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

The Preparation and Properties of Silicomolybdic Acid. II. The Preparation and Properties of β-Silicomolybdic Acid

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When silicomolybdic acid is prepared by the reaction in solution of silicic acid with normal molybdate which has been acidified with two equivalents of acid, the complex produced is not the normal α-acid. The absorption spectrum of this new silicomolybdic acid, which it is proposed to call *β-silicomolybdic acid*, has been determined and it differs markedly from that of the alpha compound. In the visual region of the spectrum the absorption of the beta complex is approximately twice that of the alpha. The difference between the two acids lies in the structure of their anions, which are probably isomeric. The β-anion changes spontaneously into the α-form by a first order transformation. The two forms of heteropoly acid also differ on reduction with stannous chloride. The beta complex forms only one product. which corresponds to α-silicomolybdous acid in consisting of the parent acid reduced in its entirety by the addition of four electrons and which will therefore be termed *β-silicomolybdous acid*. The absorption spectrum of β-silicomolybdous acid resembles that of the unreduced beta acid in the ultraviolet but in the visible region of the spectrum it is almost identical with that of α-hyposilicomolybdous acid.

Introduction

It was mentioned in the first paper of this series that solutions of silicomolybdic acid, freshly prepared by the reaction of acidified silicate and molybdate, had different properties from solutions of the normal crystalline heteropoly acid, $H_4SiMo_{12}O_{40}$. The latter has been referred to as the α-complex.

If a solution of alpha silicomolybdic acid is degraded to a mixture of silicate and molybdate by the addition of 24 equivalents of alkali, according to the equation

$$H_4(SiMo_{12}O_{40}) + 24OH^- \rightleftarrows 12MoO_4^{2-} + SiO_2 + 14H_2O$$

and then reacidified with 24 equivalents of hydrochloric acid (*i.e.*, 2 equivalents per mole of MoO_4^{2-}), silicomolybdic acid is reformed in 10–15 minutes. However, although the resulting solution still possesses the characteristic yellow color of the α-compound the extinction is over twice as great. In order to obtain reproducible and maximum extinctions it is necessary to carry out the reacidification process as rapidly as possible, using exactly 24 equivalents of acid, and in such a volume that the solution is never less than about 1×10^{-2} *M* with respect to silicon. The acidification of degraded silicomolybdate is, of course, only a convenient method of acidifying a solution containing silicate and molybdate in the correct molecular proportions for a 12-heteropoly acid formation. If additional sodium normal molybdate is added to the degraded silicomolybdate and the whole reacidified with two equivalents of hydrochloric acid per MoO_4^{2-} ion, a slightly increased extinction is generally found. This method is probably the best way of preparing a solution of this new type of silicomolybdic acid, which will be called β-silicomolybdic acid.

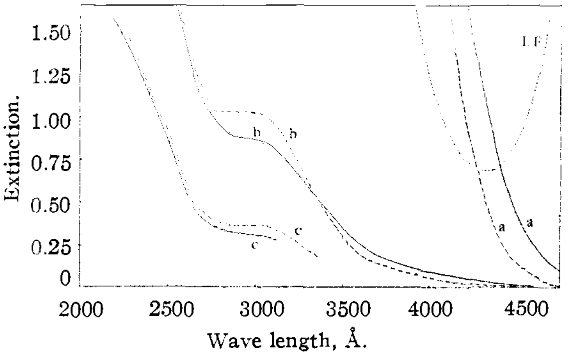

Fig. 1.—Absorption spectra of α- and β-silicomolybdic acid: - - - -, α-acid; — β-acid; I. F., Ilford filter No. 608. a, 2×10^{-3} *M;* b, 5×10^{-5} *M;* c, 2×10^{-5} *M.*

The β-acid has properties which are markedly different from those of the α-compound and a detailed study would constitute a major investigation. All that has been attempted in the work described in this paper is a brief preliminary survey of the subject.

Experimental

General Properties. Light Absorption Properties.—Figure 1 shows absorption spectra of the β-acid, determined against a suitable blank solution using a 1 cm. cell in the quartz spectrophotometer of Messrs. Hilgers and Watts. In order to increase the stability of solutions (see later) they were prepared in the presence of 1×10^{-2} *M* excess molybdate, the solutions being acidified to about *p*H 2.

