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INFRARED STUDY OF CROTONALDEHYDE OXIDATION BY 12-MOLYBDOPHOSPHORIC ACID

Tian-hsi TSAI, Ken-ichi MARUYA, Mamoru AI, and Atsumu OZAKI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama 227

IR spectra of $H_3PMo_{12}O_{40}$ (HPA) with adsorbed crotonaldehyde disclosed that HPA is reduced by crotonaldehyde only in the presence of water, giving furan as the oxidation product. Water is evidentially involved in the reaction path of crotonaldehyde oxidation, being consistent with water-enhanced catalytic oxidation of crotonaldehyde on HPA.

It has been known that crotonaldehyde is selectively oxidized to furan on heteropoly acid (HPA) ($H_3PMo_{12}O_{40}$)$^{1)}$. The oxidation reaction is enhanced by the presence of water vapor, so that water is a necessary partner of the reaction. The role of water in the HPA-catalyzed oxidation of methacrylaldehyde has been discussed by Misono et al. in terms of a reaction mechanism, on the basis of ^{18}O exchange during the reaction$^{2)}$, although the mechanism might be different for crotonaldehyde. Thus the reaction of crotonaldehyde with HPA was examined varying the extent of hydration of HPA.

First, crotonaldehyde was added to an aqueous solution of HPA (0.02 mol/dm^3) and heated to 60 °C for 10 min. The reduction of HPA was obvious by color change of the solution from yellow to green and furan was detected in the gas phase above the solution, because of limited solubility of furan in water. Thus it is clear that crotonaldehyde is oxidized by HPA to give furan in the aqueous solution at as low as 60 °C.

The oxidation of crotonaldehyde was further studied with HPA supported on silicon plate monitoring the reaction with infrared absorption. Thin film of HPA was formed on the silicon plate by adding an aqueous solution of HPA followed by drying. The degree of loading was 2 to 5 mg/cm^2. The silicon plate was then placed in an IR cell with potassium bromide window. The measurement of IR absorption was always made with IRA-2 spectrometer at room temperature.

On introduction of crotonaldehyde over the HPA sample, four absorption peaks were observed at 1725, 1710, 1170 and 1135 cm^{-1} under an equilibrium pressure of 4 torr. Since CCl_4 solution of crotonaldehyde gives strong absorptions at 1698 cm^{-1} for C=O and 1145 cm^{-1} for C-C, the above absorptions may be ascribed to analogous bonds. On evacuation of gas phase for 30 min at room temperature, those bands disappeared, presumably because of desorption and/or removal from gas phase, except one at 1170 cm^{-1} (Fig.1 curve C). The HPA sample was then heated to 120 °C

