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## Study on the Elution Behaviors of Molybdate and Tungstate in Both Hydrochloric and Perchloric Acid by Anion Exchange Chromatography

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The elution behaviors of molybdate and tungstate through anion exchange column have been investigated in the various concentration of hydrochloric and perchloric acid. A discussion is made to evaluate the existing these equilibrium and constant according to acidity. In both acids of 0.01–2.0 *M* concentration range, the existing equilibrium for molybdate and its constant calculated at 20°C is  $10^{18.9}$  for  $\text{Mo}_8\text{O}_{24}^{4-} + 20\text{H}^+ \rightleftharpoons 8\text{MoO}_2^{2+} + 10\text{H}_2\text{O}$ . In the 3–3.5 *M* hydrochloric acid it is 0.16 for  $\text{MoO}_2\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{MoO}_2\text{Cl}_3^-$  and for the case of tungstate, in the both acids of 0.01–1.0 *M* concentration range  $10^{6.6}$  for  $\text{W}_{12}\text{O}_{39}^{6-} + 6\text{H}^+ \rightleftharpoons 12\text{WO}_3 \cdot 3\text{H}_2\text{O}$ . In higher concentration than 1.0 *M* both acids the following equilibrium seems to be existed.  $12\text{WO}_3 \cdot 3\text{H}_2\text{O} \rightleftharpoons 12\text{WO}_3 + 3\text{H}_2\text{O}$

### Introduction

Molybdenum and tungsten have known to form quite different species in their acid solutions and the strength of acid also plays quite important roles in the solution. These anomalies have drawn some attentions such as UV, Raman,<sup>1</sup> the solubility, and the ion exchange studies. In the solubility study of  $\text{MoO}_3$ , Raman *et al.*<sup>2</sup> have found that  $\text{MoO}_4^{2-}$  had been converted into  $\text{MoO}_2^{2+}$  ion at pH 1 which was confirmed by Babko<sup>3</sup> and Jones<sup>4</sup>.

A similar trend has been found in the study of the distribution coefficient of molybdate using the batch method of anion exchange chromatography. Shishkov<sup>5</sup> reported that molybdenum exists only as  $\text{MoO}_4^{2-}$  species in 0.01–0.1 *M* hydrochloric acid solution and both species of  $\text{MoO}_2^{2+}$  and  $\text{MoO}_4^{2-}$  in 0.2–2.0 *M* hydrochloric acid solution. And Cook<sup>6</sup> has found that  $\text{MoO}_2\text{Cl}_2$  species existed predominantly at lower concentration than 6 *M* hydrochloric acid whereas

$\text{MoO}_2\text{Cl}_3^-$  species existed at higher than 6 *M*.

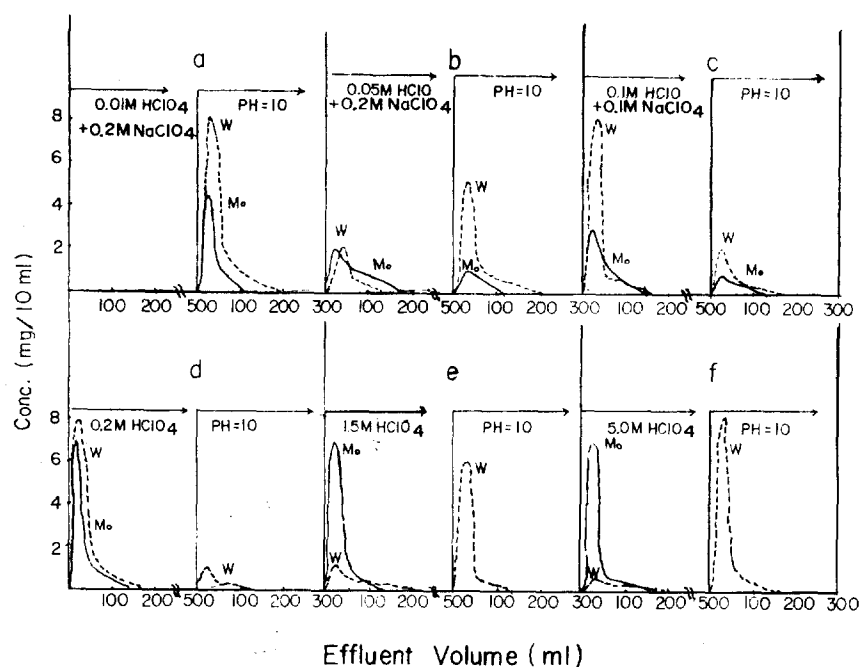
On the other hand, tungsten behaved quite differently in its acid solution. Freedman<sup>7</sup> found that tungstate ion formed a metatungstate ion at pH 1–4 and converted into polyacid with increasing the acidity, then transformed steadily to  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ . And the precipitation started to dissolve as the concentration went over 10 *M* and remained as  $\text{WO}_3^{2+}$  ion.

