Photochemical Study of the Alkylammonium Molybdates. III. Preparation and Properties

Toshihiro YAMASE and Tsuneo IKAWA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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Six alkylammonium molybdates which we have prepared were examined for photochemical and photochromic properties in a solid and in an aqueous solution. The white crystals were reddish brown or violet when irradiated with UV light. Five compounds of the six were photochromic under aerobic conditions. The thermal return to the white color was slow, taking several hours at room temperature. The irradiation of the aqueous solution (pH 4.3—6.5) by UV light caused a blue coloration; the quantum yield increased with an increase in the molybdate concentration. A UV-induced coloration in both solid and solution was ascribable to the photoreduction of Mo(VI) to Mo(V). The blue form in the aqueous solution possesses several unique characteristics, including: (1) $g=1.926$ and $a=52$ G in its ESR spectrum; (2) the oxidation of Mo(V) to Mo(VI) upon exposure to oxygen, with an accompanying bleaching, and (3) thermochromism (blue form$\leftrightarrows$greenish yellow form) with $\Delta H_r \approx 15$ kcal/mol.

In previous papers we reported the photochromism of bis(dimethylammonium) trimolybdate monohydrate and bis(isopropylammonium) dimolybdate dihydrate.[1,2] When the polycrystalline material was irradiated with UV light, the white crystals became reddish brown or violet because of the formation of Mo(V). A return to the original white color was observed in the dark in the presence of oxygen. This color change could be repeated many times. Recently, Arnaud-Neu and Schwing-Weill reported, on the basis of photochromism tests of the various molybdates of different amines, that only secondary amines yield photochromic molybdates.[3] However, their conclusion is doubtful, since some of the primary aliphatic amines yield photochromic molybdates. This report will present several generalizations regarding the photochemical behavior of the 6 alkylammonium molybdates in a solid and an aqueous solution; these generalizations should provide a better understanding of this behavior.

Experimental

Preparation of Alkylammonium Molybdates. All the chemicals were of a G. R. or reagent grade of the Tokyo Kasei Co. and were used without further purification.

Bis(isopropylammonium) dimolybdate dihydrate (IPAM),—Isopropylamine (52 ml) was added to a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (80 g) in water (50 ml). After stirring about 6 h, the solution was concentrated under reduced pressure to form a white solid, which was then filtered off and dried. One recrystallization of the crude product from water yielded colorless solids. Found: C, 13.96; H, 4.78; N, 5.96; Mo, 40.0%. Calcd for $(C_3H_{10}N)_2\ Mo_2O_7\cdot 2H_2O$: C, 15.65; H, 5.22; N, 6.09; Mo, 41.7%.

Hexakis(isopropylammonium) Octamolybdate Dihydrate (6IPA8M2),[4]—This compound was crystallized from an aqueous solution (10 ml) containing 5 g of bis(isopropylammonium) dimolybdate dihydrate at room temperature when the solution was kept in the dark for two weeks. Found: C, 13.09; H, 4.21; N, 5.40; Mo, 47.2%. Calcd for $(C_3H_{10}N)_6H_2Mo_8O_{28}\cdot 2H_2O$: C, 13.39; H, 4.09; N, 5.21; Mo, 47.6%.

Bis(dimethylammonium) Trimolybdate Monohydrate (DMAM),—$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (300 g) was added to a solution of dimethylamine (40%) in 500 ml of water. After stirring about 4 h, the solution was concentrated under reduced pressure, and the resultant white solid was allowed to crystallize. The white solid then dissolved in 1500 ml of water. This solution was warmed 50—60 °C while stirred for 2—3 h to form white precipitates. The precipitated product was filtered off, washed with cold water, and dried under a vacuum. Found: C, 8.68; H, 3.25; N, 5.12; Mo, 53.4%. Calcd for $(C_2H_7N)_2Mo_3O_{10}\cdot H_2O$: C, 8.59; H, 3.26; N, 5.01; Mo, 51.6%. DMAN could be otained by another method, too: The dioxobis(dimethyldithiocarbamato) molybdenum (VI) complex, $MoO_2[(CH_3)_2NCS_2]_2$, was made by Moore and Larson's method[5] and a nearly saturated solution of 1 g of $MoO_2[(CH_3)_2NCS_2]_2$ in 1000 ml of chloroform was refluxed for 1—2 h. After cooling, a white product was allowed to crystallize.

