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

The Preparation and Properties of Silicomolybdic Acid. I. The Properties of Alpha Silicomolybdic Acid

BY J. D. H. STRICKLAND

Silicomolybdic acid has been prepared by a new and convenient synthesis and absorption spectra of the pure acid measured with an ultraviolet spectrophotometer. Most of the reported properties of the acid in solution have been confirmed and a detailed study made of its reduction with stannous chloride. The silicomolybdate anion is reduced in its entirety, probably by the addition of hydrogen atoms, to give two blue compounds, both of which still contain the silicon and molybdenum atoms combined in the ratio 1:12. Absorptiometric and potentiometric studies have shown that one compound, α-silicomolybdous acid, corresponds to the addition of four electrons and the other, α-hyposilicomolybdous, to the addition of five electrons. Absorption spectra and other properties of these reduction products are noted.

Introduction

The determination of small quantities of silicon by the formation of silicomolybdic acid and the subsequent measurement of the light absorption of this compound, or its reduction product "molybdenum blue," is now established analytical practice.

Jolles and Neurath[1] were probably the first to suggest that the formation of silicomolybdic acid could be employed in analysis, and later Isaacs[2] introduced the subsequent reduction of this compound. The analytical literature of the past twenty-five years contains a very large number of methods, adapted for particular materials using carefully standardized conditions. In all cases, however, the analytical conditions have been determined empirically and little is known concerning the reactions which take place during the analysis. It is generally recognized that the formation and reduction of silicomolybdic acid is dependent upon time and *p*H, and most of the investigations of a more fundamental nature have been designed to determine the most suitable values for these variables. Unfortunately, very little agreement has been reached, especially with regard to *p*H, and authors give values for the optimum acidity necessary for silicomolybdate formation which often differ widely.

This unsatisfactory state of affairs makes it very difficult for the analyst to vary conditions or to design new methods without making, each time, a fresh series of investigations. It was decided, therefore, to investigate fully the mechanism of formation and reduction of silicomolybdic acid. The subject has proved to be considerably more complicated than was expected, owing to the discovery of the existence of at least two distinct forms of the silicomolybdate anion and of several reduction compounds thereof. This investigation has, therefore, been restricted to a brief preliminary survey of the subject with some emphasis on such aspects of it as may be of value in analytical work. A complete elucidation of the mechanism of formation of a molybdate heteropoly acid, such as has been achieved by Souchay and collaborators with heteropoly tungstates,[3] is impossible without a fuller knowledge of the chemistry of the parent molybdate species than we at present possess. Nevertheless, the work described in this and following papers has thrown some light on the number of molybdate species present in acidified solutions.

The discovery of the existence of two types of silicomolybdate makes it desirable to describe in this first paper some of the more characteristic properties of solutions of the only type previously recognized, which will be called α-silicomolybdic acid. This compound has the empirical formula $H_4SiMo_{12}O_{40}\cdot 29H_2O$ and its structure in the solid state has been well established.[4]

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(1) A. Jolles and F. Neurath, *Z. angew. Chem.*, **11**, 315 (1898).

(2) M. L. Isaacs, *Bull. soc. chim. biol.*, **6**, 157 (1924).

(3) For a summary of much of this work see M. Jean, *Ann. chim.*, **3**, 470 (1948).

(4) See, for example, J. F. Keggin, *Proc. Roy. Soc.* (*London*), **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935).

Solutions of this compound have been studied almost exclusively by electrometric methods. The quadribasicity predicted by the Keggin formula has been fully established by conductivity work[5] and by titration with alkali.[6,7,8] The anion is of considerable stability, degrading directly to normal molybdate and silicate when treated with alkali but, apart from this, few if any important facts concerning the structure of the silicomolybdate complex in solution are known.

Of the many reducing agents which give blue compounds when added to solutions of silicomolybdic acid stannous chloride is particularly suitable, especially in analytical work, as reduction with this compound takes place almost instantaneously to give solutions having the maximum extinction for a given concentration of silicomolybdate. Furthermore, the rate of reduction is reasonably independent of the acidity of solutions or their temperature. Stannous chloride has, therefore, been used exclusively in this investigation.

