Precipitation of Molybdenum (VI) in Strongly Acid Solutions

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Compounds precipitated from acidified Mo (VI) solutions below a pH of 1 were studied as a function of solution concentration, acid concentration, and temperature. Precipitates were identified by x-ray diffraction and chemical analysis. In the presence of polarizable cations the dominant precipitates were isomorphous compounds with variable MoO_3 to R_2O ratios of approximately 10 to 30. MoO_3 and its hydrates were obtained under other conditions. Only the hydrates crystallized from solution in a reversible manner.

THE CHEMISTRY of Mo(VI) in acid solutions is complicated by the large number of crystalline compositions which have been reported (*5*). Identification of these materials as unique compounds has required the use of x-ray diffraction, and these techniques have been systematically applied by Lindqvist to the characterization and structure determination of the major isopolymolybdates (*6*). However, as pointed out by Lindqvist, further investigation is required of the compositions of high MoO_3 to R_2O ratios which are obtained from more strongly acid solutions.

During the preparation of the molybdic oxide hydrates (*4*) precipitates giving the same x-ray diffraction pattern were obtained with sodium and ammonium salts over wide MoO_3 to R_2O ratios. These isomorphous compounds are designated as molybdenum "phase C" because of their similarity to the type C tungstic acid first reported by Morley (*7*). However, the sodium 12-molybdate whose crystal structure was partially elucidated by Lindqvist (*6*) 16-molybdates described in the literature (*2*), as judged by their methods of preparation (*8*). The work reported here is a study of the conditions of formation and of the properties of the phase C compounds. The relation of these compounds to molybdic oxide and its hydrates is also determined.

EXPERIMENTAL

Solutions of Na_2MoO_4 and of $(NH_4)_6Mo_7O_{24}$ were acidified with HNO_3 and with HCl at test temperatures of 25°, 70° and 100° C. Since appreciable time was required for precipitation to begin after acidification, the MoO_3 concentrations in the mixtures were calculated from their total volumes. The free acid concentrations were calculated on the basis of stoichiometric neutralization of the molybdenum salts. Analytical reagent grade chemicals were used. The mixtures were kept at test temperature until a substantial precipitation had taken place. The precipitates were separated by filtration, washed with acid of the same concentration as the mixture, and then with water. X-ray powder diffraction patterns and chemical analyses were made after drying both at room temperature and at 100° C.

Standard x-ray powder diffraction patterns were selected by studying precipitates prepared under different conditions. Pure compounds were then identified and mixtures were determined by comparing their diffraction patterns with the standards. Powder x-ray patterns of several phase C compounds are compared with those of MoO_3 in Figure 1. Variations in spacing of the diffraction lines at high diffraction angles indicate variations in the lattice constants of the phase C structure with changes in composition. However, resolution of the diffraction patterns was not sufficient for indexing. Interplanar spacings of the most intense diffraction lines in the order of relative intensity were observed as follows:

Molybdenum Phase C	Tungsten Phase C	$MoO_3 \cdot H_2O$
3.50 A.	3.18 A.	5.77 A.
9.32	3.90	3.34
3.06	2.46	6.70

Water contents of the sodium salts were taken as the loss in weight on igniting at 500° C. The Na_2O was then determined as NaCl by volatilizing the MoO_3 in a stream of HCl gas at 500° C. Ammonia was determined by Kjeldahl distillation, the water contents of the ammonium salts being taken as the loss in weight on ignition minus the NH_3 content. Chloride was determined by potentiometric titration with $AgNO_3$ using Ag and Pt electrodes. MoO_3 was determined by use of the Jones reductor and titration with $KMnO_4$. These methods were tested with mixtures of $Na_2MoO_4 \cdot 2H_2O$, sublimed MoO_3, and NH_4Cl and were found to give accurate results. The x-ray powder diffraction patterns were obtained with a G.E. XRD-5F unit using a 14.32-cm. camera and Ni filtered Cu K alpha radiation.

Precipitation from Na_2MoO_4 Solutions. The compounds obtained are shown in Table I. Drying to constant weight at 100° C. did not change the x-ray patterns except for $MoO_3 \cdot 2H_2O$ which was converted to MoO_3. Precipitation did not take place at 25° C. in 0.1*M* solution. The same compounds were obtained with HCl in place of HNO_3 although yields were greatly reduced at the higher acid concentrations.

