Raman Studies on Molybdenum(V) Species in HCl Solutions

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Several investigations have been made of the Mo(V) species present in HCl solutions. Sacconi and Cini have interpreted the magnetic susceptibility results in 4–7 *M* HCl in terms of the monomer–dimer interconversion [1]. In spectrophotometric studies [2], Haight has shown that the hydrolysis of $MoOCl_5^{2-}$ involves dimerization in 5–6 *M* HCl. He has also described the presence of two dimeric species in the solutions. On the basis of the ESR results [3], Hare *et al.* have shown that there are three regions according to the HCl concentration; a diamagnetic species exists below 2 *M* HCl, a paramagnetic dimer exists in the region of 4–10 *M* HCl, and a paramagnetic monomer is present above 10 *M* HCl. Colton and Rose have isolated the oxo-bridged dimer, $Mo_2O_3Cl_8^{4-}$ and proposed the equilibria occurring in HCl solutions [4]. However, there have been no definitive studies on the structures of the Mo(V) species in HCl solutions. Raman spectroscopy seems suitable for the purpose of investigating this problem since oxospecies show characteristic Raman spectra.

Experimental

Raman spectra (1200–100 cm^{-1}) were recorded on a Spex Raman spectrophotometer, Model Ramalog 5. The argon line at 488 nm was used for excitation.

Molybdenum(V) solutions were prepared from $(NH_4)_2MoOCl_5$ [5]. All chemicals were of analytical reagent grade and were used without further purification.

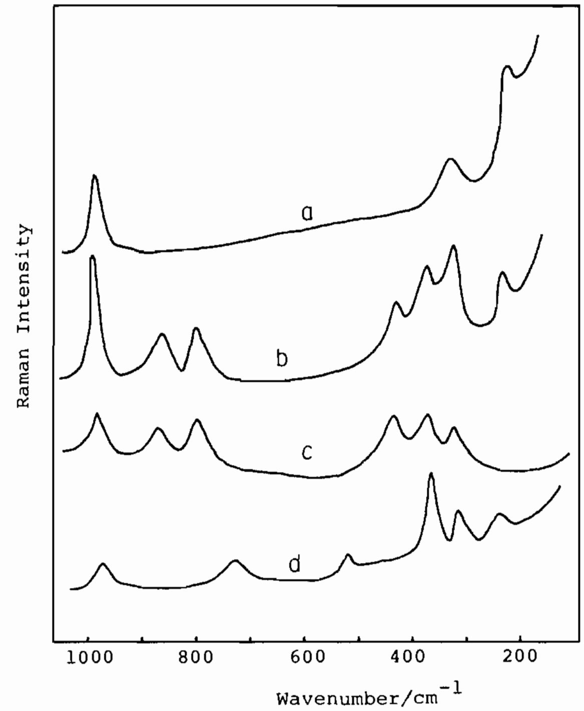

Fig. 1. Raman spectra of Mo(V) in various concentrations of HCl. HCl concentrations: a) conc.; b) 6 *M*; c) 3 *M*; d) 1 *M*.

Results and Discussion

Figure 1 shows Raman spectra of Mo(V) in various concentrations of HCl. In a concentrated HCl solution, bands were found at 997, 334 and 239 cm^{-1} (curve a). There is general agreement that the main species in this solution is the paramagnetic monomer, $MoOCl_5^{2-}$ [1–4]. No change in the spectrum was observed when the HCl concentration was decreased to 8 *M*. On dilution of the solution to 5 *M*, however, spectral change was observed; in addition to the first two bands, bands appeared at 870, 802, 436 and 378 cm^{-1} with a disappearance of the band at 239 cm^{-1} (curve c). The spectrum was independent of the HCl concentration in the range 3–5 *M*. Further dilution to 1 *M* made another spectral change (curve d); bands were found at 742, 532, 372 and 253 cm^{-1}.

TABLE I. Vibrational Frequencies (cm^{-1}) of Mo(V) in HCl.

