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Aqueous Phosphoester Bond Cleavage of Dimethyl Phosphate by Cp$_2$MoCl$_2$: First Reported Case of Hydrolytic Cleavage on an Unactivated Phosphate Diester by an Organometallic Complex

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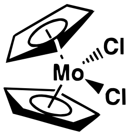
The organometallic compound bis(η^5-cyclopentadienyl) molybdenum(IV) dichloride (Cp$_2$MoCl$_2$, Cp = η^5-C$_5$H$_5$) promotes the phosphotester bond cleavage of dimethyl phosphate with rate accelerations of 10^4 at pH 4.0. NMR spectral evidence suggests this phosphoester bond cleavage proceeds through a hydrolytic pathway where the aquated Cp$_2$MoCl$_2$ binds to the phosphate diester and then carries out an intramolecular attack with either a Cp$_2$Mo-bound water or hydroxide. This is the first reported case of an organometallic complex that hydrolyzes an unactivated phosphate diester.

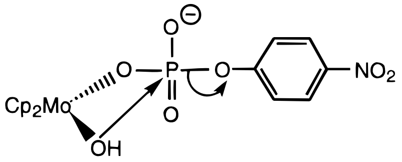
Introduction

We have recently reported the first case of an *organometallic* complex that promotes phosphoester bond cleavage of activated phosphate esters with rate accelerations comparable to the best coordination complexes.[1] This organometallic complex, bis(cyclopentadienyl)molybdenum(IV) dichloride (Cp$_2$MoCl$_2$, Cp = η^5-C$_5$H$_5$) is a metallocene that has a clamshell shape containing a tetrahedral Mo(IV) center and two chlorides in the equatorial girdle.



Cp$_2$MoCl$_2$ Cp=η^5-C$_5$H$_5$

The aqueous properties of Cp$_2$MoCl$_2$ include rapid and complete hydrolysis of the two chloride ligands to yield aquated Cp$_2$Mo(OH$_2$)$_2$$^{2+}$ in acidic solution (pH < 5.0). In water, the cyclopentadienyl ligands remain bound to the Mo(IV) center even at neutral pH.[2] This may serve to minimize metal aggregation that results in precipitation of an intractable molybdenum oxide complex. In addition, the hydrolytic stability of the Cp−Mo^{IV} ligation maintains the two Cp$_2$Mo-bound waters in the cis geometry. Functionally, it has been found that this geometric parameter is crucial for effecting phosphate hydrolysis,[3] for it localizes the phosphate ester adjacent to a metal-bound nucleophile. To this end, it was found that the Cp$_2$Mo moiety binds to *p*-nitrophenyl phosphate[1] to promote phosphoester bond cleavage with a 10^5 rate of acceleration. The proposed mechanism of phosphoester bond cleavage (pH 7.0), which is similar to that of Co(III) coordination complexes,[4] involves intramolecular nucleophilic attack by a Cp$_2$Mo-bound hydroxide on the *p*-nitrophenyl phosphate monoester.



A driving force for this hydrolytic process was proposed to be the formation of a four-membered Cp$_2$Mo−phosphate chelate; among the early transition metal metallocenes, the d^2 metallocenes have the smallest X−M−X bond angles.[5]

The diester, dimethyl phosphate (DMeP), undergoes acid-catalyzed hydrolysis (pK_a = 1.6) and is quite stable to phosphoester bond (P−O) cleavage in the monoanionic form at neutral pH.[6] Dimethyl phosphate serves as an analog to the hydrolytically stable phosphate diester backbone in DNA. Kim and Chin have calculated the rate of hydrolysis for DMeP via P−O cleavage to be 3.4×10^{-14} s^{-1} ($\tau_{1/2} \sim 600\,000$ years) at pH 7.0 and 100 °C.[7] Most nucleases use metals to hydrolyze nucleic acids with exquisite specificity and large rate acceleration.[8] Accordingly, transition-metal[9] and lanthanide[10] complexes have been used to model the phosphate hydrolysis that takes place at the nucleic acid backbone.

We now report that Cp$_2$MoCl$_2$(aq) significantly enhances the rate of hydrolytic phosphoester bond cleavage for dimethyl phosphate. This represents the first reported case of an orga-

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nometallic complex that promotes phosphotester bond cleavage of an *unactivated* phosphate diester in aqueous media.

