

폴리비닐알코올 막중에서의 헤테로다중  
음이온들의 광화학적 환원

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(1975. 4. 21 접수)

Photochemical Reduction of Some Heteropoly  
Anions in Polyvinyl Alcohol Films

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(Received April 21, 1975)

Some heteropoly anions have been known to form photosensitive systems with alcohols.<sup>1</sup> A photosensitive polyvinyl alcohol film based on this phenomenon was described by Chalkley.<sup>2</sup> We have measured absorption spectra of several photochemically reduced heteropoly anions in polyvinyl alcohol films, finding that the photochemical reduction proceeds by one-electron steps. This has allowed us to record optical spectra of the one-electron reduction products of several heteropoly anions, which cannot be obtained either chemically or electrochemically. Details are reported below.

EXPERIMENTAL

**Preparation of Compounds.**  $H_3PW_{12}O_{40}$ ,  $H_3PMo_{12}O_{40}$ ,  $(NH_4)_6P_2W_{18}O_{62}$  (A form), and  $K_6P_2Mo_{18}O_{62}$  were prepared according to Wu<sup>3</sup> and identified by their ir spectra.<sup>4</sup>  $H_4SiMo_{12}O_{40}$  ( $\alpha$  form) was prepared according to Strickland<sup>5</sup> and its Keggin structure was identified by the ir spectrum.<sup>4</sup>

**Preparation of Polyvinyl Alcohol Films.** 1 g of high viscosity, completely hydrolyzed poly-

vinyl alcohol was moistened at room temperature with a solution (5 ml) of heteropoly compound. The mixture was heated in a boiling water bath until the solution was clear. The mixture was poured onto glass and allowed to flow freely and dry at room temperature.

**Photochemical Reduction.** The dried transparent films were irradiated with a high-intensity ultraviolet lamp (Black-Ray Lamp) or a projector lamp.

**Absorption Spectra.** Spectra were recorded on a Beckman DK-2 spectrophotometer.

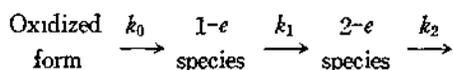
RESULTS and DISCUSSION

The color of a uv-irradiated film containing  $H_3PW_{12}O_{40}$  was almost black, as pointed out by Chalkley.<sup>2</sup> The absorption spectrum of this was identical to that of one-electron reduction product.<sup>6</sup> On further irradiation, the spectrum changed to that of the two-electron reduction species.<sup>6</sup>  $H_3PW_{12}O_{40}$  in the polyvinyl alcohol film is not reduced by visible light.

When a film containing  $P_2W_{18}O_{62}^{6-}$  (A form) was irradiated with uv light, blue color appeared.

The absorption spectrum for this stage consists of three bands at 6.6, 11.7, and 13.5 kK. The spectrum above 7 kK is similar to that of the one-electron reduction species.<sup>7</sup> However, the 6.6 kK band has not been reported before. (Incidentally this is the lowest energy band ever observed for heteropoly blues.) Apparently the region below 7 kK was not examined by other investigators. On further irradiation, the spectrum changed to that of the two-electron species.<sup>7</sup> Both spectra are shown in *Fig. 1*.

These two cases show that the photochemical reduction proceeds by one-electron steps. If the rate constant  $k_0$  for the first step



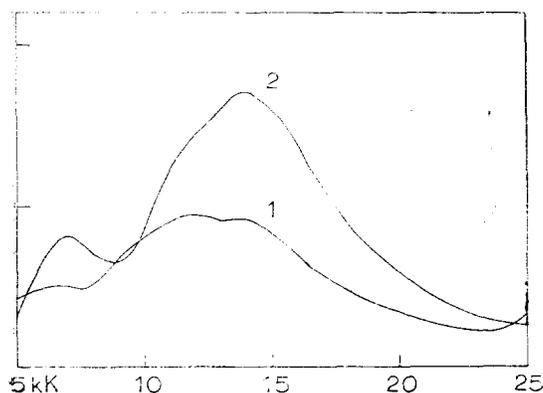
is much greater than  $k_1$ ,  $k_2$ , etc., it is possible to record the spectrum of the one-electron species. Such seem to be the cases for  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ . Now it is of interest to see whether the spectra of some one-electron reduction products, which cannot be prepared chemically or electrochemically, may be recorded in this way.

We have tested  $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ ,  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , and  $\text{SiMo}_{12}\text{O}_{40}^{4-}$ . When a film containing  $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$  was irradiated with visible light, the first spectrum that appeared showed two maxima at 8.6

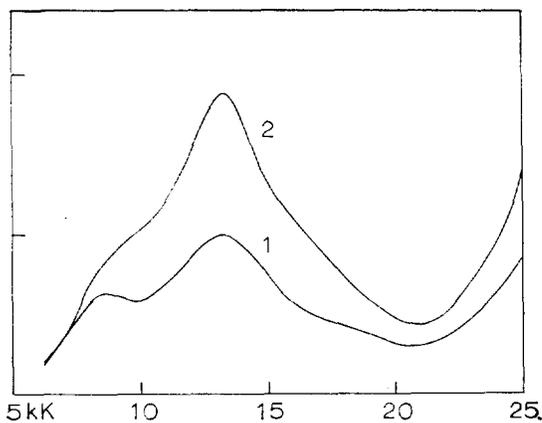
and 13.3 kK and a shoulder at 18 kK (see *Fig. 2*). On further irradiation, the 13.3 kK band grew faster than the 8.6 kK band and the latter became a shoulder. The spectrum for this stage is similar to that of the two-electron species,<sup>7</sup> which shows one maximum at 13.2 kK and a shoulder at 9.0 kK. On still further irradiation, a new band arose at 10.5 kK, which may be attributed to a higher reduction species. When a film was irradiated with uv light, the band at 10.5 kK appeared much faster, making it difficult to obtain the spectrum of the supposed two-electron species.

