Inorganica Chimica Acta, 131 (1987) 11–13

Spectrophotometric Studies on the Hexamolybdate Ion in Aqueous Organic Solutions

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(Received February 9, 1987)

On acidification of molybdate solutions, molybdates condense in definite steps to form isopolymolybdates [1, 2]. The heptamolybdate, $Mo_7O_{24}^{6-}$ is predominant at pH 4.5 or Z (= H^+/MoO_4^{2-}) = 1.14 and the octamolybdate, $Mo_8O_{26}^{4-}$ forms at higher acidifications (pH range 1.5–2.9 or $Z = 1.5$). Further acidification leads to the more aggregated species, $Mo_{36}O_{112}^{8-}$ at $Z = 1.8$. In addition to these polymerized species, the hexamolybdate, $Mo_6O_{19}^{2-}$ is known to exist [3, 4]. In recent investigations, $Mo_6O_{19}^{2-}$ was extracted into cyclohexanone [5] and tri-n-butyl phosphate [6]. However, there is uncertainty concerning the limiting conditions for the formation of $Mo_6O_{19}^{2-}$ because $Mo_6O_{19}^{2-}$ does not exist at any appreciable concentrations in aqueous solutions.

In this study, it is shown that $Mo_6O_{19}^{2-}$ is stabilized by the addition of water-miscible organic solvents. The properties of $Mo_6O_{19}^{2-}$ in aqueous organic solvents are described.

Experimental

All reagents were of analytical grade and were used without further purification. Molybdenum(VI) solutions were prepared from $Na_2MoO_4 \cdot 2H_2O$.

Ultraviolet (UV) absorption spectra were taken with a Hitachi Model 220-A spectrophotometer. Preliminary experiments showed that the equilibration in this study was attained in at least 12 h. After standing for about 24 h, therefore, UV spectra were measured at 25 ± 0.1 °C. Raman spectra were obtained with a Spex Model Ramalog-5 spectrophotometer. The argon line at 488 nm was used for excitation. Infrared (IR) spectra were recorded on a Hitachi Model 270-30 spectrophotometer as KBr pellets. A Rigaku Denki Model 8002-SD thermal analyzer was used to make thermogravimetric and differential thermal analyses (TGA–DTA).

Results and Discussion

It is well known that the yellow color of the dodecamolybdophosphate is enhanced by the presence of water-miscible organic solvents such as acetonitrile (AN) and acetone. The phenomenon has been used for the spectrophotometric determination of the orthophosphate ion [7]. However, Halasz and Pungor have pointed out that Mo(VI) solutions become yellow even in the absence of the phosphate ion when acetone concentrations > 30% (*v*/*v*), although no discussion on the phenomenon has been made [8].

Figure 1 shows UV spectra of 4.0 mM Mo(VI) in various concentrations of $HClO_4$ containing 70% (*v*/*v*) AN. The Mo(VI) solution was colorless in 0.001 M $HClO_4$ (curve a). With an increase in the $HClO_4$ concentration, the solution appeared to be yellow. In 0.02 M $HClO_4$, the yellow solution showed three absorption maxima at wavelengths 222, 257 and 325 nm. According to Cruywagen and Rypstra [6], the spectrum is characteristic of $Mo_6O_{19}^{2-}$ in AN solutions. With further increase in the $HClO_4$ concentration, the yellow color disappeared (curve d). This behavior was not observed for Mo(VI) concentrations $< 10^{-4}$ M where monomeric species are predominant.

Figure 2 shows absorbances at 250 and 325 nm as a function of the $HClO_4$ concentration. In the absence of AN (curve a), the solutions were colorless in the $HClO_4$ concentration range studied (0.001–

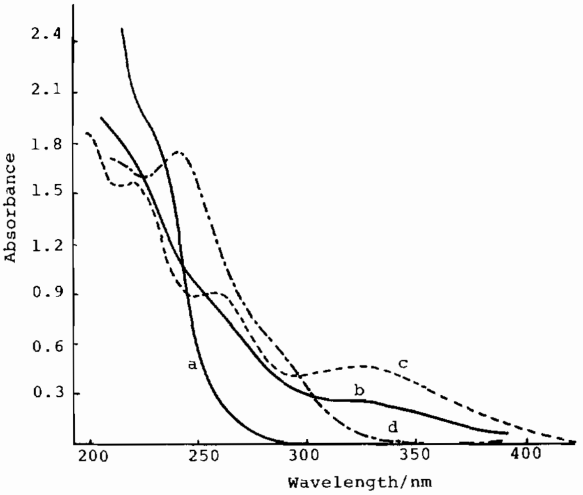

Fig. 1. UV spectra of 4.0 mM Mo(VI) in $HClO_4$ solutions containing 70% (*v*/*v*) AN. $[HClO_4]$/M: a, 0.001; b, 0.006; c, 0.02; d, 2.0. Path length, 1 mm.

