Base Hydrolysis of the Penta-ammine(trimethyl phosphate)iridium(III) Ion

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The base hydrolysis of trimethyl phosphate to yield dimethyl phosphate and methanol is accelerated 400-fold upon co-ordination to the penta-ammineiridium(III) moiety; the reaction proceeds *via* intermolecular attack of hydroxide ion at the phosphorus centre in both co-ordinated and free ligand.

As part of a study on the reactivity of co-ordinated phosphate esters, which has as a goal the elucidation of the role of metal ions in phosphate hydrolysing enzymes, the penta-ammine-(trimethyl phosphate)cobalt(III) ion $\{[(NH_3)_5CoTMP]^{3+}\}$ was synthesized.[1] The hydrolysis of this ion in base, however, showed that the reaction occurred with 100% Co–O cleavage, the only products being $[(NH_3)_5CoOH]^{2+}$ and TMP.[1,2] It was thought therefore that a complex with more robust metal–ligand bonds should reduce the rate of metal–ligand cleavage and allow the hydrolysis of the co-ordinated phosphate moiety to be observed. The analogous Ir^{III} complex, $[(NH_3)_5IrTMP](CF_3SO_3)_3$, has now been synthesized with this aim

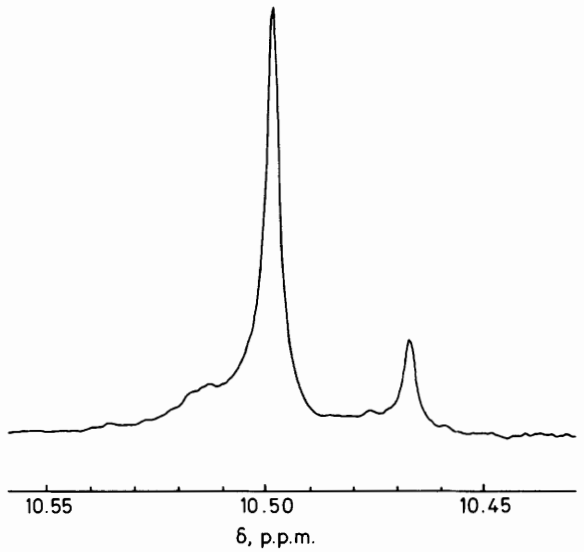

Figure 1. ^{31}P N.m.r. spectrum of hydrolysis product showing incorporation of ^{18}O into $[(NH_3)_5IrDMP]^{2+}$. Spectral acquisition parameters for Bruker CXP-200 n.m.r. spectrometer: 80.98 MHz, sweep width 500 Hz, pulse angle 90°, repetition time 16.4 s.

using a method similar to that for the analogous Co^{III} complex[1] [$^{31}P\{H\}$ n.m.r. δ 6.7 (s) p.p.m. *vs.* external H_3PO_4; ^1H n.m.r. δ 3.95 (d), *J* 11.2 Hz; satisfactory analytical data were obtained]. Base hydrolysis kinetics were studied in D_2O under pseudo first order conditions over a OD^- concentration range 0.05 M to 0.20 M; the observed rate law was $k_{obs} = k_{OD^-}[OD^-]$, with $k_{OD^-} = 5.8 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} [27 °C, μ = 1.0 M (NaCl)]. Under the same conditions the rate constant for the hydrolysis of free TMP was 1.4×10^{-4} dm^3 mol^{-1} s^{-1}, yielding a 400-fold rate enhancement upon co-ordination. The kinetics were followed by observing the disappearance of the ^1H n.m.r. signal (JEOL FX200) due to the co-ordinated TMP and the appearance of the signals due to methanol (δ 3.34) and co-ordinated dimethyl phosphate (DMP) [δ 3.65 (d), *J* 10 Hz]. The singlet at δ 3.34 was coincident with the signal of added methanol and the $[(NH_3)_5IrDMP]^{2+}$ ion, independently synthesized, has identical ^{31}P and ^1H n.m.r. spectra to the reaction product.

A question which immediately arises is: does the hydroxide ion attack occur at the phosphorus or the carbon centre? To resolve this problem, an ^{18}O tracer study was conducted. The reaction was carried out in 21% ^{18}O-labelled water. A high resolution ^{31}P n.m.r. spectrum of the products showed a single satellite peak 0.032 p.p.m. upfield from the main product peak, with intensity 17 ± 3% of the total product (Figure 1). This highfield peak was due to co-ordinated DMP ion with a single ^{18}O label on the phosphorus; the magnitude and direction of the shift were in the range previously observed for mono ^{18}O substituted phosphate esters.[3,4] A control experiment in which $[(NH_3)_5IrDMP](ClO_4)_2$ was subjected to the same conditions showed that oxygen exchange did not occur in the reaction product. This experiment shows that OH^- attacks very largely at the phosphorus centre, although some attack of OH^- at the carbon centre cannot be excluded. In this respect, the base hydrolyses of free and co-ordinated TMP are the same; tracer studies have shown that the hydrolysis of free TMP goes only *via* attack of hydroxide ion at phosphorus.[5]

Co-ordination of the phosphate ester clearly promotes an accelerated hydrolysis by the external nucleophile, but the effect is not very pronounced. It appears unlikely therefore that enzymes would use this route as a primary method of increasing reactivity at the phosphorus centre but coupled with the attack of an intramolecular nucleophile the reactivity increase should be more pronounced. Such intramolecular paths using co-ordinated aminato and hydroxo ions have been observed for the hydrolysis of co-ordinated mono-[6,7] and di-ester[8] phosphates but there is no evidence for such an intramolecular path in this study.

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