Experimental

Proton, phosphorus, and carbon NMR spectra were recorded on a Bruker QE-300 (300, 121, and 75.5 MHz, respectively). Proton chemical shifts were referenced to Me_4Si (TMS) and phosphorus chemical shifts were referenced to 85% H_3PO_4. The complex Cp_2MoCl_2 was purchased from Strem Chemical Co. and used as is. Deionized water was thoroughly purged with prepurified argon prior to use, and all manipulations were done with standard Schlenk techniques. All pD measurements were done in D_2O solution, and the reported pD values are uncorrected.

The sodium salt of dimethyl phosphate (DMeP) was prepared by adding 1.0 equiv of NaI in dry acetone to a 1 M acetone solution of trimethylphosphate (Aldrich). After stirring overnight at room temperature, the white precipitate was filtered, washed with acetone, and dried; the composition of the diester was verified by elemental analysis. Calcd: C, 16.2; H, 4.1; O, 43.2; P, 21. Found: C, 15.9; H, 4.3; O, 43.0; P, 19.6. All kinetic studies were done under an argon atmosphere at 70 °C, and the pD was adjusted (70 °C) with a concentrated NaOD or DCl solution. Preparation of Cp_2MoCl_2(aq) solutions required an initial pD adjustment after complete dissolution. This was followed by up to six hours of pD monitoring/adjusting to ensure stability of the solution pH. We have seen that the pD would drift by ±0.3 unit during our measurements. Typically we have found that the Cp_2MoCl_2(aq) solution is dark green at pD < 5, green-yellow at pD 5−8, and dark tan at pD > 8.

DMeP degradation was monitored using ^{1}H NMR (pulse delay $>10T_1$) with Me_4NCl serving as an internal standard. All NMR spectra were collected after allowing 30 min for the reaction to cool to room temperature. At pD > 8.0 an intractable solid precipitated out of solution that yielded no useful NMR information. Pseudo-first-order rate constants were obtained by reacting DMeP (5 mM) with excess Cp_2MoCl_2 (50 mM) at 70 °C in D_2O, and the DMeP signal was followed until 90% completion. Reaction orders were obtained through measuring the initial rates of DMeP degradation upon changing DMeP and Cp_2MoCl_2 concentration.

Results and Discussion

The hydrolysis of the monoanionic form of DMeP in water at pH 4 and 100 °C has been measured to be 1.0×10^{-8} s^{-1}.[6] This rate constant increases to 3.2×10^{-6} s^{-1} at pH 1.0 where more of the neutral DMeP form is present.[6] The production of methanol under these acidic conditions supports a hydrolytic mechanism for the degradation of DMeP. Accordingly, our results with Cp_2MoCl_2 under acidic conditions (pD 4.0) at 70 °C are consistent with a hydrolytic degradation of DMeP, for ^{1}H NMR spectroscopy clearly shows methanol production (3.28 ppm) with concomitant decrease of the starting DMeP at 3.53 ppm (Figure 1). In addition, the ^{1}H or ^{13}C NMR spectra show no evidence of products due to oxidation of DMeP such as formaldehyde and formic acid. However, at higher pD (>6.0) methanol production was not seen in the ^{1}H NMR spectra, and we observed a small amount of precipitation after one day.

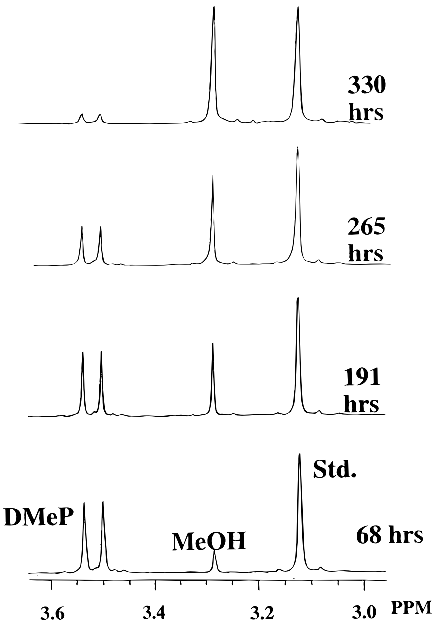

Figure 1. ^{1}H NMR spectra (300 MHz) of the DMeP (5 mM) + Cp_2MoCl_2 (50 mM) reaction at pH 4.0 and 70 °C under an argon atmosphere. Internal standard is Me_4NCl.

