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Contribution from the Department of Chemistry,
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Potentiometric and Polarimetric Studies of Complexation of Molybdenum(VI) and Tungsten(VI) by Aspartic Acid and Glutamic Acid

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Despite the extensive literature on the coordination chemistry of molybdenum(VI) and tungsten(VI), few formation constants have been reported for their complexes.[1] This situation is no doubt due to the competitive formation of isopolymolybdate and isopolytungstate species in acidic solution.[2-4] In basic solution, little or no complex forms due to the exceedingly high stability of the MoO_4^{2-} and WO_4^{2-} species.

Recently, Singh and Srivastava reported stepwise formation constants for 1:1, 1:2, and 1:3 aspartic acid and glutamic acid complexes of Mo(VI), W(VI), and V(IV).[5] The formation constants were computed from potentiometric titration data by the methods of Irving and Rossotti.[6] Since Mo(VI) and W(VI) complexes generally contain either an MO_2 or an MO_3 core with the coordination sphere of the metal completed by coordination to four or three donor atoms, respectively, it seems unlikely that complexes of 1:2 and 1:3 stoichiometry exist in aqueous solution. To determine the extent to which Mo(VI) and W(VI) are complexed by aspartic acid and glutamic acid in aqueous solution, we have studied these systems by potentiometry and polarimetry. A major objective of this communication is to describe how formation constants of Mo(VI) complexes can be correctly determined by the potentiometric titration method.

Table I. Optical Rotation (α) of Aspartic Acid as a Function of Solution Composition

pH	α	pH	α
0.050 M Aspartic Acid, 0.200 M KNO_3			
9.32	−0.171	5.07	−0.232
7.05	−0.249	3.27	0.088
5.90	−0.250		
0.050 M Aspartic Acid, 0.050 M Na_2MoO_4, 0.200 M KNO_3			
9.27	−0.142	5.12	0.661
7.37	−0.178	4.01	0.314
6.17	0.335	3.01	0.233
0.05 M Aspartic Acid, 0.050 M Na_2WO_4, 0.200 M KNO_3			
9.29	−0.147	5.00	−0.208
7.60	−0.198	4.12	−0.014
6.24	−0.198	2.19	−0.002

Table II. Continuous Variation Data for the Mo(VI)-Aspartic Acid System[a,b]

Mol fraction Mo(VI)	α(Mo + Asp)[c]	Δα[d]
0.00	−0.251	0.000
0.10	−0.043	0.183
0.20	0.131	0.332
0.30	0.213	0.389
0.40	0.280	0.431
0.50	0.286	0.412
0.60	0.254	0.354
0.70	0.210	0.285
0.80	0.141	0.191
0.90	0.080	0.105
1.00	0.000	0.000

[a] 25 °C; pH 6.19; ionic strength controlled with 0.20 M KNO_3. [b] [Mo(VI)] + [aspartic acid] = 0.050 M. [c] Optical rotation. [d] Δα = α(Mo + Asp) − α(Asp), where α(Asp) is the optical rotation of aspartic acid at the same concentration as in the Mo–aspartic acid solution.

Experimental Section

Analytical reagent grade $Na_2MoO_4{\cdot}2H_2O$ and $Na_2WO_4{\cdot}2H_2O$ were used as received. L-Aspartic acid and L-glutamic acid were obtained from Eastman Organic Chemicals and were used as received.

pH measurements were made at 25 ± 1 °C with an Orion 701 pH meter, which was calibrated with Fisher Certified standard solutions of pH 4.00, 7.00, and 10.00. Polarimetric measurements were made at 25 °C with a Perkin-Elmer Model 141 polarimeter using the 365-nm line of the mercury source. A water-jacketed cell of 100-mm length and 5-mL total volume was used. The precision of the measurements is estimated to be ±0.002 degrees of arc.

