

to the National Science Foundation for financial support. The purchase of the Varian n.m.r. instrument was made possible by a grant from the National Science Foundation. The cooperation of Drs. C. U. Pittman, Jr., George Olah, and Herman G. Richey, Jr., was most helpful.

N. C. Deno, Jane S. Liu, John O. Turner  
David N. Lincoln, Richard E. Fruit, Jr.

Department of Chemistry, Whitmore Laboratory  
Pennsylvania State University, University Park, Pennsylvania 16802

Received April 14, 1965

### Transient Intermediates in Inner-Sphere Electron-Transfer Reactions Involving Polyatomic Bridging Ligands

Sir:

One of the important questions which arises in connection with the mechanisms of inner-sphere electron-transfer reactions involving polyatomic bridging ligands, e.g., in the reductions of  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  (where X = CN,  $\text{NO}_2$ , NCS, etc.) by reductants such as  $\text{Cr}^{2+}(\text{aq})^1$  or  $\text{Co}(\text{CN})_5^{3-}$ ,<sup>2,3</sup> to give  $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$

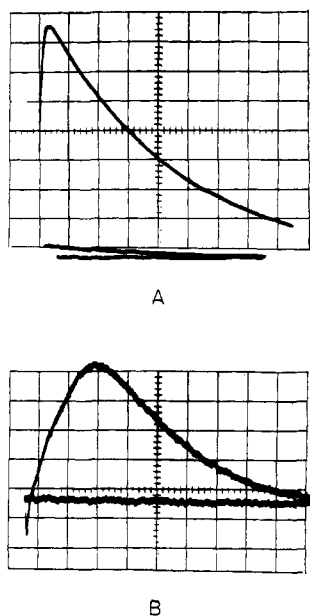


Figure 1. Stopped-flow oscillograms showing transient intermediates in the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  by pentaamminecobalt(III) complexes at 25°. (A) oxidant,  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $1.0 \times 10^{-3} M$ );  $2.0 \times 10^{-4} M \text{Co}(\text{CN})_5^{3-}$ ;  $0.0125 M \text{CN}^-$ ; wave length, 380  $m\mu$ ; time scale, 2 sec./major division. (B) Oxidant  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  ( $2.0 \times 10^{-3} M$ );  $2.0 \times 10^{-3} M \text{Co}(\text{CN})_5^{3-}$ ;  $3.0 \times 10^{-2} M \text{CN}^-$ ; wave length, 320  $m\mu$ ; time scale, 1 sec./major division.

and  $\text{Co}(\text{CN})_5\text{X}^{3-}$ , respectively, relates to the position of attack of the reductant on the bridging ligand, and to the configuration of the initial oxidation product which in some cases is thought to differ from the final product. It has been suggested,<sup>4</sup> for example, that the reduction

- (1) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).
- (2) J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).
- (3) J. Halpern and S. Nakamura, "Proceedings of the 8th Conference on Coordination Chemistry, Vienna," Springer Verlag, Berlin (W.), 1964, p. 271.
- (4) R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **6**, 217 (1958).

of  $(\text{NH}_3)_5\text{CoNCS}^{2+}$  by  $\text{Cr}^{2+}(\text{aq})$  involves attack at the S atom, followed by electron transfer *via* the intermediate  $[(\text{NH}_3)_5\text{Co}-\text{NCS}-\text{Cr}(\text{H}_2\text{O})_5]^{4+}$ , to yield the S-bonded complex  $(\text{H}_2\text{O})_5\text{Cr}-\text{SCN}^{2+}$  as the initial oxidation product; but the latter, if formed, apparently rearranges to the stable N-bonded isothiocyanato product  $(\text{H}_2\text{O})_5\text{Cr}-\text{NCS}^{2+}$  too rapidly to be detected.

The studies reported here are pertinent to this theme and appear to be the first examples in which direct evidence for the position of attack in such reactions has been obtained through the detection of the transient initial oxidation products.

The studies in question relate to the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  by several pentaamminecobalt(III) complexes,  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ . As previously shown,<sup>2,3</sup> the general rate law for these reactions has the form  $-d[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]/dt = k_i[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}] + k_o'[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}][\text{CN}^-]$ , the first term corresponding to the inner-sphere oxidation of  $\text{Co}(\text{CN})_5^{3-}$  through the bridged intermediate  $[(\text{NH}_3)_5\text{Co}-\text{X}-\text{Co}(\text{CN})_5]$ , to  $\text{Co}^{\text{III}}(\text{CN})_5\text{X}$ , and the second term to the outer-sphere oxidation of  $\text{Co}(\text{CN})_5^{3-}$  to  $\text{Co}(\text{CN})_6^{3-}$ .