The absorption resulting from the same concentrations of α-silicomolybdic acid is shown by broken lines along side the corresponding β-acid curves. With both acids absorption is negligible at wave lengths greater than about 5200 Å.

The Beer–Lambert law was obeyed if a line source of light was used but not when extinctions were measured on an absorptiometer, such as the Spekker Absorptiometer of Messrs. Hilger and Watts, with violet filters. Extinction–concentration curves for the β-acid, unlike those for the α-acid, showed extinctions of the same magnitude as found in the analytical literature for the same concentration of combined silicon.

General Chemical Properties.—The β-acid has similar properties to the α-acid. It does not exist in the solid state (attempts to isolate it result in the production of α-silicomolybdic acid) but solutions have exactly the same degree of acidity as corresponding solutions of the α-compound and the titration curves of the two acids are identical. There is also a marked positive extinction–temperature gradient for β-silicomolybdate solutions but they are much more rapidly decomposed by strong acid than are solutions of the α-compound, indicating a greater degree of dissociation of the β-complex. This increased dissociation is confirmed by the action of molybdate complexing agents such as tartrate or oxalate, but it cannot be easily studied quantitatively owing to the fact that the β-complex changes spontaneously into the α-form. This change will be described in some detail.

The Change of β-Silicomolybdic Acid into the α-Compound.—When solutions of β-silicomolybdic acid are allowed to stand for several hours the color fades considerably. On measuring the extinction changes which occur it was found that a solution of the β-acid faded until eventually its extinction was approximately equal to that of a corresponding solution of the α complex. This change required about 25–30 hours, with the solutions examined, which varied in concentration between 6×10^{-4} and 1×10^{-2} *M*. The identity of the α-silicomolybdic acid produced was confirmed by reduction experiments using stannous chloride in the presence of acidified molybdate (see the previous paper in this series).

Two typical experiments, made to follow this transforma-

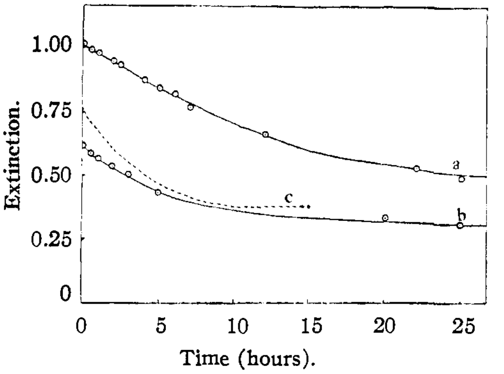

Fig. 2.—β- to α-silicomolybdate change: a, .4 cm. cell, 1.25×10^{-3} *M;* b, 2 cm. cell, 1.25×10^{-3} *M;* c, 2 cm. cell, 1.6×10^{-3} *M* in 0.15 *M* $(NH_4)_2SO_4$.

tion of the β- to α-complex, are illustrated by Fig. 2, where extinction–time curves obtained by the Spekker Absorptiometer are shown. The rate of decrease of extinction will be seen to be approximately exponential but a kinetic analysis cannot be made from these curves as neither the α- nor β-compound in solution is obeying the Beer–Lambert law. However, if β-silicomolybdate is reduced by stannous chloride in the presence of acidified molybdate a blue reduction product is formed which has an extinction which is only two-thirds of that obtained from a corresponding concentration of α-silicomolybdate (see later). Both blue solutions obey the Beer–Lambert law, and thus on reducing aliquots of a solution of the beta complex, which is in the process of changing into the α-form, the extinction *increases* with time and gives a direct measurement of the degree of transformation. The results of such experiments confirm that the change is exponential with a half-life of approximately 6 hours. This is illustrated by Fig. 3, where the percentage of the total decrease of extinction of the unreduced complex (lower curve) and the percentage of the total increase of extinction of reduced aliquots (upper curve) are plotted against time. The results are of duplicate experiments at 20 ± 1° and the curve shown for the reduction experiments is the theoretical one for a decay of half-life 5.8 hours.

