Infrared Study of 12-Molybdophosphoric Acid Reduced by Organic Compounds

Tian-hsi Tsai, Ken-ichi Maruya,* Mamoru Ai, and Atsumu Ozaki
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

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Synopsis. Reaction of 12-molybdophosphoric acid with ethyl methyl ketone, crotonaldehyde, methacrylaldehyde, 1-butene, or 1,3-butadiene is enhanced by the presence of water, and leads to preferential decrease in ν(P–O) at 1060 cm^{-1} with preference over that in ν(Mo–O–Mo) at 880 cm^{-1}, while the reaction with methanol is not dependent on the presence of water and results in rapid disappearance of ν(Mo–O–Mo) and retention of ν(P–O).

The IR spectrum of 12-molybdophosphoric acid (HPA) shows four absorption bands at 1060, 960, 880, and 790 cm^{-1} for the stretching vibrations of the anion structure, which are assigned to ν(P–O), ν(Mo=O), and two ν(Mo–O–Mo), respectively.[1)] Tsuneki *et al.*[2)] examined H_2 reduction of trisilver 12-molybdophosphate, followed by reoxidation with $^{18}O_2$, by means of IR spectroscopy, and suggested that the oxygen removed by the reduction is not from P–O but from Mo–O–Mo, because the isotope shift associated with the reoxidation by $^{18}O_2$ was observed only for ν(Mo=O) and two ν(Mo–O–Mo)'s. In this paper, we report different behaviors of IR spectral changes in reduction of HPA with various organic compounds.

Experimental

HPA was purchased from Kanto Chemical Co. and used without further purification. Organic compounds were dried on anhydrous $CaSO_4$ or molecular sieve 5A and degassed by distillation *in vacuo*. The film of HPA was prepared as described previously.[3)] The film was placed in an IR cell connected with a closed circulating system and evacuated at room temperature for 5 min or at 130 °C for 2 h, after which the vapor of an organic compound with or without water was introduced into the cell. Since the volume of the cell was about 280 cm^3, the amounts of the compound and water were in a large excess over that of HPA (2—5 mg/cm^2).

Results and Discussion

Figure 1 shows IR spectra of HPA treated with ethyl methyl ketone. ν(P–O), ν(Mo–O–Mo)$_H$ (880 cm^{-1}), and ν(Mo–O–Mo)$_L$ (790 cm^{-1}) decrease with increase in reaction temperature. The decrease for the HPA preevacuated at lower temperatures is obviously much more eminent, indicating that the reduction of HPA is enhanced by the hydrated water.

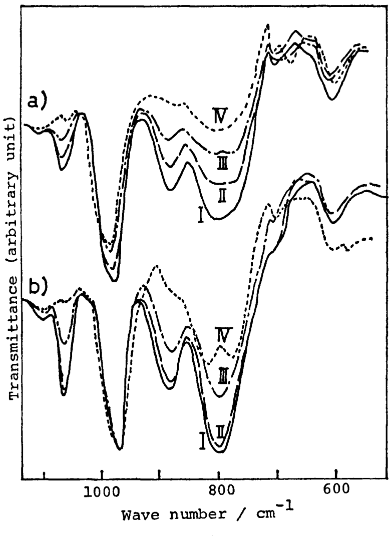

Fig. 1. IR spectra of HPA treated with ethyl methyl ketone (7 mmHg)† for 30 min. a) Preevacuated at 130 °C for 2 h and treated at I: room temp, II: 130 °C, III: 178 °C, and IV: 240 °C. b) Preevacuated at room temp for 5 min and treated at I: room temp, II: 50 °C, III: 90 °C, and IV: 125 °C.

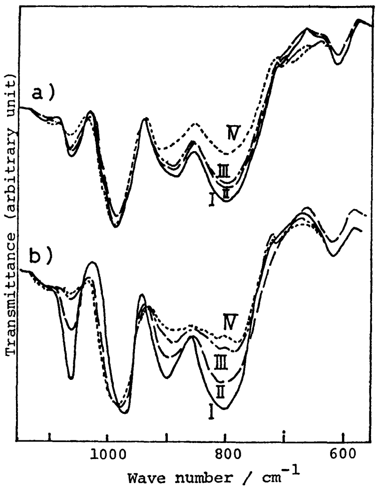

Fig. 2. IR spectra of HPA treated with 1-butene (7 mmHg) for 30 min. a) Preevacuated at 130 °C for 2 h and treated at I: room temp, II: 122 °C, III: 185 °C, and IV: 225 °C. b) Preevacuated at room temp for 5 min, after which water (4 mmHg) was added and treated at I: room temp, II: 124 °C, III: 175 °C, and IV: 220 °C.

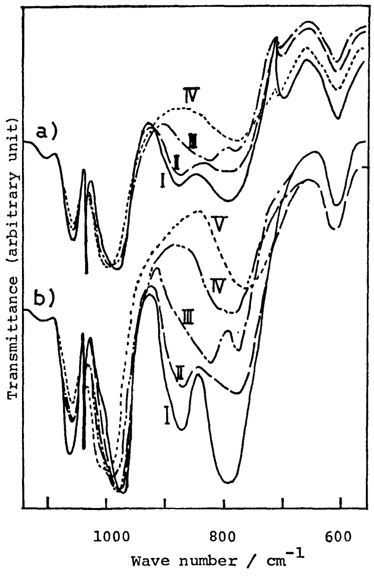

Fig. 3. IR spectra of HPA treated with methanol (4 mmHg) for 30 min. a) Preevacuated at 130 °C for 2 h and treated at I: room temp, II: 125 °C, III: 180 °C, and IV: 225 °C. b) Preevacuated at room temp for 5 min, after which water (4 mmHg) was added, and treated at I: room temp, II: 123 °C, III: 173 °C, IV: 210 °C, and V: 257 °C.