Results and Discussion

Assuming that the optical activity of aspartic acid will change upon complexation, polarimetric measurements were made to determine if Mo(VI) and W(VI) are complexed by aspartic acid. The results are given in Table I. In the presence of Mo(VI), the optical rotation is nearly the same as that of the free aspartic acid at pH 9.27. The small difference could be due to the formation of a sodium–aspartic acid complex. As the pH is decreased below pH 7, the optical rotation of the Mo–aspartic acid solution becomes increasingly different from that of aspartic acid, indicating complexation by Mo(VI). The difference reaches a maximum between pH 5 and 6 and then decreases as the pH is decreased below 5, indicating that the largest amount of complex forms in the pH range 5–6. At higher pH, the complex dissociates due to the competitive formation of MoO_4^{2-}, while at low pH isopolymolybdates form. In contrast, the optical rotation data for the W(VI)–aspartic acid solution shows only small differences from that for the aspartic acid solution, indicating little if any complexation of aspartic acid by W(VI).

The stoichiometry of the Mo(VI) complex at pH 6 was determined by the method of continuous variations. The results given in Table II indicate the stoichiometry to be 1:1.

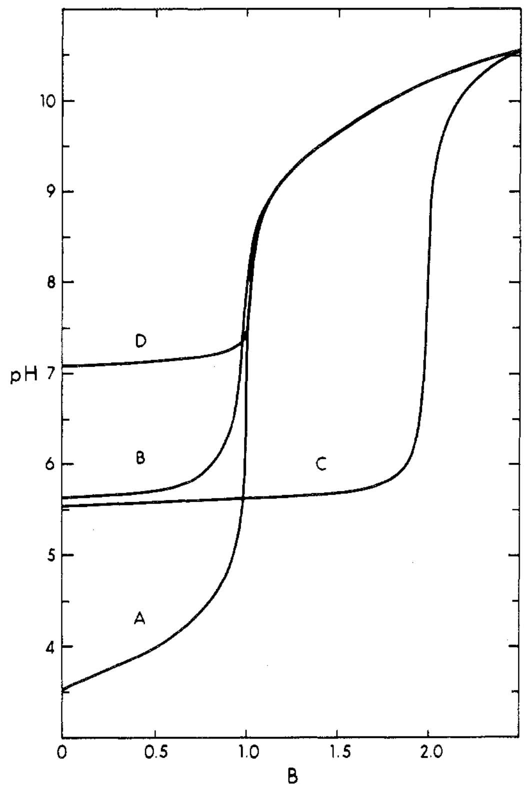

Figure 1. pH titration curves for: (A) 1.00×10^{-3} M aspartic acid and 0.16 M KNO_3; (B) 1.00×10^{-3} M aspartic acid, 1.5×10^{-2} M Na_2MoO_4, and 0.16 M KNO_3; (C) 1.5×10^{-2} M Na_2MoO_4, 2.00 $\times 10^{-2}$ M HNO_3, and 0.16 M KNO_3; (D) 1.00×10^{-3} M aspartic acid, 1.5×10^{-2} M Na_2WO_4, and 0.16 M KNO_3.

Butcher et al.[7] have shown by vibrational spectroscopy that a 1:1 Mo(VI)–aspartic acid complex isolated from neutral solution has the MoO_3 core, from which we conclude that the composition of the complex indicated by the optical rotation measurements is MoO_3L^{2-}. The formation of the complex is described by

$$MoO_4^{2-} + 2H^+ + L^{2-} \rightleftarrows MoO_3L^{2-} + H_2O \tag{1}$$

The formation constants of the Mo(VI) complexes of aspartic acid and glutamic acid were determined by the pH titration method, which is based on a shift in the ligand titration curve due to complex formation. Equation 1 indicates that complexation will cause the ligand titration curve to be displaced to higher pH. However, at pH values below the pH at which isopolymolybdate species form, which can be calculated from literature equilibrium constants,[3,4] the solution is strongly buffered and the shape of the titration curve is determined by the isopolymolybdate equilibria. Because the pH at which isopolymolybdate species form decreases as the total Mo(VI) concentration decreases, the pH range over which complexation can be studied without interference from isopolymolybdate formation depends on the Mo(VI) concentration. However, it should be noted that as the Mo(VI) concentration decreases, the extent to which complexation occurs, and thus its effect on the titration curve, also decreases.

