Communications

Platinum(II)-Catalyzed Hydrolysis of Pyrophosphate and Triphosphate: Phosphorus-31 NMR Characterization of Kinetic Intermediates

Sir:

The characterization of kinetic intermediates in the metal-catalyzed hydrolysis of phosphates is an important step toward understanding the role of metal ions in phosphoryl-transfer reactions.[1] The formation of a dinuclear intermediate has been suggested as a critical step in the hydrolysis of triphosphate ion catalyzed by cobalt(III) complexes.[2,3] Here we report the phosphorus-31 NMR characterization of kinetic intermediates in the platinum(II)-catalyzed phosphate hydrolysis of pyrophosphate and triphosphate ions.

The complex cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ was prepared,[4] and its reaction with triphosphate ion was studied in the pH range 1.0–4.0, conditions under which dimerization of the platinum complex is extremely slow.[4] Phosphorus-31 NMR spectra reveal that phosphate hydrolysis proceeds to yield orthophosphate and pyrophosphate bound to platinum as the ultimate products. From stoichiometric studies that measured orthophosphate as phosphomolybdate,[5] the ratio of initial platinum(II) concentration to the total concentration of orthophosphate ion produced was calculated to be 2.0 ± 0.1 under conditions of 4.0 mM platinum(II) and 1.0–40 mM triphosphate. The kinetics of the reaction were followed spectrophotometrically at 252 nm under pseudo-first-order conditions with at least a 10-fold excess of triphosphate over the platinum substrate in 0.5 M NaClO$_4$. The absorbance–time profile is described by consecutive first-order kinetics, and the two rate constants k_a and k_b were evaluated[6] with use of a nonlinear least-squares fit. The rate constant k_a shows a linear dependence on the triphosphate concentration while k_b is independent of the triphosphate concentration. At 40 °C and pH 4.0 the value of the first-order rate constant, k_b, is 5.8×10^{-5} s^{-1}, and the second-order rate constant, k_a/[triphosphate], is equal to 1.1×10^{-2} M^{-1} s^{-1}. The initial
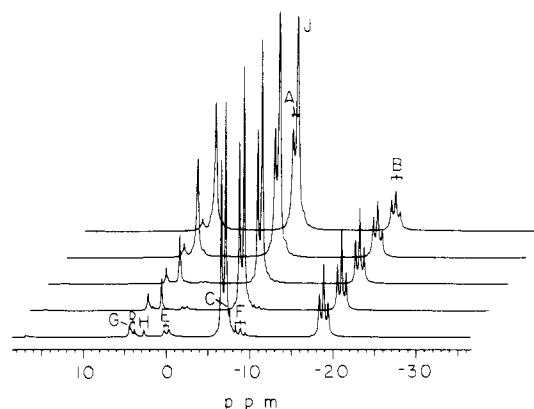

Figure 1. 36.3-MHz phosphorus-31 NMR spectra of the reaction mixture of cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ (20 mM) and triphosphate ion (40 mM) at pH 4.0 and 55 °C. The spectra were recorded at the time intervals (bottom to top) of 0.5, 1.5, 3.0, 6.0, and 10.5 h. Data acquisition conditions were as follows: 10-μs pulse (45°), 4.0-s repetition time, 8K data points, 2000-Hz spectral width, 500 accumulations.

second-order process is attributed to the formation of an intermediate that decays to the platinum-bound orthophosphate and pyrophosphate species by a first-order process (phosphate hydrolysis). The intermediate has been characterized by phosphorus-31 NMR as a dinuclear triphosphato complex as described below. The rate of phosphate hydrolysis is 2 orders of magnitude greater than the corresponding hydrolysis of free triphosphate ion under similar conditions.[7] In perchlorate medium, the hydrolyzed products slowly develop a blue color, while in nitrate media formation of such blue species is more rapid. The blue species has absorption maxima at 260, 375, 480, and 615 nm. The hydrolysis of pyrophosphate ion to generate orthophosphate ion is also catalyzed by cis-[Pt-(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ and is accompanied by the formation of a blue species having absorption maxima at 375, 480, and 610 nm.

