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FORMATION AND CONVERSION OF AN EXTRAORDINARY SPECIES OF MOLYBDOPHOSPHATE IN AQUEOUS ACETONITRILE SOLUTIONS

Toshitaka HORI* and Taitiro FUJINAGA†

Department of Chemistry, College of Liberal Arts and
Sciences, Kyoto University, Sakyo-ku, Kyoto 606
†Department of Chemistry, Kobe Gakuin University,
Tarumi-ku, Kobe 673

The existence of two species of molybdophosphate has been recognized in aqueous acetonitrile solutions. The one, which was called here as "extraordinary" molybdophosphate, forms quite rapidly and exhibits a bright yellow colour, but is unstable and undergoes a spontaneous conversion to the other. The latter complex would be of dodecamolybdophosphate in Keggin's structure.

Orthophosphate ion reacts readily with acidified molybdate reagent and produces a yellow compound of molybdophosphate. The rapid formation of the complex has long been utilized for colourimetric determinations of phosphate ion. In these determinations, molybdophosphate is generally formed in aqueous solution at the first step of the procedures and then, if necessary, successively extracted into certain organic solvents or reduced chemically to the corresponding blue compound in order to attain higher absorbances.

In some modified methods for phosphate determination, however, molybdophosphate is formed in aqueous medium containing certain water-miscible organic solvents like as acetone. This is grounded on the finding by Bernhart and Wreath1) that the presence of acetone as an auxiliary solvent intensifies the yellow colour of molybdophosphate so strongly as that achieved through its organic extraction into butanol. For such solvent effect, Chalmers and Sinclair2) gave an explanation that solvation of acetone to molybdophosphate occurs so strongly that the formation equilibrium of the complex, which is partly dissociated into phosphate and molybdate in aqueous solution, is shifted to the completion.

Besides acetone, similar solvent effect was actually observed with ethanol,3) dioxane,4) and tetrahydrofuran and others,5) and it has been appreciated quite favourable for the phosphate determinations because molybdophosphate could be brought to its quantitative formation by such solvent action but not by the addition of a large excess of reagent molybdate which produces various isopolymolybdates and possibly interferes with the absorbance measurements of the objective complex. In practice, many modified procedures for phosphate determinations using such solvent effect have been reported.

Bernhart and Wreath,1) for example, determined phosphates by making use of acetone ranging from 25 to 95 %V/V at 0.04 M (M = mol dm^{-3}) Mo(VI) in 1 M H_2SO_4. Halåsz et al.[6)] proposed two acetone-media; one is of 40 % acetone at 0.04 M Mo(VI) in 2 M $HClO_4$ suitable for differentiative determination of phosphate in mixtures with arsenate, and the other is 20 % acetone at 0.04 M Mo(VI) in 0.16 M $HClO_4$ for phosphate in mixtures with silicate. Further, Halåsz and Pungor[7)] notified that the presence of acetone more than 50 % gave a yellow colour on molybdate solution without suc hetero-ions. Chalmers and Sinclair[8)] searched for the optimum condition so precisely as that at acetone concentrations below 52 % the yellow colour of molybdophosphate once developed faded gradually, whereas above 52 % it continued to increase quite slowly for a long period, and accordingly, the use of acetone at 52 % at 0.025 M Mo(VI) in 0.22 M HCl being proposed as the best for the phosphate determination. In addition, they mentioned that the presence of extremely much amount of acetone prohibited the complex formation. Recently, Heinonen and Lahti[9)] demonstrated use of 40 % acetone at 0.018 M Mo(VI) in 0.6 M H_2SO_4 where the yellow colour of molybdophosphate faded at a rate of 2 % per hour. The authors suggested to use tetrahydrofuran[5)] and ethanol[10)] as auxiliary solvents at relatively low concentrations around 20 %, and no appreciable decrease of the yellow colour was observed.

Although the solvent effect is capable of high sensitive determinations of phosphate with relatively simple procedures, suitable conditions hitherto proposed for th stable and quantitative colour development are confused especially regarding the concentrations of the auxiliary solvents, and some of these proposals are even contradictory to each other as briefly reviewed above. This is mainly because the formation o certain extraordinary species of molybdophosphate and its conversion have been overlooked in such aqueous-organic media.