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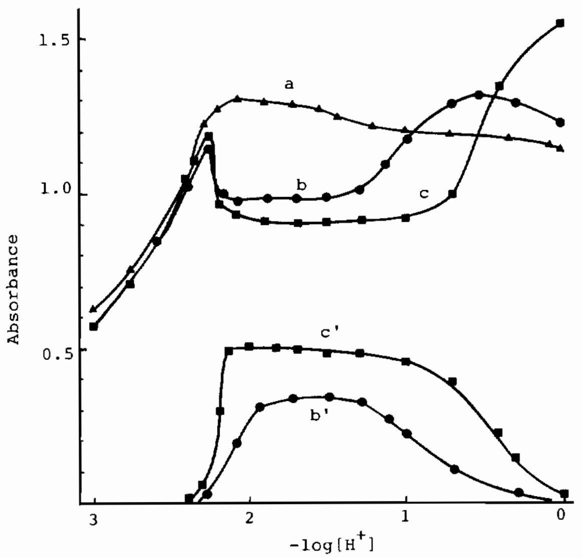

Fig. 2. Absorbances at 250 nm (a, b, c) and 325 nm (b', c') for 4.0 mM Mo(VI) in $HClO_4$ solutions containing AN. AN/% (v/v): a, 0; b, b', 40; c, c', 70. Path length, 1 mm.

1.0 M). At AN concentrations of 40% (v/v), the absorbance at 250 nm decreased with a simultaneous increase of the absorbance at 325 nm in the $-\log[H^+]$ range of 2.2–0.5, where yellow solutions resulted (curves b and b'). As the $HClO_4$ concentration was further increased, the absorbance at 250 nm went through a maximum around $-\log[H^+] = 0.5$ and then decreased. The absorbance decrease can be accounted for in terms of the formation of cationic species such as monomeric forms $Mo(OH)_5(H_2O)^+$ and $Mo(OH)_4(H_2O)_2{}^{2+}$ and a dimeric form $Mo_2O_5{}^{2+}$ [9–12]. As shown in curve c', AN concentrations of 70% (v/v) gave increased absorbances at 325 nm. This result indicates that increase of AN concentrations favors the formation of the yellow species, $Mo_6O_{19}{}^{2-}$, which agrees with the observation by Murata and Ikeda [13], who reported that the Raman line due to $Mo_6O_{19}{}^{2-}$ at 980 cm^{-1} increased in intensity by the addition of cyclohexanone.

A yellow precipitate occurred by the addition of tetramethylammonium chloride (Me_4NCl) to the 70% (v/v) AN solutions in the $-\log[H^+]$ range 2.0–1.0. The precipitate was filtered off, washed with distilled water and dried at room temperature. The IR spectrum of the precipitate is shown in curve a of Fig. 3, and the Raman lines are observed at 988, 960, 813, 602, 290 and 210 cm^{-1}. The IR and Raman spectra are in good agreement with those for the $Mo_6O_{19}{}^{2-}$ salt [3, 4]. In fact, the elemental analysis showed that the formula for the precipitate was $(Me_4N)_2Mo_6O_{19}$; the precipitate contained no water of crystallization. *Anal.* Found: C, 9.46; H, 2.37; N, 2.85; Mo, 55.96. Calc. for $(Me_4N)_2Mo_6O_{19}$: C, 9.35; H, 2.35; N, 2.73; Mo, 56.00%.

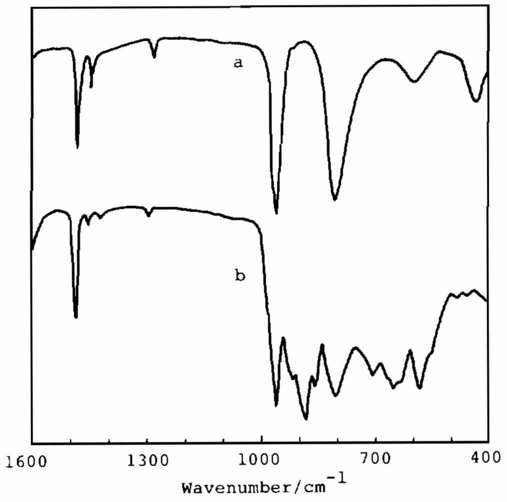

Fig. 3. IR spectra of a, $(Me_4N)_2Mo_6O_{19}$ and b, $(Me_4N)_8Mo_{36}O_{112}$.

Similarly, curve b of Fig. 3 shows an IR spectrum of a white precipitate obtained by the addition of Me_4NCl to the 40% (v/v) AN solutions in the $-\log[H^+]$ range 0.5–0.3. The precipitate showed Raman lines at 988, 954, 898, 372 and 234 cm^{-1}. The spectrum is identical with that of the $Mo_{36}O_{112}{}^{8-}$ salt [14, 15]. In the TGA–DTA curve, the $Mo_{36}O_{112}{}^{8-}$ salt showed an endothermic transformation at 75 °C with a weight loss of 8.3% due to the evolution of water. The results of elemental analysis for the salt heated at 150 °C are as follows. Found: C, 6.02; H, 1.81; N, 1.62; Mo, 58.78. Calc. for $(Me_4N)_8Mo_{36}O_{112}$: C, 6.58; H, 1.66; N, 1.92; Mo, 59.15%.

