

[CONTRIBUTION FROM THE CHEMICAL INSPECTORATE, BRITISH MINISTRY OF SUPPLY]

The Preparation and Properties of Silicomolybdic Acid. III. The Combination of Silicate and Molybdate

By J. D. H. STRICKLAND

The reaction between sodium silicate and excess sodium normal molybdate acidified with known amounts of hydrochloric acid has been studied, the pH and amount of silicomolybdic acid formed being determined after known intervals of time. The silicomolybdate is characterized and estimated by means of its absorption using reduced and unreduced solutions. In molybdate solutions acidified with up to about 1.5 equivalents of acid per mole of MoO_4^{2-} , α -silicomolybdate is the main product. After an inflection in the molybdate titration curve at just short of 1.5 equivalents of acid, progressively more β -silicomolybdate is formed. It is the sole product in solutions acidified by more than about 2 equivalents of acid, and the reaction is then first order with respect to silica. The presence of sulfate increases the proportion of α - to β -silicomolybdate formed at a given acidity. The nature of the molybdate species present in acidified solutions of the normal ion and the bearing of this work on analytical chemistry is discussed.

Introduction

In the preceding two papers of this series the existence of two forms of silico-12-molybdic acid was proved and methods were established for the absorptiometric determination of these two complexes in solution, either alone or as mixtures. It is now possible to interpret fully the results obtained from a study of the combination of silicate with acidified molybdate.

It is generally known that silicate and molybdate will not combine at either too high or too low an acidity. The analytical literature gives rather varying values for the optimum pH of silicomolybdate formation, but it is generally agreed that this lies between about pH 1 and 2.

Silicic acid in alkaline molybdate solutions is completely unreactive. It has been shown by Malaprade¹ and later by other workers, for example Davis and Bacon,² that at high acidities its velocity of combination with molybdate becomes very small. It is at acidities between these two extremes that a study of silicomolybdate formation is of greatest interest and such a study, therefore, forms the principal part of the present investigation.

As the precise molecular condition of either silicate or molybdate in acidified solutions is not known, in the experiments described here, both silicate and molybdate have been added in the form of the simple "normal" silicate and "normal" molybdate ions ($HSiO_3^{1-}$ and MoO_4^{2-}) and then acidified with a known number of equivalents of acid. In most experiments hydrochloric acid has been used, but as the effect of sulfuric acid or neutral sulfate is of some analytical interest a very brief investigation has been made of the influence of the sulfate anion.

Experimental

Prevention of Molybdenum Blue Formation.—If an attempt is made to reduce silicomolybdate by stannous chloride in the presence of excess molybdate the reduced heteropoly acid is contaminated with large quantities of "molybdate" molybdenum blue. This is best avoided by acidifying the solution sufficiently, when the molybdate is reduced to the pentavalent state, giving solutions which are only pale yellow in color and which do not interfere with the absorptiometric determination of reduced silicomolybdic acid. The degree of acidification necessary for the suppression of "molybdate" molybdenum blue formation depends upon the acid and the concentration of molybdate and stannous

chloride used. The effects of these variables are illustrated by Fig. 1, where the concentration of either sulfuric or hydrochloric acid necessary to prevent molybdenum blue formation from a given concentration of molybdate is shown for two useful stannous chloride concentrations. No great accuracy is claimed for this work but Fig. 1 serves as a useful practical guide. A reaction at concentrations represented by points within the shaded areas will give rise to some molybdenum blue formation, whereas under conditions represented by points well outside the shaded areas only pentavalent molybdenum is produced.

General Experiment Using Hydrochloric Acid.—In these experiments the amount of silicon was kept constant and sufficiently small in comparison with the molybdate for any change of acidity due to silicomolybdate formation to be almost negligible. The silicomolybdate formed at each acidity was characterized and estimated by determining the extinction of reduced and unreduced solutions.