Figure 1 shows the phosphorus-31 NMR spectra of triphosphate ion in the presence of cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ at various time intervals. The spectrum of free triphosphate ion exhibits a doublet (A) and a triplet (B) plus a small impurity of pyrophosphate ion (C). In addition to these peaks, the reaction of triphosphate ion with cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ shows a few small peaks, D–J, at the beginning of the reaction. As the reaction progresses, peaks D–G decrease while peaks H and J increase in intensity. The signal J overlaps with the

(1) Cooperman, B. S. *Biochemistry* **1969**, *8*, 5005; *Met. Ions Biol. Syst.* **1976**, *5*, 80–123.
(2) Cornelius, R. D. *Inorg. Chim. Acta* **1980**, *46*, L109–110. Norman, P. R.; Cornelius, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 2356. Norman, P. R.; Gilletti, P. F.; Cornelius, R. D. *Inorg. Chim. Acta* **1984**, *82*, L5–6. Haromy, T. P.; Gilletti, P. F.; Cornelius, R. D.; Sundaralingam, M. *J. Am. Chem. Soc.*, in press.
(3) Hubner, P. W.; Milburn, R. M. *Inorg. Chem.* **1980**, *19*, 1267–1272.
(4) Rosenberg, B. *Biochimie* **1978**, *60*, 859–867.
(5) Chen, D. S.; Toribara, Y. T.; Warner, H. *Anal. Chem.* **1956**, *28*, 1756–1761. The orthophosphate ion was first released by adding 2.0 M vanadium(II) to the solution containing platinum-bound phosphate. Platinum(II) was thus reduced to metallic platinum, and vanadium species were removed by passing the solution through a cation-exchange column.
(6) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.*, in press.

(7) Van Wazer, J. R.; Griffith, E. J.; McCullough, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 287–291.

Scheme I
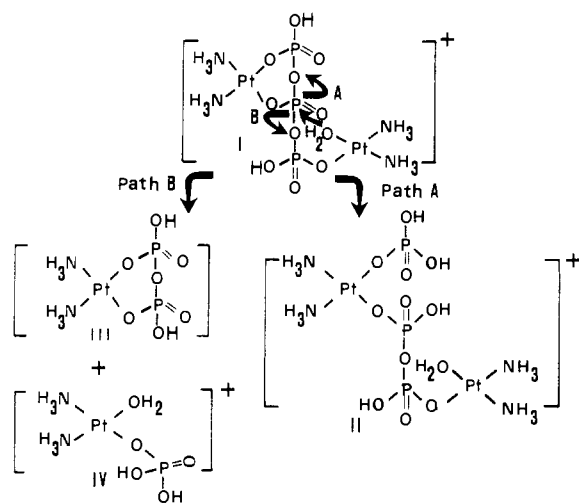
upfield component of the doublet A. The phosphorus-31 NMR spectrum of the blue product isolated at the end of the reaction exhibits the same two signals, H and J, as were observed at the end of the reaction in solution.

A plausible assignment can be made for the initial small peaks D–F to the intermediate I shown in Scheme I. The agreement of the coupling constants in the two doublets D (4.16 ppm, J = 20.8 Hz) and E (0.02 ppm, J = 21.0 Hz) and the doublet of doublets F (−8.51 ppm, J = 20.8, 21.0 Hz) and the parallel rate of disappearance of the three sets of peaks support the argument that the peaks arise from the same species. The two doublets are 7.0 and 11.0 ppm downfield, respectively, from the doublet of free triphosphate ion (A), and the doublet of doublets is 10.6 ppm downfield from the triplet of free triphosphate ion (B). The large downfield shifts of all of these resonances indicate that all three phosphates are bound to the platinum.[8] Since *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ has only two labile sites, a dinuclear platinum(II) species must be formed initially. The observed chemical shifts are consistent with the structure I shown in Scheme I. The formation of I from the respective reactants requires a series of events such as monodentate coordination, chelation, and coordination to a second platinum atom. The failure to observe any monodentate species during the reaction suggests that monodentate coordination is the rate-limiting step followed by rapid reactions leading to dinuclear complexation. This sequence of events is consistent with the kinetic results that the formation of the intermediate follows a second-order rate law, first order with respect to each of the reactants.