Some studies have also been done by the authors<sup>8</sup> for the equilibrium of molybdate and tungstate ions at pH 4–10 by using anion exchange chromatography.

In this paper we intend to elucidate the existing these equilibria and equilibrium constants at the various concentration of hydrochloric and perchloric acid through the elution behavior of molybdate and tungstate.

### Experimental

*Reagent and Apparatus.* 0.1 *M* sample solutions of molybdate and tungstate were made by dissolving the first



**Figure 1.** Elution curves of molybdate and tungstate at various concentration of perchloric acid. Resin: rexyn 201(100 200); Eluent of final stage 0.5M  $\text{NH}_4\text{Cl}$ ; Flow rate; 1.5 ml/min; Column: 3.14 $\text{cm}^2 \times 5\text{cm}$ .

grade those of sodium salts in the acid of various concentrations. Other reagents used were analytical grades. And the demineralized water was used through out in this study. Beckmann Electroscan 30 unit was used for pH measurement. Resin was Rexyn 201(100–200 mesh), exchange capacity

of 4.0 meq/g. The preparation of column and the elution curve were essentially the same as these of our earlier work<sup>8</sup>. Determination of molybdenum and tungsten were made spectrophotometrically<sup>9,10</sup>.

*Elution Behaviors of Molybdate Tungstate Ion.* In order to elucidate the relation between those ions in acidic solution, the elution curves of molybdate and tungstate ion were made at various concentration of perchloric acid since the anion of which had no ability of complex formation with metallic ion. 1 ml of each 0.1 M molybdate and 0.1 M tungstate ion solutions were loaded in the top surface of anion exchange column equilibrated with perchloric acid of various concentration and eluted with the acid solution as eluent.

The observations are given in Figure 1 and the recovery of molybdenum and tungsten eluted at first and second peaks in each curve for Figure 1 are summarized in Table 1. The elution curves of molybdate and

tungstate ions are shown in Figure 2 using hydrochloric acid instead of perchloric acid, and the recovery of molybdenum and tungsten eluted at first and second peak in each curve of Figure 2 are summarized in Table 2.

**TABLE 1: Recoveries at the First Peak and the Second Peak in the Elution Curves of Molybdate and Tungstate at the Various Concentration of Perchloric Acid**