Bis(diethylammonium) Trimolybdate Monohydrate (DEAM),—DEAM was obtained by a modification of the above DMAM-preparation procedure using an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (10 g) in 20 ml of diethylamine (40%). Found: C, 15.11; H, 4.24; N, 4.45; Mo, 47.1%. Calcd for $(C_4H_{12}N)_2Mo_3O_{10}\cdot H_2O$: C, 15.64; H, 4.23; N, 4.56; Mo, 46.9%.

Bis(propylammonium) Dimolybdate Dihydrate (PAM),—PAM was obtained by a modification of the above IPAM-preparation procedure using an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (50 g) in 100 ml of propylamine (30%). Found: C, 14.24; H, 4.68; N, 5.81; Mo, 42.1%. Calcd for $(C_3H_{10}N)_2Mo_2O_7\cdot 2H_2O$: C, 15.65; H, 5.22; N, 6.09; Mo, 41.7%.

Bis(methylammonium) Dimolybdate Dihydrate (MAM),—MAM was obtained by a modification of the above IPAM-preparation procedure using an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (350 g) in 450 ml of methylamine (30%). Found: C, 6.12; H, 3.93; N, 7.35; Mo, 46.2%. Calcd for $(CH_6N)_2Mo_2O_7\cdot 2H_2O$: C, 5.94; H, 3.96; N, 6.93; Mo, 47.5%.

Procedures. The sample was irradiated using a 500-W super-high-pressure Hg lamp. The following filters were used for the different wavelength regions: $\geq$313 nm, a liquid filter (1 cm thick) consisting of an aqueous solution of 0.5 g of potassium hydrogen phthalate/100 ml; 313 nm, conjunction with a liquid filter (3 cm thick) consisting of an aqueous solution of 46 g of $NiSO_4\cdot 6H_2O$ + 14 g of $CoSO_4\cdot 7H_2O$/100 ml and a filter (1 cm thick) of a potassium hydrogen phthalate solution; 365 nm, Toshiba UV-D1+UV-35 filters. The light intensities were measured by means of potassium ferrioxalate actinometry. The UV-induced coloration of the aerobic solution to blue was followed by the conjuction with a He-Ne laser and a photodiode.[6] The oxygen concentration was measured with a kyusuikagaku Kenkyusho D.O. Meter-TP. Thermochromism studies were done in a homemade Dewar vessel. The tempera-

ture was measured by means of a copper-constantan thermocouple kept in contact with the sample cell (1 cm internal pathlength). The evacuation of solutions was carried out by several freeze-pump-thaw cycles on 10^{-4} Torr. Molybdenum analyses were done by means of a Varian Techtron Model 1000 atomic absorption spectrophotometer. Differential scanning calorimetry showed that each of the alkylammonium molybdates was stable below 100 °C. The IR (KBr discs) and Raman spectra were recorded on Shimadzu-IR-27G and JEOL laser Raman spectrophotometers respectively. The UV and visible absorption or reflectance spectra were taken with a Hitachi 624 spectrophotometer. The ESR spectra were obtained with a Varian E-12 spectrometer.

Photometry of Mo(V) in the Aqueous Solution. On the basis of the fact that the colored IPAM powder gave a blue color when dissolved in deaerated water, the photometric determination of Mo(V) in deaerated water was carried out, assuming that all of the Mo(V) in the colored powder was converted into the blue species in water. The number of spins due to Mo(V) in the UV-irradiated IPAM powder was obtained by comparing the sum of the intensities of the Mo(V) ESR signals with the intesity of a DPPH standard (1.44×10^{15} spin in the sample powder of 230 mg). When the sample powder was dissolved in the deaerated water, DPPH had no observable effect on the blue coloration, at least not during the experimental procedure. The numerical double integration of the Mo(V) signals showed that the Mo(V) exhibiting the blue color obeys Beer's law below 4×10^{-4} M ($\varepsilon_{730}=2.3\times10^{3}$ M^{-1} cm^{-1} at 20 °C).