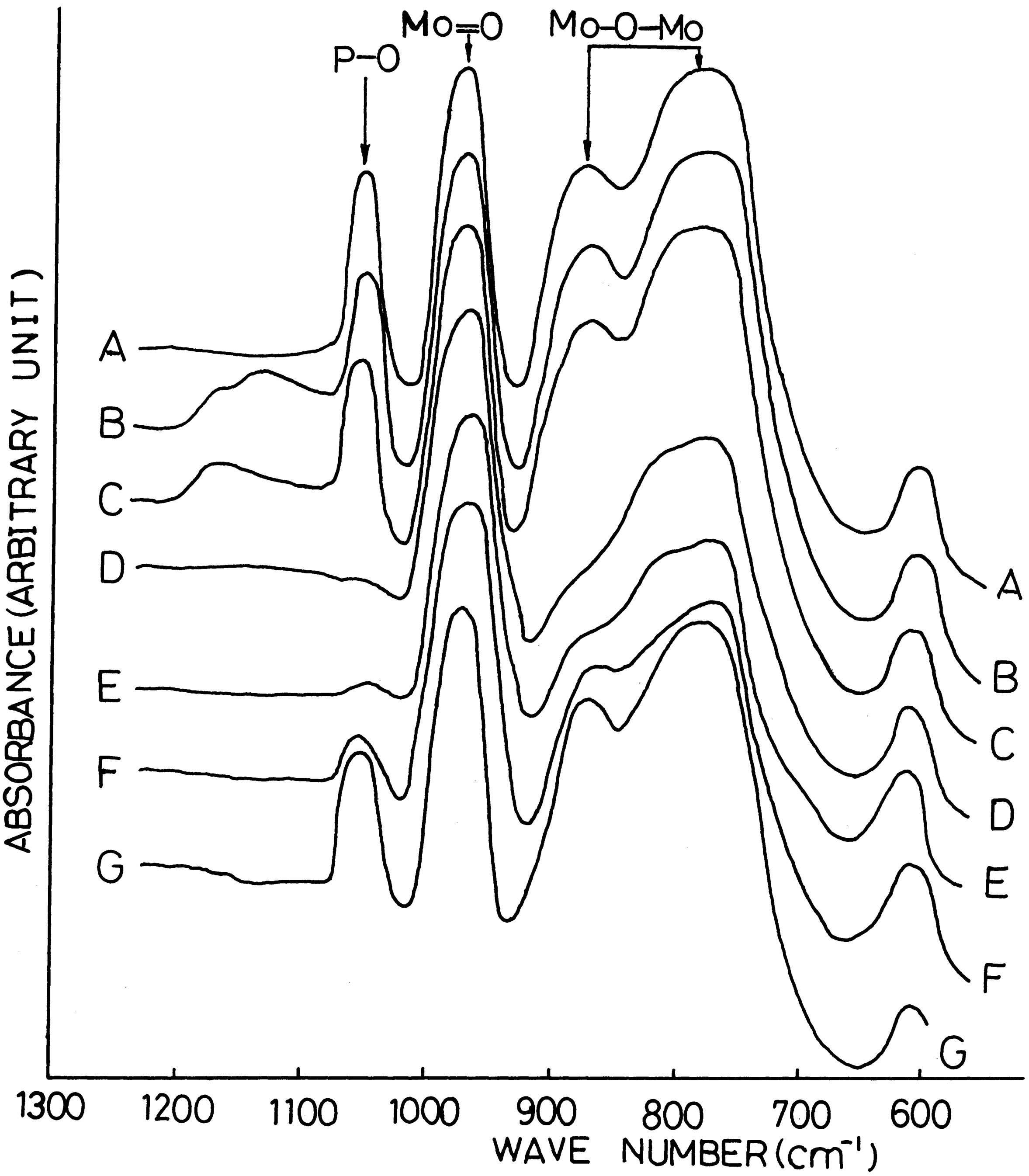

Figure 1, IR spectra of HPA with or without adsorbed crotonaldehyde

(A), HPA evacuated for 5 min at r.t. (B), After introduction of crotonaldehyde (4 torr.) on (A). (C), After evacuation of (B) for 30 min at r.t. (D), After heating(C) at 120 °C for 30 min. (E)-(G), After the heat treatment with adsorbed crotonaldehyde at 120 °C. Procedures were the same with (D) except the time of pre-evacuation, (E), 10 min and (F), 1 hr at r.t. and (G), 2 hr at 130 °C.

for 30 min. After the heat treatment, the 1170 cm^{-1} band for absorbed crotonaldehyde and 1055 cm^{-1} band for P-O bond of HPA disappeared simultaneously (Fig.1 curve D), suggesting that HPA is reduced by the reaction with adsorbed crotonaldehyde. The 1170 cm^{-1} band would be ascribed to an adsorbed reaction intermediate.

It is to be noted that the 875 cm^{-1} band usually assigned to Mo-O-Mo bond behaves similar to the 1055 cm^{-1} band, while the 775 cm^{-1} band for Mo-O-Mo changes little, on the reaction with crotonaldehyde. This behavior of IR bands for HPA is quite analogous to that observed by Tsuneki et al. in hydrogen reduction of HPA (Ag salt)3), confirming the reduction of HPA with crotonaldehyde.

Thus the reaction of HPA with adsorbed crotonaldehyde was further examined at different levels of hydration of HPA, by changing the time of preevacuation. It was confirmed by separate experiments that the original H_2O content of HPA was about 28 H_2O/mol and that the H_2O content was decreased to 21, 16 and 9 H_2O/mol after evacuation at room temperature for 5, 10 and 60 min, and to 2 H_2O/mol after evacuation at 130 °C for 2 h. The preevacuation at room or elevated temperature was followed by adsorption of crotonaldehyde at room temperature for 2 h at 4 torr, evacuation at room temperature for 30 min and the heat treatment at 120 °C for 30 min. Since the amount of HPA on the silicon plate was much less (about 1/15) than that used for the dehydration experiment, the degree of dehydration of HPA on the IR sample would be somewhat different from the above figures even if the preevacuation was made for the same duration of time. But it was clear that the degree of hydration could be changed by varying the time of evacuation at room temperature.

Figure 1 shows the effect of peevacuation of HPA sample on the IR spectra before and after the heat treatment at 120 °C. Although it is not clear from the figure, it was found that the IR absorption peaks ascribed to HPA were changed slightly (by about 5 cm^{-1}) towards lower wave number by the dehydration treatment. The wave numbers given are reffered to a state evacuated for 5 min at room temperature. As is seen from Fig.1, the IR absorption by P-O bond (1055 cm^{-1} band) observed after the heat treatment increases as the extent of dehydration of HPA increases (curves D, E and F). For the sample dehydrated at 130 °C for 2 h, the 1055 cm^{-1} band is essentially unchanged by the heat treatment at 120 °C (curve G), indicating no reduction of HPA taken place.

Interestingly the 1170 cm^{-1} band observed for the adsorbed crotonaldehyde on less dehydrated HPA sample (curve C) was missing from the spectra of more dehydrated sample even before the heat treatment at 120 °C. The observed lack of HPA reduction might be caused by complete removal of crotonaldehyde during the evacuation before the heat reatment. Thus the reaction of HPA was further studied at increasing temperatures in the presence of gas phase crotonaldehyde (4 torr) with the HPA sample preevacuated at 130 °C for 2 h. It was found that the IR spectra of HPA sample did not change after the heat treatment up to 180 °C even in the presence of gas phase crotonaldehyde. In this way, the dehydration of HPA gives rise to the lack of HPA reduction, demonstrating that it is clear that the reduction of HPA with crotonaldehyde requires the presence of water. Since the reduced HPA was proved to be reoxidized completely by molecular oxygen at 120 °C, the necessity of water in the reduction of HPA is quite consistent with the water-enhanced catalytic oxidation of crotonaldehyde over HPA.

The furan formation from crotonaldehyde was further confirmed by a separate experiment of the oxidation with HPA at 120 °C, while adsorbed methacrylaldehyde was found to be hardly able to reduce the HPA sample with or without water even at 180 °C. The water-enhanced reduction of HPA appears to be specific with crotonaldehyde. The specificity may be understood in terms of water enhanced enolization which is characteristic of crotonaldehyde$^{4)}$. The enhancement with water seems to come from water-reactant interaction.

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