CHEMISTRY LETTERS, pp. 1759-1762, 1981.

IR AND X-RAY DIFFRACTION STUDIES ON AMMONIUM SALTS OBTAINED FROM ELECTROLYTICALLY REDUCED 12-HETEROPOLYMOLYBDATE ANIONS*

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The intensities of IR bands due to the heteroatom - oxygen (P-O and Si-O) and the bridged lattice oxygen(Mo-O-Mo) in 12-heteropolymolybdate anions decreased markedly upon formation of Mo^{5+} without any elimination of their lattice oxygen. The significance of this finding in relation to the previously proposed mechanisms for the reduction of 12-molybdophosphoric acid and its salts is discussed.

The change in IR spectra of 12-molybdophosphoric acid and its salts as heterogeneous oxidation catalysts upon reduction by hydrogen has been discussed in relation to the mechanism for the reduction of these heteropoly compounds and, basing on the observed relative decrease in the intensity of IR bands due to the terminal(Mo=O) and the bridged lattice oxygen(Mo-O-Mo), the preferential elimination of the bridged lattice oxygen than the terminal one upon reduction by hydrogen has been proposed.[1-4] However, this proposal is in contrast to the mechanism of the reduction for usual MoO_3 and its related compounds in which the preferential elimination of the terminal lattice oxygen had been shown.[5-8] Additionally, there are a few papers suggesting the participation of the terminal lattice oxygen in the catalytic oxidation of hydrocarbons over 12-molybdophosphoric acid and its ammonium salt on the basis of the formation of maleic anhydride from butadiene.[9] On the other hand, the reason for the remarkable decrease in the intensity of the IR band at 1060 cm^{-1} (ν[P-O]) upon reduction by hydrogen still remains unknown although this decrease was suggested to be due to the lower symmetry of 12-molybdophosphate anions caused by the elimination of the bridged lattice oxygen.[3] Thus, the change in IR spectrum of 12-molybdophosphate anions upon reduction by hydrogen is not clearly understood even now. Then, we prepared ammonium salts of electrolytically reduced 12-heteropolymolybdic acids and studied the effect of formation of Mo^{5+} (without any elimination of the lattice oxygen) on the IR spectra of 12-heteropolymolybdate anions.

Guaranteed reagent grade 12-molybdophosphoric acid, $H_3[PMo_{12}O_{40}]$, and 12-molybdosilicic acid, $H_4[SiMo_{12}O_{40}]$, were the same as those used in our previous paper.[10] The electrolytically reduced 12-heteropolymolybdate anions were prepared following the procedure of M.T.Pope et al.[11] That is, a solution of about 2 g of 12-heteropolymolybdic acid in 10 ml of 0.5 M sulfuric acid was electrolyzed at a platinum plate cathode in a conventional H cell at room temperature. The catholyte was stirred by a current of purified argon and was separated from the anolyte(0.5 M sulfuric acid) by fritted glass. Reduction was carried out by means of controlled-current electro-

lysis,in which the cathode potential was always kept above -0.05 V ($H_3[PMo_{12}O_{40}]$) and +0.04 V ($H_4[SiMo_{12}O_{40}]$) vs. sce,respectively,to avoid the decomposition of 12-heteropolymolybdate anions. When the solution had been electrolyzed to the desired extent, the reduced 12-heteropolymolybdate anions formed were precipitated as ammonium salts by addition of about 3 g of ammonium chloride. The precipitated ammonium salts were filtered and washed with water and then dried over silica gel under vacuum at room temperature. IR spectrum was measured by KBr disk method. Molybdenum and silicon were determined by atomic absorption. Phosphorus was determined by the method reported.[12)]

The ammonium salts precipitated from non-reduced(A and D) and electrolytically reduced 12-heteropolymolybdate anions(B,C,and E) are formulated as follows;

$(NH_4)_3[PMo(VI)_{12}O_{40}]\cdot 3.2H_2O$ (A)
$(NH_4)_3H_2[PMo(V)_2Mo(VI)_{10}O_{40}]\cdot 1.4H_2O$ (B)
$(NH_4)_3H_4[PMo(V)_4Mo(VI)_8O_{40}]\cdot 1.5H_2O$ (C)
$(NH_4)_3H[SiMo(VI)_{12}O_{40}]\cdot 3.4H_2O$ (D)
$(NH_4)_3H_3[SiMo(V)_2Mo(VI)_{10}O_{40}]\cdot 3.0H_2O$ (E)

their analytical data being given in Table 1.

