On Molybdenum(IV) and Molybdenum(III) Species in HCl Solutions

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Molybdenum in oxidation states VI, V, IV and III forms a number of oxo-species. Molybdenum(VI) forms mononuclear complexes with the MoO_2^{2+} core [1–5] and dinuclear complexes with the $Mo_2O_5^{2+}$ core [6, 7]; there is evidence for the presence of the mono-oxobridged dimer in acidic solutions [8]. Di-μ-oxo Mo(VI) complexes have not been prepared so far. The structures of Mo(V) complexes are based on the MoO^{3+}, $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ cores [9–16], and these core structures are retained in HCl solutions [17]. It has been established that Mo(IV) occurs as a trinuclear species, retaining the $Mo_3O_4^{4+}$ core in solution [18–21]. The reduction product of Mo_3(IV) has been postulated as a trinuclear Mo_3(III) since the Mo(III) species is reoxidized to Mo_3(IV), and oxidation of monomeric and dimeric Mo(III) leads not to Mo_3(IV) but to dimeric Mo_2(V). A mononuclear Mo(III) complex with the formula of K_3MoCl_6 and dinuclear Mo(III) complexes with the di-μ-oxo and di-μ-hydroxo structures have been isolated [22–24]. However, less is known on the nature of Mo(III) species in solution.

Our recent interest has centered on the structural information for molybdenum ions in solution. Raman spectroscopy has proved to be suitable for studying the solution chemistry of Mo(VI) and Mo(V) ions [8, 17]. The purpose of the present study is to identify and characterize Mo(IV) and Mo(III) species present in HCl solutions.

Experimental

Raman spectra were recorded with a Spex Model Ramalog-5 spectrometer. The argon line at 488 nm was used for excitation. A Hitachi Model 220-A UV-Vis spectrophotometer was used for spectrophotometric measurements. Polarographic measurements were carried out with a PAR Model 174-A polarographic analyzer. Controlled potential electrolyses were made with a Yanagimoto Model V-8 potentiostat.

Sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, was used. The complex $(NH_4)_2MoOCl_5$ was prepared by the method of Soha and Bannerjee [25] and K_3MoCl_6 was provided by the Climax Molybdenum Co. Dowex 50W-X4 cation-exchange resin (H^+ form) was used for ion-exchange columns. All other chemicals were reagent grade and were used without further purification.

Solutions of Mo_3(IV) were prepared according to the method of Souchay [26] and stored in a refrigerator. Solutions of Mo_3(III) were prepared from Mo_3(IV) by reduction with amalgamated zinc or by controlled potential electrolyses. In a similar manner, solutions of Mo_2(III) were prepared from Mo(V).

Results and Discussion

Raman Spectroscopy

In order to obtain structural information for Mo_3(IV), Mo_3(III) and Mo_2(III) in HCl solutions, Raman spectra in the range 100–1200 cm^{-1} were recorded. The total molybdenum concentration ranged from 0.06 to 0.08 M. No previous Raman measurements on these ions have been reported. Table I summarizes the vibrational frequencies (cm^{-1}).

TABLE I. Vibrational Frequencies (cm^{-1}) of Mo_3(IV), Mo_3(III) and Mo_2(III) in HCl Solutions.

Mo_3(IV)				
1.0–10.3 M	790	550–350		
Mo_3(III)				
0.5 M	790	550–350		
1.0–6.0 M	790	550–350		285
Mo_2(III)				
1 M	740	500	374	
3–8 M	740	500	374	283

The Raman spectra of Mo_2(III) were characterized by bands at 740, 500 and 374 cm^{-1}, and an additional band at 283 cm^{-1} was observed above 3 M HCl. The spectrum in the Mo–O stretching region was unchanged in the HCl concentration in the range 1–8 M. According to Furnali and Piovesana [27], the electronic spectrum of K_3MoCl_6 above 9 M HCl is identical to that of the solid. In previous papers on Mo(VI) and Mo(V) species in acidic solutions [8, 17], we have shown that the stretching vibrations of a di-oxobridge occur at 750–500 cm^{-1}, while those of a mono-oxobridge occur outside the frequency range of 750–500 cm^{-1}, in agreement with the work by Wing and Callahan [28]. These results exclude the possibility of the presence of a

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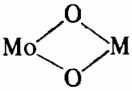
dimer with a mono-oxobridge, but indicate the formation of a dimer with a di-oxobridge in 1–8 M HCl. In general, planar molecules of the



type have six normal modes of vibration: one symmetric and three asymmetric stretching modes, and two ring deformation modes (in- and out-of-plane).

Of these, a symmetric and an asymmetric stretching mode and a ring deformation mode (in-plane) are Raman active; the 740 cm^{-1} band can be assigned to the asymmetric stretch, the 500 cm^{-1} band to the symmetric stretch and the 374 cm^{-1} band to the deformation.

