appearance of a transient (Figure 1B) which absorbed more strongly than $Co(CN)_6{}^{3-}$ at 320 m$\mu$ (consistent with a pentacyanocobaltate(III) complex containing an N-bonded ligand) and which underwent first-order decay to $Co(CN)_6{}^{3-}$ with a half-life of 1.6 sec. These observations are consistent with the sequence: $(NH_3)_5$-$Co-CN^{2+} + Co(CN)_5{}^{3-}$ ($\rightarrow [(NH_3)_5Co-CN-Co(CN)_5]^-$) $\rightarrow Co(CN)_5-NC^{3-} \rightarrow Co(CN)_6{}^{3-}$.

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 $Co(CN)_5{}^{3-}$ by two other oxidants, $Co(NH_3)_5-ONO^{2+}$ (O-bonded)[6] and $Co(NH_3)_5-NCS^{2+}$ (N-bonded isothiocyanate),[7] where the thermodynamically stable products $Co(CN)_5-NO_2{}^{3-}$ and $Co(CN)_5-SCN^{3-}$ (S-bonded thiocyanate)[8] can be formed directly by electron transfer through the intermediates $[(NH_3)_5Co-O_2N-Co(CN)_5]^-$ and $[(NH_3)_5-Co-NCS-Co(CN)_5]^-$, generated by attack of $Co(CN)_5{}^{3-}$ on a ligand atom having an exposed electron pair.

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

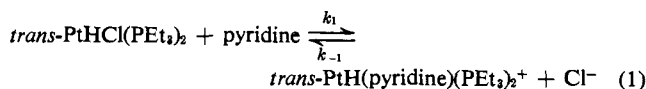(8) J. L. Burmeister, *Inorg. Chem.*, 3, 919 (1964).

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

*Sir:*

It has been reported[1] that the hydride ligand in *trans*-PtHCl(PEt$_3$)$_2$ exerts a strong labilizing influence

$$\text{\textit{trans}-PtHCl(PEt}_3)_2 + \text{pyridine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$\text{\textit{trans}-PtH(pyridine)(PEt}_3)_2{}^+ + \text{Cl}^- \quad (1)$$

is some $10^5$ times as great as that of the corresponding pyridine substitution of *trans*-PtCl$_2$(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.

*trans*-PtHCl(PEt$_3$)$_2$ was prepared by the method of Chatt and Shaw,[2] using hydrazine as the reducing agent. The corresponding deuterido compound, *trans*-PtDCl(PEt$_3$)$_2$ having an isotopic purity of 93%, was made by exchanging the hydrido compound with C$_2$H$_5$OD using 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.*[1] The reaction was found to be reversible and the kinetic data fitted the rate law[3]

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

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.*,[1] 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, $M$ [PtHCl(PEt$_3$)$_2$]$^a$ $\times 10^4$ | [Pyridine] $\times 10^3$ | $k_1$,$^b$ $M^{-1}$ sec.$^{-1}$ H | D$^c$ | $k_1$(H)/$k_1$(D) |
|---|---|---|---|---|---|
| 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 $1.44^c \pm 0.05$

$^a$ Or [PtDCl(PEt$_3$)$_2$]. $^b$ Each of these rate constants is the average of approximately four independent determinations, the reproducibility of which was generally better than $\pm 4\%$. $^c$ Corrected for the isotopic purity (93%) of the PtDCl(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[1] appears to be an artifact arising from failure to take account of the back reaction in treating the kinetic data.

these data, are $\Delta H_1^* = 10.9 \pm 0.5$ kcal./mole and $\Delta S_1^* = -17 \pm 2$ e.u. and are, within experimental error, the same for the hydrido and deuterido compounds.

The large *trans* effect of hydride cannot be associated with $\pi$-bonding effects such as have been invoked to explain the large *trans*-labilizing influence of other ligands, *e.g.*, CO and CN⁻, and has been attributed[1] instead to the high polarizability and inductive influence of the hydride ion. It is unlikely that either of these are sufficiently different for deuteride and hydride to account for the large observed kinetic isotope effect. Instead it seems likely that this isotope effect reflects weakening of the Pt–H (Pt–D) binding in the transition state, relative to the initial reactant state, owing to electron donation to the platinum by the incoming pyridine ligand. This is consistent with, and may be considered as providing some supporting evidence for, the widely accepted interpretation of the substitution reactions of square-planar platinum(II) complexes in terms of an $S_N2$ mechanism involving a five-coordinate (possibly trigonal bipyramid) transition state.

It would be of interest in the light of these observations to determine the corresponding labilizing influence and secondary isotope effect for a *cis*-hydride ligand, *e.g.*, in the substitution of pyridine for chloride in the complex *cis*-PtHCl(PEt₃)₂. Unfortunately, attempts to prepare this compound do not appear thus far to have been successful.