The conversion of DMeP to methanol can be quantitatively monitored by integrating the DMeP signal relative to the internal inert standard, tetramethylammonium chloride (Figure 1). Kinetic studies on initial rates show a first-order dependence in DMeP in the concentration range (1−200 mM) used for these studies (Supporting Information, Figure 1b). The concentration dependence on Cp_2MoCl_2 is not first-order, but is almost half-order (Supporting Information, Figure 1a).[11] The half-order dependence in Cp_2MoCl_2 suggests that another process precedes the actual DMeP hydrolysis by Cp_2MoCl_2(aq). In this connection, we propose that upon dissolution of Cp_2MoCl_2, there is first a dimer−monomer equilibrium,[12] and that the active species responsible for the hydrolysis of DMeP is the monomer (mathematical proof enclosed in Supporting Information). Such a hypothesis for this half-order dependence is reasonable on two grounds. First, dimeric forms of Cp_2Mo have been prepared from the corresponding dihydride in aqueous acetone solutions.[13] Crystallographic analysis show that both Cp_2Mo moieties are held together by two μ-hydroxo bridges to form the $[Cp_2Mo(\mu\text{-OH})_2MoCp_2](OTs)_2$ complex. It was suggested that the OH^- functionality had a greater ability to serve as bridging ligands than halide anions, and that the monomer and dimer may coexist in equilibrium.[13] Moreover, dimeric forms of mono-permethylated metallocenes have been isolated in aqueous solution and have been shown to be in equilibrium with its corresponding monomer.[14] Secondly, there is clear precedence for this type of half-order dependence in metal-promoted phosphate hydrolysis

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(11) See Supporting Information, Figure 1a. Although there is a slight deviation from a perfect half-order dependence in Cp_2MoCl_2, the plot definitely falls within the half-order regime in the 15−200 mM concentration range. In order to obtain a reasonable pseudo-first-order rate constant, the 50 mM Cp_2MoCl_2 concentration was used because of the limitations in its water solubility at high concentrations and the detection of DMeP at low [Cp_2MoCl_2].

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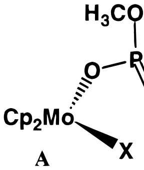
that suggests the active species is a monomer which is in equilibrium with a dimer. We have already reported such a metal concentration dependence in our previous studies on *p*-nitrophenyl phosphate hydrolysis by Cp_2MoCl_2.[1] This dependence in metal concentration was also observed in the *p*-nitrophenyl phosphate hydrolysis by $Cu([9]aneN_3)Cl_2$, and the half-order dependence in metal was interpreted as a monomeric active copper coordination species that was in equilibrium with a dimer.[15]

The hydrolytic degradation of DMeP exhibits clean pseudo-first order kinetics with a measured k_1 of 8.3×10^{-7} s^{-1} when a 10-fold excess of Cp_2MoCl_2 is used (Supporting Information). From this DMeP hydrolysis, we calculated the rate constant k to be 3.8×10^{-6} $M^{-1/2}$ s^{-1} wherein

$$\text{rate} = -d[\text{DMeP}]/dt = k_1[\text{DMeP}] = k[Cp_2MoCl_2]^{1/2}[\text{DMeP}] \quad (1)$$

To quantitatively assess how $Cp_2MoCl_2(aq)$ accelerates the hydrolysis of DMeP, we chose to compare this rate constant with that obtained by Bunton and co-workers who performed a DMeP hydrolytic reaction in water under conditions close to what was done with Cp_2MoCl_2. One therefore uses the observed k_1 of 1.0×10^{-8} s^{-1} at 100 °C (pH 4.0 with P−O bond cleavage)[6] and the $\Delta H^{\ddagger}$ (35.5 kcal mol^{-1}) for DMeP hydrolysis as calculated by Chin.[7] This finally gives an approximate rate for DMeP hydrolysis of 6.3×10^{-10} s^{-1} at 70 °C and pH 4.0, assuming that the $\Delta H^{\ddagger}$ value does not change at this lower pH. In comparing the rate constants of DMeP hydrolysis in water versus $Cp_2MoCl_2(aq)$, it is clear that the Cp_2MoCl_2 + DMeP reaction represents a 10^3−10^4 rate enhancement compared to DMeP hydrolysis in pH 4 water alone.

