Catalytic Effect of MO_4^{2-} (M=Cr, Mo and W) on Hydrolyses of Carbon and Phosphorus Esters

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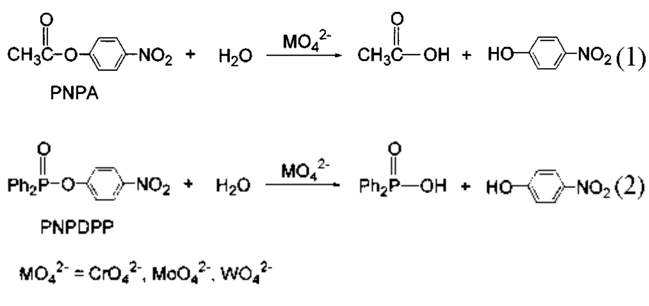
Second-order rate constants have been measured spectrophotometrically for the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl diphenylphosphinate (PNPDPP) with MO_4^{2-} (M = Cr, Mo and W) in phosphate buffer (pH = 8.00) at 35.0 °C. These MO_4^{2-} species exhibit large catalytic effect in the hydrolysis of PNPA and PNPDPP except WO_4^{2-} in the reaction with PNPA. The catalytic effect of these MO_4^{2-} species has been observed to be much more significant in the hydrolysis of PNPDPP than in the hydrolysis of PNPA. Since the smallest CrO_4^{2-} would be most highly solvated by H_2O molecules, CrO_4^{2-} is expected to exhibit the least catalytic effect, if solvation effect is the most important factor. However, in fact, CrO_4^{2-} shows the highest catalytic effect toward PNPA, indicating that solvation effect is not solely responsible for the catalytic effect. The most basic CrO_4^{2-} shows the highest catalytic effect, while the least basic WO_4^{2-} is least reactive toward PNPA, indicating that the basicity of MO_4^{2-} might be an important factor. However, in the hydrolysis of PNPDPP, no correlation is observed between the basicity and catalytic effect, suggesting that basicity alone can not be responsible for the catalytic effect shown by the MO_4^{2-} species. Formation of a chelate is suggested to be responsible for the high catalytic effect of MO_4^{2-} in the hydrolysis reaction of PNPA and PNPDPP. The formation of chelate is considered to be more suitable for the reaction with PNPDPP than with PNPA based on the larger catalytic effect observed in the reaction with PNPDPP than with PNPA.

Introduction

Acyl group transfer reactions are widely spread in nature, and their reaction mechanisms have been extensively investigated.[1-5] It has been reported that monovalent alkali metal ions as well as divalent metal ions such as Zn^{2+} and Cu^{2+} behave as a Lewis acid catalyst in acyl group transfer reactions.[6-8] Buncel *et al.* found that alkali metal ions exhibit catalytic effect for the reaction of alkali metal ethoxides with *p*-nitrophenyl diphenylphosphinate (PNPDPP) in anhydrous ethanol.[6] The catalytic effect was found to increase with decreasing the size of alkali metal ion. However, on the contrary, Li^+ ion exhibited inhibitory effect while K^+ ion showed catalytic effect in the corresponding reaction with *p*-nitrophenyl benzenesulfonate (PNPBS).[6c] We have found that alkali metal ions exhibit inhibitory effect on the reaction of PNPDPP with alkali metal phenoxides in anhydrous ethanol.[7] Clearly, the effect of alkali metal ions is dependent on the type of substrates and nucleophiles as well as on the size of alkali metal ions.

Some years ago, Byers found that MoO_4^{2-} exhibits significant catalytic effect for the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *S*-*p*-nitophenyl thioacetate (PNPTA).[9] Two possible explanations were suggested for the high catalytic effect shown by MoO_4^{2-}, *e.g.*, electrophilic catalyst by forming a chelate and solvation effect.[9] However, the hydrolysis of 2,4-dinitrofluorobenzene (DNFB) was also found to be catalyzed significantly by MoO_4^{2-}, in which a chelation role by MoO_4^{2-} is not possible. Therefore, the role of electrophilic catalysis was ruled out, and solvation effect was attributed to the large catalytic effect.[10]

In order to obtain more information for the catalytic role shown by MoO_4^{2-} in the hydrolysis of PNPA, we have performed a systematic study as shown in equations (1) and (2). We employed PNPA and PNPDPP as substrates and a series of MO_4^{2-} (M = Cr, Mo and W) as catalysts in the hydrolysis reactions. Such changes in the substrate structure from carbon to phosphorus center and the central metal in MO_4^{2-} would give us useful information for the catalytic role of MO_4^{2-} in the hydrolysis of esters.