As a result of the study of the reduction of ferric iron etc., Weiss and others[9] have shown that stannous chloride generally acts *via* the stepwise oxidation of the $SnCl_4^{2-}$ anion and rarely *via* cationic Sn^{2+}. The velocity of reduction is greatly accelerated by the presence of chloride. Probably the most reliable values for the oxidation-reduction potentials of stannous-stannic couples are given by Huey and Tartar[10] who obtained values of −0.15 and −0.13 v. (sign convention of Lewis and Randall) for the couple

$$Sn^{II} \longrightarrow Sn^{IV} + 2e^-$$

in 0.5 and 2 *M* hydrochloric acid, respectively. They showed that smooth platinum formed an unsatisfactory electrode for recording equilibrium voltages in tin solutions, which were best obtained using a mercury pool. Unfortunately, platinum has had to be used for the potentiometric work described in this paper because mercury rapidly reduces silicomolybdate solutions containing chloride.

Most of the present investigation has been made by characterizing the absorption properties of reduced silicomolybdate solutions, a technique of great value in the determination of the state of reduction of these compounds. An absorptiometric method of identifying the reduction products of heteropoly compounds is capable of much greater accuracy than that obtained by gravimetric analysis but the value of such a method has been appreciated by only a few authors[11,12] who have worked almost exclusively with phosphomolybdic acid.

Experimental

Preparation and Properties. Synthesis.—Originally the best modern synthesis, that given by North and Haney,[13] was used. However, as a result of the present investigation, it has been possible to devise an even better synthesis, giving a 100% yield of very pure material, with no serious experimental difficulties. The technique is not essentially different from that given by North and Haney but by avoiding heat, excess silicon and acid almost complete combination of the silicate and molybdate takes place. The yield obtained by this method was so much higher than that found with existing published processes that an account of it will be given. Multiples of the stated quantities may be taken:

Dissolve 24.5 g. of pure finely powdered molybdenum trioxide in 20% sodium hydroxide solution until the solution is just alkaline to phenolphthalein. Carefully acidify with 5 *N* hydrochloric acid and then add 75 ml. in excess. Make the solution up to a volume of 250 ml. with water. Dissolve 3.2 g. of good quality sodium silicate crystals ($Na_2SiO_3 \cdot 5H_2O$) in 50 ml. of cold water and add the solution to the acidified molybdate while the latter is being vigorously stirred. Allow the mixture to stand for at least 15 minutes.

Take 50-ml. portions of the solution in a separating funnel, add 15 ml. of concentrated hydrochloric acid to each portion and extract vigorously for a minute with 35 ml. of pure diethyl ether. Allow the funnel to stand for about 10 minutes. Run off the bottom layer of silicomolybdate-ether complex (the funnel should have a short stem) into a measuring cylinder and to the combined ether extracts add 0.2 times the volume of water. Mix and transfer the liquid to a large evaporating dish. If at any stage the solution becomes green it should be restored to a full yellow color by the addition of a few drops of dilute bromine water.

Remove the bulk of the ether by warming the dish to a temperature which must *not* exceed 35°. Place the dish in a vacuum desiccator over potash and maintain at the highest vacuum obtainable by the water-pump until crystals of the 29 hydrate have completely separated. Maintain the vacuum for another 12–18 hours, after substituting concentrated sulfuric acid for the potash. Remove the solid with a bone or plastic spatula, grind it to a fine powder and replace for a few more hours in the desiccator until an approximately constant weight is obtained. Store the solid in a tightly stoppered bottle.

A typical analysis of a sample of acid prepared in this manner[13] gave results corresponding to a solid of formula $H_4SiMo_{12}O_{40} \cdot 8.08H_2O$. Assuming a molecular weight of 1970 the acid required 4.01 equivalents of base (electrometric titration with a glass electrode) and had a Si:Mo ratio of 1:12.05.

Absorption Spectra.—Figure 1 shows the absorption spectra at 20° of solutions 2×10^{-3}, 4×10^{-4}, 2×10^{-4}, 5×10^{-5} and 2×10^{-5} *M*, as determined with a 1-cm. cell using the Uvispek quartz prism spectrophotometer of Messrs. Hilger and Watts, Ltd. The extinction values were determined immediately on diluting a stock solution, in order to eliminate errors from the slow dissociation of the anion noticeable at concentrations less than about 5×10^{-5} *M*. Light absorption was negligible at wave lengths greater than about 5200 Å. Solutions obeyed the Beer-Lambert law if a narrow wave band (*ca.* 10 Å.) was used and the spectrophotometer proved a useful means of determining the con-