Precipitation at 100° C. was further studied by adding measured volumes of HNO_3 to boiling Na_2MoO_4 solutions to obtain mixtures 0.10, 0.33, and 0.50*M* in MoO_3 over a free acid range of 0 to 5*N*. The mixtures were prepared from a 2.5*M* Na_2MoO_4 stock solution and the total volumes were 100 ml. at 0.5*M* and 200 ml. at the other concentrations. The acidified solutions were boiled for a few minutes

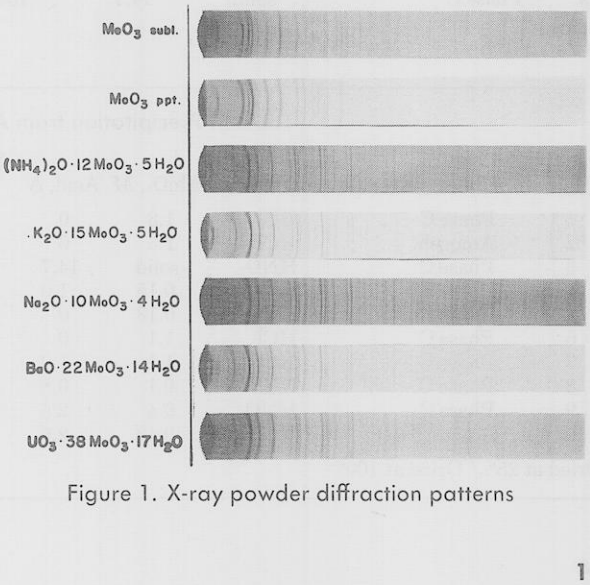


Figure 1. X-ray powder diffraction patterns

and then placed on a hot plate at 90 to 95° C. for 4 hours to complete the reaction. The precipitates were recovered by filtration, washed with H_2O, and dried at 100° C. for 3 days. Small portions of selected samples were reserved for x-ray examination while the remainder were ignited at 500° C. to determine combined H_2O and yields. Figure 2 gives the results of these tests. The dashed lines show the water contents (right hand scale). These indicate the compositions of mixtures since the H_2O contents of individual compounds are 1.5 to 2.0% for MoO_3, 4.0 to 5.0% for phase C, and 8 to 10% for $MoO_3 \cdot H_2O$. The compositions as determined by x-ray are shown on the curves. Separate tests were made to determine the stability of these compounds at the precipitation conditions. Neither was changed by boiling for 4 hours in $1N$ or in $3N$ HNO_3, as determined by x-ray diffraction.

The tests were repeated with HCl, but precipitates were not obtained at HCl concentrations greater than $2N$ due to the high solubility of Mo(VI) in HCl. In contrast also to the results with HNO_3 were the high phase C yields obtained with stoichiometric HCl addition. These were 57, 95, and 98% for 0.1, 0.3, and $0.5M$ Na_2MoO_4 respectively.

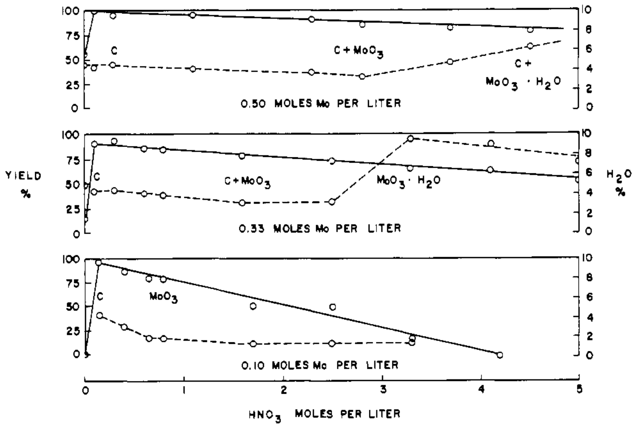


Figure 2. Precipitation from Na_2MoO_4 solution at 100° C.

