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Mg^{2+}-Promoted P–O vs. S–O Bond Cleavage in the Alcoholyses of Phenyl Phosphatosulfate

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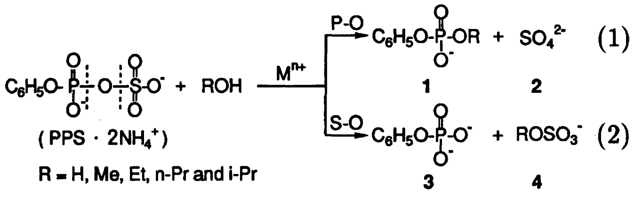
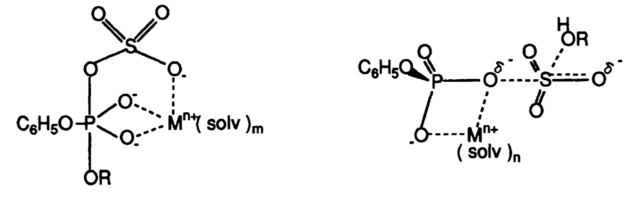
In order to obtain insight into the selectivity of Mg^{2+} at the site of bond cleavage of P–O and S–O of the P–O–S linkage, metal ion-promoted alcoholyses of phenyl phosphatosulfate were studied. Mg^{2+} quantitatively promoted P–O bond cleavage in the methanolysis, but mixed cleavage of the P–O bond, which occurred partly due to hydrolysis by trace water and the S–O bond in the reaction of ethanol, 1- or 2-propanol. The ratio of the S–O bond cleavage against the mixed cleavage increased in a order EtOH (11.5%)<*n*-PrOH (13.3%)<*i*-PrOH (29.0%). On the other hand, Ca^{2+} and Zn^{2+} promoted selective P–O and S–O bond cleavage, respectively, in the reaction of 2-propanol as well as methanolysis.[1] The medium-dependent change in the selectivity of Mg^{2+} at the site of bond cleavage was discussed.

Mg^{2+} is an essential cofactor for biochemical sulfuryl group-transfer reactions from 3′-phosphoadenosine-5′-phosphatosulfate (PAPS) to numerous acceptors, such as amines, phenols, steroids, and polysaccharides.[2] A particularly interesting subject concerning the sulfuryl group-transfer reactions is the role of Mg^{2+}: How the metal ion affects the rate and selects S–O over P–O bond cleavage of the P–O–S linkage. By contrast, Mn^{2+} or Co^{2+} was suggested to catalyze the P–O bond cleavage in the enzymatic hydrolysis of PAPS.[3] However, many aspects of the mechanisms of metal-ion catalysis have been left unclarified.

In such nonenzymatic reactions as Mg^{2+}-catalyzed hydrolysis and aminolysis of phenyl phosphatosulfate (PPS) and related substrates under neutral or basic conditions in aqueous media, the P–O–S linkage underwent selective P–O bond cleavage.[4—6] It was previously found that in the methanolysis of PPS in a mixed solvent of MeOH–DMF (1:1, v/v), Mg^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, and Ca^{2+} catalyzed selective P–O bond cleavage (Eq. 1, R=Me); by contrast, Be^{2+}, Al^{3+}, Fe^{3+}, and Zn^{2+} promoted selective S–O bond cleavage (Eq. 2, R=Me).[1] The kinetic studies showed that P–O bond cleavage occurred along with a dimolecular nucleophilic attack of methanol on phosphorus proceeding via the formation of a pentavalent phosphorus intermediate, as depicted hypothetically in **5** (R=Me), and the S–O bond cleavage occurred along with a monomolecular elimination of sulfur trioxide involving a molecule of solvent in the transition state, as illustrated in **6** (R=Me) (Chart 1).





5 **6**

Chart 1. Proposed structures **5** and **6**.

The selectivity of the metal ion at the site of the bond cleavage could be explained by assuming a different coordination, i.e., a metal ion with octahedral or trigonal bipyramidal coordination assisted the formation of the P(V) intermediate (**5**, R=Me), resulting in P–O bond cleavage and a metal ion with tetrahedral coordination participating in stabilizing the transition state (**6**, R=Me) to promote S–O bond cleavage.[1,7]

As described above, Mg^{2+} always catalyzed selective P–O bond cleavage in nonenzymatic reactions, but not S–O bond cleavage, as in biochemical sulfuryl group-transfer reactions. It is suggested that although Mg^{2+} with octahedral or trigonal bipyramidal coordination catalyzes P–O bond cleavage, Mg^{2+} with tetrahedral coordination promotes S–O bond cleavage. It must be important for obtaining a better understanding of the roles of Mg^{2+} in biochemical reactions to test whether or not Mg^{2+} can actually promote S–O bond cleavage in nonenzymatic reactions under neutral or basic conditions; the effects of the metal ion on the alcoholyses of PPS have thus been studied.