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† 1 mmHg≈133.322 Pa.

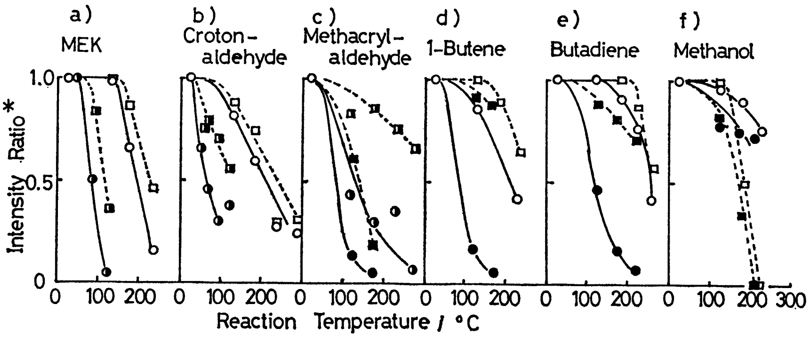

Fig. 4. Changes in peak intensity ratio.
*: $\log(I_0/I)_{\mathrm{react.\ temp}}/\log(I_0/I)_{\mathrm{room\ temp}}$ ○ (1060 cm^{-1}) and □ (880 cm^{-1}): evacuated at 130 °C for 2 h. (1060 cm^{-1}) and ◧ (880 cm^{-1}): evacuated at room temp for 5 min. ● (1060 cm^{-1}) and ■ (880 cm^{-1}): evacuated at room temp for 5 min, after which water (4 mmHg) was added.

The decreases in ν(P–O) and ν(Mo–O–Mo)$_H$ are nearly parallel to each other.

The same dependence on the coexistence of water vapor is found in the reaction with 1-butene, as shown in Fig. 2. The spectra shown in Fig. 2b display quicker decrease of ν(P–O) than that of ν(Mo–O–M)$_H$. On the other hand, the reaction with methanol results both in almost complete retention of the absorption of ν(P–O) and in disappearance of ν(Mo–O–Mo)$_H$, as shown in Fig. 3.

The change in both the bands obtained with the above three compounds is plainly plotted together with those obtained with crotonaldehyde, 1,3-butadiene, and methacrylaldehyde in Fig. 4, where it is assumed that either the preevacuation or the reaction conditions have no effect on ν(Mo=O) since the absorption seems to be always superposed as seen in Figs. 1, 2, and 3. Each spectrum is, therefore, normalized on the basis of the intensity of ν(Mo=O), and each change in absorption is represented as the ratio of intensity at a reaction temperature to that at room temperature. With 1-butene and 1,3-butadiene, the intensities of ν(P–O) decrease steeply with increase in reaction temperature, while the lowering of ν(Mo–O–Mo)$_H$ is very dull, the ratio remaining still more than 0.8 even at 170 °C. With ethyl methyl ketone and crotonaldehyde, too, the decrease in ν(P–O) always precedes that of ν(Mo–O–Mo)$_H$, although they seem to be nearly parallel. The behavior of the decrease in the two bands with methacrylaldehyde is similar to that with 1-butene in the absence of water and to that with ethyl methyl ketone in its presence. It was reported in our previous paper³⁾ that absorbed methacrylaldehyde could hardly reduce HPA with or without water at 180 °C, which should be revised. It is, therefore, obvious that the reaction of HPA with all the above five compounds, except methanol, is enhanced by the presence of water and gives rise to the preferential decrease in ν(P–O). The catalytic oxidation of the compounds by HPA is known to depend on the amount of water,⁴,⁵⁾ in conformity with the reduction of HPA. Thus, the lowering of ν(P–O) may be characteristic of reactions in which water participates.

On the other hand, the reaction with methanol results in the striking decrease in ν(Mo–O–Mo)$_H$ and the almost complete retention of ν(P–O), which seems to be much less affected by water as shown in Figs. 3 and 4f. The catalytic reaction by HPA to produce formaldehyde is not enhanced by water.⁵⁾ The decrease in ν(Mo–O–Mo)$_H$, therefore, may be attributed to the loss of oxygen in Mo–O–Mo.

The results of Fig. 4 show that there would be no appreciable interaction between ν(P–O) and ν(Mo–O–Mo)$_H$, indicating no fast oxygen exchange between them. In addition, the oxygen mixing between ν(Mo–O–Mo)$_H$ and ν(Mo–O–Mo)$_L$ appears to be very slow even at 257 °C, because the latter band remains while the former disappears, as shown in Figs. 2 and 3. In the reduced state, the latter band often splits into two bands at 825 and 780 cm^{-1}, and the splitting was observed both in the disappearance (Figs. 1 and 2) and in the retention (Fig. 3) of ν(P–O), indicating a very complicated behavior. At present, the relation between ν(Mo–O–Mo)$_L$ and the reduction of HPA is obscure. Katamura *et al.*⁶⁾ investigated the mechanism of the H_2 reduction of HPA and the interaction of water with it by means of TPD and IR measurements, suggesting that lower symmetry of the anion structure caused by the reduction may explain the change in IR spectra in the P–O region. It might, however, be suggested from no interaction between the bands that the decrease in ν(P–O) relates to loss of the bridged oxygen showing ν(Mo–O–Mo)$_L$ but not ν(Mo–O–Mo)$_H$, if Tsuneki's²⁾ and Katamura's⁶⁾ suggestions would be taken. Another interpretation might be loss of the oxygen in P–O, though there seems to be no change in the band at 610 cm^{-1} which is assigned to δ(O–P–O)²⁾ as shown in Figs. 1, 2, and 3.

References

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