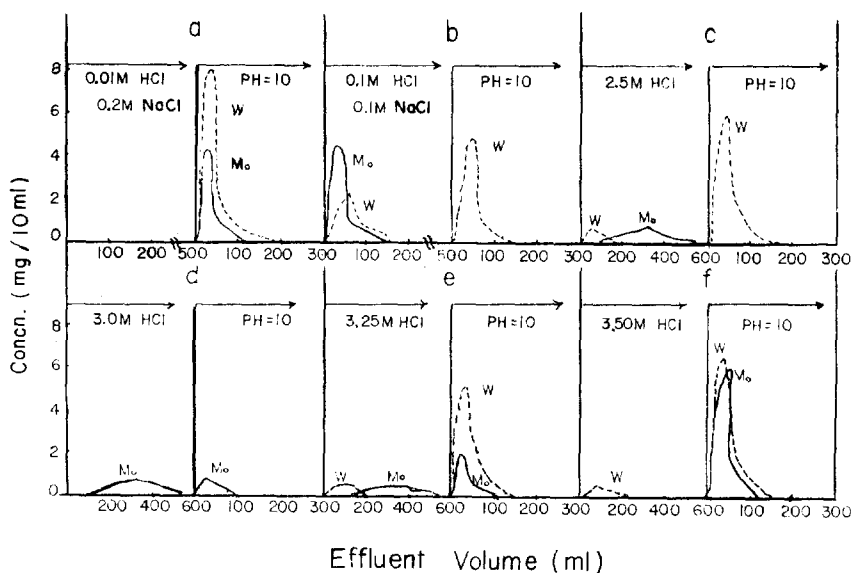
Conc. of $\text{HClO}_4$ (M)	Amount taken (mmole)	Recovery at the first peak (mole)	Recovery at the second peak (mmole)
0.01 + 0.2 M $\text{NaClO}_4$	Mo=0.1	Mo=none	Mo=0.1
	W =0.1	W =none	W =0.1
0.05 + 0.2 M $\text{NaClO}_4$	Mo=0.1	Mo=0.068	Mo=0.032
	W =0.1	W =0.013	W =0.087
0.1 + 0.1 M $\text{NaClO}_4$	Mo=0.1	Mo=0.084	Mo=0.016
	W =0.1	W =0.080	W =0.020
0.2	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.089	W =0.011
0.5	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.088	W =0.012
1.0	Mo=0.1	Mo=0.1	Mo=0.00
	W =0.1	W =0.080	W =0.020
1.5	Mo=0.1	Mo=0.1	Mo=0.00
	W =0.1	W =0.044	W =0.56
2.0	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.018	W =0.082
2.4	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.013	W =0.087
3.5	Mo=0.1	Mo=0.1	Mo=0.00
	W =0.1	W =-	W =-
4.0	Mo=0.1	Mo=0.1	Mo=0.00
	W =0.1	W =-	W =-
5.0	Mo=0.1	Mo=0.1	Mo=0.00
	W =0.1	W =0.004	W =0.096

## Result and Discussion

The species variation of molybdate and tungstate according to acidity Figure 1 and Table 1 show that the shapes of the elution curves of molybdate and tungstate are varied according to the concentration of perchloric acid.

In the curve of Figure 1a, molybdenum and tungsten are not eluted up to 500 ml with the eluent when the composi-

tion of eluent are 0.01 M perchloric acid and 0.2 M sodium perchlorate. However the elution started slowly within 200 ml in the case of 0.5 M ammonium chloride solution at pH 10. In Figure 1b curve, a part of molybdenum and tungsten are eluted within 200 ml by the acidic eluent. And the remaining molybdenum and tungsten in the resin phase are eluted slowly by 0.5 M ammonium chloride solution at pH 10. In Figure 1d curve, the total molybdenum and 90 % tungsten are eluted in the acidic eluent and the remaining tungsten is eluted in the 0.5 M ammonium chloride solution at pH 10.



**Figure 2.** Elution curves of molybdate and tungstate at various concentration of hydrochloric acid. Resin: Rexyn 201(100-200); Eluent of final stage: 0.5 M NH<sub>4</sub>Cl; Flow rate: 1.5 ml/min; Column: 3.14 cm<sup>2</sup>x5 cm,

Our interpretation for the observation of Figure 1a is that molybdate and tungstate ion should have only one species as polymer which is not eluted in the 0.01 M perchloric acid. Then Figures 1b and c curves may imply that molybdate and tungstate ion exist as two species. Therefore the possible interpretation of the species eluted in perchloric acid should be neutral or positive charged species because it is eluted early, and the species eluted in 0.5 M ammonium chloride solution at pH 10 are then negative charged polymeric species, which convert to monomer state at pH 10.