We report here that if one accepts this suggestion, it appears to be easy to understand the observations.

Experimental

The diammonium salt of PPS was prepared by a reaction of phenyl phosphate with the DMF–sulfur trioxide complex in DMF at room temperature according to a previously reported method.[1,5] Alcohols, DMF, and *N*-ethylmorpholine were distilled before use. Metal ions were of analytical grade.

Table 1. Analytical Data for Product Analyses

Compounds	UV[a)]	R_f	^{1}H NMR[c)]			
	λ_{max}(nm)(ε)	value[b)]	$\delta_{C_6H_5}$	δ_{CH_3}	δ_{CH_2}	δ_{CH}
Phenyl phosphatosulfate (PPS)	262(440)	0.65	7.30(m)	—	—	—
Methyl phenyl phosphate (**1**, R=Me)	262(580)	0.82	7.30(m)	3.69(d)	—	—
Ethyl phenyl phosphate (**1**, R=Et)	262(580)	0.83	7.30(m)	1.27(t)	4.05(m)	—
Phenyl propyl phosphate (**1**, R=*n*-Pr)	262(580)	0.82	7.30(m)	0.91(t)	1.65(m) 3.94(q)	—
Phenyl isopropyl phosphate (**1**, R=*i*-Pr)	262(580)	0.82	7.30(m)	1.27(d)	—	4.53(m)
Phenyl phosphate (**3**)	267(740)	0.48	7.30(m)	—	—	—
Ethyl sulfate (**4**, R=Et)	—	—	—	1.31(t)	4.13(q)	—
Propyl sulfate (**4**, R=*n*-Pr)	—	—	—	0.95(t)	1.70(m) 4.04(t)	—
Isopropyl sulfate (**4**, R=*i*-Pr)	—	—	—	1.32(d)	—	4.64(m)

a) In 0.1 N NaOH. b) Toyo Filter Paper, No. 50; *n*-PrOH–NH_3(28%)–H_2O(6 : 3 : 1). c) D_2O and from sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

Table 2. Kinetic Parameters for Metal Ion Promoted Alcoholyses of Phenyl Phosphatosulfate (PPS) and Fraction of Different Bond Cleavage[a)]

ROH	M^{2+}	K/mol^{-1} dm^3	k/s^{-1}	Fraction of the bond cleavage (%)		
				S–O	P–O	P–O(hydrolysis)
MeOH	Mg[b)]	85.0	4.38×10^{-5}	0	93.5	6.5
EtOH	Mg[b)]	337	9.80×10^{-5}	11.5	72.0	16.5
n-PrOH	Mg[b)]	628	2.98×10^{-4}	13.3	49.9	36.8
i-PrOH	Mg[b)]	—	(5.33×10^{-4})[e)]	29.0	11.0	60.0
i-PrOH	Ca[c)]	609	9.09×10^{-4}	0	13.4	86.6
i-PrOH	Zn[d)]	81.4	2.60×10^{-3}	100	0	0

a) [PPS]=1.0×10^{-3} mol dm^{-3}, [*N*-ethylmorpholine]=2.5×10^{-2} mol dm^{-3}, at 55 °C. b) $Mg(ClO_4)_2\cdot2.2H_2O$. c) $CaCl_2\cdot1.1H_2O$. d) $ZnCl_2\cdot0.02H_2O$. e) $k_{obsd}(Mg^{2+}=2.50\times10^{-3}$ mol dm^{-3}), see text.

Since $ZnCl_2\cdot6H_2O$ precipitated as hydroxide. in 2-propanol including *N*-ethylmorpholine, hydrated water was expelled as HCl and SO_2 overnight while refluxing thionyl chloride. An excess of thionyl chloride was removed by distillation under reduced pressure, and the thus-obtained $ZnCl_2\cdot0.02H_2O$ was dried over KOH. $CaCl_2\cdot1.1H_2O$ was obtained by heating the hexahydrate at 250 °C under reduced pressure. The content of hydrated water of the metal ion was estimated by EDTA titration.