Precipitation from Ammonium Paramolybdate Solutions. Typical results are shown in Table II. Some NH_3 as well as H_2O was lost on drying the phase C compounds at 100° C., but the x-ray patterns were not changed by drying and matched those of the sodium compounds. The great difference between the products obtained from sodium and ammonium solutions suggest the importance of the cation in fixing the course of precipitation. Tests 1 and 2 of Table I were then repeated with the addition of NH_4NO_3 to the Na_2MoO_4 solution to provide a $1M$ NH_4^+ concentration. The ammonium phase C was now obtained instead of MoO_3 or $MoO_3 \cdot H_2O$. Similarly, when the tests were repeated with the addition of $NaNO_3$ instead of NH_4NO_3 the sodium phase C was obtained in both cases. In contrast, Li_2MoO_4 and $MgMoO_4$ solutions both at 0.1 and $0.5M$ precipitated only MoO_3 at 100° C. with a free HNO_3 concentration of $1N$. However, mixtures of MoO_3 and phase C were obtained from these solutions at $0.5M$ when the reaction time was shortened to a few minutes.

Precipitation from $MoO_3 \cdot 2H_2O$ Solutions. The use of $MoO_3 \cdot 2H_2O$ solutions permits the study of precipitation in the absence of cations as well as in the presence of neutral salts. Thus, boiling a solution of $MoO_3 \cdot 2H_2O$ in water precipitated MoO_3 while the phase C was obtained instead in $1M$ NaCl. The letter procedure is similar to that used by Rosenheim to make his sodium and potassium octomolybdates (5). Both $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ produced the phase C in a few days at room temperature when added to $1M$ NaCl solution. MoO_3 did not exhibit this reaction.

Slurries of 5 grams of $MoO_3 \cdot 2H_2O$ in 100 ml. of H_2O were heated in a hot-air oven. A mixture of MoO_3 and $MoO_3 \cdot H_2O$ was obtained in a day at 70° C. Only $MoO_3 \cdot H_2O$ was obtained at 50° C. although a month was required for the conversion. $MoO_3 \cdot H_2O$ crystallized in a few hours at 70° C. with 1 or $3N$ HNO_3.

Table I. Precipitation from Na_2MoO_4 Solutions with HNO_3

No.	Compd.	MoO_3,M	HNO_3,N	Temp., ° C.	Time	H_2O,%[1]	Na_2O,%[1]	H_2O,%[2]	Yield, %
1	MoO_3	0.1	0.8	100	10 min.	2.90	0.00	2.07	64
2	$MoO_3 \cdot H_2O$	0.1	0.8	70	2 days	11.10	0.09	10.07	74
3	$MoO_3 \cdot H_2O$	0.18	3.3	100	1 hour	10.08	0.04	10.02	13
4	Phase C	0.4	2.5	100	5 min.	7.37	2.02	4.57	71
5	$MoO_3 \cdot 2H_2O$	0.4	2.5	25	3 wks.	20.07	0.00	1.84	68
6	$MoO_3 \cdot H_2O$	0.4	2.5	70	2 days	11.35	0.03	10.41	87
7	Amorph.	1.0	1.0	25	1 hour	14.62	2.38	4.84	18
8	Phase C	1.0	1.0	100	5 min.	14.05	2.70	3.62	86
9	Phase C	solid	14.7	100	30 min.	7.04	2.39	5.68	95

[1] Sample dried at 25°. [2] Sample dried at 100°.

Table II. Precipitation from Ammonium Paramolybdate Solutions

No.	Compd.	Acid	MoO_3, M	Acid, N	Temp., ° C.	Time	H_2O, %[1]	NH_3, %[1]	H_2O, %[2]	HN_3, %[2]	Yield, %
1	Phase C	HCl	1.3	0	100	5 min.	6.23	1.73	4.43	1.40	97
2	Amorph.	HCl	1.3	0	25	5 min.	14.10	1.72	5.85	1.51	87
3	Phase C	HNO_3	solid	14.7	100	30 min.	6.49	1.73	5.12	1.40	99
4	Phase C	HCl	0.15	1.0	70	1 hour	...	...	3.42	1.40	47
5	Phase C	HCl	0.13	0	100	10 min.	...	...	4.94	1.33	95
6	Phase C	HCl	1.1	0	100	2 min.	6.81	1.82	...	...	93
7	Phase C	HCl	1.1	1.0	100	2 min.	8.87	1.46	4.70	1.21	97
8	Phase C	HCl	0.1	0.8	100	5 min.	...	...	5.42	0.86	66
9	Phase C	HNO_3	0.4	2.5	100	2 min.	...	...	5.56	0.73	79
10	$MoO_3 \cdot 2H_2O$	HNO_3	0.43	2.6	25	3 wks.	20.13	0.03	2.18	0.03	62