Results and Discussion

Photosensitive Properties in the Solid. In Fig. 1 alkylammonium molybdates are divided into two categories according to the similarity among the IR spectra of the compounds in the Mo–O vibrational region (400—1000 cm^{-1}). The IR spectra of Group (1) compounds (IPAM, 6IPA8M2, PAM, and MAM) were very similar to those of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$. The IR spectra of Group (2) compounds (DMAM and DEAM) showed characteristic strong bands at ≈500 and ≈640 cm^{-1}. Table 1 lists the solubility in water, the absorption maximum (λ_{max}) which is observed after irradiation with UV light, and the approximate speeds of the coloration and return reactions. Under irradiation with UV (313 or 365 nm) light, the white crystals were

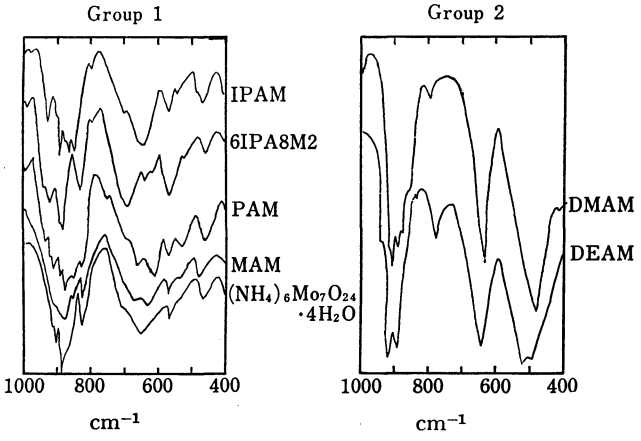

Fig. 1. IR spectra (KBr discs) of alkylammonium molybdates.

Table 1. Photosensitive alkylammonium molybdates

Group	Alkylammonium molybdate		λ_{max}, nm	Approx. coloration time, min[b]	Approx. return time, h[c]
(1)	IPAM	(108)[a]	510	5—7	7—10
	6IAP8M2	(11)	480	≈3	15—20
	PAM	(90)	490	5—7	4—5
	MAM	(330)	480	1—2	—
(2)	DMAM	(1.4)	470	<1	2—3
	DEAM	(1.0)	475	<1	2—3

a) Numbers in parentheses are solubilities in water (100 ml) at 20 °C. b) Numbers indicate the irradiation time required to obtain the reflectance of ≈50% at λ_{max} when the white briquetted powder is exposed to UV (≥313 nm) light at a distance of 30 cm from the light source. c) Numbers indicate the half-life period of the colored species at room temperature under aerobic conditions.

reddish brown or violet. No significant changes in the IR spectra and X-ray diffraction powder patterns after irradiation were observed. The effect of oxygen on the coloration seemed to be negligible. The apparent coloration decreased in this order: DMAM, DEAM> MAM>6IPA8M2>IPAM, PAM. For DMAM, DEAM, 6IPA8M2, IPAM, and PAM, a return to the original white color was observed in the dark under aerobic conditions. Although the entire bleaching did not obey the simple first-order law, the half-life period of the colored species was several hours at room temperature and increased in this order: DMAM, DEAM< PAM<IPAM<6IPA8M2. The return reaction was the thermal process which was catalyzed by oxygen, since irradiation with visible light or the deaerated system brought about no observable bleaching. Therefore, the stronger bleaching effect was obtained by thermal treatment in oxygen. For example, ≈1 atm of oxygen at 50 °C changed the return half-life of DMAM from 2—3 h under aerobic conditions at room temperature to less than 10 min. MAM was UV-sensitive, but did not return to the white color in the dark. It should be noted that Group (2) compounds exhibit lower solubilities in water, higher UV sensitivities, and faster return rates than Group (1) compounds. All of the colored polycrystallines exhibited an ESR signal due to Mo(V), while the white crystallines exhibited no significant ESR signal of Mo(V).[1,2] The colored samples in Group (1) turned blue (λ_{max} 730 nm, λ_{sh} 620 nm), when dissolved in deaerated water. The resulting solution gave rise to a single intense line (g= 1.926), with six weak satelite lines, three on each side and equally spaced (a=52 G), in its ESR spectrum, as was previously reported for IPAM.[2] This equal spacing of the six weak lines indicated a hyperfine structure (hfs) due to isotopes with a nuclear spin of 5/2. The line-width was too great to allow the resolution of separate lines from ^{95}Mo and ^{97}Mo. This is not surprising, since the nuclear magnetic moments differ by only 2%.[7] The exposure of the blue solution to oxygen brought about the oxidation of Mo(V) to Mo(VI), with an accompanying bleaching, resulting in no observable ESR signal of Mo(V). The colored samples in Group (2) gave no detectable amount of Mo(V) in their