The silica was added as a $5.0 \times 10^{-3} M$ solution of alkali degraded α -silicomolybdate. Further additions of molybdate were made by a solution of sodium normal molybdate. This salt was prepared by fusing equimolecular proportions of sodium carbonate and molybdic oxide, filtering the extracted melt, and adjusting the pH of the solution, if necessary, to 6.5. The molybdate content was standardized by precipitating the molybdenum as oxinate. The stock solution so prepared was $2.46 \times 10^{-1} M$ with respect to the ion MoO_4^{2-} .

5.00 ml. of standard molybdate solution and a desired volume of standard N hydrochloric acid were introduced into a 50-ml. measuring flask and the volume made to about 45 ml. with water. Two ml. of the standard silicate solution was then added with rapid mixing and by this means the silicate was made to react with the bulk of the molybdate at almost the desired final acidity. The volume of the solution was made to exactly 50 ml. and mixed. About 15 ml. of this solution was used for pH measurement and the remainder transferred to a 4-cm. cell for absorption measurement. A stop watch was started when the silicate was added to the molybdate and after 10 minutes: (a) The pH was measured by the glass electrode pH meter (standardized before each reading at pH 4.00 by 0.05 M phthalate). (b) The extinction of the solution in the 4-cm. cell (kept at $20 \pm 1^\circ$ throughout the period of reaction) was measured by the Spekker Absorptiometer of Messrs. Hilgers and Watts fitted with Ilford No. 601 violet filters. (c) As rapidly as possible a 25-ml. aliquot of the solution in this cell was pipetted into a flask containing 17 ml. of water, 5 ml. of 10 N hydrochloric acid and 2 ml. of 0.25 M ammonium paramolybdate (0.25 M with respect to Mo). The strong acidity of this solution prevented further combination of silicate and molybdate (see later) and hence "froze" the combination after 10 minutes from the commencement of the reaction. The acidity also prevented interference from "molybdate" molybdenum blue, see above, so that on adding 1.0 ml. of 0.1 N stannous chloride three minutes after adding the acid only the silicomolybdate complex was reduced to a blue compound. The extinction of this solution (50 ml.) was measured in a 1-cm. cell by the Spekker Absorptiometer using Ilford No. 608 red filters. This extinction was corrected for the slight blank (0.01–0.02) arising from pentavalent molybdenum.

In these experiments the solution in which the reaction took place was $2 \times 10^{-4} M$ with respect to silica and $2.70 \times$

(1) L. Malaprade, *Ann. chim.*, 11, 104 (1929).

(2) H. C. Davis and A. Bacon, *J. Soc. Chem. Ind. London*, 67, 316 (1948).

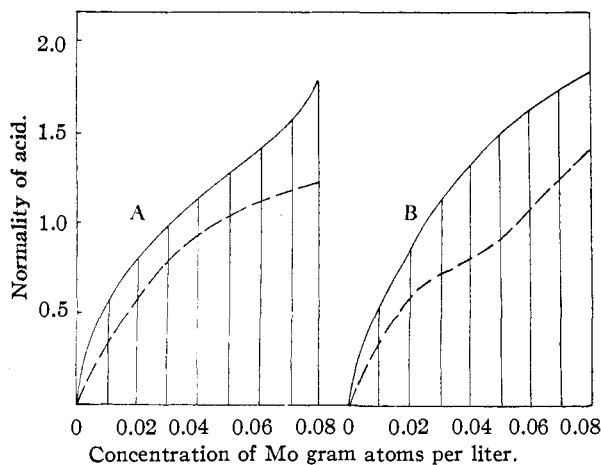


Fig. 1.—Molybdenum blue formation: A, 3×10^{-3} N SnCl₂; B, 6×10^{-3} N SnCl₂; —, sulfuric acid; - - -, hydrochloric acid.

10^{-2} M with respect to Mo. In the 50 ml. of reduced solution the silica concentration was 1×10^{-4} M. The experiments were repeated with a total molybdate concentration of 3.685×10^{-2} M in the reacting solution.

