{\text{HCOO}^-}[\text{HCOO}^-][\text{MnO}_4^-]$$

corresponding to contributions from separate paths involving reactions of MnO_4^- with HCOOH and HCOO^- . In the light of the comparison revealed by Table II it is tempting to draw the conclusion that the oxidation of

 TABLE II
 COMPARISON OF KINETIC PARAMETERS

Reductant	$k_{25^\circ}, M^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal./mole}$	$\Delta S^\ddagger, \text{e.u.}$	$k_{\text{C-H}}/k_{\text{C-D}}$
$(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$	0.21	13.3	-17	10.5
HCOO^- ^a	3.0	12.4	-15	7-10
HCOOH ^a	1.6×10^{-8}	15.8	-19	1.0

^a Based on data in ref. 4.

$(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$ and of free HCOO^- proceed through similar mechanisms, *i.e.*, that the reaction of HCOO^- with MnO_4^- also involves transfer of an H atom rather than, as previously suggested,^{4,5} of an H^- ion. The recent suggestion of Stewart and Moeck⁶ that the permanganate oxidation of various alkoxide ions may also involve H atom, rather than H^- ion, transfer is of interest in this connection.

(6) R. Stewart and M. M. Moeck, *Can. J. Chem.*, **41**, 1160 (1963).

Studies are in progress on the oxidation of $(\text{NH}_3)_5\text{Co}\cdot\text{OCHO}^{2+}$ by other oxidants. Preliminary results suggest that oxidation by $\text{Co}_{\text{aq}}^{3+}$ produces $(\text{NH}_3)_5\text{Co}\cdot\text{OH}_2^{3+}$ in nearly quantitative yield. $(\text{NH}_3)_5\text{Co}\cdot\text{OH}_2^{3+}$ is also the major product of the Ag^+ -catalyzed oxidation by $\text{S}_2\text{O}_8^{2-}$.⁷ These results contrast with the behavior previously reported for the corresponding oxalato and *p*-aldehydobenzoato complexes, both of which yield predominantly Co^{2+} with these oxidants. The significance of these unexpected differences is not altogether clear and is being further examined.

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(7) R. A. Palmer and J. Halpern, unpublished results.

(8) National Research Council of Canada Postdoctoral Fellow, University of British Columbia, 1961-1962.

(9) Alfred P. Sloan Research Fellow.

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RECEIVED JUNE 21, 1963

A Quantitative Test for a Classical Carbonium Ion Mechanism

Sir:

The mechanism given in Chart I has been proposed to explain the highly stereospecific nature of the open carbonium ion intermediates presumed to have been formed during deamination of (+)-1,2,2-triphenylethyl-1- C^{14} -amine (Ia).¹⁻³ We also have reported⁴⁻⁷ the results of several stereospecific ketone-forming deaminations of amino alcohols which demand the presence of open carbonium ion intermediates. In spite of these facts,³⁻⁷ however, there is still considerable reluctance to abandon the idea that open carbonium ions are essentially racemic intermediates.^{8,9}

(1) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.*, **81**, 466 (1959).

(2) C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961).

(3) See also: (a) S. Winstein and E. Grunwald, *ibid.*, **70**, 835 (1948); (b) S. Winstein and B. K. Morse, *ibid.*, **74**, 1134 (1952); (c) S. Winstein and L. L. Ingraham, *ibid.*, **77**, 1739 (1955).

(4) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

(5) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961).

(6) B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3662 (1961).

(7) C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27**, 3525 (1962).

(8) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

(9) W. Hückel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963).