[1] Dried at 25°. [2] Dried at 100°

The effect of specific cations was determined by heating slurries of $MoO_3 \cdot 2H_2O$ in $1M$ solutions of various salts at 50° C. Phase C formed in a few hours with solutions of NH_4Cl, KCl, and NaCl. No reaction was observed in 2 weeks with solutions of LiCl, $MgCl_2$, $AlCl_3$, $CaCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, $CdCl_2$, and $HgCl_2$. The $MoO_3 \cdot 2H_2O$ dissolved completely in $CrCl_3$ solution, apparently to form a molybdochromic acid. $BaCl_2$ produced a precipitate whose analysis corresponded to $BaO \cdot 2.66MoO_3 \cdot 3H_2O$, while $UO_2(NO_3)_2$ solution precipitated $UO_3 1.99MoO_3 \cdot 3H_2O$. These polymolybdates were converted to compounds which gave the phase C x-ray diffraction pattern by boiling with concentrated HNO_3. The analyses of the products then corresponded to $BaO \cdot 22MoO_3 \cdot 14H_2O$ and $UO_3 \cdot 38MoO_3 \cdot 17H_2O$.

The reaction of hot, concentrated HNO_3 on solid normal or isopolymolbdates is a general method of synthesizing phase C providing the cation is suitable. Li, Ca, and Mg phase C compounds were obtained by this method in admixture with MoO_3 and these were entirely converted to MoO_3 by boiling in $1N$ HCl for 10 minutes. However, ethylenediamine molybdate produced a relatively stable phase C.

Amorphous Precipitates. A white precipitate was formed by adding HNO_3 or HCl to $1M$ Na_2MoO_4 and allowing the solution to stand at room temperature. The precipitates formed most rapidly at $1N$ free acidity and the rate of formation was greatly accelerated by warming. Thus, 13.5 ml. of $12N$ HCl was added to 50 ml. of $1M$ Na_2MoO_4 and the mixture was heated at 70° C. for an hour. The bulky, white precipitate was separated by centrifuging and washed 5 times with $1N$ HCl in the centrifuge tube. The precipitate was then washed out of the tube with a few milliliters of H_2O and the resulting solution was dried to a glassy gel in vacuo at room temperature. Yield: 2 grams (23%) of cream colored powder. Anal. H_2O 15.37; Na_2O, 2.16; MoO_3, 80.3; Cl, 2.69. This powder was soluble in water, but became insoluble after drying to constant weight at 100° C. Anal. H_2O, 5.36; Cl, 1.98. Both solids were amorphous to x-rays. However, an insoluble product which gave the C phase diffraction pattern was obtained by allowing the initial precipitate to stand in $1N$ HCl for 2 weeks. Anal. H_2O, 14.33; Na_2O, 1.64; MoO_3, 84.1; Cl, 0.39. In contrast, ammonium paramolybdate solutions under the same conditions rapidly precipitated an amorphous solid in high yield with a composition similar to the ammonium phase C. This was readily filtered and washed entirely free of HCl with water.

Sodium Phase C. Byé's sodium hexamolybdate phase (*2*) resembles phase C in having a wide compositional range, from 6- to 12- molybdate. Lindqvist studied this phase and observed the sodium and ammonium octomolybdates to be isomorphous (*5*). The following tests were made to differentiate between phase C and the octomolybdate phase. One ml. of $12N$ HCl was added to 50 ml. of boiling $Na_4Mo_8O_{26}$ solution $1M$ in MoO_3 to establish the octomolybdate composition. The solution was kept hot for an hour and the precipitate was then filtered, washed with water and dried at 100° C. Yield: 5.8 grams (73%), phase C. Anal. Na_2O, 3.75; H_2O, 5.76; MoO_3, 90.4 ($Na_2O \cdot 10.4 \cdot MoO_3 \cdot 5.3H_2O$). The filtrate was evaporated to 20 ml. and kept at room temperature for 4 days to obtain 1.4 grams (15%) of colorless crystals which were identified by x-ray diffraction as $Na_4Mo_8O_{26} \cdot 12H_2O$. This salt was completely dehydrated at 100° C. and its x-ray pattern altered as was also $Na_2MoO_4 \cdot 2H_2O$ and $Na_6Mo_7O_{24} \cdot 19H_2O$.