The results of these experiments are shown in Fig. 2. Before the inflection point the pH values for the experiments using 3.685×10^{-2} M molybdate were so near to those for 2.70×10^{-2} M molybdate that they have not been shown. With both these concentrations the inflection occurred at a point corresponding to the addition of 1.47-1.48 equivalents of acid per mole of MoO₄²⁻. By making each pH measurement in the same volume of solution these titration curves are free from any "dilution" error.

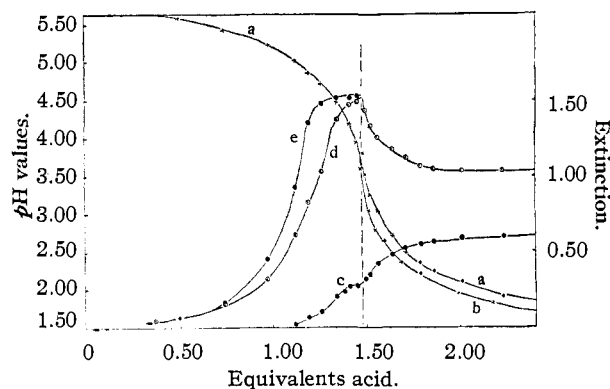


Fig. 2.—Formation of silicomolybdate: 10 minutes reaction time; a, pH curve for $[Mo] = 2.700 \times 10^{-2}$ M; b, pH curve for $[Mo] = 3.685 \times 10^{-2}$ M; c, extinction curve of unreduced complex; d, extinction curve of reduced complex; e, as d after 2 hours.

The yellow extinction values (shown in Fig. 2 at twice their actual value) were practically the same for both molybdate concentrations. The extinctions of the blue reduced aliquots have only been shown for the experiments using 2.70×10^{-2} M molybdate (curve d). A few experiments were made in which the silicate and acidified molybdate were allowed to stand for 2 hours, a period found by trial to be sufficient for practically all reaction to take place. Only when less than 1.5 equivalents of acid were present were reproducible extinction values found. Those for the unreduced solutions were slightly greater than those shown by curve c and the extinctions of reduced aliquots were much greater (see curve e).

The Combination of Various Concentrations of Silica.—The effect of fivefold variation in the concentration of the silica combining with the molybdate is shown in Fig. 3. In these experiments the amount of molybdate chosen was such that the excess after all the silica had combined was 2.50

$\times 10^{-2}$ M in each case. The experiments were carried out exactly as described above, except that the acidified molybdate was poured rapidly into the degraded α -silicomolybdate. This ensured that no reaction took place in a solution more acid than the final desired value. The reaction time in all cases was 10 minutes. The horizontal lines crossing the extinction curves of the unreduced solutions show the extinction values to be expected for full combination of the silica as α -silicomolybdate.

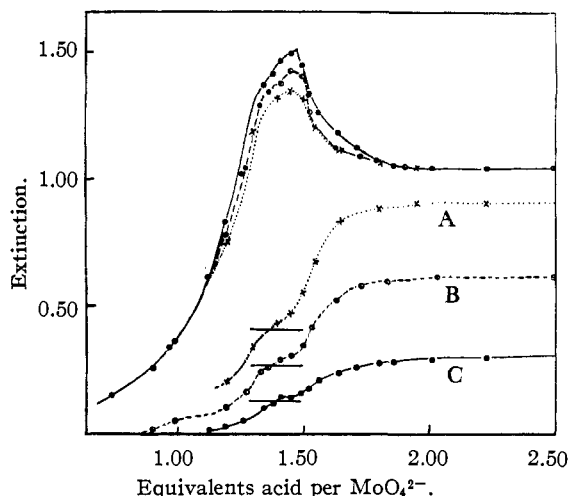


Fig. 3.—Formation of silicomolybdate: —, $[SiO_2] = 2.0 \times 10^{-3}$ M; —o—o—, $[SiO_2] = 5.0 \times 10^{-3}$ M;x.....x..... $[SiO_2] = 9.5 \times 10^{-3}$ M. A, B, C curves for unreduced solutions 4-cm. cell and other curves for reduced aliquots.

