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REGULARITY OF THE OXIDIZING ACTIVITY OF Mo^{6+} IONS IN VARIOUS 12-HETEROPOLYMOLYBDATES*

Masamichi AKIMOTO, Yoshitaka TSUCHIDA, and Etsuro ECHIGOYA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The oxidizing activity of Mo^{6+} ions in 12-heteropolymolybdates was found to correlate with the electronegativity of counter ion (H^+, alkali, and alkali-earth metal ions) as well as of hetero atom (P^{5+}, As^{5+}, and Si^{4+}).

Heteropoly acids and their salts function not only as acidic catalysts but also as active and selective catalysts in the oxidation of hydrocarbons.[1] Although various heteropoly compounds, especially 12-heteropolymolybdates containing various kinds of counter ions and hetero atoms, are often found as catalysts for vapor-phase oxidation of methacrolein, and isobutyric acid,[1,2] the effect of these catalyst components on the catalytic activity and selectivity of oxidation reactions are not evidently understood. In this paper, we tried to measure the oxidizing activity of Mo^{6+} ions in various 12-heteropolymolybdates and found such regularity as described above.

Guaranteed reagent grade 12-molybdophosphoric acid($H_3PMo_{12}O_{40}$, abbreviated as H_3P, P = Keggin unit, i.e, $PMo_{12}O_{40}$) was purchased from Kanto Chemical Co., Inc.. Its alkali, and alkali-earth metal salts, and 12-molybdosilicic acid(H_4Si) were prepared according to the methods reported.[3,4] Ammonium 12-molybdophosphate(NH_4P) and 12-molybdoarsenate(NH_4As) were prepared from ammonium paramolybdate and H_3PO_4 or H_3AsO_4, respectively.[5] These heteropolymolybdates were then calcined at 300°C in air for 3 hr. ESR measurements were carried out at room temperature with a JEOL JES-PE type spectrometer operating in the X band, 100 kHz of modulation frequency being adopted. The g values of paramagnetic species and radical concentrations were determined by use of 2,2-diphenyl-1-picrylhydrazyl. Solutions of various aromatic hydrocarbons in dehydrated n-hexane were prepared at 1/10 - 1/50 molar concentrations.

Table 1 summarizes the concentration of Mo^{5+} ions formed on the reaction of H_3P, its alkali, and alkali-earth metal salts with aromatic hydrocarbons. The samples (100 mg in 3-mm I.D. quartz tubes) were first dehydrated by heating in flowing dried air at 250°C for 3 hr, and approximately 800 μl of the appropriate solution was injected at room temperature. After purging with nitrogen, the tubes were sealed with glass caps and were kept for 20 hr at room temperature. Although the dehydrated samples remained yellow, a small amount of Mo^{5+} ions up to 0.1×10^3 $Gauss^2\cdot mm^2/cm$ Mn was found in those suspended in n-hexane. The Mo^{5+} concentrations listed in Table 1 are thus corrected values. The Mo^{5+} ions formed in H_3P had g value of 1.952 - 1.955, and 9.63×10^3 peak area units correspond to the formation of one Mo^{5+} ion per 400 Keggin units(H_3P - pyrene). Comparison of the Mo^{5+} concentrations between different salts

Table 1 Formation of Mo^{5+} on the reaction of 12-molybdophosphates with various aromatic hydrocarbons[a]

Catalyst	Surface area (m^2/g)	E.N. of counter ion[b]	Peak area of Mo^{5+}($Gauss^2 \cdot mm^2$/cm Mn) $\times 10^{-3}$ [d]				
			Benzene 9.43-9.52[c]	o-Xylene 8.56	Naphthalene 8.10	Anthracene 7.58	Pyrene 7.55
H_3P	5.6	2.1	0.15	1.79	4.58	8.27	9.63
NaH_2P	2.2	---	0.04	1.06	3.12	4.53	4.35
Na_2HP	3.6	---	0.32	1.23	1.09	2.70	2.97
Na_3P	5.8	0.9	Neg[e]	0.02	0.90	1.80	2.87
Li_3P	3.4	1.0	1.13	0.05	1.50	13.55	18.95
K_3P	111.8	0.8	Neg	Neg	0.10	4.08	2.05
Rb_3P	163.7	0.8	Neg	Neg	0.10	7.09	2.91
Cs_3P	129.9	0.7	Neg	Neg	0.05	4.50	2.68
$Ca_{1.5}P$	0.1	1.0	0.12(0.02)[f]	0.65(0.01)	0.43(0.64)	0.76(0.21)	1.23(0.59)
$Mg_{1.5}P$	0.1	1.2	Neg(Neg)	0.19(0.08)	0.86(0.87)	0.52(0.70)	0.62(1.26)
$Sr_{1.5}P$	0.5	1.0	Neg(Neg)	0.40(0.02)	0.10(0.07)	0.57(0.69)	0.83(0.67)
$Ba_{1.5}P$	1.7	0.9	Neg(Neg)	1.02(0.03)	2.11(0.80)	3.30(0.66)	4.53(1.65)