Result

All the kinetic reactions in the present study obeyed pseudo-first-order kinetics over 90% of the total reactions. Pseudo-first-order rate constants (k_{obs}) were calculated from the equation, $\ln(A_\infty - A_t) = -k_{obs}t + c$. Correlation coefficients of the linear regressions were usually higher than 0.9995. In Figure 1 are graphically demonstrated the dependence of k_{obs} on the concentrations of MO_4^{2-} for the hydrolysis of PNPA in aqueous phosphate buffer (pH = 8.00) at 35.0 ± 0.1 °C. The corresponding plots for the hydrolysis of PNPDPP are illustrated in Figure 2. The second-order rate constants k_2 were calculated from the slope of the linear plots in

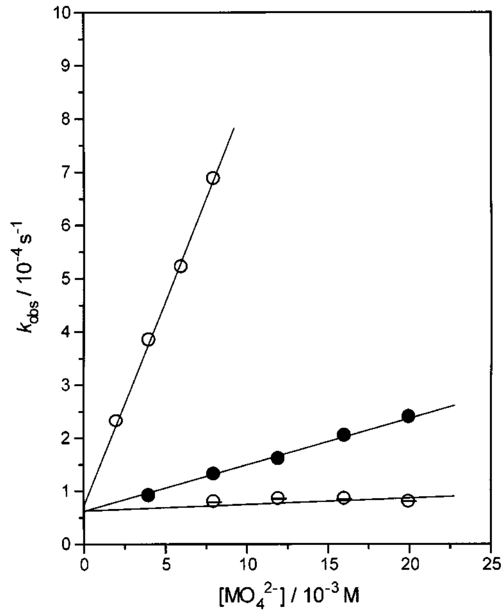


Figure 1. Plots showing dependence of k_{obs} on the concentration of MO_4^{2-} for the hydrolysis of PNPA with the MO_4^{2-} species in phosphate buffer (pH = 8.00) at 35.0 °C. M = Cr (○); M = Mo (●); M = W (⊖).

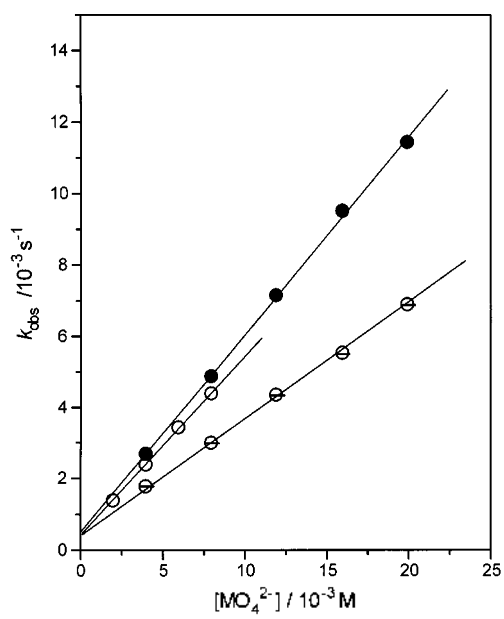


Figure 2. Plots showing dependence of k_{obs} on the concentration of MO_4^{2-} for the hydrolysis of PNPDPP with the MO_4^{2-} species in phosphate buffer (pH = 8.00) at 35.0 °C. M = Cr (○); M = Mo (●); M = W (⊖).

Figures 1 and 2. Four or five different concentrations of MO_4^{2-} were used to calculate second-order rate constants. The second-order rate constants obtained in this way are summarized in Table 1. The second-order rate constants for the reaction of a series of aryloxides with PNPA and PNPDPP are also summarized in Table 2 for a comparison purpose.