Experiments Using Sulfate.—When sulfuric acid was used in place of hydrochloric acid in the above experiments with 2.7×10^{-2} M molybdate little difference was noted when up to 1.5 equivalents were added. This was not the case when over about 1.5 equivalents of acid were present, as will be seen from the pH—equivalents and extinction—equivalents curves shown in Fig. 4, where the results of sulfate and chloride experiments are shown side by side.

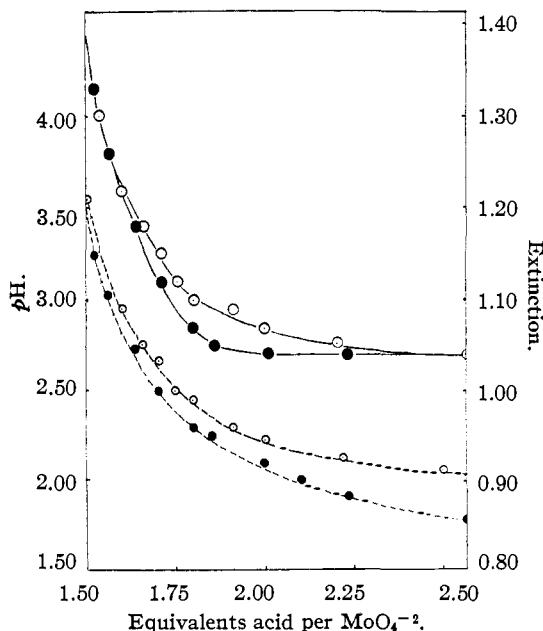


Fig. 4.—Formation of silicomolybdate: sulfuric acid; —o—o—, extinction; - - -o- - -, pH curve. Hydrochloric acid: —●—, extinction; - - -●- - -, pH curve.

In some further experiments $2.70 \times 10^{-2} M$ molybdate solutions were acidified with sulfuric acid, as before, but an additional concentration of sulfate ion was introduced by means of neutral solutions of either sodium or ammonium sulfate. All solutions were at the same acidity, 2.21 equivalents, and the extra sulfate was added to the bulk of acidified molybdate before adding the silicate. The results are shown in Table I. The column headed "E. 4 cm. yellow" gives the extinction in a 4-cm. cell of the unreduced solutions after 10 minutes. The theoretical extinction of such a solution, containing all the silica ($2 \times 10^{-4} M$) combined as β -silicomolybdate, was 0.29. The column head "E. 1 cm. blue" shows the extinction of a stannous chloride reduced aliquot of combined silica concentration $1 \times 10^{-4} M$. The standard extinction for such a solution, assuming only β -silicomolybdic acid formation, was 1.04.

Effect of Silica Concentration.—When up to $6 \times 10^{-4} M$ silicate combines with $5.6 \times 10^{-2} M$ molybdate the excess molybdate concentration and hydrogen ion activity vary by only a few per cent. as combination takes place. Under these conditions the reaction would be expected to be a first order one with respect to the silica concentration. Although the rate of formation is generally too great for measurement, if it is reduced by the presence of a sufficient number of equivalents of acid the "first order" nature of the reaction can be tested, either by a direct determination of the rate of combination or, more conveniently, by finding whether the fractional formation of silicomolybdic acid after a given time is independent of the concentration of silica initially present.

The results of a typical experiment of the later type are shown in Table II. Here a $5.6 \times 10^{-2} M$ molybdate solution, after acidification with 9.0 equivalents of hydrochloric acid, was allowed to react with various concentrations of silica and the amount of β -silicomolybdate formed after exactly 10 minutes was determined, either by direct extinction measurement of the unreduced solution in a 4-cm. cell or by reduction of a suitable aliquot with stannous chloride. A comparison of these extinctions shows that only the beta complex is formed even at high acidities.

It will be seen that the reaction is first order, the half-life of the combining silica being about 15 minutes. An approximate indication of the effect of acid on the rate of combination of silica ($5 \times 10^{-4} M$) with $5.6 \times 10^{-2} M$ molybdate is given from the half-life values shown in Table III. The pH values of these solutions were difficult to measure with any accuracy, especially after the larger additions of acid.