The acidification procedure was repeated at room temperature and the solution was allowed to evaporate to ⅓ volume in a week. Approximately 4 grams of colorless, readily soluble crystals were obtained. Their analysis corresponded to $Na_2O \cdot 7.6MoO_3 \cdot 15.3H_2O$. The x-ray pattern was different from that given by phase C and was not changed by drying at 100° C. The composition of this compound is similar to the octomolybdate prepared by Lindqvist using similar procedures. Also, the stability of the crystals to drying at 100° C. is consistent with Lindqvist's suggestion of an infinite ion structure for this compound.

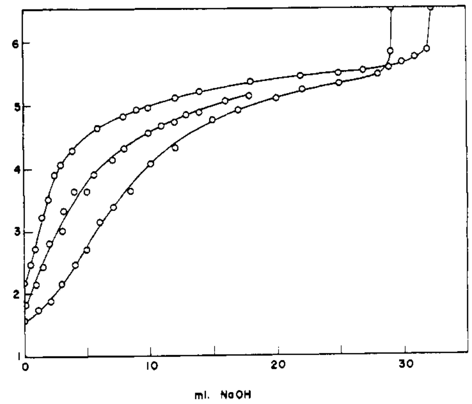


Figure 3. Titration of sodium phase C compounds

The range of homogeneity of the sodium phase C was studied for samples precipitated at different acidities. After drying to constant weight at 100° C., the analyses of seven compounds obtained at free acid concentrations of 0 to $0.8N$ and washed with water varied from 3.87% Na_2O and 4.46% H_2O to 3.11% Na_2O and 4.07 H_2O for an average of $Na_2O \cdot 11.3MoO_3 \cdot 4.3\ H_2O$. The analysis of six samples precipitated at acid concentrations greater than $1N$ and washed with $0.1N$ HCl varied from 1.80% Na_2O and 3.75% H_2O to 2.66% Na_2O and 4.88% H_2O for an average composition of $Na_2O \cdot 20.0MoO_3 \cdot 7.70\ H_2O$. A sample initially 3.27% in Na_2O was boiled under reflux forsix hours in $3.5N$ HNO_3. The x-ray pattern was unchanged, and the Na_2O content was reduced only to 3.01%. Refluxing with $1N$ HCl under the same conditions reduced the Na_2O content to 0.87%, but produced a mixture of MoO_3 and phase C.

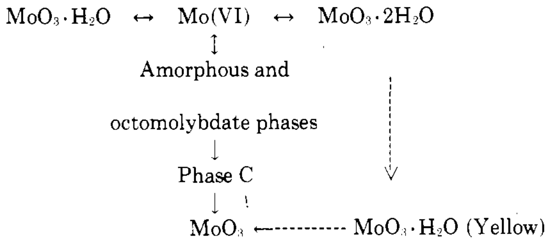
Cation exchange properties of the acid washed compounds were investigated by titration with $0.1N$ NaOH in $3M$ $NaNO_3$ (*3*). Figure 3 shows the titration curves for 0.25 gram samples suspended in 50-ml. of $3M$ $NaNO_3$. The bottom curve is for two amorphous samples. These were entirely dissolved at a pH of 4.5 while a pH of 5.5 was required for complete dissolution of the other samples. The upper curve is for two samples obtained from dilute solution at 100° C. while the middle curve is for two samples precipitated from $1M$ Na_2MoO_4,one at 100° C. and the other at 25° C. One of each set of samples was precipitated with HCl and the other with HNO_3 The titration curves show that the compounds are homogeneous, that is, they do not consist of mixtures of crystalline and amorphous material. The amorphous compounds (bottom curve) dissolve at a lower pH than the well crystallized compounds (upper curve). A mixture of the two should follow the lower curve initially and then rise to the upper curve. However, compounds of poor crystallinity (diffuse x-ray patterns) follow their own (middle) curves. Also, there is no indication of exchange of H^- for Na^-. While the compounds dissolved progressively the undissolved residues had a higher Na_2O content than the original materials. A sample of 20-molybdate composition was titrated to a pH to 5.0 in aqueous suspension. The residue of phase C, after separation by filtration and water washing, had the composition of a 10-molybdate, but was recovered in only 50% yield.