The spectrum of reduced  $\text{PMo}_{12}\text{O}_{40}^{3-}$  has not been reported so far. When a film containing this anion was irradiated with visible light, a spectrum with a maximum at 13.5 kK and a shoulder at 10.8 kK appeared. When irradiated with uv light, the same spectrum was obtained at first, but on further irradiation the shoulder disappeared (see *Fig. 3*). These two spectra probably originate in the one- and two-electron reduction products, respectively.

$\text{SiMo}_{12}\text{O}_{40}^{4-}$  was examined similarly. The first spectrum showed three bands at 10.3, 12.3, and 14.8 kK (see *Fig. 4*). On further irradiation, the middle band grew much faster than the



*Fig. 1.* Absorption spectra of one- and two-electron reduction species of  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ .



*Fig. 2.* Absorption spectra of one- and two-electron reduction species of  $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ .

other, the spectrum approaching that shown in Fig. 2. Since the reported spectrum of the two-electron species shows only one band at 12.8 kK<sup>8</sup>, the two bands at 10.3 and 14.8 kK may be attributed to the one-electron species. The band at 12.3 kK in the first spectrum may belong to the two-electron species, some of which was produced at the early stage.

The new spectral bands measured in this work are summarized in Table 1. The spectra of the

reduced heteropoly anions are not still well understood. We have attributed the lowest energy band to the intervalence charge-transfer transition, M(V)→M(VI) (M=Mo or W) and pointed out that this band always occurs at 9±2 kK.<sup>9</sup> This is roughly true for the compounds studied here.

Heteropoly anions can also be reduced photochemically in other alcoholic solutions. But some reduced species are oxidized rapidly in the air, making it difficult to record their absorption spectra. When these are generated in polyvinyl alcohol films, they are stable from air oxidation.

The detailed mechanism of the photochemical reduction has not been elucidated. Two mechanisms are possible: (1) hydrogen radicals generated photochemically from polyvinyl alcohol may reduce heteropoly anions, and (2) the charge-transfer excited state of the molybdenyl or tungstenyl group in the heteropoly anion may behave just like a free radical abstracting the hydrogen atom from polyvinyl alcohol. The first mechanism is probably not important in this experiment, where visible and long-wave(300~400 nm) ultraviolet lights were used. Some observations that support the second mechanism have been made. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is white, and films containing this are not reduced by visible light, while all others, which are yellow, are reduced in polyvinyl alcohol films by visible light. But reduction proceeds much fas-

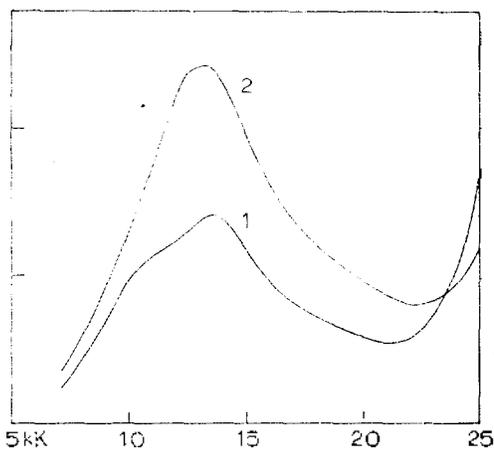


Fig. 3. Absorption spectra of the first and second stages of reduction for  $\text{PMo}_{12}\text{O}_{40}^{3-}$ .

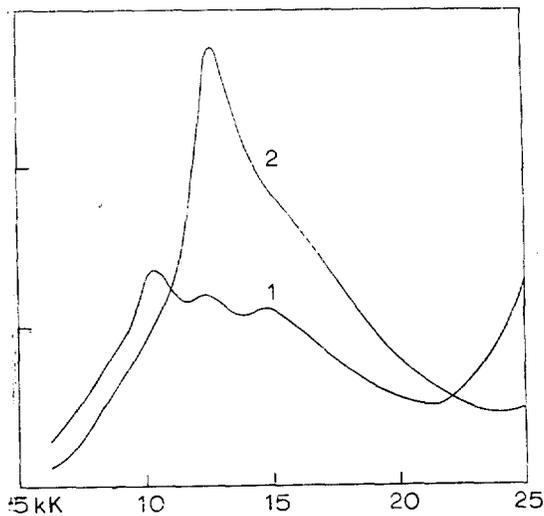


Fig. 4. Absorption spectra of the first and second stages of reduction for  $\text{SiMo}_{12}\text{O}_{40}^{4-}$ .

Table 1. Spectral maxima of reduced heteropoly anions.

Anion	Bands <sup>a</sup>		
$\text{P}_2\text{W}_{15}\text{O}_{62}^{7-}$	6.6	11.7 <sup>b</sup>	13.5 <sup>b</sup>
$\text{P}_2\text{Mo}_{15}\text{O}_{62}^{7-}$	8.6	13.3	
$\text{PMo}_{12}\text{O}_{40}^{4-}$	10.8 <sup>c</sup>	13.5	
$\text{SiMo}_{12}\text{O}_{40}^{3-}$	10.3	12.3 <sup>d</sup>	14.8

<sup>a</sup> in units of kK, <sup>b</sup> reference 7, <sup>c</sup> shoulder,

<sup>d</sup> This band may belong to the two-electron species. See the text.

ter when irradiated with uv light. This can be explained by the fact that the oxygen-to-metal charge-transfer band occurs in the ultraviolet region. The yellow color originates in the tail of this band that comes into the visible region. Mechanisms of the photochemical reduction are being studied in this laboratory.

#### ACKNOWLEDGMENT

This research was supported by the Korean Traders Scholarship Foundation.

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