Table 1. Summary of the second-order rate constants for the hydrolysis of PNPA and PNPDPP with the MO_4^{2-} species in phosphate buffer (pH = 8.00) at 35.0 ± 0.1 °C

	MO_4^{2-}	pK_a (MO_4H^-)[a]	k_2, $M^{-1}s^{-1}$	
			PNPA	PNPDPP
1	WO_4^{2-}	3.7	4.29×10^{-5}	0.318
2	MoO_4^{2-}	4.1	9.22×10^{-3}	0.553
3	CrO_4^{2-}	6.49	7.55×10^{-2}	0.503

[a]pK_a data taken from reference 13.

Table 2. Summary of the second-order rate constants for the reaction of PNPA and PNPDPP with a series of aryloxides in H_2O at 25.0 °C

	X-C_6H_4O	pK_a(ArOH)	k_2, $M^{-1}s^{-1}$	
			PNPA[a]	PNPDPP[b]
4	4-CNC_6H_4O	7.73	0.030	–
5	4-ClC_6H_4O	9.35	0.685	0.341
6	C_6H_5O	9.95	1.13	–
7	4-MeC_6H_4O	10.07	2.13	–

[a]Data taken from reference 15a. [b]Data taken from reference 16b

Discussion

The effect of solvation on catalytic effect. As shown in Figures 1 and 2, the magnitude of k_{obs} values increases linearly with increasing the concentration of MO_4^{2-}. However, the k_{obs} value for the reaction of PNPA with WO_4^{2-} remains almost constant upon increasing the concentration of WO_4^{2-}, indicating that the catalytic effect of WO_4^{2-} in the hydrolysis reaction of PNPA is nearly negligible.

Byers found that MoO_4^{2-} is 170 times more reactive than a phosphate dianion having similar basicity in the hydrolysis of PNPA.[9] Since MoO_4^{2-} is larger (Mo-O bond length = 1.82 Å) than phosphate dianion (P-O bond length = 1.54 Å),[9] solvation by H_2O molecules would be less significant for MoO_4^{2-} than for phosphate dianion. Therefore, solvation effect was suggested to be responsible for the high reactivity of MoO_4^{2-} over phosphate dianion in the hydrolysis of PNPA.[9]

As shown in Table 1, CrO_4^{2-} exerts the highest catalytic effect, while WO_4^{2-} exhibits nearly negligible catalytic effect in the hydrolysis of PNPA. The electronegativity of the central metal is not much different (*e.g.*, 1.56, 1.30 and 1.40 for Cr, Mo and W, respectively).[11] However, the size of MO_4^{2-} increases in the order $CrO_4^{2-} < MoO_4^{2-} \approx WO_4^{2-}$.[12] Therefore, solvation of the MO_4^{2-} species in H_2O would be most significant for CrO_4^{2-}. If solvation effect is the solely important factor, one would expect that CrO_4^{2-} shows the lowest reactivity among the three MO_4^{2-} species. However, in fact, CrO_4^{2-} is most reactive, while WO_4^{2-} exhibits almost no catalytic effect in the hydrolysis of PNPA. Therefore, solvation effect is not considered to be solely responsible for the catalytic effect of the MO_4^{2-} species in the hydrolysis reaction of PNPA.

The effect of basicity on catalytic effect. It is well known that nucleophilicity is proportional to the basicity of nucleophiles. As shown in Table 1, WO_4^{2-} is least basic (pK_a = 3.7)[13] and least reactive, while CrO_4^{2-} is most basic (pK_a = 6.49)[13] and most reactive toward PNPA. Therefore, one might suggest that the low basicity of WO_4^{2-} is responsible for its low reactivity in the hydrolysis of PNPA. In order to correlate the effect of basicity on catalytic effect, a Brønsted-type plot has been constructed in Figure 3 for the reaction of PNPA with a series of aryloxides and the MO_4^{2-} species. Interestingly, as shown in Figure 3, the point for WO_4^{2-} lies on the same line consisted of the aryloxides. Such a linear Brønsted-type plot would indicate that the transition state structure for the reaction of PNPA with aryloxides and WO_4^{2-} is similar. However, the two points for CrO_4^{2-} and MoO_4^{2-} show significant positive deviations from the linearity, indicating that the transition state for the reaction of PNPA with CrO_4^{2-} and MoO_4^{2-} is different from the one with WO_4^{2-}. Therefore, it is clear that the high reactivity shown by CrO_4^{2-} and MoO_4^{2-} can not be attributed to their high basicity.