The kinetics and product-analysis procedures were essentially the same as those previously used.[1,5,6] In addition, the NMR spectrum, UV spectrum and R_f value of paper chromatography of alkyl phenyl phosphates (**1**, R=Me, Et, *n*-Pr or *i*-Pr) were identical with those of authentic samples prepared by the hydrolysis of alkyl phenyl phosphorochloridate according to methods described in the literature.[8] The analytical data for product analyses are summarized in Table 1.

Results

The reaction was carried out in methanol, ethanol, 1-propanol or 2-propanol containing the diammonium salt of PPS (1.0×10^{-3} mol dm^{-3}), $Mg(ClO_4)_2$, $CaCl_2$ or $ZnCl_2$ including hydrated water (0—0.1 mol dm^{-3}) and *N*-ethylmorpholine (2.5×10^{-2} mol dm^{-3}) at 55.0 °C. The alcoholyses were followed by three monitoring techniques: Alkyl phenyl phosphate (**1**) and phenyl phosphate (**3**) were analyzed by UV and HPLC, and inorganic sulfate (**2**) was colorimetrically analyzed by barium chromate.[9] It was previously reported that a counter anion, such as perchlorate or chloride, did not affect the selectivity, and that *N*-ethylmorpholine was unreactive toward PPS in both the presence and absence of a metal ion.[1,3]

The alcoholysis was very slow unless some metal ion was added. Mg^{2+} enhanced the rate of P–O bond cleavage to give **1** (R=Me) and **2** in quantitative yields in the methanolysis (Eq. 1). However, in the reaction in 2-propanol, the metal ion promoted mixed reactions of P–O bond cleavage to give **1** (R=*i*-Pr) and **2**, S–O bond cleavage to give **3** and isopropyl sulfate (**4**, R=*i*-Pr, Eq. 2) and hydrolysis by trace water contained in the

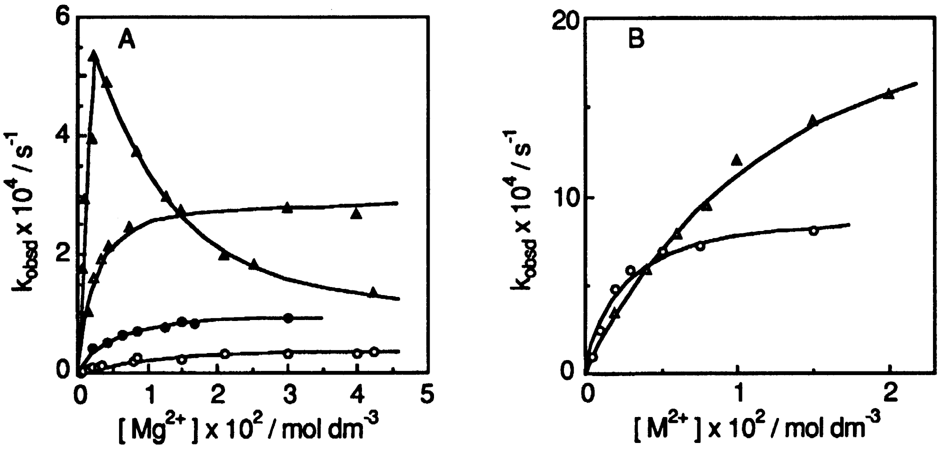


Fig. 1. Plots of k_{obsd} vs. the metal ion concentration in the reaction of PPS in alcohol. (A) Alcoholyses by methanol (○), ethanol (●), 1-propanol (△), and 2-propanol (▲). Metal ion: $Mg(ClO_4)_2 \cdot 2.2H_2O$. (B) Alcoholysis by 2-propanol. $CaCl_2 \cdot 1.1H_2O$ (○), $ZnCl_2 \cdot 0.02H_2O$ (△). $[PPS]=1.0\times10^{-3}$ mol dm^{-3}, [*N*-ethylmorpholine]$=2.5\times10^{-2}$ mol dm^{-3} at 55.0 °C.