Representative titration curves for the Mo(VI)–aspartic acid system are shown in Figure 1. As predicted, the titration curve for a solution containing Mo(VI) and aspartic acid (curve B) is displaced to higher pH from the curve for aspartic acid (curve A) up to $B = 1$, where B = moles of base added/moles of total ligand. At $B > 1$, the pH is sufficiently high so that essentially all the Mo(VI) is present as MoO_4^{2-} and its presence has no effect on the titration of the second proton of aspartic acid. For comparison, the titration curve of an acidified MoO_4^{2-} solution is also shown in Figure 1 (curve C). As the Mo(VI)–aspartic acid solution is titrated with base, the pH increases slowly up to $B = 0.7$ (pH 5.8) due to titration of the isopolymolybdates and the $B = 0.0$ to 0.7 portion of curve B is superimposable with the $B = 1.0$ to 1.7 portion of curve C. The $B = 0.7$ to 1.0 portion of curve B is at higher pH than the $B = 1.7$ to 2.0 portion of curve C due to complex formation according to eq 1. For the solution conditions in Figure 1, the maximum shift of curve B from curve C in the region $B = 0.7$ to 1.0 is 0.2 pH units.

A value was calculated for the formation constant of the MoO_3L^{2-} complex, defined by eq 2, from each of the data

$$K_f = \frac{[MoO_3L^{2-}]}{[MoO_4^{2-}][H^+]^2[L^{2-}]} \tag{2}$$

points in the $B = 0.7$ to 1.0 range of curve B in Figure 1 and from similar titrations on solutions containing 1.00×10^{-3} M aspartic acid and 5.00×10^{-3} M Na_2MoO_4 and 1.00×10^{-3} M aspartic acid and 1.00×10^{-3} M Na_2MoO_4. The formation constant was calculated at each point with

$$K_f = \frac{[L_t][H^+]K_2 + 2[L_t]K_2K_3 - A(K_2K_3 + K_2[H^+] + [H^+]^2)}{A[MoO_4^{2-}][H^+]^2K_2K_3} \tag{3}$$

where $A = B[L_t] + [H^+] - [OH^-]$, $[L_t]$ is the total ligand concentration, and K_2 and K_3 are the ligand dissociation constants (determined to be $pK_2 = 3.68$ and $pK_3 = 9.66$ for the ionic strength conditions (0.16 M) used here). pH measurements were converted to hydrogen ion concentrations with activity coefficients estimated with the Davies equation.[8,9] The calculation of K_f was done by first setting $[MoO_4^{2-}]$ equal to the total Mo(VI) concentration and then iteratively correcting the MoO_4^{2-} concentration with the calculated K_f values. Convergence was always achieved by the fourth iteration. The mean of 34 individual values from the three titrations is 6.23×10^{16} with a standard deviation of 0.57×10^{16}. The individual values are constant over the $B = 0.7$ to 1.0 range and are identical in the three experiments even though the pH ranges are different due to the different Mo(VI) concentration. The agreement of the results from the individual experiments supports the correctness of the model used to interpret the pH titration data. From similar experiments, the formation constant of the analogous Mo(VI)–glutamic acid complex was determined to be $6.11 \pm 0.49 \times 10^{16}$. Interestingly, the formation constants of the Mo(VI) complexes of both aspartic acid and glutamic acid are approximately two orders of magnitude smaller than the Mo(VI) complexes of the isomeric tridentate iminodiacetic acid and methyliminodiacetic acid ligands.[10]

Potentiometric titration curves were also obtained for the W(VI)–aspartic acid and W(VI)–glutamic acid systems. The titration curve for a solution containing 1.5×10^{-2} M Na_2WO_4 and 1.00×10^{-3} M aspartic acid is shown in Figure 1 (curve D). The pH is shifted to even higher pH values than in the Mo(VI)–aspartic acid titration due to the more extensive formation of the isopolytungstates. The titration curve is controlled by the isopolytungstate equilibria up to $B = 1$, at which point the W(VI) has all been converted to WO_4^{2-} and the titration curve becomes identical with curve A. These results and similar data for the W(VI)–glutamic acid system provide no evidence for complexation of W(VI) by aspartic acid and glutamic acid.

