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PHOTOCHROMISM OF ISO-PROPYLAMMONIUM MOLYBDATE

Toshihiro YAMASE, Hiroh HAYASHI, and Tsuneo IKAWA
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

Iso-propylammonium dimolybdate dihydrate, which shows a photochromic activity in the solid state and forms a blue color in the aqueous solution on exposure to UV, has been investigated by ESR. It was confirmed that the signal responsible for the color corresponded to the formation of Mo(V).

In our previous paper, the photochromism of dimethylammonium trimolybdate monohydrate (DMAM) $(C_2H_8N)_2\ Mo_3O_{10}\cdot H_2O$ has been reported.[1)] Molybdates of various amines have been synthesized. In this letter the results of ESR measurements of iso-propylammonium dimolybdate dihydrate (PAM) $(C_3H_{10}N)_2\ Mo_2O_7\cdot 2H_2O$ are used to study the color formation responsible for the photochromism. PAM was prepared by the reaction with iso-propylamine and ammonium heptamolybdate (amine to molybdenum ratio of 1 : 1) in water.[2)] Crystalline material obtained was washed by ethanol and ethylether. Recrystallization from water yielded a white crystalline material. According to the differential scanning calorimetry, PAM was stable below 110°C. Its solubility in water of 100 ml at 20°C was about 108 gram, while that of DMAM was 1.4 gram. The sample was irradiated with 365 nm light obtained through the use of a combination of filters and a 500 W-superhigh-pressure Hg lamp. White crystalline samples of PAM colored to reddish violet on exposure to UV and were changed back to the original white by thermal bleaching when UV was cut off. Aerobic and deaerated samples responded in the same way to UV light. The colored samples in the dark might be kept indefinitely in a vacuum at about 70°C without changing in any way, while the thermal treatment in oxygen brought about a rapid bleaching. This result suggests that the thermal bleaching is catalysed by oxygen. IR spectra and X-ray diffraction powder pattern of the material were unchanged by UV irradiation. ESR spectra were recorded at room temperature on a Varian E-12 X-band spectrometer with 100 kHz magnetic field modulation.

In Fig.1 is shown the powder ESR spectrum of PAM after the development of color by UV irradiation. Spectrum can be interpreted in terms of species with fixed orientations and with principal g values 1.908, 1.930, and 1.944, although anisotropic hyperfine structure is obscured. When the absorption responsible for the color was determined by reflectance spectra from colored briquetted powder, ESR signals in Fig.1 correlated with the optical densities at the band maximum of 510 nm. It was found that the colored sample was very soluble in water just as original white sample, and formed a blue colored solution having absorption maxima at 620 and 730 nm as shown in Fig.2a. The deaerated blue-colored solution exhibited the thermochromic property. The blue color faded when the solution was heated to about 60°C and reappeared rapidly on cooling. The fading was not observed by the irradiation of red light corresponding to the absorption band. In contrast to the deaerated solution, the aerobic one did not show the thermochromism. The blue color faded gradually on exposure to oxygen and did not reappear on cooling. When white powder of PAM was dissolved in water, blue coloration by UV-irradiation was observed for both aerobic and deaerated solutions. UV-induced blue-coloration was characteristic of the aqueous solution containing PAM. The ESR spectrum of the blue-colored solution exhibited a large single line and hyperfine structure (hfs) of six lines with a coupling constant of 52.0 gauss at $g = 1.926$, as shown in Fig.2b, although the resolution of hfs components at higher field was incomplete due to the broadening. The six line structure is obviously the result of hyperfine interaction with molybdenum isotopes (^{95}Mo, natural abundance 15.7%, $I = 5/2$, $\mu_N = -0.9134$; ^{97}Mo, natural abundance 9.45%, $I = 5/2$, $\mu_N = -0.9326$). Then, the large single line originates from ^{96}Mo(V) with $I = 0$. The assignment of the lines at $g = 1.926$ in the ESR spectrum of the blue-solution is considerably important in view of the correlation with the solid state photochromism of PAM, since the colored crystalline samples brought about the blue coloration in aqueous solution and the white crystalline samples exhibited no ESR signal of Mo(V) in both solid state and aqueous solution. It is not clear only from these observations what acts as an electron donor, but at least it is possible to say that the photoreduction of Mo(VI→V) occurs in the solid. The fact that in both IR spectra and X-ray diffraction powder patterns, no significant difference between white and deep-colored samples was observed may exclude a possibility of the photolysis of iso-propylammonium cation in the solid. The effect of oxygen on the oxidation of Mo(V→VI) can not be explained at present.

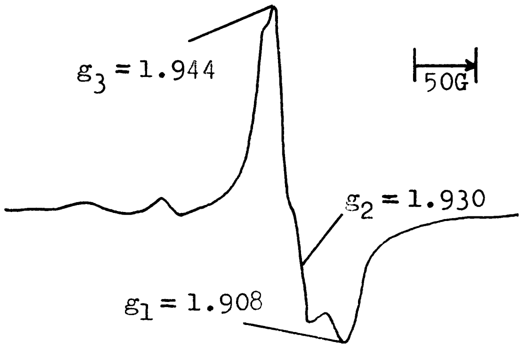

Fig.1. Powder ESR spectrum of PAM.

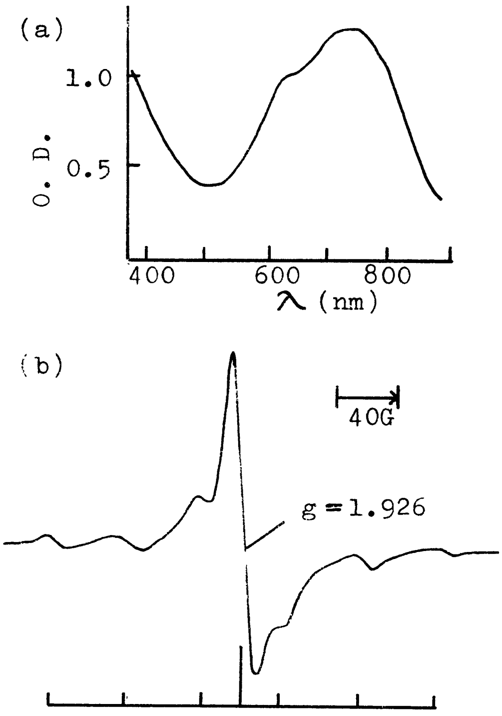

Fig.2. Absorption (a) and ESR (b) spectra of blue-colored aqueous solution.

REFERENCES

1) T.Yamase, T.Ikawa, H.Kokado, and E.Inoue, Chem. Lett., 615 (1973).

2) A.C.Krause and F.C.Krauskopf, J. Amer. Chem. Soc., 47, 1689 (1925).

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