Experiments on the Reduction of Molybdate.—The existence of more than one type of molybdate in acidified normal molybdate can be inferred by the behavior of such solutions toward reduction with stannous chloride. As mentioned above, unless the molybdate is strongly acidified "molybdate" molybdenum blue is produced on adding stannous chloride and Fig. 1 shows the approximate acidity necessary to suppress this formation. This only applies, however, provided that the acidified solutions are allowed to stand for some time before the stannous chloride is added,

otherwise molybdenum blue may be formed, according to the condition of the molybdate before the solutions are strongly acidified.

For example, when 10 ml. of an 0.05 M molybdate solution, acidified by up to 1.5 equivalents of hydrochloric acid, was added to 40 ml. of 1.25 N hydrochloric acid and reduced immediately by 1 ml. of 0.1 N stannous chloride, no molybdenum blue was ever formed. If, however, the 0.05 M molybdate had first been acidified with more than 1.5 equivalents before it was introduced into the 40 ml. of more concentrated acid, a considerable amount of molybdenum blue was produced. To prevent this the molybdate had to react with the strong acid with which it was finally mixed for a certain time, the longer it thus reacted the less blue being formed when the tin solution was added. An 0.05 M molybdate solution acidified by 3 equivalents of hydrochloric acid (pH 1.3) required about 40 seconds of strong acidification before no blue could be detected.

Such experiments show that a "molybdenum blue" forming molybdate, which is presumably produced when the normal ion, MoO_4^{2-} , is acidified by over 1.5–2 equivalents of acid, has a transient stability in strong acid before it is converted into another form which reduces directly to Mo^V .

The presence of sulfate lessens the amount of molybdenum blue forming molybdate present at a given acidity. For example in the above experiments, with 3 equivalents of acid, no blue was noted even on immediate reduction if the molybdate solution was also initially 0.4 M with respect to ammonium sulfate. If such a solution was acidified to pH 3, which required about 6 instead of 3 equivalents of acid, only about 15 instead of 40 seconds acidification were necessary to destroy all the molybdenum blue forming species. If the sulfate was added to the strong acid, instead of to the molybdate, it had no noticeable effect and the acidification time was as long as if no additional electrolyte had been present.

Molybdate Absorption Spectra.—Figure 5 shows the absorption spectra of solutions of sodium normal molybdate acidified to varying extents with hydrochloric acid. The spectra were measured by the Uvispek quartz spectrophotometer of Messrs. Hilgers and Watts, against blank solutions containing the same concentration of sodium and chloride ions as the solution under examination. The solutions were

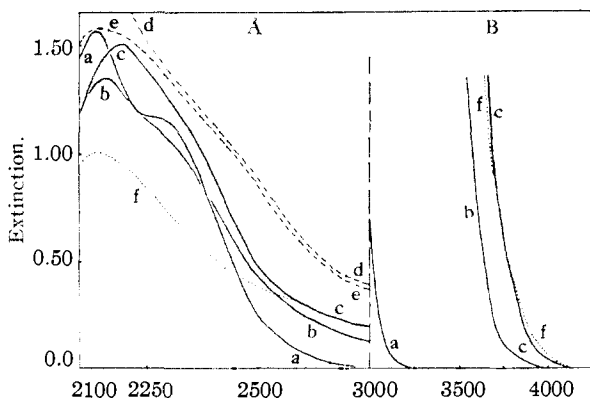


Fig. 5.—Absorption spectra of the molybdates: A, 1-cm. cell, $2.4 \times 10^{-4} M$ with respect to Mo; B, 1-cm. cell, $2.4 \times 10^{-2} M$ with respect to Mo. Curves d and e are spectra of α and β silicomolybdic acid.