One can also see a poor correlation between the basicity of MO_4^{2-} and catalytic effect on the hydrolysis of PNPDPP with the MO_4^{2-} species. As shown in Table 1, the more basic CrO_4^{2-} is less reactive than the less basic MoO_4^{2-} in the reaction with PNPDPP. Furthermore, as shown in Tables 1 and 2, WO_4^{2-} is nearly as reactive as CrO_4^{2-} and 4-$ClC_6H_4O^-$, although WO_4^{2-} is less basic than CrO_4^{2-} and 4-$ClC_6H_4O^-$ by *ca.* 2.8 and 5.6 pK_a units, respectively. Therefore, one can suggest that basicity alone can not be responsible for the high catalytic effect shown by the MO_4^{2-} species in the hydrolysis reaction of PNPA and PNPDPP.

The effect of chelation on catalytic effect. Nucleophilic substitution reactions of esters of various types have been intensively investigated due to importance in organic chemistry as well as in biochemistry.[1-5,14,15] It has been well understood that reactions of esters with amines proceed through an addition intermediate, and the rate-determining step is dependent on the basicity of the leaving group and the incoming amine.[2-4,14] However, reactions of esters with oxyanionic nucleophiles have not completely been understood but have been remained under a subject of controversy.[3,5,15] For example, Williams *et al.* concluded that the reaction of PNPA with aryloxides proceeds through a concerted mechanism,[3,5] while Buncel *et al.* suggested a stepwise mechanism for reactions of anionic nucleophiles with PNPA and related esters.[15] Byers reported that hydrolysis of PNPA catalyzed by MoO_4^{2-} proceeds through an addition intermediate which hydrolyzes spontaneously.[10] The rate-determining step was suggested to be the attack of MoO_4^{2-} on the basis of solvent kinetic isotope effect of unit.[10] Since the central metal of the MO_4^{2-} species in the present system could serve as an electrophilic catalyst, a chelate like II would be possible. The chelate II would stabilize the tetrahedral addition intermediate I. Therefore, Byers once suggested that a chelating effect would be responsible for the high catalytic effect shown by MoO_4^{2-} in the hydrolysis of PNPA.[9,10] However, Byers found that the hydrolysis of 2,4-dinitrofluorobenzene proceeds 1300 times faster in the presence of 0.5 M MoO_4^{2-} than in

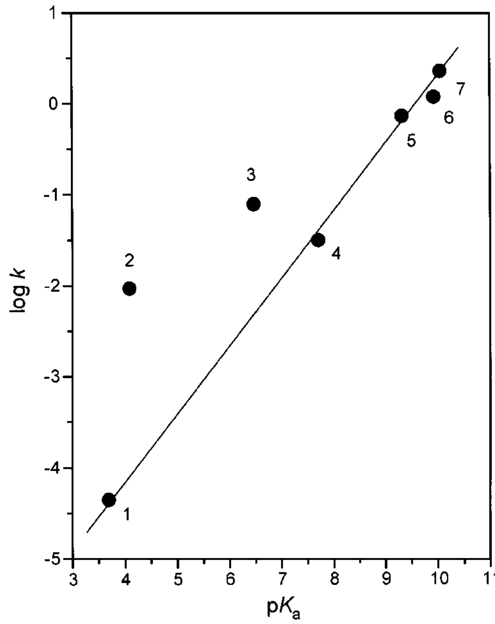
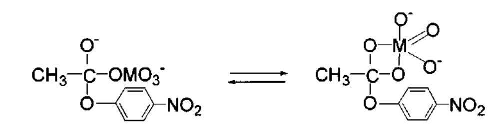


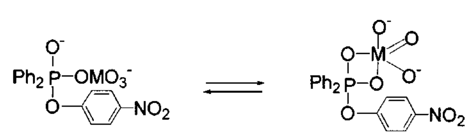
Figure 3. A Brønsted-type plot for the reaction of PNPA with a series of aryloxides and the MO_4^{2-} species. The numbers on the plot refer to the nucleophiles in Tables 1 and 2.