For  $(\text{NH}_3)_5\text{Co}-\text{NO}_2^{2+}$  (containing an N-bonded nitro ligand)<sup>5</sup> as oxidant, the values of  $k_i$  and  $k_o'$ , at 25° and  $\mu = 0.2$ , were found to be  $3.4 \times 10^4 M^{-1} \text{sec}^{-1}$  and  $3 \times 10^4 M^{-2} \text{sec}^{-1}$ , respectively. At 0.0125  $M \text{CN}^-$  about 99% of the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  proceeds by the inner-sphere ( $k_i$ ) path to yield  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$  ( $\text{NO}_2$  also N-bonded to Co) as the final product. Stopped flow measurements<sup>2</sup> (Figure 1A) clearly reveal that under these conditions the disappearance of  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $t_{1/2} = 0.1 \text{ sec.}$ ) does not coincide with the formation of the final product but rather of a transient intermediate which decays much more slowly ( $t_{1/2} = 7 \text{ sec.}$ ) to  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$ . The transient exhibits strong absorption in the wave length region ( $\sim 380 m\mu$ , Figure 1A) where both  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{3+}$  and  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$  are nearly transparent, but which is characteristic of pentacyanocobaltate(III) complexes containing O-bonded ligands (e.g.,  $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$   $\lambda_{\text{max}} 380 m\mu$ ,  $\epsilon_{\text{max}} 240$ ). These observations are consistent with attack of  $\text{Co}(\text{CN})_5^{3-}$  on an oxygen atom of the bridging  $\text{NO}_2$  ligand, resulting in electron transfer through the intermediate  $[(\text{NH}_3)_5\text{Co}-\text{NO}_2-\text{Co}(\text{CN})_5]^-$  to produce O-bonded  $\text{Co}(\text{CN})_5\text{ONO}^{3-}$  initially, and subsequent isomerization of the latter to  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$ . The first-order rate of isomerization was unaffected by increasing the  $\text{Co}(\text{CN})_5^{3-}$  concentration from  $1 \times 10^{-5}$  to  $2 \times 10^{-4} M$ , suggesting that the isomerization under these conditions occurs intramolecularly rather than *via* ligand transfer between  $\text{Co}(\text{CN})_5\text{ONO}^{3-}$  and  $\text{Co}(\text{CN})_5^{3-}$ .

Similar evidence for a transient intermediate was obtained with  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  (C-bonded)<sup>6</sup> as oxidant. The values of  $k_i$  and  $k_o'$  for this oxidant at 25° and  $\mu = 0.2$  were found to be  $2.9 \times 10^2 M^{-1} \text{sec}^{-1}$  and  $4.5 \times 10^3 M^{-2} \text{sec}^{-1}$ , respectively, both paths in this case giving rise to  $\text{Co}(\text{CN})_6^{3-}$  as the final product. At 0.03  $M \text{CN}^-$ , with the inner-sphere path accounting for some 70% of the reaction, the disappearance of  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  ( $t_{1/2} = 0.8 \text{ sec.}$ ) coincided with the

- (5) R. B. Penland, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 887 (1956).
- (6) H. Siebert, *Z. anorg. allgem. Chem.*, **327**, 63 (1964).

appearance of a transient (Figure 1B) which absorbed more strongly than  $\text{Co}(\text{CN})_6^{3-}$  at 320  $m\mu$  (consistent with a pentacyanocobaltate(III) complex containing an N-bonded ligand) and which underwent first-order decay to  $\text{Co}(\text{CN})_6^{3-}$  with a half-life of 1.6 sec. These observations are consistent with the sequence:  $(\text{NH}_3)_5\text{Co}-\text{CN}^{2+} + \text{Co}(\text{CN})_5^{3-} \rightarrow [(\text{NH}_3)_5\text{Co}-\text{CN}-\text{Co}(\text{CN})_5]^- \rightarrow \text{Co}(\text{CN})_5-\text{NC}^{3-} \rightarrow \text{Co}(\text{CN})_6^{3-}$ .

Thus it appears that, in each of the above cases, attachment to the bridging ligand occurs at an atom which exposes an unshared electron pair to the attacking reductant even when this position of attack does not lead to the thermodynamically stable product.

It is also significant in this context that similar experiments failed to reveal any evidence for analogous transient intermediates in the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  by two other oxidants,  $\text{Co}(\text{NH}_3)_5-\text{ONO}^{2+}$  (O-bonded)<sup>6</sup> and  $\text{Co}(\text{NH}_3)_5-\text{NCS}^{2+}$  (N-bonded isothiocyanate),<sup>7</sup> where the thermodynamically stable products  $\text{Co}(\text{CN})_5-\text{NO}_2^{3-}$  and  $\text{Co}(\text{CN})_5-\text{SCN}^{3-}$  (S-bonded thiocyanate)<sup>8</sup> can be formed directly by electron transfer through the intermediates  $[(\text{NH}_3)_5\text{Co}-\text{O}_2\text{N}-\text{Co}(\text{CN})_5]^-$  and  $[(\text{NH}_3)_5\text{Co}-\text{NCS}-\text{Co}(\text{CN})_5]^-$ , generated by attack of  $\text{Co}(\text{CN})_5^{3-}$  on a ligand atom having an exposed electron pair.