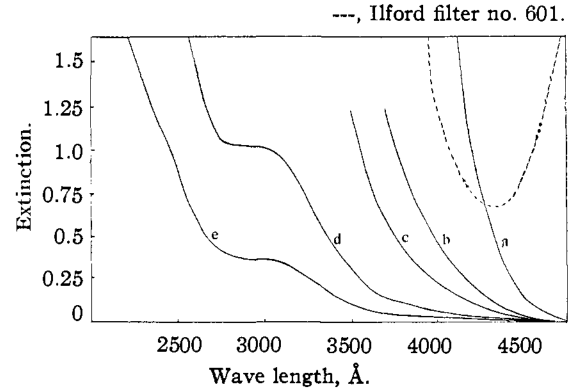

Fig. 1.—α-Silicomolybdate absorption spectra: a, 2×10^{-3} *M*; b, 4×10^{-4} *M*; c, 2×10^{-4} *M*; d, 5×10^{-5} *M*; e, 2×10^{-5} *M*.

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[5] W. Asch, *Z. anorg. Chem.*, **28**, 294 (1901).

[6] L. Malaprade, *Ann. chim.*, **11**, 104 (1929).

[7] R. Ripan and C. Liteanu, *Compt. rend.*, **224**, 196 (1947).

[8] P. Souchay and A. Tchakirian, *Ann. chim.*, **1**, 249 (1946).

[9] J. Weiss, *J. Chem. Soc.*, 309 (1944); T. R. Ball, W. Wulfkuehler and R. E. Wingard, THIS JOURNAL, **57**, 1729 (1935).

[10] C. S. Huey and H. Tartar, *ibid.*, **56**, 2585 (1934).

[11] F. Hein, I. Buraway and H. Schwedler, *Kolloid Z.*, **74**, 35 (1936).

[12] W. Treadwell and Y. Schaeppi, *Helv. Chim. Acta*, **29**, 771 (1946).

[13] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 127.

centration of α-silicomolybdate in solution. As a spectrophotometer was available for only a limited time during this investigation concentrations were generally determined by means of the Spekker Absorptiometer of Messrs. Hilger and Watts using a tungsten filament lamp light source and Ilford No. 601 filters, the characteristic absorption of which is also shown in Fig. 1. With this broad wave band of incident light the Beer–Lambert law was no longer obeyed and the concentration of silicomolybdate had to be read from calibration curves. A pronounced extinction–temperature gradient existed and, for accurate measurement of concentrations, solution temperatures had to be controlled to within a few degrees.

Chemical Properties.—In general, the chemical properties given in the literature have been confirmed. *p*H measurements with the glass electrode showed that the acid ionized into an anion and four hydrogen ions to the extent which would be expected from a "completely dissociated" mineral acid. Oxalates, citrates and tartrates, known to form complexes with molybdate, bleached the color of silicomolybdate solutions slowly at room temperature, the rate of bleaching increasing rapidly with an increase of *p*H or temperature. In solutions more concentrated than about 2.5 × 10^{-3} *M* heat alone brought about decomposition, a turbidity consisting of decomposition products, silicic acid and hydrated molybdenum trioxide, being observed. This decomposition was caused by the acidity of solutions and did not take place with the neutralized acid. The effect was found even in the cold with very dilute solutions of silicomolybdate which had been strongly acidified, although no solid separated. The reaction between the silicomolybdate complex and alkali was sluggish, unless the solutions were heated, when complete bleaching occurred on the addition of about 16 equivalents of OH^{1-} to the anion, $SiMo_{12}O_{40}^{4-}$.

Reduction with Stannous Chloride.—Stannous chloride solutions were prepared from a stock 10^{-2} *N* solution, prepared by dissolving 1.5 g. of pure $SnCl_2 \cdot 2H_2O$ in 10 ml. of concentrated hydrochloric acid and diluting the solution to 1 liter with air-free water. This stock supply was stored under carbon dioxide and, for immediate use, was diluted suitably with air-free water. Diluted solutions were kept under a stream of carbon dioxide and standardized every 30 minutes by means of 10^{-2} *N* iodate.

Absorptiometric Experiments. First Reduction Stage.—10-ml. aliquots of a 2.50, 3.75 or 5.00 × 10^{-4} *M* solution of silicomolybdic acid were introduced, together with 5 ml. of 10 *N* sulfuric acid, into a series of 150-ml. flasks containing measured volumes of air-free water. Carbon dioxide was passed through each solution for 5 minutes to ensure the complete absence of oxygen and finally a known volume of standardized 2.5 × 10^{-3} *N* stannous chloride solution was added from a small buret. The final volume in each experiment was 50 ml., the solution being 1 *N* in sulfuric acid, with practically no chloride present. The solutions were mixed and transferred for extinction measurement to a 1-cm. cell fitted with a tightly fitting cover slip. Constant extinction values were obtained after less than one minute, indicating a very rapid reduction. The extinctions were measured on the Spekker absorptiometer fitted with Ilford No. 608 filters, which transmit light of wave lengths greater than 6250 Å.