By comparing with the previous reports<sup>2,3,7,8</sup> the tungsten species eluted in acidic solution must be  $WO_3 \cdot \frac{1}{4}H_2O(H_6W_{12}O_{37})$  and molybdenum is  $MoO_4^{2-}$ . Hence the degree

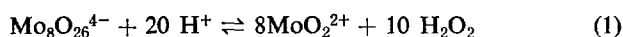
**TABLE 2: Recoveries at the First Peak and the Second Peak in the Elution Curves of Molybdate and Tungstate at the Various Concentration of Hydrochloric Acid**

Conc. of HCl (M)	Amount taken (mmole)	Recoveries at the first (mmole)	Recoveries at the second peak (mmole)
0.01 + 0.2 M NaCl	Mo=0.1	Mo=0.00	Mo=0.1
	W =0.1	W =0.00	W =0.1
0.1 + 0.1 M NaCl	Mo=0.1	Mo=0.1	Mo=.00
	W =0.1	W =0.046	W =0.054
0.4	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.045	W =0.055
0.8	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.10	W =0.075	W =0.025
1.0	Mo=0.10	Mo=0.10	Mo=0.00
	W =0.10	W =0.080	W =0.20
1.4	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.05	W =0.050
2.0	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.018	W =0.082
2.5	Mo=0.1	Mo=0.10	Mo=0.00
	W =0.1	W =0.022	W =0.017
3.0	Mo=0.1	Mo=0.083	Mo=0.017
	W =0.1	W =-	W =-
3.2	Mo=0.1	Mo=0.066	Mo=0.034
	W =0.1	W =-	W =-
4.0	Mo=0.1	Mo=0.00	Mo=0.10
	W =0.1	W =0.009	W =0.091
5.0	Mo=0.1	Mo=0.00	Mo=0.10
	W =0.1	W =0.007	W =0.093

of depolymerization of the polymer will be increased with rising perchloric acid concentration and the amount of molybdenum and tungsten eluted in acidic solution will be increased with acidity as shown in Figures 1c and d curves at the higher concentration than 0.2 M perchloric acid all the molybdenum is eluted in the first peak. Whereas in the case of tungsten, the most of tungsten is eluted in the second peak at the higher concentration than 0.5 M perchloric acid as shown in Figures 1e and f curve.

From the foregoing discussion, we have concluded that molybdate and tungstate have two species according to the concentration of perchloric acid and these two species equilibrate each other. And the species absorbed in the resin at the beginning may not follow the equilibrium rule during the elution but the ion exchange reaction rule<sup>8</sup>.

In the molybdate, the following equilibrium seems to be existed in the 0.01–0.2 M hydrochloric and perchloric acid solution.

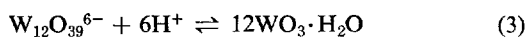


Here the species eluted from the first peak is considered as  $\text{MoO}_2^{2+}$  and the second peak as  $\text{Mo}_8\text{O}_{26}^{4-}$ , which is converted to monomer form in the ammonium chloride solution at pH 10.

At the higher concentration than 0.2 M perchloric acid, molybdate has only one peak eluted in acidic solution as shown in Figures 1d, e and f. The equilibrium constant of Eq. (1) can be calculated using data of 0.05 M perchloric acid eluent by

$$K = \frac{[\text{MoO}_2^{2+}]^8}{[\text{Mo}_8\text{O}_{26}^{4-}] [\text{H}^+]^{20}} = \frac{(0.068)^8}{0.004 \times (5 \times 10^{-2})^{20}} = 8 \times 10^{18} \quad (2)$$

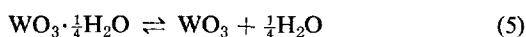
In the case of tungstate, the equilibrium in 0.01–0.5 M perchloric acid solution may be given by



Here  $\text{WO}_3 \cdot \frac{1}{4}\text{H}_2\text{O}$  species corresponds to first peak and  $\text{W}_{12}\text{O}_{39}^{6-}$  species is the second peak in Figures 1a, b and c. The equilibrium constant of Eq. (3) may be calculated using the data from Table 1.

$$K = \frac{[12\text{WO}_3 \cdot 3\text{H}_2\text{O}]}{[\text{W}_{12}\text{O}_{39}^{6-}] [\text{H}^+]^6} = \frac{0.007}{0.0017 \times 10^{-6}} = 4 \times 10^6 \quad (4)$$

From the elution behavior of tungstate shown in Figures 1e, f, we have concluded that  $\text{WO}_3 \cdot \frac{1}{4}\text{H}_2\text{O}$  species losses water molecule at the higher concentration than 0.5 M perchloric acid and it becomes  $\text{WO}_3$ .