To obtain further information on the nature of $Mo_2(III)$ we took the UV–VIS spectrum of 0.4 mM $Mo_2(III)$ in 1 M HCl. The spectrum showed absorption peaks at 360 and 660 nm, being independent of the HCl concentration in the range 1–5 M. Above 7 M HCl the solution gave an absorbance decrease at 360 nm with the formation of peaks at 420 and 520 nm, characteristic of the spectrum of $MoCl_6^{3-}$. This behavior is explained in terms of the monomer–dimer interconversion as a function of [HCl]. In order to confirm this, a deaerated solution of 5 mM K_3MoCl_6 in 1 M HCl was stirred with nitrogen over a mercury pool. The potential of the mercury pool was held at –0.70 V to avoid the oxidation of Mo(III). After *ca.* 40 h, the solution showed absorption peaks at 360 and 660 nm; the increase in the absorbance was observed over *ca.* 70 h. These results demonstrate that the monomeric Mo(III) is dimerized spontaneously to $Mo_2(III)$ in 1 M HCl, but the reaction rate is slow.

The Raman spectra of $Mo_3(IV)$ showed a band near 790 cm^{-1} and a very broad band extending from 550 to 350 cm^{-1}; no change in the spectrum was observed for HCl concentrations in the range 1.0–10.3 M. Solutions of $Mo_3(III)$ gave essentially the same Raman spectra as those of $Mo_3(IV)$, except for a band in the former at 285 cm^{-1}. The band at 285 cm^{-1} increased in height with increasing HCl concentration. The exciting line is absorbed by the molybdenum solutions due to their intense color, which restricts the concentration range of molybdenum. Although there is a possibility of the appearance of bridge vibrations in the frequency range expected for di-oxobridge groups, we could not detect them. From the observed bands, we cannot conclude the entire structures of $Mo_3(IV)$ and $Mo_3(III)$ species, but the results support the assumption that the reduction of $Mo_3(IV)$ to $Mo_3(III)$ occurs with retention of an identical trinuclear structure.

The appearance of the band at 283–285 cm^{-1}, which is characteristic of a Mo–Cl stretching vibration [29, 30], provides evidence that both $Mo_2(III)$ and $Mo_3(III)$ form chloro-complexes in HCl solutions. No bands in the Mo=O stretching region (900–1000 cm^{-1}) were observed for $Mo_3(IV)$, $Mo_3(III)$ and $Mo_2(III)$ solutions.

Ion-exchange Chromatography

All ion-exchange experiments were carried out in an anaerobic glovebox. When a solution of $Mo_2(III)$ in 1 M HCl was placed on a cation-exchange column which had been treated with 1 M HCl, a green band was adsorbed on the top of the column. The green band was eluted with 4 M HCl. Similarly, a green solution of $Mo_3(III)$ in 0.7 M HCl was adsorbed onto the resin and was eluted with 4 M HCl. The cation-exchange behavior shows that $Mo_2(III)$ and $Mo_3(III)$ exist as positively charged species below 1 M HCl, while anionic chloro-complexes are formed in 4 M HCl, in agreement with the Raman results.

A red-purple solution of $Mo_3(IV)$ in 4 M HCl passed through the column without being adsorbed, which indicates that negatively charged species exist. To see whether Mo(IV)–chloro complexes were formed, chloride ions in a $Mo_3(IV)$ solution were removed by precipitation with $AgNO_3$. The precipitate of AgCl was removed by filtration and the filtrate was placed on the column which had been treated with 4 M $HClO_4$. Under these conditions the $Mo_3(IV)$ solution was adsorbed on the column. The red-purple band was eluted with 4 M HCl, which shows the formation of anionic Mo(IV)–chloro complexes. As shown in Table I, however, no Raman bands due to the Mo–Cl stretching were observed for $Mo_3(IV)$ in 1.0–10.3 M HCl, but we did not examine this feature in detail.

Polarographic Behavior

Figure 1(A) shows a differential pulse polarogram of 0.8 mM $Mo_3(IV)$ in 0.1 M HCl. A well-defined peak was observed at –0.48 V. The peak-potential (E_p) was independent of the $Mo_3(IV)$ concentration in the range 0.01–5 mM, which suggests that the trinuclear structure is retained even for concentrations as low as 0.01 mM. With an increase in HCl concentration the peak shifted to more positive potentials, and a broad peak appeared near –0.47 V above 2 M HCl (curve B). Similar double-wave behavior has been observed in sulfuric acid [31], *p*-toluenesulfonic acid [32] and trifluoromethanesulfonic acid [33]. This behavior has been accounted for in terms of the formation of the mixed-valent intermediate, $Mo_3(III,III,IV)$. The Raman spectra of both $Mo_3(IV)$ and $Mo_3(III)$ were identical in the Mo–O stretching region, which seems to support the proposition by Richens and Sykes that the intermediate retains the essential trinuclear structure [32].

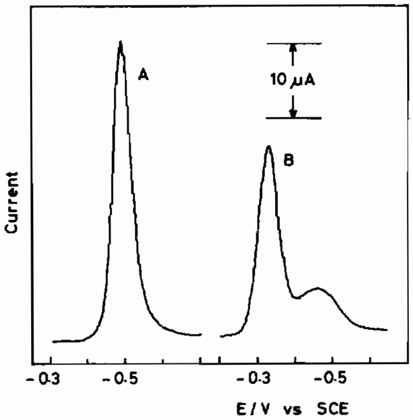


Fig. 1. Differential pulse polarograms of 0.8 mM Mo_3(IV) in hydrochloric acid. [HCl]/M; A, 0.1; B, 4.0. Drop time, 1 s; ΔE, 25 mV; scan rate, 2 mV/s.

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