Table 1 Analytical Data

Ammonium salt	Number of electrons injected/KU	Found (wt%)					Calcd (wt%)				
		P	Si	Mo	N	H	P	Si	Mo	N	H
A	0	1.62	---	58.8	2.32	0.98	1.60	---	59.5	2.17	0.95
B	2	1.61	---	60.9	2.21	0.88	1.63	---	60.5	2.21	0.88
C	4	1.65	---	59.4	2.12	1.02	1.62	---	60.4	2.20	1.01
D	0	---	1.42	59.4	2.35	1.02	---	1.45	59.5	2.17	1.03
E	2	---	1.45	59.7	2.34	1.01	---	1.46	59.6	2.18	1.10

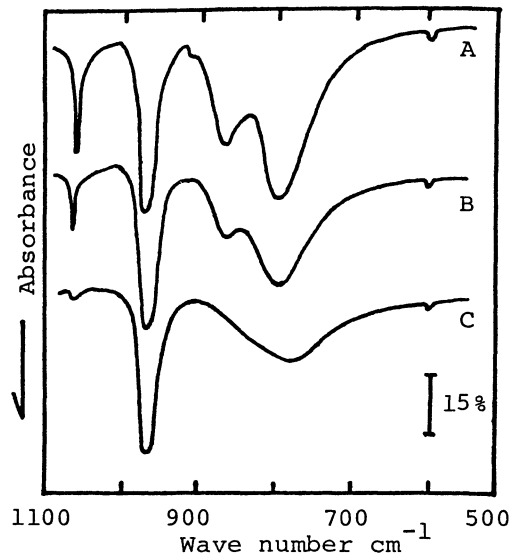

Fig.1 IR spectra of ammonium 12-molybdophosphates. ν[P-O]:1063cm^{-1}, ν[Mo=O]:963cm^{-1},ν[Mo-O-Mo]:868,795 cm^{-1}, δ[O-P-O]:595cm^{-1}

The IR spectra of these ammonium 12-heteropolymolybdates are shown in Figs. 1 and 2 , below which the assignment of each band following Ref(13) is also shown. When 12-molybdophosphate anions were subjected to the first two-electron reduction,the intensities of the P-O and the Mo-O-Mo bands decreased to 60 and 70% of the initial levels,respectively,whereas the intensity of the Mo=O band changed little. Frequency shift was observed for the Mo-O-Mo bands: 868 → 862 cm^{-1} and 795 → 790 cm^{-1} (Fig.1, A and B). This finding is very similar to the previously reported changes in the IR spectra of 12-molybdophosphoric acid and its trimetal salts upon reduction by hydrogen.[1-4)] The decrease in the intensity of these bands upon electrolytic reduction was much more obvious after the second two-electron reduction: both the P-O and the Mo-O-Mo(at 868 cm^{-1}) bands almost disappeared and the Mo-O-Mo band at 790 cm^{-1} further shifted to 780 cm^{-1}. Although the Mo=O

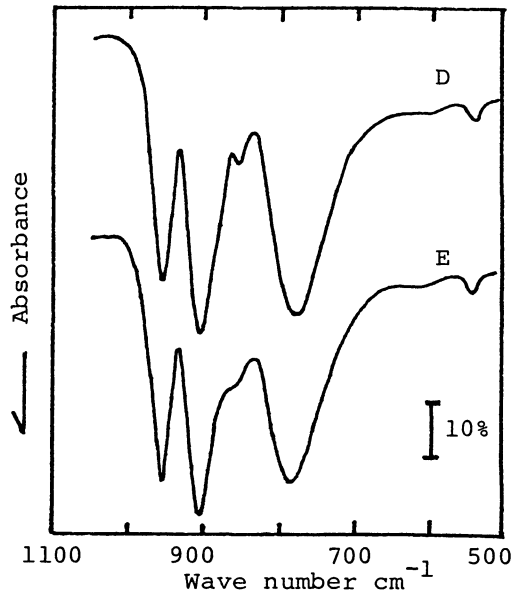

Fig.2 IR spectra of ammonium 12-molybdosilicates. ν[Si-O]:907 cm^{-1}, ν[Mo=O]:958 cm^{-1}, ν[Mo-O-Mo]:858,783 cm^{-1}, δ[O-Si-O]:540 cm^{-1}

band broadened a little,its intensity determined as peak area remained nearly unchanged(Fig.1,C).

Analogous behavior of IR spectrum upon electrolytic reduction was seen with 12-molybdosilicate anions. However, the change in the intensity of IR bands upon electrolytic reduction was not so drastic as the case of the phosphate analogues. That is,the intensities of the Si-O and the Mo-O-Mo bands decreased by about 5 and 20%,respectively,upon first two-electron reduction,and no remarkable frequency shift was observed(Fig.2).