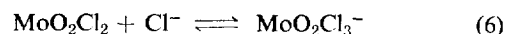


Here the species eluted in the first peak of Figures 1e and f is considered as  $\text{WO}_3 \cdot \frac{1}{4}\text{H}_2\text{O}$  form and the second peak as  $\text{WO}_3$  which is dissolved in the ammonium chloride solution at pH 10 and eluted.

*Effect of Chloride Complex.* Comparing Figure 1 with Figure 2, the elution behavior of tungstate is similar in both Figure's except that molybdenum behave different at

the higher solution than 2.5 M hydrochloric acid. This may be due to the chloric complex effect. At the lower concentration than 2.5 M hydrochloric acid the elution behavior of molybdate ion is similar to that in perchloric acid which is shown in Figure 2a and b. In Figure 2b all the molybdate is eluted within 100 ml eluent but in Figure 2c, the elution curve showed a rather broad shape from 100 ml to 550 ml eluent. In Figure 2d molybdenum showed two bands. One of them is eluted in the 100–500 ml eluent and the other which is not eluted in the 3 M hydrochloric acid is eluted with ammonium chloride solution at pH 10. In Figure 2c, the pattern is similar to that of Figure 2d except the molybdenum is eluted more in the second peak. In Figure 2f the elution is observed until 550 ml by 3.5 M hydrochloric acid and all of it is eluted with ammonium chloride solution at pH 10.

The possible interpretation of this observation is that there are two species of molybdenum under these conditions and they are in equilibrium. This phenomenon implies that molybdenum forms chloride complex in these conditions. As shown in Figures 1d, e and f, molybdate ion exists as  $\text{MoO}_2^{2-}$  in the acidic solution and the species forms a complex with chloride ion in hydrochloric acid. In Figure 2c the elution curve of molybdenum is quite spread comparing with that in Figure 1b. This indicates the formation of  $\text{MoO}_2\text{Cl}_2$  species between  $\text{MoO}_2^{2+}$  and  $\text{Cl}^-$ . The following reaction seems to be exist in Figures 2d and e.



Here  $\text{MoO}_2\text{Cl}_2$  species corresponds to the first peak and  $\text{MoO}_2\text{Cl}_3^-$  to the second peak. In Figure 2f molybdenum is not eluted in 3.5 M hydrochloric acid and only by ammonium chloride solution at pH 10. This means that another type of molybdenum exists. The equilibrium constant of Eq. (6) can be calculated using the data of Table.

$$K = \frac{[\text{MoO}_2\text{Cl}_3^-]}{[\text{MoO}_2\text{Cl}_2] [\text{Cl}^-]} = \frac{0.034}{0.066 \times 3.25} = 0.16$$

## Conclusion

Anion exchange resin column was used to investigate the species behaviors of molybdate and tungstate in the various concentration of perchloric and hydrochloric acid.

We have concluded that molybdate and tungstate have one or two species according to the concentration of both acids and these species equilibrate each other.

The species absorbed in the resin at the beginning may not follow the equilibrium rule during the elution but the ion exchange reaction rule.

The elution behavior of  $\text{WO}_4^{2-}$  is similar to that of  $\text{MoO}_4^{2-}$  except that molybdate behave differently at the higher concentration than 2.5 M hydrochloric acid.

Molybdate ion exists as  $\text{MoO}_2^{2-}$  in the acidic solution and the species forms a complex with chloride ion in hydrochloric acid.

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## S<sub>N</sub>2 Transition State Variation in the Benzenesulfonyl Chloride Solvolysis\*

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For solvolyses of benzenesulfonylchlorides we determined transfer enthalpies of transition states, and solvent (TFE+EtOH) and substituent effects on rates. We have used the More O'Ferrall plots to show that transition states variation caused by solvent and substituent changes is consistent with an associative S<sub>N</sub>2 mechanism for the nucleophilic substitution reaction of benzenesulfonylchlorides.