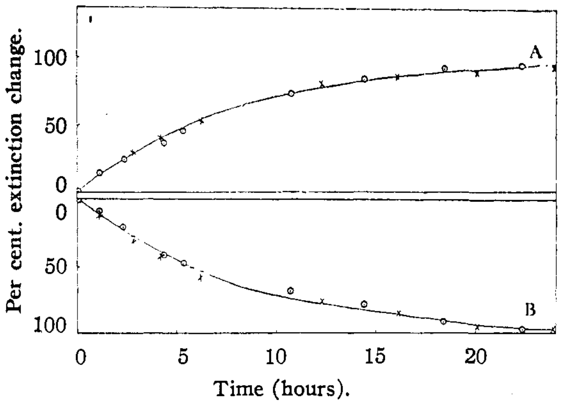

Fig. 3.—Beta to alpha silicomolybdate change: A, reduced solutions; B, unreduced solutions.

Heating solutions greatly accelerates the change of the β-complex into the α-complex, a change which is complete in less than 20 minutes at 100°. The addition of excess neutral electrolyte (an excess over the concentration of sodium chloride introduced during the preparation of the β-acid) also accelerates the transformation. An example of this action is shown by curve c in Fig. 2, where the β-acid (1.6×10^{-3} *M*) is in the presence of 0.15 *M* ammonium sulfate. The change was complete in about 6 hours in 0.2 *M* ammonium sulfate solutions. Finally, the rate of change increases in solutions less concentrated than 5×10^{-4} *M, i.e.,* of *p*H greater than about 2.5, or when the *p*H of more concentrated solutions is raised by the addition of alkali. No kinetic study has been made but the transformation was observed to be very rapid (within 15–30 minutes) when the β-acid was neutralized with four equivalents of alkali.

The change of β-silicomolybdate into the α-form appears to be spontaneous and it has not been found possible to prevent its occurrence or to bring about the reverse change. In the experiments outlined above, the β-acid was prepared with no excess molybdate present and was probably never entirely free from the α-species, which would commence to be formed from the moment of acidifying the molybdate. When the acid is produced by acidifying an excess of molybdate, over the amount needed to combine with the silica, although the beta to alpha change still occurs it is considerably retarded (half-life about 25 hours) and is much less susceptible to acceleration by heat, electrolyte or alkali. The reason for this "stabilization" is not known. The excess of molybdate required to "stabilize" the acid is much too little to permit an added molybdate molecule to be associated with each molecule of heteropoly acid formed. No gain of stability appears to be achieved by greatly increasing the concentration of excess molybdate.

Reduction Experiments. General.—Irrespective of conditions, *i.e.*, acidity or sulfate or chloride concentration, β-silicomolybdic acid when reduced by stannous chloride appeared to give only one reduction product. This was formed almost instantly on adding tin solutions and was a royal blue in color, being almost indistinguishable visually from α-hyposilicomolybdous acid.

Furthermore, the extinction coefficient of this compound, as measured on the Spekker Absorptiometer fitted with Ilford No. 608 filters, was practically identical with that of α-hyposilicomolybdous acid (1.03–1.04 for a solution 1×10^{-4} *M* with respect to silicon). Solutions obeyed the Beer–Lambert law with the absorptiometer, had no significant extinction-temperature variation and, in the absence of oxidation, were stable when strongly acid (despite the marked instability of the unreduced beta complex).

Absorption Spectra.—Curve a in Fig. 4 shows the absorption spectrum of a 5×10^{-5} *M* solution of freshly prepared β-silicomolybdic acid reduced with a slight excess of stannous chloride in 1 *M* hydrochloric acid. The absorption was measured against a suitable blank using a tightly stoppered 1 cm. cell.

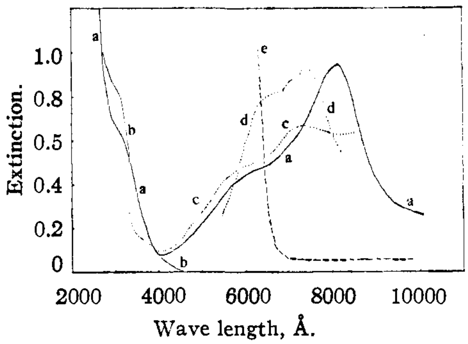

Fig. 4.—Absorption spectra of various silicomolybdate compounds: a, reduced β-acid; b, unreduced β-acid; c, α + 5e⁻ blue; d, α + 4e⁻ blue; e, Ilford filter No. 608.

Also shown in Fig. 5 is the absorption spectrum of a 5×10^{-5} *M* solution of unreduced beta acid (curve b), which will be seen to coincide with the spectrum of the reduction product in many places. Sections of the absorption spectra of both α-silicomolybdous acid and the α-hypo compound, at a 5×10^{-5} *M* concentration, are also given.