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## Chemistry of Polypyrones. A Model for Acetogenin Biosynthesis

*Sir:*

In marked contrast to our intimate knowledge of the (reductive) condensation of acetate and malonate units in fatty acid biosynthesis,[1] the details of metabolism intermediary between acetate–malonate primers and their "polyketide"-derived natural products can at present only be inferred by structural analogy. Thus, satisfactory *rationalization* of the biogenesis of many plant and fungal products can be made by assuming intervention of an acetate–malonate chain (*e.g.*, I),[2] followed by appropriate aldol condensation and decarboxylation.[3–5]

(1) See, *e.g.*, F. Lynen and M. Tada, *Angew. Chem.*, **73**, 513 (1961); R. Bressler and S. J. Wakil, *J. Biol. Chem.*, **237**, 1441 (1963), and references cited.
(2) An arbitrary choice employing acetoacetate as primer.
(3) A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).
(4) J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins," W. A. Benjamin, Inc., New York, N. Y., 1964.
(5) R. Robinson, "Structural Relations of Natural Products," Clarendon Press, Oxford, England, 1955.
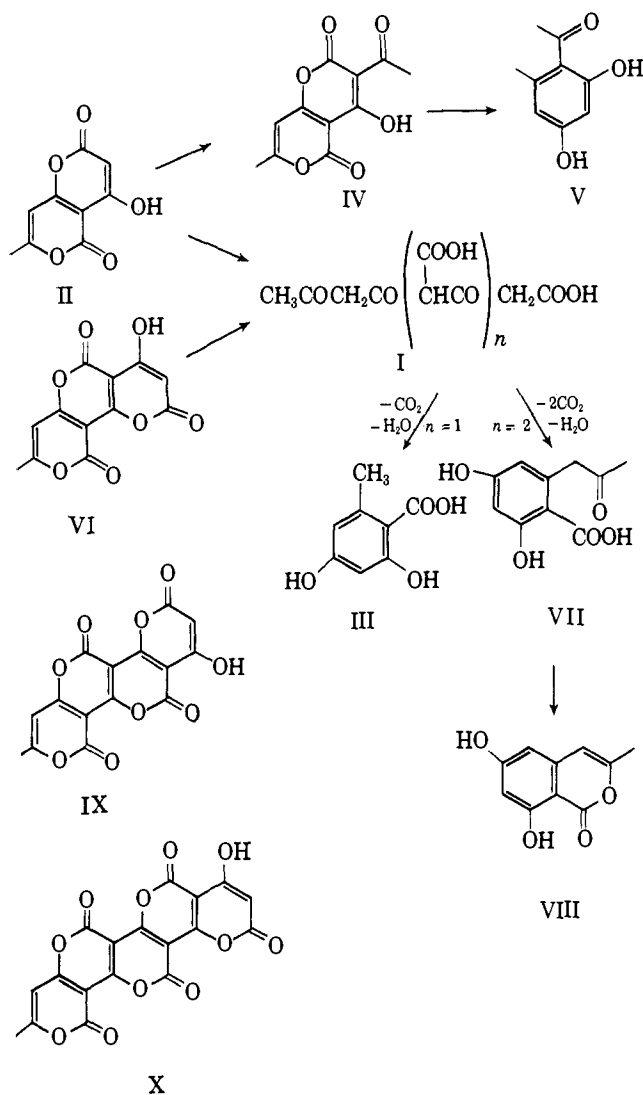


The chemistry of polypyrones (as II) offers not only facile construction of any desired number of acetate–malonate units condensed in a stable, highly crystalline progenitor of the proper head-to-tail sequence but also the opportunity to study for the first time the reactions of poly-$\beta$-ketones containing five or more acetate residues.[6]

Thus, treatment of II[7] [$\lambda_{max}^{EtOH}$ 270 and 330 m$\mu$ (log $\epsilon$ 3.81 and 3.76)] (prepared from malonyl dichloride and triacetic acid lactone) with methanolic potassium hydroxide solution affords orsellinic acid (III), the prototype of numerous fungal constituents,[4] presumably *via* the anion of I ($n = 1$). Similarly, the acetylpyronopyrone (IV) [$\lambda_{max}^{EtOH}$ 230, 240, 260, and 347 m$\mu$ (log $\epsilon$ 3.84, 3.81, 3.72, and 3.93)] (from II and acetyl chloride) is transformed into 2,4-dihydroxy-6-methylacetophenone (V).[8]

This simulation of polyacetate aromatic biosynthesis is further maintained in the trispyrone (VI) [from II and malonyl chloride; $\lambda_{max}^{EtOH}$ 253, 280, and 373 m$\mu$ (log $\epsilon$ 3.83, 3.94, and 4.04)] which undergoes decarboxylative

(6) *Cf.* A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).
(7) The identities of III, V, VII, and VIII were established by mixture melting point and spectroscopic comparison with authentic samples. Satisfactory analytical data and mass, n.m.r., and infrared spectra were obtained for the new compounds described.
(8) K. Hoesch, *Chem. Ber.*, **48**, 1122 (1915); D. J. Cram and F. W. Cranz, *J. Am. Chem. Soc.*, **72**, 595 (1950).