To probe how the diester is hydrolyzed by Cp_2MoCl_2, the fate of the DMeP was monitored with ^{31}P NMR spectroscopy (proton coupled) at pD 4.0. The final products of the DMeP + Cp_2MoCl_2 reaction (pD 4) have ^{31}P signals at −3.0 and 6.0 ppm that were assigned as pyrophosphate and inorganic phosphate, respectively by addition of authentic samples. There was no evidence of accumulated free or Cp_2Mo-bound monomethyl phosphate. This observation is consistent with our previous work that showed Cp_2MoCl_2 was effective in hydrolyzing monoesters.[1] In addition, there is a small intermediate septet (**A**) at 8 ppm that always appears as the first species when Cp_2MoCl_2 is added to DMeP. We attribute this 8 ppm septet, which collapses to a singlet upon proton decoupling ($J^3_{H,P} \sim 7$ Hz), as the initial Cp_2Mo-DMeP adduct (**A**) with two methoxy groups.



X = OH
or OH_2^+

A

That $[Co(cyclen)(OH_2)_2](ClO_4)_3$ binding to DMeP also results in a ^{31}P signal displaced 7 ppm downfield of DMeP[7] supports the hypothesis that species **A** in Figure 2 is the Cp_2Mo−DMeP monodentate adduct.

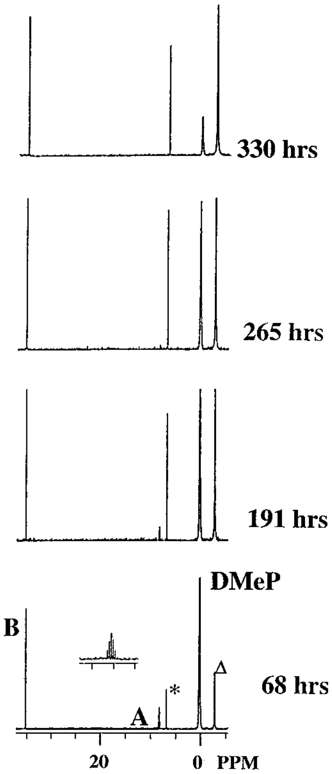
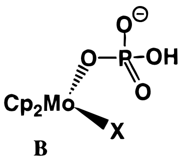


Figure 2. ^{31}p NMR spectra (^1H-coupled, 121 MHz) of DMeP (5 mM) + Cp_2MoCl_2 (50 mM) reaction (pH 4.0 and 70 °C). The monodentate Cp_2Mo−phosphate adduct (**B**), free inorganic phosphate (*) and pyrophosphate (△) are produced with time. Complex **A** (8 ppm) is the initial Cp_2Mo−DMeP adduct that appears as a quartet of quartet due to the two nonequivalent methoxy groups of the coordinated DMeP.

The second species to appear is a singlet at 35 ppm that is assigned as a monodentate Cp_2Mo−phosphate complex (**B**). This complex has been seen in the hydrolysis of *p*-nitrophenyl phosphate by Cp_2MoCl_2[1] which results after intramolecular attack by Cp_2Mo-OH on the coordinated *p*-nitrophenyl phosphate. Further support for the identity of species **B** at 35 ppm comes from the fact that a singlet appears at the identical chemical shift when Na_2HPO_4 is added to $Cp_2MoCl_2(aq)$.



X = OH
or OH_2^+

B

Compound **B** could either result from the hydrolysis of **A** or from binding of $Cp_2MoCl_2(aq)$ to free inorganic phosphate in solution. The monodentate nature of this complex is supported by the 30 ppm downfield displacement in the ^{31}P NMR spectrum of complex **B** relative to free inorganic phosphate. This displacement in the ^{31}P chemical shift is consistent with previous crystallographic and NMR studies on monodentate Cp_2Mo−phosphate complexes.[2] In summary, the ^{31}P spectral data of the final products from the DMeP + Cp_2MoCl_2 reaction are consistent with a hydrolytic process for the phosphoester bond cleavage.

When the ^{13}C NMR spectrum of the DMeP + Cp_2MoCl_2 reaction was taken in the $^{18}OH_2/^{16}OH_2$ solution, the methanol signal at 49.00 ppm remained unchanged as a singlet. This suggests no oxygen from the solvent was incorporated into the methanol which would give an ^{18}O isotope-induced ^{13}C shift

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of 0.04 ppm.[16] One mechanism consistent with the ^{31}P and ^{13}C NMR spectra at pD 4.0 is for a phosphoester bond cleavage pathway that proceeds mainly through P−O cleavage as opposed to C−O cleavage. An intermolecular attack on the CH_3 of DMeP would result in 50% ^{18}O incorporation in the free methanol at 49 ppm which was not seen in the ^{13}C NMR spectrum.