Degree of Reduction.—A potentiometric titration of β-silicomolybdic acid with stannous chloride could not be used to determine the number of electrons gained during reduction, as the β- to α-complex change during the titration would prevent a satisfactory completion of the latter. An absorptiometric study similar to that described in the previous paper was, however, practicable, provided that it was made within the space of about 15 minutes from the time of full formation of the β-acid.

Experimental details were similar to those already given (Part I) and will not be repeated in full. The results of such an experiment are shown in Fig. 5, where it will be seen that full extinction was obtained after adding 4 equivalents of

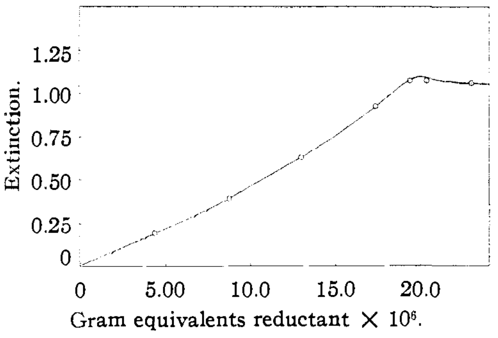

Fig. 5.—Reduction of β-silicomolybdic acid: 5.00×10^{-6} mole β-silicomolybdate, 1 cm. cell, Spekker absorptiometer, Ilford 608 filters.

stannous chloride to each mole of β-silicomolybdic acid. When β-silicomolybdate is prepared in the absence of excess molybdate it is difficult to obtain a product entirely free from the α compound and this accounts for the slight maximum in the extinction curve. The results shown in Fig. 5 are taken from the most successful of several experiments. The others have not been reported as the β-acid used was either not completely formed, had been decomposed by the acid present, or had changed appreciably into the α-form. In all cases, however, the number of equivalents of stannous chloride required approximated to 4 and not to 3 or 5.

Oxidation Experiments.—The $+4e^-$ β-acid reduction product is not oxidized by acidified molybdate or by an equimolecular ferro-ferricyanide mixture (oxidation potential *ca.* −0.5 v.). In air the extinction of solutions gradually decreases, indicating oxidation, and the rate of bleaching is slightly increased in the presence of an iodine–iodide mixture of oxidizing potential *ca.* −0.6 v.

Oxidants such as ceric cerium rapidly bleached the color and by using comparatively strong solutions of the reduced β-complex it was shown that the β-form of the unreduced acid is quantitatively reformed on oxidation. This occurred in solutions which were too strongly acidic for silica to combine with either penta- or hexavalent molybdenum, thus proving that the β-complex resembles the α-acid in being reduced in its entirety.

Polarographic Studies.—To compare the behavior of the α- and β-anion on polarographic reduction, polarograms were taken of 1×10^{-4} *M* solutions in water at 25°. These solutions were polarographed within a few minutes of dilution, to minimize dissociation and, in the case of the β-acid, to prevent any appreciable transformation into the α-state. The supporting electrolyte in both cases was 0.1 *N* potassium sulfate and the *p*H approximately 3.5.

A polarogram of the β-acid is shown in Fig. 6 and one for the α-acid in Fig. 7, both being corrected for residual current. The small step of about 0.4 microamp. at −0.25 v. in the α-acid polarograms is reproducible and characteristic of this compound, not appearing in the polarogram of the β-acid. Otherwise the polarograms were difficult to reproduce exactly, but were of the characteristic shape shown provided that the acidity remained constant. The value of $m^{2/3}t^{1/6}$ for the capillary used was 1.89 mg.$^{2/3}$ sec.$^{-1/2}$.

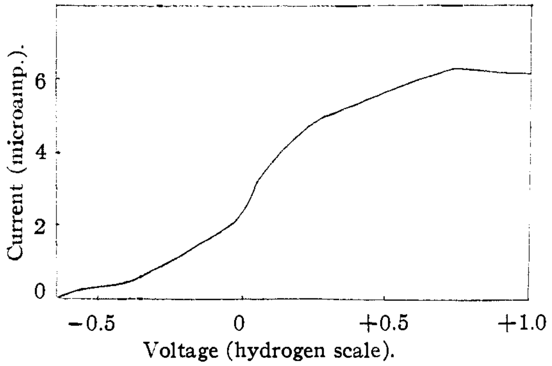

Fig. 6.—Polarogram: 1×10^{-4} *M* β-complex.