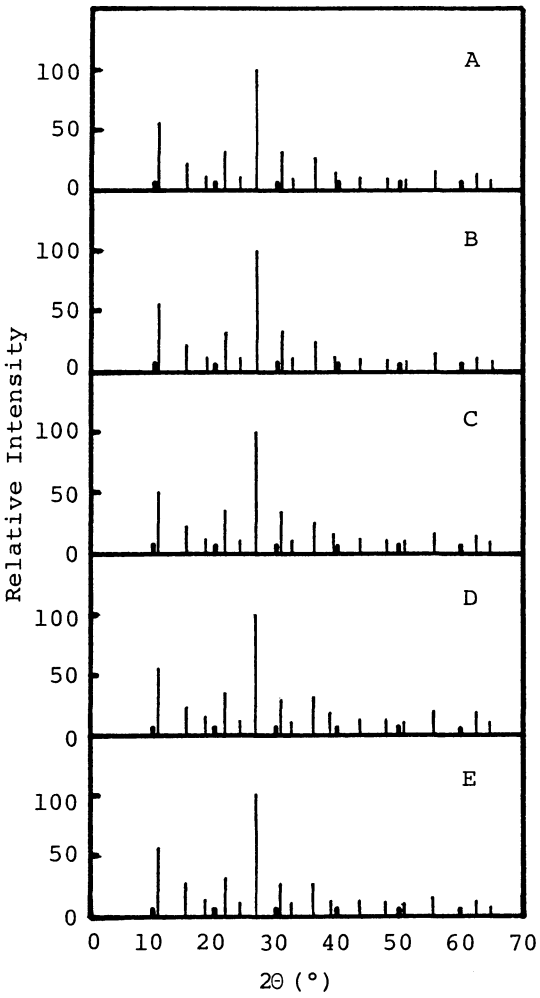

Fig.3 X-Ray diffraction patterns of ammonium 12-heteropolymolybdates. X-Ray: Cu-Kα. Filter: Ni

The X-ray diffraction patterns of these five triammonium salts were measured in order to confirm that no decomposition of the 12-heteropolymolybdate anions during the electrolytic reductions took place. The ammonium salts precipitated from non-reduced,two-,and four-electron reduced 12-molybdophosphate anions were highly crystalline: they showed nearly the same X-ray diffraction patterns at 2θ = 26.5°(strong), 10.7,15.2,21.5,30.6,and 36.1°(medium strong)(Fig.3,A,B,and C),characteristic of the ammonium salt,$(NH_4)_3[PMo(VI)_{12}O_{40}]$.[14] This was also the case with the silicate analogues: the ammonium salts precipitated from non-reduced and two-electron reduced 12-molybdosilicate anions showed nearly the same and sharp X-ray diffraction patterns at 2θ = 26.4°(strong),10.7,15.1,21.5,30.6,and 36.1°(medium strong)(Fig.3,D and E). The observation of nearly the same X-ray diffraction patterns for these five triammonium 12-heteropolymolybdates may be explained by the small difference in ionic radius between P^{5+}(~0.4Å) and Si^{4+}(0.39Å) and by the existance of nearly the same

number of crystal water in these triammonium salts as shown previously in this paper. At any rate,the result of X-ray diffraction analysis obtained in the present work indicates in accordance with the previous report[15] that no decomposition of 12-molybdophosphate anions and the silicate analogues took place when they were subjected to the electrolytic reductions mentioned above. Hence,it appears that the intensity of IR bands due to the heteroatom - oxygen(P-O and Si-O) and the bridged lattice oxygen in 12-heteropolymolybdate anions decreases upon formation of Mo^{5+} without any elimination of their lattice oxygen. This finding does not agree with the previous suggestion.[3] The effect of the protons in these ammonium salt molecules(B,C,D,and E) on the IR spectra of the 12-heteropolymolybdate anions seems negligible because these protons usually exist as hydrated ones[16] and because water might have additionally been absorbed into the ammonium salts during the IR experiments. Therefore,the observed decrease in the intensity of these IR bands upon electrolytic reduction(Figs.1 and 2) is presumably attributed to the lower symmetry of the 12-heteropolymolybdate anions caused by the formation of Mo^{5+}. The negligible change in the intensity of the Mo=O band upon electrolytic reduction(Figs.1 and 2) may be explained by the difference in vibrational mode between the Mo=O and the others. At any rate,the above finding made in the present work clearly shows that the intensity of the IR bands due to the bridged lattice oxygen decreases upon formation of Mo^{5+} without any elimination of this lattice oxygen. Therefore,we would like to point out the possibility that the roles of the bridged lattice oxygen in the reduction of 12-molybdophosphoric acid and its salts were overestimated in the previously proposed mechanisms of reduction.[1-4]

Acknowledgement The authors are greatly thankful to Prof.S.Aoyagui and Dr.K.Suga in Department of Chemical Engineering in Tokyo Institute of Technology for the use of a controlled-potential electrolyzer.

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(Received September 19, 1981)