Ammonium Phase C. Titration curves for amorphous and crystalline ammonium phase C samples were very similar to those obtained with the sodium compounds. However, the ammonium compounds exhibited a broader compositional range and also contained somewhat less combined water. Six samples with MoO_3 to $(NH_4)_2O$ ratios of 12 to 30 contained 0.3 to 0.4 moles of H_2O per mole of MoO_3 for an average of 0.36, when dried at 100° C. The compositions of the sodium compounds are more closely represented by $Na_2O \cdot 10\text{–}30(MoO_3 \cdot 0.4H_2O)$.

The ammonium compounds were also more stable in acid solution. A sample which had been dried at room temperature had the composition of $(NH_4)_2O \cdot 11.9MoO_3 \cdot 6.06H_2O$. A 5-gram portion was recovered in nearly quantitative yield after refluxing for six hours with 50 ml. of 1*N* HCl. However, the composition now corresponded to $(NH_4)_2O \cdot 33.5MoO_3 \cdot 14.2H_2O$, and the x-ray pattern indicated only the phase C.

DISCUSSION

The course of precipitation from acidified Mo(VI) solutions below a nominal pH of one is summarized as follows:



The phase C compounds are the predominant precipitates from hot solutions when high concentrations of ammonium or alkali salts are present at acid concentrations below 2.5*N*. The amorphous and octomolybdate phases, which include the water soluble 6- to 16-molybdates reported in the literature (5), are converted to insoluble phase C on heating or standing in acid suspension. The only further reaction observed for phase C in acid suspension is conversion to MoO_3. However, there is a second route to MoO_3 through the thermal decomposition of $MoO_3 \cdot 2H_2O$. This reaction takes place in the solid state via the unstable, yellow $MoO_3 \cdot H_2O$ and must have its counterpart in solution. MoO_3 and $MoO_3 \cdot H_2O$ are precipitated from hot, acidified Mo(VI) solutions singly or in admixture although they are not interconvertible under the conditions or precipitation. Only the hydrates crystallize from solution reversibly, and the crystallization rate of $MoO_3 \cdot 2H_2O$ is very slow at acid concentrations below 2.5*N*. The irreversibility of the reactions which produce MoO_3 and phase C are responsible for the appearance of these compounds where the hydrates would be expected. Precipitation from acidified Mo(VI) solutions is thus controlled by kinetic factors rather than by equilibrium solubility relations.

Molybdenum phase C resembles tungsten phase C in methods of preparation and properties although they are not isomorphous. The tungsten phase C reversibly exchanges a portion of its cation content while such action was not evident with molybdenum phase C. Both phases have as precursors the amorphous precipitates which form from colloidal suspension. Of these the molybdenum compounds are more stable since they convert to phase C in acid suspension while the amorphous tungsten compounds convert to $WO_3 \cdot 2H_2O$.

Phase C compounds form in the presence of easily polarizable cations of large size and low ionic charge (K^+, NH_4^+, Na^+, Ba^{+2}) or with oxo cations (UO_2^{2+}). These cations must be an integral part of the phase C structure since it does not exist in their absence. The ammonium compounds form most rapidly and are most stable while the less polarizable Li^+, Ca^{2+}, and Mg^{2+} form very unstable phase C compounds. The phase C might be considered as an inverted heteropoly complex with the cation as a ligand since, by contrast, the molybdenum heteropoly complexes form with polarizing cations of small size and high charge as the central atom (Al^{3+}, Cr^{3+}, Co^{3+}, etc.) or with oxo anions (PO_4^{3-}, SiO_4^{4-}, etc.) However, the phase C compounds can also be considered as acid analogues of the well known basic salts (*1*).

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