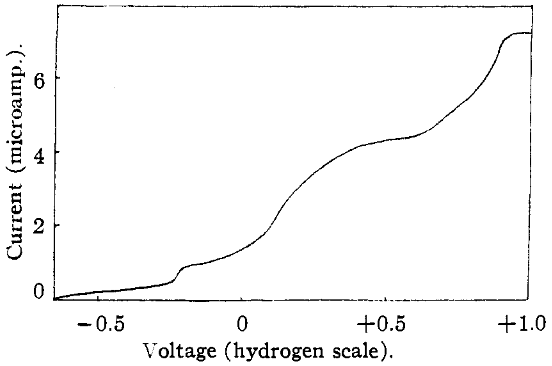

Fig. 7.—Polarogram: 1×10^{-4} α-complex.

Discussion

The existence of two forms of silicomolybdic acid is unexpected and, so far as is known, has not been reported in the literature. What is more surprising is that the β-compound appears to contain silicon and molybdenum atoms combined in the ratio of 1:12. Although it cannot be isolated in the solid state for analysis, the presence of at least twelve molybdate molecules per silicate molecule is necessary for the full production of this compound. This has also been shown (absorptiometrically) by Krumholtz,[1] using conditions under which the β-acid would have been produced. The α- and β-complexes are identical with respect to their behavior as acids and the difference between these two forms of heteropolymolybdate presumably exists in the structure of the anions.

The spontaneous change of the β-anion into that of the alpha requires more detailed study but has certain of the characteristics of an irreversible depolymerization. The decrease of extinction noted when β-silicomolybdic acid solutions are allowed to stand accounts for the fading of yellow silicomolybdate solutions noted during many analytical methods reported in the literature and generally assumed to be the result of a decomposition of the complex.

The markedly different absorption spectra of the two compounds will be seen in Fig. 1, the crossover of the two curves at 3350 Å. resulting in the difference in extinction of the two acids when measured between 3800 and 4800 Å. with an absorptiometer. At wave lengths exceeding 4000 Å. the curves are sufficiently parallel for the color of the solutions of these compounds to be visually indistinguishable. This probably accounts for the long delay in the recognition of the existence of two species of silicomolybdate complex.

There are indications that the β-anion hydrolyzes into molybdate much more readily than does the α-anion and it is also markedly different from the latter in its reaction with stannous chloride. Apparently only one reduction product is formed, which resembles α-silicomolybdous acid (ref. Part I) in being produced almost instantaneously, even in the virtual absence of chloride, and in consisting essentially of the unchanged β-anion reduced to a state corresponding to the addition of four electrons. In view of this similarity the compound will be called *β-silicomolybdous acid*, but it will be

[1] P. Krumholtz, *Z. anorg. Chem.*, **212**, 91 (1933).

noted that its absorption in the visible region of the spectrum, Fig. 4, is very similar to that of α-hyposilicomolybdous acid, which it therefore resembles closely in color. The oxidation–reduction potential of the couple

$$\beta\text{-silicomolybdous} \longrightarrow \beta\text{-silicomolybdic} + 4e^-$$

is estimated from chemical evidence to be similar to the corresponding α-acid couple, *i.e.*, about −0.6 v.

As β-silicomolybdous acid is stable in the presence of excess acidified molybdate, whereas any α-hyposilicomolybdous acid is oxidized to α-silicomolybdous acid, the result of reducing say a 1×10^{-4} M α-silicomolybdic acid solution with stannous chloride in the presence of molybdate is to give a solution having an extinction on the absorptiometer of about 1.5, whereas if a 1×10^{-4} M β-silicomolybdic acid solution is reduced under similar conditions an extinction of only about 1.0 results. As the extinctions of solutions of the unreduced acids also differ, the β-acid having an extinction about twice that of the α-acid, it is possible from absorptiometric measurements to determine the condition of the silicomolybdate ion, whether in the α- or β-state, or a mixture of the two. This fact, as will be described later, has been of great use when investigating which form of the heteropoly acid is formed from molybdate and silicate under various conditions.