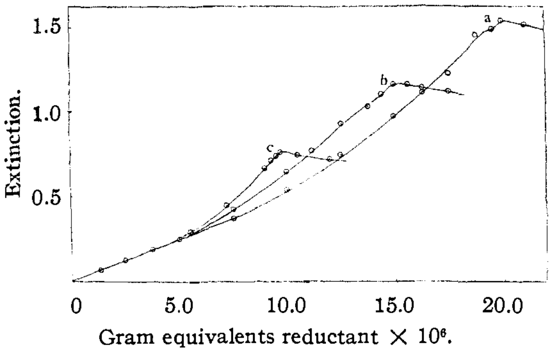

Fig. 2.—Reduction of α-silicomolybdic acid: a, 5.00 × 10^{-6} mole $H_4SiMo_{12}O_{40}$; b, 3.75 × 10^{-6} mole $H_4SiMo_{12}O_{40}$; c, 2.50 × 10^{-6} mole $H_4SiMo_{12}O_{40}$.

The results of these experiments are illustrated by Fig. 2, where the maxima in the three curves each occur when exactly four equivalents of reductant have been added per mole of silicomolybdate. The solutions at the maxima were sea-green in color and obeyed the Beer–Lambert law, even on the Spekker absorptiometer. Unlike the unreduced complex the extinction–temperature gradient was negligible and the color did not fade on standing solutions in strong acid, provided that oxygen was excluded. No solid could be salted out on the addition of ammonium sulfate, etc., as occurred with solutions of normal "molybdate" molybdenum blue.

The absorption spectrum of a 5 × 10^{-5} *M* solution of the silicomolybdate reduction compound (*i.e.*, solution c, Fig. 2, at the maximum) is shown by curve b in Fig. 3. To minimize errors from oxidation the absorption spectrum was measured in two parts, from 2500 to 5000 Å. using one solution and from 5000 to 10,000 Å. using a second identical solution, neither solution standing for more than 45 minutes.

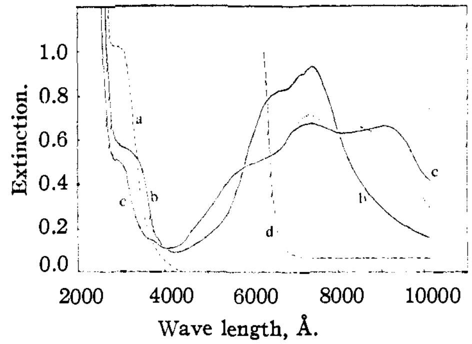

Fig. 3.—Absorption spectra of the reduction product of α-silicomolybdic acid: a, unreduced solution; b, first reduction; c, second reduction; d, Ilford filter No. 608; 5 × 10^{-5} *M* solutions, 1-cm. cell.

Second Reduction Stage.—The addition of more than 4 equivalents of stannous chloride caused a gradual decrease in extinction until, on the addition of a very large excess, an approximately constant value was reached. The commencement of this decrease is shown in Fig. 2. This decrease was found to be the result of a secondary reduction which was very slow under the conditions used in the first series of experiments above. The rate of reduction rapidly increased with the concentration of chloride but was retarded by the presence of sulfate. The experiments made to find this degree of reduction were similar to those used to find the degree of reduction of the first compound formed, except that reduction took place in 2 *N* hydrochloric acid and the greatest possible care had to be taken to exclude oxygen. Extinctions were measured in tightly closed 1-cm. cells about 5 minutes after adding the tin solution, when a constant extinction was obtained.

The results of these experiments are shown in Fig. 4, where it will be seen that after the addition of 2 × 10^{-5} equivalent of stannous chloride to 5 × 10^{-6} mole of silicomolybdate the

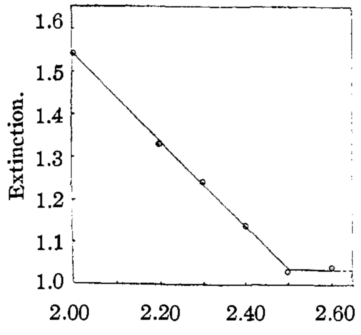

Fig. 4.—Reduction of α-silicomolybdic acid: 5.00 × 10^{-6} mole $H_4SiMo_{12}O_{40}$; 2 *N* HCl.

extinction decreases in a linear manner until 2.5 × 10^{-5} equivalent of reductant have been added. It seems fairly conclusive, therefore, that this second reduction product corresponds to the addition of 5 electrons to the silicomolybdate molecule and the compound will be referred to, for brevity, as the $+5e^-$ blue.