TABLE I

| Concn. of $(NH_4)_2SO_4$, M | Concn. of Na_2SO_4 , M | Total concn. of SO_4^{2-} , M | pH | E. 4 cm. Yellow | E. 1 cm. Blue | α Complex, % | HCl pH |
|--------------------------------|----------------------------|-----------------------------------|------|-----------------|---------------|---------------------|--------|
| Nil | Nil | 0.03 | 2.11 | 0.285 | 1.05 | 2 | 2.25 |
| 0.05 | Nil | .08 | 2.20 | .265 | 1.11 | 14 | |
| Nil | 0.05 | | 2.19 | .265 | 1.10 | 12 | 2.4 |
| 0.10 | Nil | .13 | 2.32 | .250 | 1.18 | 28 | |
| Nil | 0.10 | | 2.31 | .250 | 1.18 | 28 | 2.7 |
| 0.20 | Nil | | 2.48 | .210 | 1.29 | 50 | |
| Nil | 0.20 | .23 | 2.50 | .230 | 1.26 | 44 | 3.0 |

TABLE II

| Initial concn. $SiO_2 \times 10^4$ | Concn. β -silicomolybdate $\times 10^4$ calculated from: | Per cent. initial SiO_2 reacted in 10 min., % | |
|------------------------------------|----------------------------------------------------------------|-------------------------------------------------|----|
| | Reduced solutions | Unreduced solutions | |
| 6.00 | 2.16 | 2.2 | 36 |
| 5.00 | 1.87 | 2.0 | 37 |
| 3.00 | 1.06 | 1.1 | 35 |
| 2.00 | 0.70 | 0.75 | 35 |
| 1.00 | 0.36 | 0.35 | 36 |

TABLE III

| Equivalents of HCl added to MoO_4^{2-} | Approx. half-life of reacting SiO_2 |
|------------------------------------------|---------------------------------------|
| 6 | Very small (pH approx. 0.85) |
| 7 | 2.5 min. (pH approx. 0.80) |
| 8 | 6 min. (pH approx. 0.75) |
| 9 | 15 min. |
| 10 | 40 min. |
| 11 | 3 hours |
| 12 | 11 hours |

initially prepared and the spectra measured at a concentration of $2.40 \times 10^{-2} M$ with respect to Mo. In order to obtain measurements in the far ultraviolet, it was necessary to dilute these solutions to $2.40 \times 10^{-4} M$. The spectra thus obtained did not change significantly on standing the solutions for a period of 24 hours.

Curves a are of the molybdate as normal molybdate in solutions of pH 6.5. Curves b are of solutions acidified by 1.5 equivalents of acid, at pH 4.1 and 3.5 for dilute and concentrated solutions, respectively. Curves c show the spectra of a solution acidified by 5 equivalents of acid (the dilute solution was at pH 3). These last two spectra changed very little on further acidification except to tend toward curves f which are the spectra of molybdate in very strongly acidic solutions (1 N).

The accuracy of measurement by the spectrophotometer below wave lengths of 2200–2150 Å. is open to question, owing to interference from stray radiation, but in all the experiments illustrated by the curves in Fig. 5 the optical conditions were identical and the resulting spectra are mutually comparable.

Discussion

The most noticeable feature of Fig. 2 is the coincidence at 1.48 equivalents of added acid of the inflection in the molybdate titration curves, the small "plateau" in the extinction curve of the unreduced solution and the maximum in the extinction curve of aliquots reduced by stannous chloride in the presence of excess molybdate. These extinctions, 0.28 and 1.51, respectively, approximate to those shown from previous work (see Part I) to be expected from a $2 \times 10^{-4} M$ solution of combined silica if all the silica is combined as α -silicomolybdate. Similarly when more than about 2 equivalents of hydrochloric acid are added the extinctions in Fig. 2 show that the silica is all combined to form the beta complex (see Part II). In 2 hours the α -silicomolybdate formation at less than 1.5 equivalents, which was incomplete in 10 minutes, has increased to an equilibrium value. The dissociation of the α -complex at a high pH is responsible for the incomplete formation when the pH exceeds about 4.5. The onset of the β - and α -silicomolybdate transformation made the 2-hour experiments inaccurate at acidities over 1.5 equivalents, when the β -complex was being formed in quantity.