homogeneous deaerated solution, although the solution obtained was slightly blue. This seemed to be ascribable to the fact that each compound in Group (2) was much less soluble in water than these in Group (1). The difference in photosensitivity, reversibility, or the return rate among the 6 molybdates in the solid state may be strongly connected with their crystal structures. However, we have not made a crystal structure determination of any compounds except for 6IPA8M2.

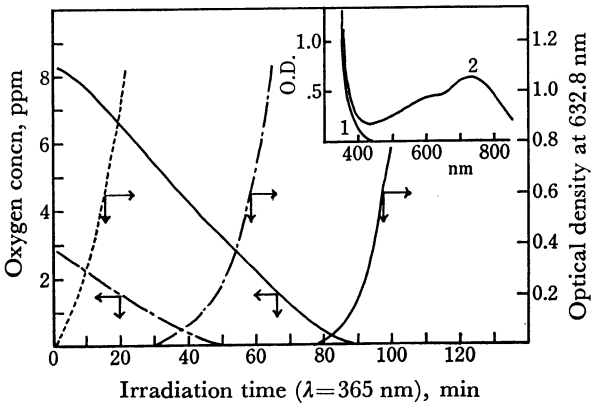

Fig. 2. Effect of oxygen on the UV-induced coloration of the aqueous solution containing 4% IPAM at 20 °C: $[O_2]_{ini}$=8.3 ppm (———), $[O_2]_{ini}$=3.0 ppm (—·—), N_2-bubbled (·····). Incident light intensity is 3.0×10^{-5} E/l min. Optical path length of the solution is 45 mm. Small figure shows spectral changes of a deaerated solution with 1 cm of its thickness: (1) before irradiation, (2) after 5 min of 365 nm irradiation with incident intensity of 2.4×10^{-4} E/l min.

Photosensitive Properties in the Aqueous Solution. Each of the fresh aqueous solutions exhibited pH levels of 4.3—6.5. Under the irradiation of a deaerated solution with UV light, the color changed from colorless to blue, as is shown in Fig. 2. Oxygen inhibited the UV-induced blue coloration of the solution: For the 4% solution of IPAM with initial oxygen levels of 8.3 3.0, and ≈0 ppm, UV irradiation caused the consumption of oxygen in the course of the induction period, and coloration at the steady state was observed when the oxygen level reached about 1 ppm (Fig. 2). The inhibiting effect of oxygen on the coloration may be explained in terms of the rapid oxidation process of Mo(V) to Mo(VI), judging from the fact that the blue form was oxidized by oxygen to yield the colorless form. The blue form was considered to be essentially the same as the blue form on the dissolution (in water) of a colored polycrystalline sample, judging from the similarity between their ESR spectra, giving g=1.926 and a=52 G. The blue forms in the deaerated solution exhibited thermochromism (blue⇄greenish yellow) over the temperature range from 0 to 70 °C.[8] Analysis of the temperature-dependent spectral changes in the IPAM solution revealed a single isosbestic point at 480 nm between the blue and greenish yellow forms, as is shown in Fig. 3(a). With OD_h and OD_l referring to the optical densities at 730 nm at the highest and the lowest temperatures respectively, a plot of (ODh—OD)