[a] Catalyst:100 mg. [b] Pauling's electronegativity. [c] Ionization potential(eV). [d] 1×10^3 $Gauss^2 \cdot mm^2$/cm Mn $=8.5\times10^{15}$ spins. [e] Negligible. [f] Peak area of aromatic radicals.

is not always meaningful because the concentration is affected not only by the oxidizing activity of Mo^{6+} ions as well as by the electron-donating nature of adsorbing molecules but also by the size of adsorbing molecules,the surface area and pore-size distribution of these salts. Nevertheless,it is worthwhile to note that the concentration decreased roughly with decreasing electronegativity of counter ion and with increasing ionization potential of adsorbing molecules. The low concentrations observed on contact of K_3P,Rb_3P,and Cs_3P with pyrene molecules may be attributed to size effect. At any rate,it can be reasonably but qualitatively said that Mo^{6+} ions have high oxidizing activity when they are able to oxidize hydrocarbon molecules of a low electron-donating nature or a high ionization potential. As shown in Table 1,the Mo^{6+} ions in H_3P,NaH_2P,Na_2HP,and Li_3P are able to oxidize benzene molecules whereas those in Na_3P can not oxidize benzene but are able to oxidize o-xylene. Similarly,the Mo^{6+} ions in K_3P,Rb_3P,and Cs_3P can not oxidize benzene and o-xylene molecules but are able to oxidize naphthalene. Thus,it is to be noted that the oxidizing activity of Mo^{6+} ions decreased with decreasing electronegativity of counter ion. This is also the case with the alkali-earth metal salts(Table 1). However,$Ca_{1.5}P$ showed higher oxidizing activity than $Mg_{1.5}P$ though Pauling's electronegativity follows the order Ca < Mg. This may be attributed to the higher electronegativity of Ca^{2+} ions than Mg^{2+} as estimated from their heats of formation of oxide(151.7 kcal/g-mol for CaO and 143.8 kcal/g-mol for MgO).

Formation of Mo^{5+} ions upon contact of the 12-molybdophosphates with these aromatic hydrocarbons was always accompanied by that of positive hydrocarbon radical ions. The ESR spectra of the latter paramagnetic species were symmetrical and sharp,the g value ranging from 2.002 to 2.003 and the peak to peak width from 4.2 to 9.4 Gauss, characteristic of aromatic radical cations.6) Their radical concentrations agreed fairly well with those of Mo^{5+} ions, especially at relatively high concentrations, as illustrated in the case of the alkali-earth metal salts(Table 1). The radical concentration in this kind of system was shown to increase exponentially with decreasing ionization potential of aromatic hydrocarbon molecule.7) In the present work, however, such a clear relationship was not observed.

The oxidizing activity of Mo^{6+} ions was also qualitatively evaluated by the reaction of gaseous oxygen with Mo^{5+} ions. The samples(100 mg in 3-mm I.D. quartz tubes) were reduced with 30 Torr hydrogen at 300°C for 1 hr and were then evacuated for 30 min at the same temperature. After the concentration of Mo^{5+} ions(C_0, number of Mo^{5+} ions formed per 100 Keggin units) was determined, gaseous oxygen was introduced at 25 Torr at room temperature and the samples were then heated for 30 min at various temperatures(Fig.1 and Table 2). The Mo^{5+} ions formed in H_3P were hardly oxidized even at 250°C, but 20.3% and 67.0% of them were oxidized at 300°C and 330°C, respectively. Although the initial radical concentration decreased when H^+ of H_3P was step by step substituted by less electronegative Na^+ ion(C_0 = 4.0 for NaH_2P, and 2.2 for Na_2HP), the reactivity of Mo^{5+} ions to gaseous oxygen rather increased: 53.5%, 57.8%, and 97.1% of the initial Mo^{5+} ions in NaH_2P, Na_2HP, and Na_3P were oxidized at 300°C, respectively. It is to be noted that the temperature, at which the reaction was initiated, decreased in a drastic manner with decreasing electronegativity of counter ion though the initial concentration did not vary widely(Fig.1). This is also the case with the alkali-earth metal salts. However the Mo^{5+} ions in these salts were not so easily oxidized as those in the tri alkali metal salts. The reaction became observable at 200°C, but 22.5% - 54.1% of the initial Mo^{5+} ions remained unoxidized at 330°C(Table 2).