The effect of varying the amount of silica combining with the molybdate is to increase the relative amount of β -complex found when less than 1.8 equivalents of acid are added. This is illustrated by Fig. 3, where the "peaks" at 1.45–1.5 equivalents of acid are progressively lowered as the concentration of combined silica is increased. At the same time it will be seen that the "plateaus" in the extinction curves of the unreduced complex becomes less distinct and progressively higher than the correct alpha value. It will also be noticed from Fig. 3 that at very low acidities appreciable extinctions are obtained from α -silicomolybdous acid, or some similar blue compound, before any recordable yellow extinction is noticed from the unreduced heteropoly compound. The amounts of silicomolybdate in solution, as estimated directly and by reduction experiments, do not tally exactly in the 10-minute experiments until 1.3 equivalents of acid are present and at 0.75 equivalent the reduction experiments indicate the presence of up to 10 times the amount of complex that would be inferred from direct extinction measurement. The

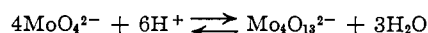
reason for this behavior cannot be stated for certainty without further experimental work, but the presence of a relatively colorless form of the silicomolybdate complex, which is indicated by the above work, may be the result of the formation at very low acidity of traces of, say, a silico-11-molybdate, analogous to the corresponding germanium compound, etc.

The formation of α - and β -silicomolybdate will be seen to act as a useful "indicator" of a change in molybdate structure when acid is added to the normal molybdate ion, MoO_4^{2-} . It would appear that there are at least three species of molybdate present, an α -silicomolybdate forming molybdate, which is found in solutions acidified with up to 1.5 equivalents of hydrochloric acid, a β -silicomolybdate forming species which is predominant at an acidity greater than 1.5 equivalents but which probably exists in solutions to which as little as 1.1 equivalents have been added and finally a form of molybdate, present in strongly acidified solutions, which is completely unreactive toward silica. It is proposed here to refer to these three types of molybdate as α -, β - and γ -molybdate, respectively.

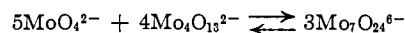
Further evidence for the presence of at least these three different forms is to be found in the behavior of solutions on reduction, described in this paper, the β -molybdate having some transient stability in very strong acid before it is converted into the γ -form. Similarly, the absorption spectra in Fig. 5 show the difference between a solution acidified by 1.5 equivalents (curve b), the same solution acidified with well over 1.5 equivalents (curve c) and a strongly acidified molybdate solution (curve f).

The solution chemistry of the molybdates is still, unfortunately, very obscure and an exceptionally large number of mutually conflicting statements are to be found in the literature. Recently a measure of agreement has been reached on certain points, chief amongst which is the fact that the normal and meta molybdate ions are by far the most stable ions in solution. Polymerization and depolymerization of the molybdate species occurs during the progressive acidification of normal molybdate solutions, depending to some extent on the concentration of molybdate, and Britton and German, Travers, and Malaprade³ and others have all assumed that a condensation can occur between normal and meta molybdate ions. In a very comprehensive investigation Byé⁴ has elaborated earlier theories and as a result of his work and that of Carpéni⁵ the most likely molybdate equilibria appear to be:

(a) In solutions more dilute than about 0.01 M, the acid dependent



(b) In somewhat more concentrated solutions, at a suitable acidity, the condensation

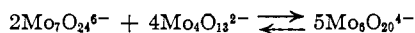


(3) L. Malaprade and A. Travers, *Bull. soc. chim. France*, **39**, 1408, 1543 (1926); H. T. S. Britton and W. L. German, *J. Chem. Soc.*, 2154 (1930).

(4) J. Byé, *Ann. chim.*, **20** 463 (1945).

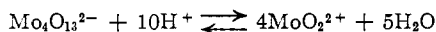
(5) G. Carpéni, *Bull. soc. chim. France*, **14**, 490, 501 (1947).