Solutions of this substance were a royal blue in color (*i.e.*, the color normally encountered in "molybdenum blue" analytical methods for silicon, phosphorus etc.) and visually quite distinct from solutions of the first reduction product ($+4e^-$ blue). The $+ 5e^-$ blue was stable to acid, had no appreciable extinction-temperature coefficient and solutions obeyed the Beer-Lambert law when using the Spekker absorptiometer.

The absorption spectrum of a 5 × 10^{-5} *M* solution of the $+5e^-$ blue in a 1-cm. cell, is shown by curve c in Fig. 3. Also in Fig. 3 is shown the absorption curve of a 5 × 10^{-5} *M* solution of unreduced α-silicomolybdic acid, curve a, and that of an Ilford No. 608 filter curve d. The curve of the latter explains why a solution of the $+4e^-$ blue has about 1.5 times the extinction of a solution of the $+5e^-$ blue (1.54 and 1.04, respectively, for a 1 × 10^{-4} solution) when measured on the Spekker absorptiometer. (The selenium cells in the absorptiometer are insensitive to light of wave length greater than about 8000 Å.)

The dotted portion of curve c shows the absorption change noted when the $+5e^-$ blue stands for some time in the presence of a large excess of stannous chloride. It is unlikely that this alteration of extinction indicates yet a further reduction taking place, as the presence of a large excess of chloride ions, which would increase the reducing power of stannous chloride, actually decreases the extent of this absorption change.

Potentiometric Experiments. First Reduction Stage.—Potentiometric titrations were carried out using a smooth platinum foil electrode and a dip type saturated calomel half-cell (*ca.* −0.24 v.) with the liquid junction through a small ground glass sleeve on the half-cell. The e.m.f. of the assembly was measured using the valve type potentiometer of the Cambridge Instrument Company. To prevent atmospheric oxidation the titrations took place in a stoppered beaker. The stopper admitted the electrodes and a buret and, in addition, a glass tube through which passed carbon dioxide. This tube terminated in a flat spiral on the bottom of the beaker through fine perforations in which the gas passed into the liquid and thence up through a small escape hole. The buret was connected to a reservoir of stannous chloride, both buret and reservoir being kept air free by a stream of carbon dioxide.

In the first experiment 5.00 ml. of a 1.25 × 10^{-3} *M* α-silicomolybdic acid solution was added to the beaker followed by sulfuric acid and sodium chloride solutions to make the volume to about 90 ml. At the end of the titration the solution was approximately 1 *M* with respect to sulfuric acid and 0.5 *M* with respect to sodium chloride. A stable potential was recorded after a few minutes during the earlier part of the titration but after the first inflection the reaction was very slow and at least 30 minutes were required before relatively constant values for the potential were obtained. The final curve is shown by curve a in Fig. 5 which has inflections at points corresponding to the addition of about 3.4 and 5.5 electrons per molecule of silicomolybdate complex. Approximately an hour and a half elapsed between commencing the titration and reaching the first inflection, during which time appreciable amounts of the unreduced acid were decomposed by the acid present and the first reduction was being interfered with badly by the second. Curve a therefore, although confirming the existence of two reducing reactions, was not sufficiently accurate for quantitative deductions.

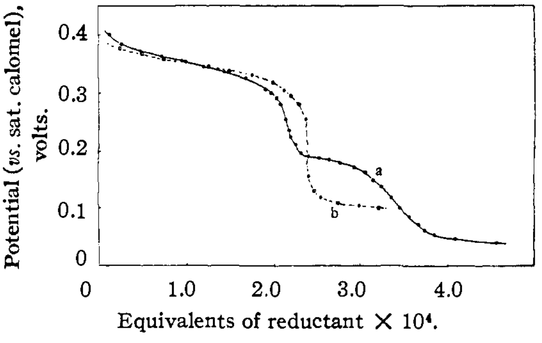

Fig. 5.—Titration of α-silicomolybdic acid with stannous chloride: a, 2 *N* acid, 1.0 *M* sulfate, 0.5 *M* chloride; b, 2 *N* acid, 1.0 *M* sulfate, less than 0.01 *M* chloride.