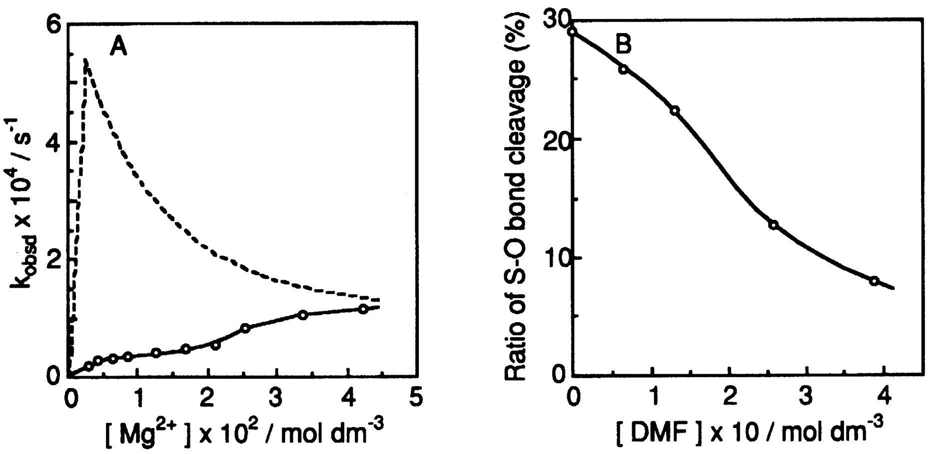


Fig. 2. Effect of DMF on a Mg^{2+}-promoted reaction in 2-propanol. (A) Plots of k_{obsd} vs. concentration of Mg^{2+} in the presence (solid line) and absence (dashed line) of DMF, $[DMF]=0.38$ mol dm^{-3}. (B) Plots of the concentration of Mg^{2+} vs. the ratio of S–O bond cleavage against mixed cleavage in the reaction of 2-propanol. $[Mg^{2+}]=1.3\times10^{-2}$ mol dm^{-3}. The other reaction conditions were the same with those shown in Fig. 1.

reaction medium to give **2** and **3** in a ratio of about 1 : 3 : 6, respectively. Although the Mg^{2+}-promoted reaction in either ethanol or 1-propanol was essentially similar to that in 2-propanol, the ratio of the S–O bond cleavage or the hydrolysis against the mixed reactions increased in the order ethanol<1-propanol<2-propanol, as shown in Table 2. In the reaction in 2-propanol, Ca^{2+} promoted P–O bond cleavage and hydrolysis in a ratio of about 1 : 7, respectively; no metal ion-promoted S–O bond cleavage could be observed. On the other hand, Zn^{2+} promoted selective S–O bond cleavage, as expected, to give **3** and **4** (R=*i*-Pr) in the alcoholysis by 2-propanol, suggesting that the presence of trace water was less important for S–O bond cleavage. In other words, it was considered that Mg^{2+} or Ca^{2+} promoted the hydrolysis of PPS by trace water occurring along with selective P–O bond cleavage.

The pseudo-first order rate constants (k_{obsd}) for metal ion-promoted reactions against the concentration of metal ions are plotted in Fig. 1. The rates, except those for the Mg^{2+}-promoted reaction in 2-propanol, tend to saturate with increasing concentration of the metal ion. This observation can be explained by assuming a reaction scheme (Eq. 3) involving a preequilibrium formation of a binary complex (SM) of PPS (S) and metal ion (M). Equation 4 is formulated in accordance with this scheme,[1,6,7] where $[S]_T$ and $[M]_T$ are the initial stoichiometric concentration of PPS and metal ion, respectively, and k and K are the rate constant and the formation constant for SM, respectively. The calculated curves in Fig. 1, except the curve for Mg^{2+}-promoted alcoholysis by 2-propanol, were obtained by Eq. 4, using the evaluated values of k and K given in Table 2.

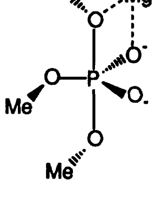
$$\mathrm{S} + \mathrm{M} \overset{K}{\rightleftarrows} \mathrm{SM} \xrightarrow{k} \text{products} \tag{3}$$

$$k_{\text{obsd}} = \frac{kK[\mathrm{M}]_{\mathrm{T}}}{1 + K[\mathrm{M}]_{\mathrm{T}} + K[\mathrm{S}]_{\mathrm{T}}\,(1 - k_{\text{obsd}}/k)} \tag{4}$$

