CHEMISTRY LETTERS, pp. 615-616, 1973. Published by the Chemical Society of Japan

PHOTOCHROMISM OF DIMETHYLAMMONIUM MOLYBDATE

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A new photochromic compound was found. Dimethylammonium molybdate (DMAM) represented by the ideal formula $\{(CH_3)_2NH_2\}_2O \cdot 3MoO_3 \cdot H_2O$ colored remarkably to the reddish brown on exposure to UV and returned to the original white by thermal fading. DMAM exhibited photochromic phenomena in the solid state and the correlation between coloration and UV-induced ESR signals was found.

There have been no reports on the photochromic compound consisting of dimethylamine and molybdenum trioxide. Many metal oxides including molybdenum have been reported to be phototropic with or without a dopant. For example, TiO_2 coprecipitated with MoO_3, TiO_2 doped with Fe-Mo, or Ba_2 $NaNb_5O_{15}$ doped with Fe-Mo darken when exposed to UV or short wavelength visible light. In general photochromic effects of metal oxide have been interpreted on the basis of electron trapping in defects within the crystal.1)

We wish to report that dimethylammonium molybdate (DMAM) represented by the ideal formula $\{(CH_3)_2NH_2\}_2O \cdot 3MoO_3 \cdot H_2O$ is a new photochromic material that exhibits photochromic phenomena in the solid state. Preparations of DMAM were carried out (1) by a reaction with dimethylamine and molybdic acid or molybdenum trioxide in water2) and (2) by thermal decomposition of molybdenum dimethyldithiocarbamate3) in chloroform or methylene dichloride solvent. White precipitates obtained by both methods were filtered off, washed with chloroform several times and dried at room temperature. The dry powder was extracted with hot water. After repeated extraction, final crystallization in the dark gave fine white crystals. As to a white crystalline material obtained by both methods of (1) and (2), analytical data, UV and IR spectra, and X-ray diffraction powder patterns were almost the same, respectively. The structure of the DMAM crystalline is not determened yet.

High-pressure mercury lamp (100W) was used as a UV light source. To prevent possible rise of a sample temperature, air-cooling was used during irradiation. The photosensitive wavelength region of DMAM was determined by using a Narumi Grating Spectrograph (PM-2-3-1) with an Xe lamp and an optical wedge. Coloration could be caused by irradiation with UV light in the range 260 to 400 nm. Weakly colored samples appeared pink while more strongly colored samples were a deep reddish brown. The absorption responsible for this color was a single broad band centered around 470 nm as determined by reflectance spectra from briquetted powder as shown in Fig 1. Aerobic and deaerated samples responded in the same way to UV light. The absorbance at 470 nm increased with an increase of irradiation time. The UV-induced color of DMAM faded gradually at room temperature in the dark. The fading was promoted by heating but not by visible light. When DMAM was dissolved in solvent such as water, no coloration of solutions was observed by both steady irradiation and flash photolysis (400 J, 20 μsec). This suggests that the photochromism of DMAM is restricted to solid state. The powder ESR spectrum of DMAM was studied in the microwave cavity of a Japan Electron Optics electron spin resonance apparatus model JES-3BS-X at room temperature. When powdered photochromic DMAM was colored, ESR signals at g_1=1.885, g_2=1.930 and g_3=1.935 were observed as shown in Fig 2. UV-induced signals may correspond to the formation of Mo^{5+}ion4), even if the type of structure was associated with g anisotropy. UV-induced ESR signals were unaffected by oxygen. Thermal fading in the dark brought about the decrease of relative intensities of UV-induced signals. The rates of change in these signals are likely to correlate with the rate of photochromic changes. Observation of UV-induced ESR signals suggests the electron transfer in the lattice but the origin of the spectrum line is not clear yet.

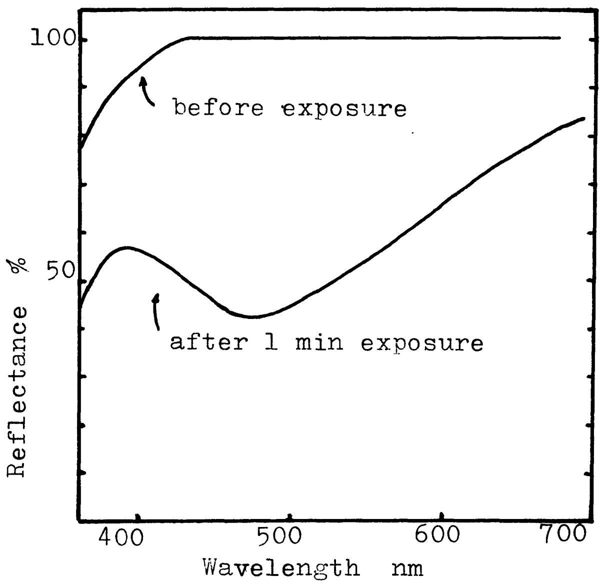

Fig. 1. Reflectance curves of DMAM before and after exposure to UV light.

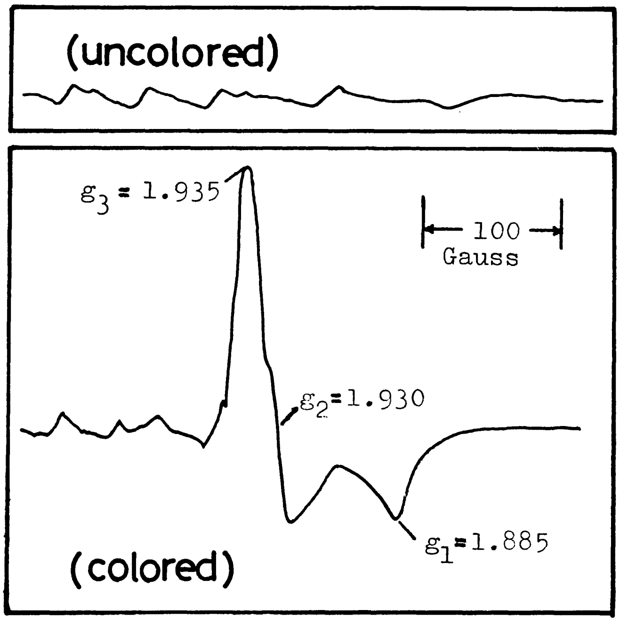

Fig. 2. Powder ESR spectra of DMAM (top) before and (bottom) after exposure to UV light.

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(Received March 30, 1973)