In order to obtain a more satisfactory inflection corresponding to the formation of the first reduction product, the experiment was repeated in the absence of added chloride, which made the velocity of the secondary reduction almost negligible. The result is shown by curve b in Fig. 5. Stable values for the potential were obtained comparatively rapidly and the inflection, which is greatly sharpened, was reached in less than half the time previously required. The inflection corresponds to the addition of 3.85 electrons to the silicomolybdate molecule and differs by only some 4% from the value of 4.0 obtained absorptiometrically, a difference easily explicable by the slight acid decomposition which would still have taken place during the titration.

Second Reduction Stage.—In order to obtain a more accurate estimate of the degree of reduction of the second reduction product, the titrations described above were repeated, titrating stannous chloride with silicomolybdic acid. The results of two such titrations are shown by curves a and b in Fig. 6. In curve a the solution was approximately 1 *M* with respect to sulfuric acid and 0.5 *M* with respect to sodium chloride. In curve b, which has a sharper end-point, the sulfate was absent and the titration took place in 2 *N* hydrochloric acid. In the earlier parts of the titration between 30 and 50 minutes were required after each addition of silicomolybdate before stable potential was recorded but after the inflections the voltages became constant after a few minutes.

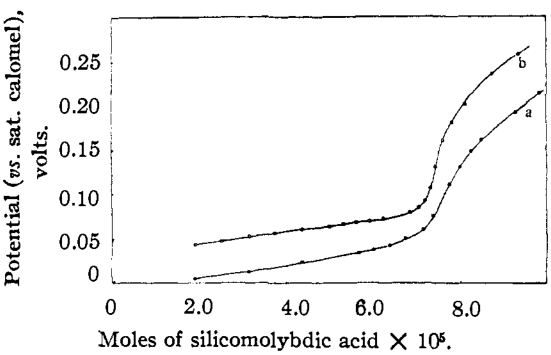

Fig. 6.—Titration of stannous chloride with α-silicomolybdic acid: a, 3.83 × 10^{-4} equivalent Sn^{II}, 1.0 *M* sulfate, 0.5 *M* chloride; b, 3.59 × 10^{-4} equivalent Sn^{II}, 2 *N* acid, no sulfate, 2.0 *M* chloride.

In these experiments the second stage of the reduction of silicomolybdic acid was favored, as the silicomolybdate complex reacted with an excess of reductant. As the complex was reduced almost instantaneously to the $+4e^-$ blue, the first parts of curves, a and b, are effectively the result of titrating Sn^{II} with the $+4e^-$ blue. As would be expected, therefore, there is only one inflection. After this inflection the oxidant is no longer the $+4e^-$ blue but unreduced α-silicomolybdic acid and hence the titration curves are not of the symmetrical form to be expected from a simple reversible reaction. The maximum rate of change of potential, however, should occur very near to the equivalence point and the values of 5.07 and 4.92 electrons per molecule of silicomolybdate, obtained from these curves, are excellent confirmation of the value of 5.0 obtained absorptiometrically.

Oxidation Experiments.—Solutions of the $+5e^-$ blue oxidized in air rapidly to give the $+4e^-$ blue (with a resulting increase in the extinction as measured on the absorptiometer) and then the $+4e^-$ blue itself was oxidized with a resulting fading of the solution. An iodine–iodide solution (5 × 10^{-4} *N*, with an I/I^- ratio of 1:2.5; oxidation–reduction potential *ca.* −0.6 v.) oxidized the $+5e^-$ blue almost instantaneously and the resulting $+4e^-$ blue was bleached more rapidly than by air alone. A solution which was 2.5 × 10^{-4} *M* with respect to ferricyanide and 1 × 10^{-3} *M* with respect to ferrocyanide (oxidation–reduction potential *ca.* -0.38 v.) oxidized $1 \times 10^{-4} M$ $+5e^-$ blue solution to the $+4e^-$ stage but no further. Stronger oxidants, such as ceric cerium or permanganate, oxidized both reduction products almost instantaneously.

Oxidation in Strongly Acid Solutions.—Working in 1-2 N hydrochloric acid solutions, where it can be shown that neither penta- nor hexavalent molybdenum will combine with silicic acid, the $+5e^-$ or $+4e^-$ blue reduction compounds of α-silicomolybdic acid were both rapidly oxidized by nitric acid to give a quantitative yield of the original α-acid (as determined absorptiometrically).