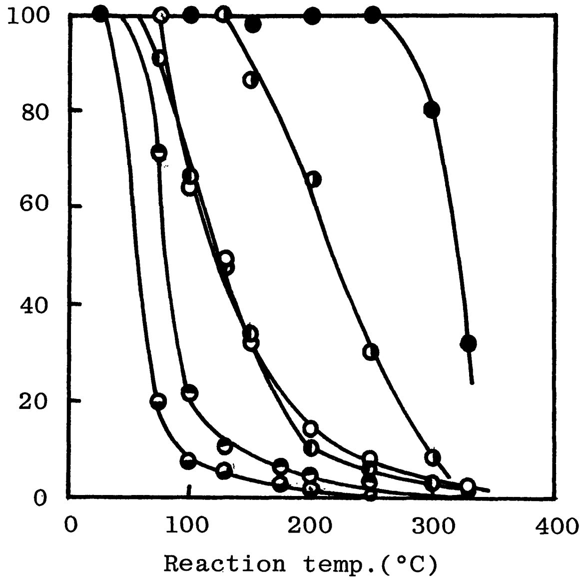

Fig.1 Reaction of Mo^{5+} with O_2 formed in H_3P, and its tri alkali metal salts
●: H_3P(C_0 =9.5), ◑: Li_3P(0.17), ○: Na_3P(1.2), ◐: K_3P(1.5), ◓: Rb_3P(1.2), ◒: Cs_3P(1.6)

Table 2 Reaction of Mo^{5+} with O_2 formed in the alkali-earth metal salts

Catalyst	C_0	Mo^{5+}(%) oxidized at			
		200°C	250°C	300°C	330°C
$Ca_{1.5}P$	1.6	4.2	15.0	30.8	45.9
$Mg_{1.5}P$	2.6	7.4	23.3	42.2	59.7
$Sr_{1.5}P$	0.88	2.2	23.0	50.9	74.5
$Ba_{1.5}P$	0.74	14.6	29.0	57.5	77.5

It was already reported that oxidation of Mo^{5+} ions to Mo^{6+} by gaseous oxygen at the surface of previously reduced MoO_3 proceeds with accompanying formation of adsorbed oxygen species, O_2^- and O^-: $O_2(gas) \rightarrow O_2^- \rightarrow O^- \rightarrow O^{2-}(lattice)$.8) In the present case, however, no formation of such negatively charged adsorbed oxygen species was observed by means of ESR even at 77°K and at temperatures at which the oxidation took place. This indicates that the activation energy is the highest for the formation of O_2^- through donation of an electron from Mo^{5+} ion to diatomic oxygen molecule, formed O_2^- being then converted rapidly to lattice oxygen O^{2-} via O^-. In another words, the oxidation of Mo^{5+} ions is decisively affected by their electron-donating nature in the case of 12-heteropolymolybdates. Comparing this with the result of Fig.1, it is not unreasonable to believe that the electron-donating nature of Mo^{5+} ions to oxygen formed in these 12-molybdophosphates is relatively high when the electronegativity of counter ion is low. As the oxidizing activity of Mo^{6+} ions will be inversely proportional to the electron-donating nature of Mo^{5+} ions in the reduced salts, the result of Fig.1 and Table 2 well agrees with that of Table 1.

Table 3 Reaction of Mo^{5+} with O_2 formed in various 12-heteropolymolybdates

Catalyst	Surface area (m^2/g)	E.N. of hetero atom[a]	C_0	Mo^{5+}(%) oxidized at 75°C	100°C	130°C	175°C	200°C	300°C
H_3P	5.6	2.1	9.5	Neg	Neg	Neg	Neg	Neg	20.3
H_4Si	3.2	1.8	2.9	6.8	6.7	16.1	26.6	36.6	81.6[b]
NH_4P	34.7	2.1	3.0[c]	Neg	32.0	59.6	70.6	86.0	95.1
NH_4As	23.6	2.0	0.76[c]	26.4	44.5	---[d]	---	---	---

[a] Pauling's electronegativity. [b] 290°C. [c] Calculated assuming formation of tri ammonium salt. [d] ESR spectrum broadened.

In the case of H_4Si, the oxidation of Mo^{5+} ions proceeded even at 75 - 100°C; approximately 7% and 16.1% of them were oxidized at 100°C and 130°C, respectively. This is in contrast to the case with H_3P. Similarly, the Mo^{5+} ions in NH_4As were more easily oxidized than those in NH_4P (Table 3). Decomposition of H_4Si during the reaction was negligible because almost portion of acid reoxidized at 290°C was dissolved in water. Thus, the oxidizing activity of Mo^{6+} ions is also correlated with the electronegativity of hetero atom and will follow the order of hetero atom, $Si^{4+} < As^{5+} < P^{5+}$. This is an increasing order of the electronegativity of hetero atom. Therefore, it is believed that the oxidizing activity of Mo^{6+} ions parallels with the electronegativity of counter ion as well as of hetero atom in 12-heteropolymolybdates.

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