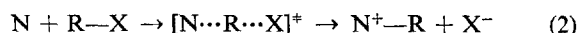
### Introduction

Benzenesulfonyl chloride is known to solvolyze by a borderline mechanism<sup>1</sup> as in the solvolysis of benzyl chloride<sup>2</sup>. There have been however much dispute over the mechanism as to whether it is an S<sub>N</sub>2 or an S<sub>A</sub>N process; Rogne and Lee favor an S<sub>N</sub>2<sup>3</sup> whereas Ciuffarin favors an S<sub>A</sub>N<sup>4</sup> mechanism. Extensive work on the transition state structure for benzyl solvolysis have been reported by Jencks<sup>5</sup> and Harris.<sup>6</sup> Jencks made a detailed analysis of the transition state variation as the medium is changed using the extended Grunwald-Winsten<sup>7</sup> equation (1),

$$\log(k/k_0) = mY + lN \quad (1)$$

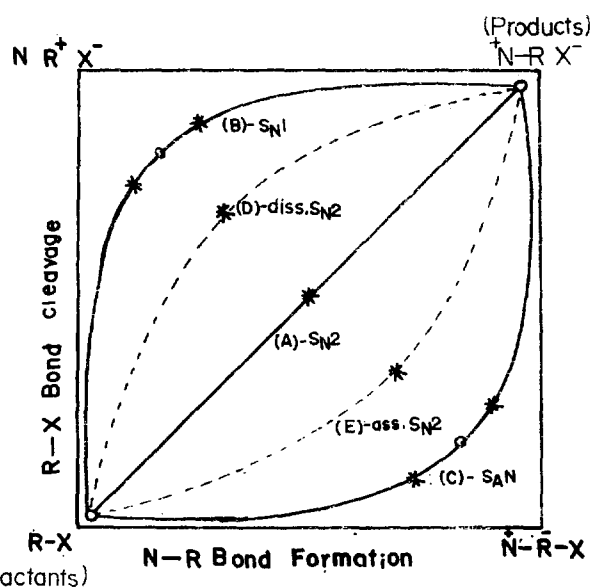
in which *Y* and *N* are the ionizing power and nucleophilicity of the medium, respectively, and *m* and *l* are reaction constants describing the susceptibility to *Y* and *N*.

Harris and coworkers<sup>6</sup>, on the other hand, made use of the More O'Ferrall type of plots<sup>8</sup> in predictions of the S<sub>N</sub>2 transition state variation for a series of substituted benzyl derivatives. Such plots were possible by application of Hammond's postulate<sup>9</sup> and Thornton's theory to direct displacement reactions, (2).



Hammond's postulate<sup>9</sup> can lead us to predictions of new transition state structures along ("parallel" to) the reaction coordinate, while predication of movement of transition state other than that along the reaction coordinate are possible using Thornton's rule.<sup>10</sup>

In the More O'Ferrall approach<sup>8</sup> the two dimensional potential energy diagram (Figure 1) includes two possible



**Figure 1.** A More O'Ferrall plot for a nucleophilic displacement reaction, where N is the nucleophile, X is the leaving group, and minima and maxima corresponding to the stable intermediates and transition state respectively are represented by circles and star marks. Path A, path B and path C represent the reaction coordinates for an S<sub>N</sub>2, S<sub>N</sub>1 and S<sub>A</sub>N reactions, respectively. Path D and path E represent the reaction coordinates for borderline mechanisms of a dissociative and associative S<sub>N</sub>2 reactions, respectively.

intermediates at two corners (upper left and lower right corners), making it possible to translate substituent and medium effects on intermediate stability into effects on the transition state structure even when the intermediates are not involved in the reaction. The More O'Ferrall plots can be used by applying following three rules:<sup>6</sup> (1) if species corresponding to a corner along the reaction coordinate are

\*This work is taken as Part 14 of the series "Nucleophilic Displacement at Sulfur Center".