Oxidation by Acid Molybdate.—Solutions of strongly acidified molybdate, with a standard oxidation–reduction potential of *ca.* -0.4 to -0.5 v.[14] oxidized the $+5e^-$ blue to the $+4e^-$ blue but had no effect on the latter. Thus when stannous chloride is added to a dilute α-silicomolybdate solution in the presence of acidified molybdate only the $+4e^-$ compound is produced. In such experiments the stannous chloride must be reacting with the heteropoly acid very much more rapidly than with the excess molybdate, as the latter is also reduced within a few seconds to the pentavalent state. The extinction of a solution of the $+4e^-$ blue thus formed is remarkably constant and it would appear that the pentavalent molybdenum present must undergo, preferentially, any oxidation that occurs when solutions are exposed to the air.

Discussion

Absorptiometric methods are of great use for the rapid determination of the concentration of silicomolybdic acid. Unfortunately, the use of the wave lengths of the "plateau" between 2700 and 3100 Å. is impossible with the Spekker absorptiometer and if the spectrophotometer is used the measurement is restricted to extremely dilute solutions. The calibration curves obtained with pure silicomolybdate solutions are similar to those found in many published analytical methods except that the extinctions are only about one-half of what they should be for a given concentration of combined silicon. This is explained by the fact that the type of silicomolybdate prepared from the solid acid and investigated in this paper is not the same as the type of complex commonly produced immediately silicic acid and acidified molybdate react. The exact relationship will be discussed in a later paper but it should be noted that the type of silicomolybdate studied here will be termed α-silicomolybdic acid to distinguish it from the other form, which will be called β-silicomolybdic acid.

Titration and *p*H measurements class silicomolybdic acid as a "fully ionized" acid comparable in strength with a strong mineral acid. As first suggested by Malaprade,[6] the anion must be of considerable stability and probably retains much of the structure found by X-ray work to exist in the solid acid, although some degree of polymerization, hydration, etc., may occur. The remarkably strong acidity and stability of this compound would be expected from the Keggin formula, because of the complete valency saturation possible with a central SiO_4 tetrahedron. The corresponding phospho or arseno compounds, which contain a pentavalent atom in the central tetrahedron, have a relatively poor stability.

The fact that the presence of a large concentration of a molybdate complexing agent (such as tartrate) causes the slow decomposition of silicomolybdic acid indicates that the anion must dissociate to some extent to give a molybdate species. This would explain the decomposition brought about in hot acid solutions, as under these conditions molybdate is known to decompose irreversibly to give hydrated oxides. The degree of dissociation must normally be very small, however, as solutions have to be more dilute than $5 \times 10^{-5} M$ before any dissociation can be detected by the spectrophotometer.

In view of the "strength" of the acid its sodium salt would not be expected to undergo hydrolysis and the fact that solutions of $Na_4SiMo_{12}O_{40}$ have a *p*H around 3.5 must arise from the dissociation of the anion, giving rise to hydrogen ions. As at *p*H 3.5 the molybdate species would almost certainly be in the metamolybdate conditions (*cf.*[15]), we can write the dissociation, or more accurately hydrolysis, of the anion most simply as

$$SiMo_{12}O_{40}^{4-} + H_2O \rightleftarrows SiO_2(aq.) + 3Mo_4O_{13}^{2-} + 2H^+$$

This would account for the acidity of the sodium salt, the action of molybdate complexing agents and the decomposition brought about by alkali. In the latter case, after first neutralizing the 4 hydrogen ions associated with the acid, the anion is slowly decomposed, the above equilibrium being moved to the right both by the removal of hydrogen ions and by the decomposition of the metamolybdate to give normal molybdate

$$Mo_4O_{13}^{2-} + 6OH^- \rightleftarrows 4MoO_4^{2-} + 3H_2O$$

Although complete hydrolysis of the anion (as indicated by the complete bleaching of the color) occurred at about *p*H 5.5, after the addition of 16 equivalents of alkali, complete decomposition of the molybdate thus formed did not occur until a further 4 equivalents had been added (*p*H about 6.5).

Both absorptiometric and potentiometric work indicate that the first reduction product formed when α-silicomolybdic acid is treated with stannous chloride corresponds to the addition of four electrons to the heteropoly complex. The strong absorption of visible light by the $+4e^-$ blue thus formed would be expected, as the molybdenum atoms then have a net valency of 5.67, bringing about a resonant state in the molecule as a whole.

The absorption spectra of the unreduced and reduced acids show some similarity in the ultraviolet and all evidence points to the fact that the α-silicomolybdate anion reduces in its entirety to give a compound still containing the silicon combined with molybdenum in an atomic ratio of 1:12. This would be expected in view of the great stability of the silicomolybdate anion and is proved by the fact that the $+4e^-$ blue can be rapidly oxidized to give a quantitative yield of the unreduced α-acid, under conditions in which silica and molybdate do not combine.