Conclusion

The results presented in this paper demonstrate that formation constants of Mo(VI) complexes can be obtained from potentiometric titration measurements at pH values between the pH at which isopolymolybdates form and the pH at which the complex is completely dissociated due to MoO_4^{2-} formation. Because of the more extensive formation of isopolytungstates, the pH range over which formation constants of W(VI) complexes can be measured is much smaller.[10] The results presented for the complexation of Mo(VI) and W(VI) by aspartic acid and glutamic acid indicate that the work of Singh and Srivastava[5] is incorrect, presumably because they did not account for the consumption of titrant, and thus the control of solution pH, by the isopolymolybdate and isopolytungstate equilibria.

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Registry No. Aspartic acid, 6899-03-2; glutamic acid, 6899-05-4; MoO_4^{2-}, 14259-85-9; WO_4^{2-}, 14311-52-5; MoO_3L^{2-} (L = aspartic acid), 62005-75-8; MoO_3L^{2-} (L = glutamic acid), 62005-77-0.

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Chemistry of Chromyl Fluoride.
5.[1] New Preparative Routes to CrO_2F_2

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The literature contains a number of reports on the synthesis of chromyl fluoride that involve the use of such reagents as fluorine,[2] hydrogen fluoride,[3] sulfur tetrafluoride,[4] cobalt trifluoride,[5] or iodine pentafluoride[6] in reaction with chromium trioxide. Treatment of chromyl chloride with fluorine[7] or chlorine monofluoride[8] also has been used to produce chromyl fluoride. These methods are useful for preparation of relatively small quantities of CrO_2F_2 but are not particularly practical for the production of the large amounts needed for chromyl fluoride reaction studies.

In this paper four new preparative routes to chromyl fluoride are presented, among which are the most convenient methods of synthesis yet reported.

Experimental Section

Chromium trioxide (Mallinkrodt, Reagent Grade) was thoroughly dried under vacuum before use. Chlorine monofluoride (Ozark-Mahoning) was used as received after its infrared spectrum showed no extraneous absorbances.[9] Carbonyl fluoride (PCR), tungsten hexafluoride (Ozark-Mahoning), and molybdenum hexafluoride (prepared by the method of Pitts and Jache[10]) were condensed over NaF to remove HF and then distilled into the reaction vessel. Sulfur hexafluoride (Matheson, 99.8%) was used as received.

Infrared spectra were taken on a Perkin-Elmer 467 infrared spectrophotometer. Gas-phase spectra were obtained with a Monel cell using either AgCl or KRS-5 windows. The path length of the cell was 8.25 cm. Chromyl fluoride analyses were done in the authors' laboratory by condensing and hydrolyzing a freshly prepared sample in a fused silica vessel. Hexavalent chromium was determined iodometrically, using standardized thiosulfate solution. Acidity was measured by titration with standard base using phenolphthalein indicator and is reported as milliequivalents of acid. One mole of chromyl fluoride hydrolyzes to yield 4 equiv of acid in the form of 2 mol of HF and 1 mol of H_2CrO_4. Other chemical analyses were performed by Beller Laboratories of Göttingen, West Germany. Molecular weight determination of gases was accomplished using the vapor density method.