The decay of intermediate I to yield hydrolyzed products may proceed by two pathways as shown in Scheme I. In path A, attack by the coordinated aquo or hydroxo group on the β-phosphorus atom and cleavage of the phosphorus–oxygen bond (indicated by A) should result in the formation of a transient intermediate, which upon hydrolysis yields product II. Alternatively, cleavage of the phosphorus–oxygen bond at the position indicated by B would result in complexes III and IV. The two peaks H and J are 1.5 and 1.4 ppm downfield relative to the peaks for othophosphate and pyrophosphate, respectively. These two peaks can readily be interpreted as originating from product II. The singlet H is assigned to the monodentate orthophosphate ligand and peak J to the bridging pyrophosphate ligand. The two phosphate groups in the py-

rophosphate ligand are nearly equivalent in structure II; the small difference in chemical shifts between the two phosphate groups may contribute to the broadness of peak J as compared to that of H. The phosphorus-31 NMR spectrum (at pH 8.0) of the pyrophosphato chelate, III, has been shown[9] to give a singlet about 8 ppm downfield from free pyrophosphate with two satellites originating from the 33.7% abundant platinum-195 nucleus (I = $^1/_2$). The absence of a peak at this position confirms that path A in Scheme I is the predominant path for formation of products at pH 4.0. At pH 6 and above, the peak due to the pyrophosphato chelate (III) was observed, indicating a possible contribution from path B.

The phosphorus-31 NMR spectra of pyrophosphate ion in the presence of *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ at various time intervals exhibit the same two signals, G and H, as observed in the triphosphate reaction, with peak G decreasing and peak H increasing with time. The peak G, about 12 ppm downfield from free pyrophosphate ion, is attributed to a dinuclear species with pyrophosphate bridging between the two platinum atoms. Upon hydrolysis this dinuclear species would produce orthophosphate ions (peak H) bound to platinum.

The blue color for the hydrolyzed product is consistent with a redox titration using cerium(IV), which reveals that the average oxidation state of platinum in the blue species is 2.3 ± 0.2. A reasonable description of the blue species would be the combination of two dinuclear species (product II in Scheme I) through an axial platinum–platinum bond with one platinum(III) for every three platinum(II) ions. The broader line widths of peaks H and J compared to line widths previously reported[6] for coordinated phosphates are consistent with the fact that the blue species is paramagnetic and EPR active. The different average oxidation state also accounts for the different coordination chemical shift observed for the platinum blue.

(9) Bose, R. N.; Cornelius, R. D., submitted for publication.

Department of Chemistry　　　　　　　　　　**Rathindra N. Bose**
Wichita State University　　　　　　　　　　**Richard D. Cornelius***
Wichita, Kansas 67208

Department of Chemistry　　　　　　　　　　**Ronald E. Viola**
Southern Illinois University
Edwardsville, Illinois 62026

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Observation of an Intervalence Charge-Transfer Band in a Mixed-Valence Ruthenium Dimer Bridged by a Nonconjugated Nitrogen Donor Ligand

Sir:

We wish to communciate the synthesis, spectra, and electrochemistry of a new ruthenium dimer containing the nonconjugated bridging ligand 1,4-cyclohexanedione dioximate (1) and the observation of an intervalence charge-transfer band upon generation of the Ru(II)–Ru(III) dimer.

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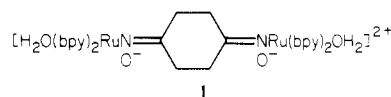
(8) The phosphorus-31 NMR spectra of the two isomeric chelates, the α,γ and β,γ isomers, show 5–9 ppm downfield coordination chemical shifts for only the coordinated phosphate groups. The uncomplexed phosphate groups, namely the β-phosphate in the α,β isomer and the α-phosphate in the β,γ isomer show 1–2 ppm upfield changes in chemical shifts.[6]