The actual structure of the reduced molecule is not known but must consist, basically, either of the

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(14) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

(15) For two of the most modern and authoritative researches into molybdate structure in aqueous solutions, see G. Carpéni, *Bull. soc. chim. France*, **14**, 490, 501 (1947); J. Byé, *Ann. chim.*, **20**, 463 (1945).

original heteropoly acid less two oxygen atoms or of the heteropoly anion plus four hydrogen atoms. The latter is more probable. According to the Keggin formula, the silicomolybdate anion consists of four $Mo_3O_9^{1-}$ groups round the central SiO_4 tetrahedron, there being twelve oxygen atoms on the periphery of the anion, three for each $Mo_3O_9^{1-}$ group. The rapid removal of two oxygen atoms from such a structure is unlikely, as the anion is entirely symmetrical and no two $Mo_3O_9^{1-}$ groups or oxygen atoms are different from any other, but the addition of one hydrogen atom to each of the four $Mo_3O_9^{1-}$ groups would keep the structure and symmetry of the molecule almost unaltered. The first reduction, therefore, is most probably represented by the couple

$$(H_4SiMo_{12}O_{40})^{4-} \longrightarrow (SiMo_{12}O_{40})^{4-} + 4H^+ + 4e^-$$

Very similar conclusions to the above have already been reached by Treadwell and Schaeppi[12] about the structure of the corresponding reduction product of phospho-12-molybdate, which they showed contained molybdenum atoms of mean valency 5.67. They also suggested a mechanism involving the addition of four hydrogen atoms, the resulting formula being the same as that given by Auger and Ivanoff[16] for a compound isolated by them in 1937, $H_3PO_4(Mo_6O_{17})_2 \cdot xH_2O$, rewritten as $H_3(H_4PMo_{12}O_{40}) \cdot x - 2H_2O$.

The oxidation–reduction potential of the couple shown above, in approximately normal acid, can been estimated potentiometrically to be −0.59 v. As would be expected from the suggested mechanism, the voltage of this couple became less negative by about 0.06 v. from a tenfold decrease of hydrogen ion concentration. As the $+4e^-$ compound is basically similar to the unreduced acid it is proposed to call it *α-silicomolydous* acid.

The reduced silicomolybdate molecule differs from the unreduced compound in that it is not decomposed by strongly acidic solutions. This would indicate that it does not dissociate into hexavalent molybdenum to anything like the same extent as does the oxidized form of the complex. It should also be noted that the characteristic sea-green color of α-silicomolybdous acid is not found when using any reductant other than stannous chloride. This reaction is specific to stannous tin, probably to the stannous ion Sn^{2+}, as the reduction is very rapid even in solutions containing only traces of chloride.

The royal blue $+5e^-$ reduction product, containing molybdenum of a mean valency of 5.58, resembles α-silicomolybdous acid in consisting of the parent heteropoly acid reduced in its entirety. The presence of chloride is necessary for this reduction, which clearly involves the more common stannous chloride reduction mechanism, *i.e.*, the action of the chloro ion, $SnCl_4^{2-}$.

Because the $+5e^-$ blue is in a lower state of oxidation than α-silicomolybdous acid the compound will be called α-hyposilicomolybdous acid.

It has not been possible to evaluate potentiometrically the standard oxidation–reduction potential of the couple

$$+\ 5e^-\ \text{blue} \longrightarrow +\ 4e^-\ \text{blue} + 1e^-$$

owing to the unsatisfactory nature of the platinum electrode, but from chemical evidence the oxidation–reduction potential can be placed at approximately −0.25 ± 0.03 v.

A characteristic of the α-form of the silicomolybdate complex is the formation of α-silicomolybdous acid on reducing solutions with stannous chloride in the presence of excess acidified molybdate. This reaction has been of the greatest value (see later papers) in the identification and determination of the α-acid in solution. A comparison of the reduced silicomolybdate solutions, obtained during most analytical methods, with solutions of silicon combined as α-silicomolybdous acid again proves that the α-form of the silicomolybdate complex is not formed during analysis. Instead of the sea-green $+\ 4e^-$ blue a royal blue compound, resembling the α-hypo reduction product but which cannot be this substance, is produced. A full investigation of this matter will be described in the next paper of this series.

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[16] V. Auger and N. Ivanoff, *Compt. rend.*, **204**, 1424 (1937).