the absence of MoO_4^{2-}.[10] Since chelation is not possible in the reaction of 2,4-dinitrofluorobenzene with MoO_4^{2-}, the chelate like II was ruled out in the hydrolysis of PNPA with MoO_4^{2-}.[10]



I II

One can find from Table 1 that the catalytic effect of MO_4^{2-} is more significant for the reaction with PNPDPP than with PNPA, *i.e.*, WO_4^{2-}, MoO_4^{2-} and CrO_4^{2-} are 7400, 60 and 6.6 times more reactive toward PNPDPP than toward PNPA, respectively. One might consider that PNPDPP is intrinsically more reactive than PNPA toward anionic nucleophiles. However, as shown in Table 2, PNPDPP is less reactive than PNPA toward 4-$ClC_6H_4O^-$ anion. Besides, PNPDPP has been also reported to be less reactive than PNPA toward 2,3-butanedione monoximate anion.[16] Therefore, one can conclude that PNPDPP is not intrinsically more reactive than PNPA. Then, why does PNPDPP show higher reactivity than PNPA toward these MO_4^{2-} species? Extra stabilization such as chelation IV is considered to be responsible for the higher reactivity shown by these MO_4^{2-} species toward PNPDPP than toward PNPA.



III IV

One can expect that the bond length of M-O should be similar to that of C-O or P-O in order to form strong chelation like II or IV. The bond length of C-O and P-O has been reported to be 1.42 and 1.54 Å respectively, while that of Cr-O, Mo-O and W-O has been reported to be 1.57, 1.82 and 1.81 Å, respectively.[12] The difference in the bond length between C-O and M-O is much larger than the one between P-O and M-O. Therefore, one can expect that the chelation IV would be more favorable than the chelation II. This is consistent with the fact that the catalytic effect is much larger in the hydrolysis of PNPDPP than in the hydrolysis of PNPA as shown in Table 1.

Experimental Section

Material. PNPA and PNPDPP were easily prepared from the reaction of *p*-nitrophenol with acetyl chloride and with diphenylphosphinyl chloride in anhydrous ether in the presence of triethylamine. Their purity was checked by means of melting ponts and spectral data such as IR and ^{1}H NMR characteristics. Other chemicals used were of the highest quality available and used without further purification. Doubly glass distilled water was further boiled and cooled under nitrogen just before use. The buffer solution (pH = 8.00 ± 0.02) was made of 0.1 M NaOH and 0.1 M Na_2HPO_4 solutions. The stock solution of MO_4^{2-} was made by dissolving calculated amount of Na_2MO_4 in the 0.1M phosphate buffer solution of pH 8.00.

Kinetics. The pH measurement was done using an Orion Research Digital Analyzer/501 and the kinetic study was performed using a Hitachi U-3210 UV-vis spectrophotometer equipped with a Leslab RTE-110 constant temperature circulating bath to keep the reaction mixture at 35.0 ± 0.1 °C. All the kinetic studies were performed under pseudo-first order conditions in which the concentration of MO_4^{2-} is much greater (at least 20 times) than that of the substrate. No evidence for accumulation of the addition intermediate was found during the hydrolysis reaction, indicating that the intermediate hydrolyzes spontaneously. The reactions were followed by monitoring the appearance of *p*-nitrophenoxide at 400 nm for the reactions with MoO_4^{2-} and WO_4^{2-}, and at 450 nm for the reaction with CrO_4^{2-} in order to avoid the absorption by CrO_4^{2-}. All the solutions were prepared just before use and transferred by Hamilton gas tight syringes. Other details in kinetic experiments were reported previously.[16]

Conclusions

The present MO_4^{2-} species exhibit large catalytic effect in the hydrolysis of PNPA and PNPDPP in pH 8.00 phosphate buffer solution except WO_4^{2-} in the reaction with PNPA. The catalytic effect is more significant in the hydrolysis of PNPDPP than in the hydrolysis of PNPA. The effect of solvation and basicity on the catalytic effect would be important, however, solvation or basicity alone can not be responsible for the catalytic effect. The electrophilic catalysis by the central metal of MO_4^{2-} to form a chelate II or IV is considered to be also responsible for the catalytic effect in the hydrolysis reactions of PNPA and PNPDPP with the MO_4^{2-} species.

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