In this letter, the authors substantiate the formation of two different species of molybdophosphate in aqueous acetonitrile solutions by means of spectrophotometry and flow-coulometry. Concerning with the solvent effect on molybdophosphate, acetonitrile was not essentially different from the other auxiliary solvents like as acetone, dioxane, and ethanol, and therefore the results obtained with acetonitrile woul well represent those with the other solvents. Acetonitrile was employed here only because it allowed molybdophosphate to be electrolyzed more reversibly on account to its inherent potentiality as solvent.

Each 50 ml (ml = 10^{-3} dm^3) of mixed molybdate reagent composed of 0.05 M Mo(VI), 1.2 M HCl, and varing amounts of acetonitrile ranging from zero to 70 % was prepared and equilibriated at 25 ± 0.2 °C. A 4 ml portion of each reagent was transfered into a quartz cuvette with a pathlength of 1 cm and reacted with a 40 µl of 0.1 M phosphat standard solution by mixing it quickly and thoroughly. At the mixing, the time was set to zero and the absorbance changes at 420 nm were auto-

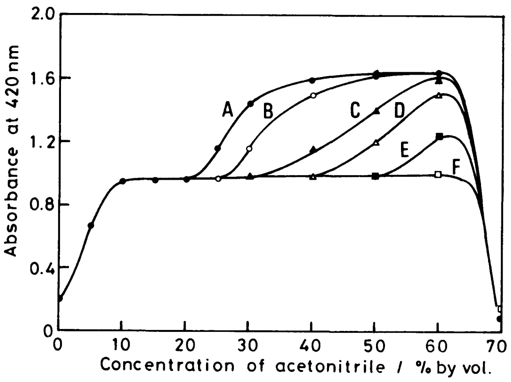

FIG. 1, FORMATION PROFILE OF MOLYBDOPHOSPHATE AS FUNCTIONS OF ACETONITRILE CONCENTRATION AND STANDING TIME (A) 2 MIN, (B) 20 MIN, (C) 2 HOUR, (D) 5 HOUR, (E) 14 HOUR, AND (F) 38 HOUR AFTER PREPARING SOLUTIONS CONSISTING OF 1X10^{-3} M PHOSPHATE, 0.05 M MO(VI), 1.2 M HCL, AND VARING AMOUNTS OF ACETONITRILE.

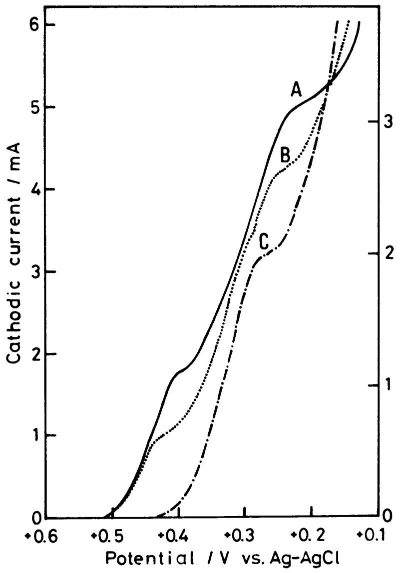

FIG. 2, COULOPOTENTIOGRAMS OF MOLYBDOPHOSPHATE FORMING IN A SOLUTION CONSISTING OF 2X10^{-4} M PHOSPHATE, 0.05 M MO(VI), 1.2 M HCL, AND 50 % ACETONITRILE AT (A) 2-10 MIN, (B) 4 HOUR, AND (C) 24 HOUR. SCAN RATE: 50 MV/MIN, FLOW RATE OF THE SAMPLE SOLN.: 5.0 ML/MIN.

matically recorded against the time at the thermostated temperature. For particularly slow reactions, the absorbances were read off manually at a 12-hour interval.