*Acknowledgment.* Support of this work by the National Science Foundation (Grant GP 654) is gratefully acknowledged.

(7) M. Linhard, R. Siebert and M. Wiegel, *Z. anorg. allgem. Chem.*, **278**, 287 (1955).

(8) J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).

Jack Halpern, Shuzo Nakamura

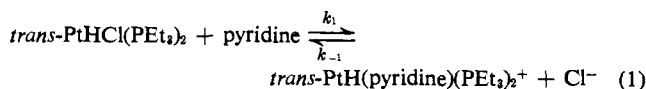
Department of Chemistry, The University of Chicago  
Chicago, Illinois

Received May 12, 1965

## A Secondary Kinetic Isotope Effect in a Substitution Reaction of a Square-Planar Complex

Sir:

It has been reported<sup>1</sup> that the hydride ligand in  $\text{trans-PtHCl}(\text{PEt}_3)_2$  exerts a strong labilizing influence



is some  $10^5$  times as great as that of the corresponding pyridine substitution of  $\text{trans-PtCl}_2(\text{PEt}_3)_2$ . In view of the magnitude of this *trans* effect and of the important questions of interpretation associated with it, it appeared of interest to measure the kinetic isotope effect on the rate of reaction 1 arising from the deuterium substitution of the hydride ligand. We report here the results of these measurements which reveal an unusually large secondary kinetic isotope effect.

$\text{trans-PtHCl}(\text{PEt}_3)_2$  was prepared by the method of Chatt and Shaw,<sup>2</sup> using hydrazine as the reducing agent. The corresponding deuterido compound,  $\text{trans-PtDCl}(\text{PEt}_3)_2$  having an isotopic purity of 93%, was made by exchanging the hydrido compound with  $\text{C}_2\text{H}_5\text{OD}$  using  $\text{DCl}$  as catalyst. Successive batches of the hydrido and deuterido complexes, obtained by such repeated exchanges, yielded reproducible results. The kinetic measurements were made in anhydrous ethanol solution, the reaction being followed conductometrically according to the method of Basolo, *et al.*<sup>1</sup> The reaction was found to be reversible and the kinetic data fitted the rate law<sup>3</sup>

$$-d[\text{PtHCl}(\text{PEt}_3)_2]/dt = k_1[\text{PtHCl}(\text{PEt}_3)_2](\text{pyridine}) - k_{-1}[\text{PtH}(\text{pyridine})(\text{PEt}_3)_2^+][\text{Cl}^-] \quad (2)$$

Values of  $k_1$  were computed from this rate law using a value of 0.030 for the equilibrium constant ( $=k_1/k_{-1}$ ) of the reaction, determined by the method of Basolo, *et al.*,<sup>1</sup> and in good agreement with the value found by them. Over the range of our measurements (Table I), this value was, within experimental error, independent of the isotopic substitution and of the temperature.

The results of our kinetic measurements are summarized in Table I and reveal a remarkably large secondary kinetic isotope effect, corresponding to a decrease in  $k_1$  by a factor of approximately 1.4 when the hydride ligand is replaced by deuteride. The activation parameters of the reaction, derived from

Table I. Summary of Kinetic Data

Temp., °C.	Initial concentrations, M		$k_1, {}^b M^{-1} \text{sec.}^{-1}$		$k_1(\text{H})/k_1(\text{D})$
	$[\text{PtHCl}(\text{PEt}_3)_2]^a$ $\times 10^4$	$[\text{Pyridine}]$ $\times 10^3$	H	D <sup>c</sup>	
0	2.0	1.2	1.73	1.20	1.44
0	4.0	1.2	1.60	1.16	1.37
0	8.0	1.2	1.55	1.08	1.44
0	4.0	3.6	1.56	1.05	1.48
0	4.0	6.0	1.60	1.08	1.48
0	8.0	3.6	1.50	1.06	1.42
0	8.0	6.0	1.52	1.06	1.43
-10	4.0	6.0	0.702	0.503	1.40
-20	4.0	6.0	0.295	0.209	1.41
-10	2.0	1.2	0.718	0.490	1.47
-20	2.0	1.2	0.317	0.219	1.45

Mean kinetic isotope effect  $1.44^e \pm 0.05$

<sup>a</sup> Or  $[\text{PtDCl}(\text{PEt}_3)_2]$ . <sup>b</sup> Each of these rate constants is the average of approximately four independent determinations, the reproducibility of which was generally better than  $\pm 4\%$ . <sup>c</sup> Corrected for the isotopic purity (93%) of the  $\text{PtDCl}(\text{PEt}_3)_2$ .

(*trans* effect) on the chloride ligand, this being reflected in the observation that the rate of reaction 1

(1) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

(2) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

(3) No contribution to the forward rate of reaction 1 could be detected from a pyridine-independent path. The contribution from such a path reported earlier<sup>1</sup> appears to be an artifact arising from failure to take account of the back reaction in treating the kinetic data.