The polarograms of the α- and β-complexes (Figs. 6 and 7) are further illustrations of the differences in behavior of these two compounds. The small wave at −0.25 v. in the alpha polarogram is characteristic and is at about the half-wave potential to be expected from the α-silicomolybdous to α-hyposilicomolybdous reduction. The first reduction of the two complexes to the $+\ 4e^-$ blues is in both cases at too negative a potential to be recorded and shows only as a slope due to anodic dissolution. With both acids highly irreversible waves occur (associated with considerable over-voltage) which may be assumed from their magnitude to be the result of a general decomposition of the whole anion down to silica and Mo^{V} or Mo^{III}. However, the difference in structure between the two anions shows itself by the fact that these waves are of different shapes, the β-anion decomposition occurring, as would be expected, at a slightly more negative potential than that of the α-anion decomposition.

The exact relation between the two types of silicomolybdate complex remains to be discussed.

The relatively simple behavior of silicomolybdic acid in degradation with alkali, etc., probably explains why the properties of this compound in solution have been so little investigated. By contrast, other heteropoly acids in solution have been studied extensively, in the main by Souchay and coworkers.[2] The heteropoly tungstates have all been shown to exist as both "12" and "11" acids, the latter being formed from tungstate and the parent acid at a comparatively high *p*H, or directly from the 12 tungstate by the addition of alkali. The conversion of the 12 to 11 acids is reversible, under certain conditions, but the general behavior of these compounds varies according to the nature of the parent acid.

The molybdenum heteropoly acids have been similarly investigated but rather less thoroughly. The free arseno-12 acid does not exist in solution at room temperature and the phospho compound is so unstable that on titrating it with alkali no inflection is observed, only a smooth curve corresponding to the complete decomposition of the anion. The germano-12 acid is more stable, giving on titration an inflection due to the neutralization of a strong quadribasic acid. On the addition of more alkali, however, the 12-germanomolybdate anion is not converted to germanic acid and molybdate but into an 11-germanomolybdate, this conversion being reversible between *p*H 3.5 and 4.5. (Solutions of 11-germanomolybdic acid are yellow but are paler in color than solutions of the 12 acid.) Finally 11-germanomolybdate degrades into the simple ions of the constituent acids.

Throughout the known series of heteropoly tungstates and molybdates there is thus a tendency for molecules of the parent and isopoly acid to combine together in several different ratios, some of the compounds produced being directly interconvertible. Silicomolybdic acid is a marked exception in being comparatively stable but degrading directly to silicate and molybdate without any intermediate 11 acid formation, etc. There is, nevertheless, a superficial resemblance between the 12 and 11 heteropoly acids on the one hand and β- and α-silicomolybdate on the other hand.

There can be no doubt, however, that α-silicomolybdic acid is a 12 and not an 11 acid and the relationship between the α- and β-forms of the silicomolybdate complex is not directly analogous to any known relationship within the heteropoly acids as a group.

There remains the possibility that the beta complex contains silicon and molybdenum combined together in an atomic ratio greater than 1:12; the experimental accuracy of the work described here does not rule out the possibility of the ratio being between 1:12 and about 1:12.5. It is more likely, however, that the β-acid is simply an unstable isomer (probably a polymer) of the more stable (alpha) 12 acid. Such a relationship, moreover, may not be unique and may result when other "terminal" heteropoly molybdic acids are freshly prepared from acidified molybdate. In this connection it is interesting to note that Krumholtz[1] found that the extinction of a freshly prepared solution of 12-germanomolybdic acid reached a maximum shortly after preparation and then rapidly decreased to a constant limiting value.

Acknowledgments.—The author wishes to acknowledge the helpful advice and criticism given by many of his colleagues. The paper is published by permission of the Chief Scientist, British Ministry of Supply, and forms a part of a Thesis submitted for the degree of Doctor of Philosophy in the University of London.

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RECEIVED JUNE 15, 1951

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(2) See, for example, P. Souchay, *Bull. soc. chim. France*, **9**, 289 (1942); *Ann. chim.*, **19**, 102 (1944); *ibid.*, **20**, 73, 96 (1945); *ibid.*, **2**, 203 (1947). Also: A. Tchakirian and P. Souchay, *Ann. chim.*, **1**, 232, 249 (1946); S. Dubois and P. Souchay, *ibid.*, **3**, 105 (1948).