Although a larger rate enhancement took place in a Mg^{2+}-promoted reaction in 2-propanol, excess Mg^{2+} over PPS inhibited the reaction, as shown in Fig. 1A. The maximum rate in the plot of k_{obsd} vs. the concentration of Mg^{2+} suggests that a 1 : 1 complex of PPS and Mg^{2+} (SM) is a more catalytically active species than a higher order complex. Such a maximum rate cannot be observed in the presence of DMF (0.38 $\text{mol}\,\text{dm}^{-3}$), as shown in Fig. 2A. The values of k_{obsd} of a Mg^{2+}-promoted reaction in 2-propanol containing DMF increase stepwise to saturate with increasing concentration of Mg^{2+}, suggesting that DMF inhibits more strongly Mg^{2+} from the formation of the higher order complex than from that of the SM complex. Figure 2B shows that the ratio of S–O bond cleavage against mixed cleavage in Mg^{2+}-promoted alcoholysis by 2-propanol readily decreases with an increasing concentration of DMF. Zn^{2+} promotes selective S–O bond cleavage in alcoholysis by 2-propanol in both the presence[1)] and absence of DMF. Mg^{2+} and Zn^{2+} are different from one another regarding the effect of DMF on S–O bond cleavage.

Discussion

As described earlier, there were two groups of metal ions which catalyzed either P–O or S–O bond cleavage in the methanolysis of PPS.[1)] The correlation of second-order rate constants for metal ion-catalyzed P–O and S–O bond cleavage, k_2(P–O) and k_2(S–O), with ionic radii (r) of metal ions showed two rate maxima in the vicinity of 0.51 (Al^{3+}) and 0.69 Å (Cr^{3+}), corresponding to S–O and P–O bond cleavage, respectively. With the exception of Mg^{2+}, there was a linear correlation between $\Delta(1/r)$ and $\log k_2$(S–O) or $\log k_2$(P–O), where $\Delta(1/r)$ was the difference in $1/r$ between a metal ion and Al^{3+} or Cr^{3+}.[7)] Such a linear correlation is not unexpected, since in coordination chemistry a linear correlation is known to exist between the logarithms of the stability constants of metal chelates or the ionization potential of metal ions and the $1/r$ values.[10)] Thus, the metal ion-catalyzed P–O and S–O bond cleavage were different from one another, not only regarding the optimum ionic radius, but also in the slope of linear correlation of rate, i.e., −5.1 and −0.60 for P–O and S–O bond cleavage, respectively. The large difference in the slope between P–O and S–O bond cleavage could be explained by assuming a chelate effect, i.e., tridentate and bidentate coordination with strict geometrical requirements in **5** and **6**, respectively. However, the observed value of k_2(P–O) for Mg^{2+}-catalyzed P–O bond cleavage alone was about 20-fold smaller than the expected value based on the linear correlation of rate, suggesting that the coordination structure of the Mg^{2+}–P(V) intermediate is different from that illustrated in **5**. At this point, it is interesting to note the investigation of the molecular orbital calculation recently reported by Uchimaru et al.[11)] They showed that the coordination of Mg^{2+} between two equatorial oxygen atoms of dianionic trimethoxyphosphorane was unlikely, and that Mg^{2+} coordination preferably occurred in the region between the axial oxygen and the equatorial phosphoryl oxygen, as illustrated in **7** (Chart 2). According to this, it is considered that Mg^{2+} coordination in the P(V) intermediate cannot occur in the region among the three oxygen atoms, as illustrated in **5**. In other words, Mg^{2+} appears to be too small to coordinate favorably between two equatorial oxygen atoms of the P(V) intermediate (**5**) with a large bond angle of metal-ion chelation ($\angle^{-}$O–P–O^{-} near to 120°). However, Mg^{2+} could not promote S–O bond cleavage proceeding through the transition state (**6**) with a small bond angle of metal-ion chelation ($\angle^{-}$O–P–O^{-} near to 109°) in the methanolysis. On the other hand, Mg^{2+} promoted a mixed cleavage of the P–O and S–O bonds in alcoholysis by ethanol, 1-propanol or 2-propanol. Zn^{2+} and Ca^{2+} promoted S–O and P–O bond cleavage, respectively, in alcoholysis by 2-propanol. It was most conceivable, as described before, that Mg^{2+}- and Zn^{2+}-promoted S–O bond cleavage occurred along with a monomolecular elimination of sulfur trioxide involving a molecule of solvent in the transition state, and that Mg^{2+}- and Ca^{2+}-promoted P–O bond cleavage and hydrolysis occurred along with a dimolecular nucleophilic attack of alcohol and water, respectively, on phosphorus. Table 2 shows that a ratio of the S–O bond cleavage against the mixed cleavage for Mg^{2+}-promoted alcoholysis increases in a order methanol<ethanol<1-propanol<2-propanol. DMF inhibited the Mg^{2+}-promoted S–O bond cleavage in alcoholysis by 2-propanol, as shown in Fig. 2B, but not Be^{2+}-promoted S–O bond cleavage in alcoholysis by 2-propanol.[1)] Be^{2+} and Ca^{2+} promoted S–O and P–O bond cleavage, respectively, in alcoholysis by either 2-propanol or methanol.[1)] Interestingly, Mg^{2+} alone changed cleavage site from P–O bond in methanolysis to mixed P–O and S–O bonds in alcoholysis by 2-propanol. It appears to