The proposed intramolecular pathway would occur through a series of nucleophilic attacks by a Cp_2Mo-bound water or hydroxide on the phosphate ester. It should be noted that at pD's 3.0, 4.0, 5.0, and 5.5 the observed initial rates of DMeP hydrolysis are 8.3×10^{-7}, 4.4×10^{-7}, 6.5×10^{-7}, and 1.0×10^{-7} s^{-1}, respectively. Given the uncertainty and error in measuring these initial rates of methanol production, this random eight-fold difference in rates is rather insignificant indicating that the rate of DMeP hydrolysis is fairly independent of the $H(D)^+$ concentration. This is suggestive that a Cp_2Mo-bound water molecule may also be the nucleophilic species.

At pD 6.0 and 7.0 (70 °C), the starting DMeP decreases with clean pseudo-first order kinetics with k_1 values ($\sim 10^{-7}$ s^{-1}) similar to the low pD (≤ 5.0) rates. However, there is no evidence of free methanol in solution or even dissolved methane. It is interesting to note that precipitation also occurs when Cp_2MoCl_2 is combined with methanol at pD 7; we have been unable to characterize this precipitate as it is probably a combination of several molybdenocene-based complexes. At the same time both ^{13}C and ^{1}H NMR reveal no oxidative degradation products, and the ^{31}P spectra are identical to what was observed at pD 4.0 (Figure 2). The NMR results at pD 6 and 7 suggest that the phosphoester bond cleavage of DMeP by Cp_2MoCl_2 may proceed through a hydrolytic pathway similar to what was described for the pD 4 case. One can only hypothesize that at near neutral pH, there is a side reaction between methanol and Cp_2MoCl_2 that may form an insoluble precipitate. If this is indeed the process, then one can make the case that there is an even larger rate acceleration at neutral pH. When we use Chin's calculations,[7] the k_1 for DMeP hydrolysis by water at 70 °C and pH 7.0 is estimated to be 5.8×10^{-16} s^{-1}. This shows that Cp_2MoCl_2 accelerates the phosphoester bond cleavage of DMeP by 10^8 at near neutral pH, assuming a hydrolytic process. This is the same rate enhancement that we reported in the phosphotester bond cleavage of the bis(4-nitrophenyl)phosphate diester by $Cp_2MoCl_2(aq)$ at pH 7.0.[1]

Rate accelerations by previous coordination complexes lend further credence to the proposed intramolecular attack by a Cp_2Mo-bound water or hydroxide nucleophile on the DMeP phosphodiester. Lewis acid activation by Cp_2Mo coordination alone is not sufficient to explain the observed rate acceleration, for it has been found that Co(III)-phosphate coordination yields only a 10^2 enhancement in phosphate hydrolysis.[17] This implies Co(III) coordination complexes that accelerate phosphate hydrolysis by 10^{10} provide an additional 7−8 orders of magnitude rate acceleration through intramolecular attack of Co(III)-bound hydroxide. If the assumption that DMeP is degraded by Cp_2MoCl_2 via a hydrolytic process at pD 7, then the rate acceleration (10^8) can be attributed to Cp_2Mo providing Lewis acid activation (10^2) and a nucleophilic hydroxide/water (10^6). Even at lower pD 4.0, the 10^4 rate acceleration of DMeP hydrolysis cannot be attributed to Lewis acid activation by Cp_2Mo alone, but rather through the additional intramolecular attack of a Cp_2Mo-bound water or hydroxide molecule.

Conclusion

We have shown that the organometallic compound Cp_2MoCl_2 promotes the hydrolytic cleavage of dimethyl phosphate, a phosphate ester that mimics the diester functionality of DNA. This is the first report that shows an organometallic compound can promote the phosphoester bond cleavage of an unactivated phosphate diester. Moreover, Cp_2MoCl_2 accelerates the rates of phosphoester bond cleavage by 10^4 at pH 4.0. These rate accelerations and the NMR data are consistent with a mechanism that proceeds through coordination of aquated Cp_2MoCl_2 to DMeP followed by intramolecular attack of a Cp_2Mo-bound hydroxide or water nucleophile. The Cp_2Mo moiety acts as both a Lewis acid to activate the phosphate diester and as a delivery system for intramolecular nucleophilic attack on the coordinated phosphate diester. These findings add to the potential use of Cp_2MoCl_2 and its derivatives for the hydrolytic cleavage reactions of other unactivated phosphate esters.

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Supporting Information Available: Graphs of observed rate constant versus concentration of organometallic complex, a reaction equilibrium scheme, and reaction kinetics of DMeP + Cp_2MoCl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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