HCl/*M*	ν(Mo=O)	ν(Mo–O)	δ(O=Mo–O)	ν(Mo–Cl)	δ(Mo–O–Mo)	δ(Mo=O)
1	982	742 532	372	323	253	
3–5	984	870 802 436	378	326		
8-conc.	997			334		239

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The Raman frequencies are summarized in Table I. These results provide direct evidence for the existence of three species in these solutions.

It is known that Mo=O stretching vibrations occur in the 900–1000 cm^{-1} region [6]. The bands at 982–997 cm^{-1} are found over the HCl concentration range studied, which indicates that the three Mo(V) species contain terminal oxygens.

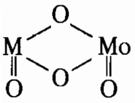
The band at 334 cm^{-1} observed in a concentrated HCl solution is generally assigned to a Mo–Cl stretching vibration [7, 8]. The band at 239 cm^{-1} can be assigned to the rocking mode of the terminal oxygen, since the frequency seems to be too low to be ascribed to the Mo–Cl stretching mode.

Various dimeric complexes with the cores of $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ have been isolated from aqueous solutions [9–15]. According to Wing and Callahan [16], asymmetric and symmetric stretching frequencies of a mono-oxobridge occur at frequencies higher than 750 cm^{-1} and at frequencies lower than 500 cm^{-1} respectively, because of the large angle of the Mo–O–Mo bond.

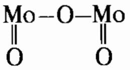
On the other hand, stretching vibrations of a dioxobridge are expected to occur at 750–500 cm^{-1}. On this basis, we can assign the 870, 802 and 436 cm^{-1} bands in 3–5 *M* HCl to the stretching mode of the mono-oxobridge, and the 742 and 532 cm^{-1} bands in 1 *M* HCl to that of the di-oxobridge. This agrees with work by Ardon and Pernick [17], who have postulated the existence of a dimer with the Mo_2O_4 core in 1 *M* HCl. This conclusion is further supported by the fact that Mo(V) complexes with the Mo_2O_4 core are diamagnetic [9,14, 15, 18]; according to Hare *et al.* [3], a diamagnetic ion is present below 2 *M* HCl.

Concerning other bands found in 1–5 *M* HCl, those at 323–326 cm^{-1} presumably arise from the Mo–Cl stretching mode [7, 8]. The bands at 372–378 cm^{-1} are close in frequency to those due to the Mo–Cl stretching vibration. However, the bands near 380 cm^{-1} are always observed in Mo(VI) solutions without Cl^- ions [19], and have been assigned to the deformation mode of a *cis*-MoO_2 group [20]. From the above results, the bands could be assigned to the deformation mode of the O=Mo–O unit. The band at 253 cm^{-1} in 1 *M* HCl can be tentatively assigned to the deformation mode of the dioxobridge.

The results described above lead to the conclusion that the principal species of Mo(V) in 1 *M* HCl is a dimeric chloro complex with the



core, while a dimer with the



$$\begin{array}{ccc} Mo & -O- & Mo \\ \| & & \| \\ O & & O \end{array}$$

core predominates in 3–5 *M* HCl. It is generally assumed that terminal oxygens are *cis*-directed [21]. Monomeric chloro complexes with the terminal oxygen exist above 8 *M* HCl.

The intensities of the bands near 990 and 330 cm^{-1} were significantly greater in 6–7 *M* HCl than in 3–5 *M* HCl and the band at 239 cm^{-1} was found in 6–7 *M* HCl (curve b in Fig. 1), which indicates that the monomer is in equilibrium with the dimer with the Mo_2O_3 core in 6–7 *M* HCl. This result is in agreement with the spectrophotometry reported by Haight [2]. Similarly, Raman spectra showed the co-existence of the two dimers in 2 *M* HCl.

It is not possible to deduce the precise formulae of the Mo(V) species from the present Raman data. Spectrophotometric and polarographic studies are being made to determine the stoichiometry and the equilibrium constants.

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