7

Chart 2. Structure **7**.

be difficult to explain both the difference in the selectivity between Mg^{2+} and Be^{2+} or Ca^{2+} and the medium-dependent change in the selectivity of Mg^{2+} at the site of bond cleavage by only medium effects. As described below, the selectivity of Mg^{2+} can be easily explained by assuming a different coordination.

Be^{2+} and Al^{3+} with smaller ionic radii generally favor a tetrahedral coordination,[12] and promote selective S–O cleavage in the alcoholyses of PPS by 2-propanol or methanol.[1] On the other hand, although octahedral coordination is commonly found in compounds of Mg^{2+}, tetrahedral coordination is not rare. It has been suggested that the steric control of coordination of Mg^{2+} plays an important role in both the structure and conformation.[13] For example, a larger phenyl or alkyl group, a large halogen and ether donnor, as in $PhMgBr{\cdot}2O(C_2H_5)_2$ or $C_2H_5MgBr{\cdot}2O(C_2H_5)_2$, leads to tetrahedral coordination. It is then highly likely that a large alkyl group of alcohol as a ligand more strongly affects the type of coordination of Mg^{2+} with a small ionic radius than that of Ca^{2+} with a large ionic radius. It is most conceivable that Mg^{2+} with an octahedral or trigonal bipyramidal coordination assists in a nucleophilic attack of methanol on phosphorus, thus resulting in P–O bond cleavage in methanolysis. On the other hand, it is considered that because of a steric repulsion among the molecules of the bulky alcohol attached to Mg^{2+} with a small ionic radius in SM complex, two different events simultaneously occur more readily in ethanol, 1-propanol or 2-propanol than in methanol, i.e., Mg^{2+} tends to decrease its coordination number from six or five to four with increasing size of the alkyl group in contrast to this, trace water contained in the medium tends to readily attach to Mg^{2+} to increase its coordination number from four to five or six. Mg^{2+}, with a coordination number of four, i.e., tetrahedral coordination, participates in the stabilization of the transition state (**6**) to promote S–O bond cleavage. The water or hydroxide ion attached to Mg^{2+} with tetrahedral coordination may act as an intramolecular nucleophile on phosphorus of the SM complex, resulting in P–O bond cleavage.

DMF did not affect the selectivity of Zn^{2+} or Be^{2+} in alcoholysis by 2-propanol, but inhibited Mg^{2+}-promoted S–O bond cleavage. The inhibition can be readily explained by assuming that DMF acts as a ligand to change the coordination structure of Mg^{2+} from tetrahedral coordination for S–O bond cleavage to trigonal bipyramidal or octahedral coordination for P–O bond cleavage in 2-propanol. By contrast, Be^{2+} and Zn^{2+} are considered to favor tetrahedral coordination alone in 2-propanol, irrespective of the presence of DMF.

Meanwhile, in water Zn^{2+} always catalyzed selective P–O bond cleavage, e.g., in the reaction of PPS with 2-pyridinecarbaldehyde oxime,[5] and in the hydrolysis of 2-pyridyl phosphonosulfate;[7] however, it promoted selective S–O bond cleavage in the alcoholyses of PPS. It was suggested that the change in the selectivity of Zn^{2+} at the site of bond cleavage was also due to a change in the type of coordination, i.e., octahedral or trigonal bipyramidal coordination in water to tetrahedral in alcohol.[1] Thus, the selectivity of Zn^{2+} is highly dependent on the medium. Mg^{2+} is phenomenally similar regarding this point to Zn^{2+}, but different from Ca^{2+}.

Much remains to be clarified about the effects of Mg^{2+} on the reaction of P–O–S linkage. Nevertheless, it must be important to note that the coordination structure of the Mg^{2+}-substrate complex appears to play a central role in determining the selectivity in the S–O or P–O bond cleavage of the P–O–S linkage of phosphatosulfate: S–O bond cleavage through tetrahedral coordination and P–O bond cleavage through trigonal bipyramidal or octahedral coordination.

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