(c) In solutions more concentrated than 0.05 – 0.1 *M* and acidified with between 1 and 1.5 equivalents



From this it is clear that the β -molybdate species is almost certainly the simple meta ion, $\text{Mo}_4\text{O}_{13}^{2-}$. The nature of the α -molybdate ion is, however, obscure. In the dilute solutions used in this investigation there would be, according to Byé, little or no hexamolybdate, $\text{Mo}_6\text{O}_{20}^{4-}$, although some paramolybdate should be produced (the inflection in the titration curve in Fig. 2 is at slightly less than 1.5 equivalents, confirming the observations of Byé). It will be seen that from the absorption spectra, Fig. 5, that the curve for α -molybdate in very dilute solutions, curve b, is not that of the normal ion, curve a, as is asserted by Carpéni, or a composite curve of a and c, as would be assumed from the work of Byé. Thus, in the absence of further investigation, the α -molybdate ion cannot be identified with any known species. There remains the possibility that there can exist some isomerism of the meta molybdate species, analogous for example to the isomerism of the paratungstate ions,⁶ both empirically (HW_6O_{21}),⁵ but no other evidence of this has been reported in the literature.

γ -Molybdate is almost certainly the cationic form (presumably molybdyl) indicated by diffusion experiments⁷ and produced from β -molybdate by a reaction such as



If this equilibrium is rapidly established, the activity of the β -molybdate in very strongly acid solutions would be expected to be small but to remain constant, hence explaining the observed slow first order formation of β -silicomolybdate in these solutions.

The effect of sulfate is to increase the amount of α -silicomolybdate formed at any given number of equivalents of acid. This is illustrated by Fig. 4 and Table I. Although here the *pH* is increased by the presence of sulfate this increase is not solely responsible for the increase in α -complex formation, as will be seen from the last column in Table I. The *pH* values given there are the *pH* values necessary to give the same fractional formation of the alpha acid when hydrochloric acid alone is used. These are appreciably higher than the actual *pH* values of the sulfate containing solutions. The effect of equimolecular concentrations of sodium and ammonium sulfates is the same and may, in fact, be largely a function of the ionic strength of solutions. The supposition that the presence of excess electrolyte increases the amount of α -molybdate at the expense of the β -form is supported by the molybdate reduction experiments, where it was

shown that the amount of "molybdenum blue" forming molybdate (beta) was greatly reduced in the presence of a high concentration of ammonium sulfate.

Analytical Considerations

There are three main sources of error and confusion in the literature dealing with methods for silicon analysis based on the formation of silicomolybdic acid.

Firstly, mixtures of α - and β -silicomolybdate are sometimes formed which, because of the visual similarity of solutions of these two compounds, are mistaken for incomplete combination of the silicon into one yellow complex. Similarly, on reduction, mixtures of α -silicomolybdous (greenish-blue) and β -silicomolybdous (royal blue) acids may be formed with widely differing molar extinction coefficients for light of wave lengths exceeding 6250 Å. Finally, even if β -silicomolybdic acid is quantitatively formed, it may be formed under conditions such that its spontaneous transformation into the α -complex becomes appreciable before extinction measurements are made.

It is commonly supposed that *pH* is the essential factor in silicomolybdate formation. However, as a result of the present work, it would appear inadvisable to consider the *pH* without reference to the amount of molybdate used or to the quantity of other electrolyte present. The more fundamental condition is the number of gram equivalents of hydrogen ion added per gram ion of MoO_4^{2-} and this should be between about 3 and 5 to ensure that all the silicon combines as the β -complex.

A concentration of molybdate such that $[\text{Mo}] = 0.05$ after the silica has combined is suitable for all quantities of silica but the total ionic strength of all other ions in solution should be restricted (less than about 0.5) to prevent any α -silicomolybdate formation. If the acid added exceeds 7–10 equivalents the rate of reaction (see Table III) will become impracticably slow. When the β -silicomolybdate has been formed, the measurement of its extinction or the subsequent reduction of this complex should not be delayed for longer than a further 15 minutes, especially if much excess electrolyte is present, or its transformation to the alpha complex may become appreciable.

If the above considerations are borne in mind no difficulty will be experienced in designing analytical methods for silicon in a wide variety of materials.

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