By using the absorbance vs. time curves thus provided at various acetonitrile concentrations, formation of molybdophosphate was profiled with respect to both acetonitrile concentration and time as shown in Fig. 1. Curve *A* in the Figure represents the complex formation at an early stage around t = 2 min, two discrete levels of absorbances being appeared: one was occurred in solutions containing 10-20 % acetonitrile and exhibited a yellow colour in an ordinary intensity and the other was in 40-60 % and an extraordinarily intensified yellow. The appearance of the extraordinary yellow should rather be attributed to the formation of certain extraordinary species of molybdophosphate at such an early stage, but not to somewhat bathochromism arising from the strongly solvated species of molybdophosphate. Because, the yellow shows a tendency to fade gradually with a specific rate depending on the acetonitrile concentration, suggesting a conversion reaction to other species of molybdophosphate. Here, it was quite noteworthy to observe that the extraordinary yellow actually *faded*, but *never faded away*. This fact can be seen clearly in absorbance changes depicted by curves through *B* (t = 20 min), *C* (t = 2 hour), *D* (t = 5 hour), and *E* (t = 14 hour) in Fig. 1. As indicated by curve *F* (t = 38 hour), at the equilibrium state a constant absorbance level is achieved over a wide concentration range of acetonitrile of 10 % through 60 %. It is needless to say that the final absorbance level is mostly the same as that attained directly in 10-20 % acetonitrile solutions. Accordingly, it can be concluded that the extraordinary complex is only formed kinetically and stabilized in more concentrated acetonitrile, but is unstable thermodynamically and converts to the more stable complex. The latter complex would be regarded as dodecamolybdophosphate in Keggin's structure,[11)] i.e., so-called α-molybdophosphate, but was here conventionally called as "ordinary" molybdophosphate.

The extraordinary complex can also be distinguished from the ordinary one according to the difference in their electrochemical behaviours. The extraordinary

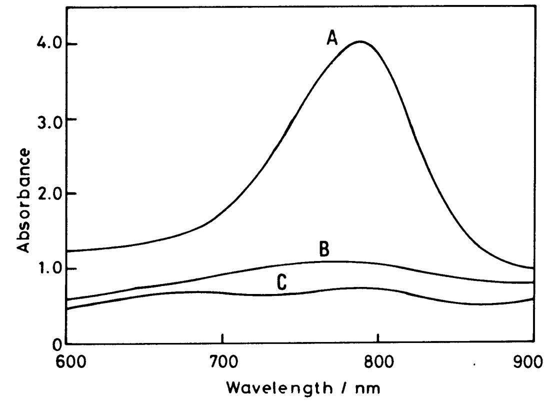

FIG. 3, TYPICAL ABSORPTION SPECTRA OF REDUCED FORMS OF (A) EXTRAORDINARY COMPLEX AT +0.38 V, (B) ORDINARY COMPLEX AT +0.27 V, AND (C) EXTRAORDINARY COMPLEX AT +0.23 V.

complex was formed similarly as before at 25 °C in solution consisting of 2 X 10^{-4} M phosphate, 0.05 M Mo(VI), 1.2 M HCl, and 50 % acetonitrile and the solution was electrolyzed immediately by means of a flow-through column electrode packed with glassy carbon fibre,12) resulting in a coulopotentiogram,13) i.e., Q - E curve in the flow-coulometry. Curve A in Fig. 2 shows a coulopotentiogram thus measured at the duration of 2-10 min after the preparation of the solution and, hence, it should be of the extraordinary complex, two well-defined cathodic waves appearing at potentials around +0.38 V and +0.23 V vs. Ag-AgCl reference electrode in saturated KCl solution. The plateau currents at the respective potential ranges allowed to calculate the number of electrons involved as n = 1 and n = 3, respectively, though these are of approximate values and should be ascertained further by some other methods. Whereas, the ordinary complex, which was formed through the conversion from the extraordinary complex in the same solution as used above, gives a well-defined cathodic wave aroung +0.27 V as shown by curve C. The number of electrons involved in the reduction step can be calculated as approximately n = 2. At a transient stage during the conversion, the molybdophosphate solution gives apparently a complicated coulopotentiogram as represented by curve B. However, now it is evident that the coulopotentiogram came from a mixture of both the molybdophosphate complexes existing together after such standing time as t = 4 hour.

Fig. 3 represents absorption spectra of blue products from the electrolysis of molybdophosphate; curve A is the spectrum of the blue form of the extraordinary complex reduced at a constant potential of +0.23 V with n = 3, having an absorption maximum at 788 nm; curve B, the blue form of the ordinary complex reduced at +0.27 V with n = 2 and an absorption maximum around 770 nm; curve C, the blue of the extraordinary complex reduced at +0.38 V, and absorption maxima of around 680 nm and around 790 nm.

The conversion reaction ascertained here for the extraordinary complex is quite irreversible and never reversed by the addition of auxiliary solvents when the conversion is once completed. Therefore, it could also be predicted that dodecamolybdophosphate solidified as the Keggin's structure would not produce such extraordinary complex even when dissolved into aqueous-organic solvents like as a 50 % aqueous dioxane.14) This fact is quite paralell to that observed on the relation between α- and β-dodecamolybdosilicate.15) Detailed results and discussion on this matter will be given in the successive reports.

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