Recently, the existence of the $Mo_{12}O_{37}{}^{2-}$ ion in weakly acidic solutions is claimed [13]. Calc. for $(Me_4N)_2Mo_{12}O_{37}$: C, 5.08; H, 1.28; N, 1.48; Mo, 60.86%, being slightly different from the experimental values.

$Mo_6O_{19}{}^{2-}$ is formed in solutions containing dimethyl formamide (DMF), acetone, ethanol and 1,4-dioxane. On the other hand, $Mo_6O_{19}{}^{2-}$ does not occur in any of the Mo(VI) solutions containing formamide or n-methyl formamide (NMF). Figure 4 shows the effect of concentrations of organic solvents on absorbances at 325 nm for 4.0 mM Mo(VI) in 0.02 M $HClO_4$; for acetone-containing solutions, absorbances at 400 nm were measured because of the absorption of acetone at 325 nm. It was observed that concentrations of organic solvents up to 20% (v/v) had no effect but concentrations >30% (v/v) gave increased absorbances. Constant absorbances were obtained at concentrations >70% (v/v) of AN, DMF and acetone. At AN concentrations of 70% (v/v) or more, the molar absorption coefficient per molybdenum, ϵ is calculated as 1090 and 375 cm^{-1} M^{-1} at 325 and 380 nm respectively; for $Mo_6O_{19}{}^{2-}$ in AN, the corresponding values are 1140 and 390

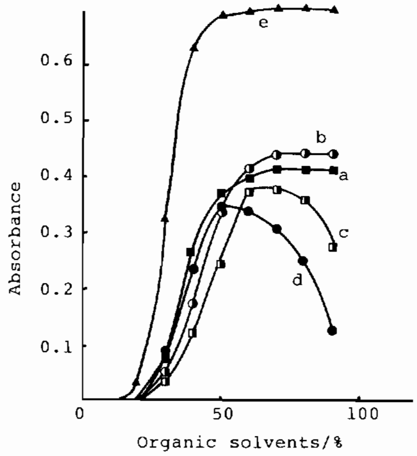

Fig. 4. Effect of concentrations of organic solvents on absorbances at 325 nm (a–d) and 400 nm (e) for 4.0 mM Mo(VI) in 0.02 M $HClO_4$ containing a, AN; b, DMF; c, ethanol; d, 1,4-dioxane; e, acetone. Path length: a–d, 1 mm; e, 1 cm.

cm^{-1} M^{-1}, which suggests that *ca.* 96% of Mo(VI) forms $Mo_6O_{19}^{2-}$ under these conditions. For ethanol and 1,4-dioxane, on the other hand, absorbances at 325 nm decreased at higher concentrations. This behavior agrees with the result that $(Me_4N)_2Mo_6O_{19}$ is insoluble in ethanol or 1,4-dioxane.

We then examined the temperature effect on absorbances at 250 and 325 nm of solutions consisting of 4.0 mM Mo(VI), 0.05 M $HClO_4$ and 40% (*v*/*v*) AN. As the temperature was raised, absorbances at 325 nm showed a gradual increase with a decrease of absorbances at 250 nm. The following experiments were made to confirm the temperature effect. A solution containing 100 mM Mo(VI), 1.0 M HCl and 40% (*v*/*v*) AN was stirred at 10 °C for 12 h. The $Mo_{36}O_{112}^{8-}$ salt was precipitated by the addition of Me_4NCl to the cold solution. However, different results were obtained when the solution was heated to boiling before adding Me_4NCl; the $Mo_{36}O_{112}^{8-}$ salt was no longer obtained but the $Mo_6O_{19}^{2-}$ salt was precipitated. When Mo(VI) concentrations >200 mM, there appeared a white precipitate before the addition of Me_4NCl. The precipitate showed an X-ray diffraction pattern identical with that of anhydrous molybdenum oxide in hexagonal form [16]. After filtration, the $Mo_6O_{19}^{2-}$ salt was obtained by adding Me_4NCl to the supernatant hot solution. The results of temperature effect on absorbances suggest that the behavior is not due to the solubility difference between the $Mo_6O_{19}^{2-}$ and $Mo_{36}O_{112}^{8-}$ salts but that $Mo_{36}O_{112}^{8-}$ is converted into $Mo_6O_{19}^{2-}$ at higher temperatures.

In addition, it was found that an increase of the ionic strength is unfavorable for the formation of $Mo_6O_{19}^{2-}$.

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