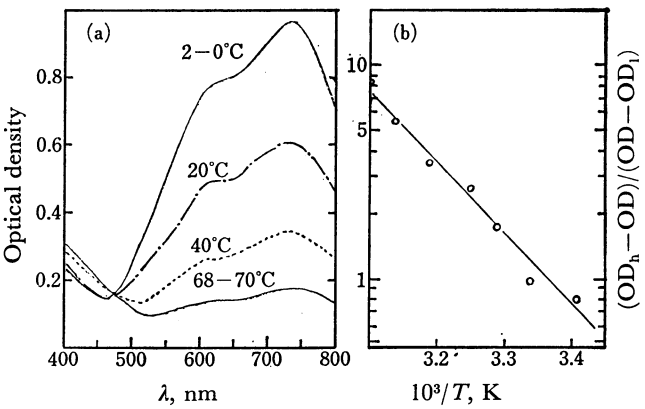

Fig. 3. Thermochromism of the blue form in the deaerated aqueous solution containing 4.3% IPAM: Mo(V)=2.6×10^{-4} M.

/(OD–OD_l) corresponding to the ratio of the concentration of the blue form to that of the greenish yellow form against the reciprocal absolute temperature was approximately linear, giving≈15 kcal as the value of the heat of reaction (ΔH_r) on the equilibrium of the blue form⇄ the greenish yellow form, as is shown in Fig. 3(b). The same value of ΔH_r was obtained for the MAM solution, supporting the idea that the chemical structure of the blue form is independent of the molybdates. The Mo(V) formation quantum yields (η) of the deaerated solution at 20 °C are summarized in Table 2. A comparison of these data shows that the blue form is photochemically produced at pH=4.3—6.5 without any significant difference in η between irradiations with 313 nm and 365 nm light and that η increases with an increase in the molybdate concentration. There have been no reports of the formation of blue species in an aqueous solution containing molybdates at pH 4.3—6.5. In aqueous solutions containing Na_2MoO_4 or $(NH_4)_6Mo_7O_{24}$, $Mo_7O_{24}^{6-}$, which is the predominant species at pH 4.8—6.8, is not reducible, although more acidic solutions (pH≤1.2) are easily reduced to a blue species, which is written as $H_2Mo_2^{V}Mo_4^{VI}O_{19}^{2-}$.[9,10] These

Table 2. Quantum yield of the deaerated aqueous solutions for the Mo(V) formation

Alkylammonium molybdate	Initial concn, wt%	Fresh solution pH	Quantum yield[a] η_{313}	η_{365}
IPAM	4.3	5.3	0.48	0.48
	2.8		0.32	—
	1.2		0.30	—
	0.4		0.03	—
6IPA8M2	2.8	6.2—6.5	0.38	0.30
MAM	4.8	5.6	0.05	0.04
DMAM	1.4	4.3	0.04	—
$(NH_4)_6Mo_7O_{24}\cdot4H_2O$	4.0	5.3	0	—

a) η_{313} and η_{365} indicate the quantum yields obtained by using the exciting light of 313 nm and 365 nm respectively. The incident light intensities at 313 nm and 365 nm are 4—5×10^{-5} E/l min and 2.3—2.4×10^{-4} E/l min respectively.

conclusions are also supported by these of our experimental results: bands in the Raman spectra of the molybdate solution appeared at 925, 890, 350, and 220 cm^{-1} and were close to those of the solid $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Furthermore, the solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at pH 5.3 gave no blue species photochemically (Table 2). The tendency for η to increase with an increase in the molybdate concentration suggests that the primarily-formed photoproduct reacts with the ground-state molybdate to yield the mixed-valence blues containing molybdenum cluster groups. The possibility of a molybdenum cluster containing more than two atoms of Mo(V) (for example, $H_2Mo_2^{V}Mo_4^{VI}O_{19}^{2-}$ which may be produced when $pH \leq 1.2$), may be excluded, since Mo(V) should not obey Beer's law if this possibility is operative. In order to understand the reaction mechanism of the blue coloration, the structure of the blue form must be revealed at least. However, further speculation is inappropriate, since the true formula of the blue species is not known at present.

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