Reaction of Chromium Trioxide and Chlorine Monofluoride. Dried CrO_3 (45 mmol) was added to a 100-ml stainless-steel reaction vessel in a drybox followed by the addition of 94 mmol of ClF at −196 °C. The reaction mixture was then warmed to 0 °C and kept at that temperature for 12 h after which time the vessel was evacuated at −196 °C. The only volatile product at this temperature was found to be O_2, identified by its molecular weight. (Requires: 32.0 g/mol. Found: 32.1 g/mol.) At −78 °C, the volatile products were ClF and ClO_2F, as identified by their characteristic infrared absorbances,[9,11] and Cl_2, identified as yellow-green liquid at −78 °C with approximately 100 mm of vapor pressure at that temperature. At room temperature, the only volatile product was CrO_2F_2, identified by its infrared spectrum.[12] The yield of CrO_2F_2 was 45 mmol or 100% based on CrO_3.

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 6.36 mequiv. Found: Cr, 42.43; acidity, 6.30 mequiv.

Following a procedure similar to that outlined above, 25 mmol of CrO_3 and 24 mmol of ClF were brought to 0 °C in a stainless-steel reaction vessel. Upon evacuation of the vessel at −196 °C, oxygen was removed. The infrared spectrum of the volatile products (at −78 °C) showed only ClO_2.[13] At room temperature the only volatile product was CrO_2F_2.

Reaction of Carbonyl Fluoride and Chromium Trioxide. To a 100-ml stainless-steel reaction vessel 9 mmol of dried CrO_3 was added. Carbonyl fluoride (24 mmol) was transferred into the vessel and the reaction mixture was heated to 185 °C for 12 h. Upon cooling the vessel to −78 °C and opening it to an evacuated −196 °C trap, white bands formed immediately in the liquid-nitrogen-cooled receiver. The trap contents were shown to be COF_2 and CO_2 by infrared analysis. The room-temperature volatile product was CrO_2F_2 as shown by its infrared spectrum. The yield of chromyl fluoride was 100% based on chromium trioxide.

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 4.16 mequiv. Found: Cr, 42.71; acidity, 4.15 mequiv.

In another run, using the above outlined procedure, 12 mmol of dried CrO_3 and 9 mmol of COF_2 were added to a reaction vessel and heated to 185 °C for 12 h. When the vessel was evacuated at −78 °C, the only volatile product observed in the infrared spectrum was CO_2. A molecular weight determination was performed on the −78 °C volatile product. (Requires: 44.0 g/mol. Found: 43.9 g/mol.) After evacuation at room temperature, which removed 9 mmol CrO_2F_2, the vessel was found to contain 3 mmol of unreacted CrO_3.

Reaction of Molybdenum Hexafluoride and Chromium Trioxide. To 24 mmol of CrO_3 contained in a 200-ml stainless-steel vessel 11 mmol of MoF_6 was added at −78 °C via vacuum distillation. The reaction vessel was heated to 125 °C for 12 h and then evacuated at room temperature. The only volatile product was found by infrared analysis to be chromyl fluoride. The weight loss indicated that the total amount of CrO_2F_2 produced was 11 mmol.

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 6.01 mequiv. Found: Cr, 42.51; acidity, 5.92 mequiv.

Sublimation of the solid residue yielded a white solid which had a melting point of 95–97 °C. The reported melting point of $MoOF_4$ is 97 °C.[14]

Anal. Calcd for $MoOF_4$: Mo, 51.0; F, 40.4. Found: Mo, 51.0; F, 40.0. The yield was quantitative based on MoF_6.

In another experiment, 23.57 mmol of CrO_3 was placed in a 30-ml fused silica reaction vessel. The vessel was evacuated and 9.623 mmol of MoF_6 was vacuum distilled into the vessel and condensed at −78 °C. The reaction mixture was allowed to warm to room temperature and reddish-brown vapors were evident immediately upon melting of the MoF_6. The reaction mixture was stirred for 2 h at room temperature and the reddish-brown color of the vapors became increasingly intense. The vessel was evacuated at room temperature and chromyl fluoride and silicon tetrafluoride were the only volatile components to be observed in the infrared spectrum.