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The stability of 12-molybdosilicic, 12-tungstosilicic, 12-molybdophosphoric and 12-tungstophosphoric acids in aqueous solution at various pH

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The stabilities of the solid superacids $H_3Mo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ in aqueous solution have been measured at various values of pH by use of ion chromatographic analyses. The aforementioned acids are completely decomposed at values of pH, 4.0, 5.2, 7.0 and 11.0, respectively. The stabilities in aqueous solution with respect to pH follow the order $H_4SiW_{12}O_{40} > H_3PW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_3PMo_{12}O_{40}$.

Keywords: metal–oxygen cluster compounds; heteropoly acids; stability; pH; aqueous solutions

1. Introduction

Interest in solid superacids as catalysts has accelerated markedly in recent years, in part resulting from environmental considerations in those processes currently employing liquid acids, but also as a consequence of the perceived potential for solid acids in a variety of processes, in particular those related to the petroleum industry [1].

Metal–oxygen cluster compounds (MOCC) (also known as heteropoly oxometalates) exist in a variety of stoichiometries and structures [2]. Those with Keggin structure have received considerable attention as catalysts in recent years [3]. These are ionic solids with large, high molecular weight anions (fig. 1) containing a central atom, in the present work phosphorus or silicon, surrounded by four oxygen atoms arranged tetrahedrally. Twelve octahedra with oxygen atoms at their vertices and a peripheral metal atom at their approximate centres envelope the central tetrahedron and share oxygen atoms with each other and the tetrahedron.

A variety of cations may be associated with the Keggin anions. With protons

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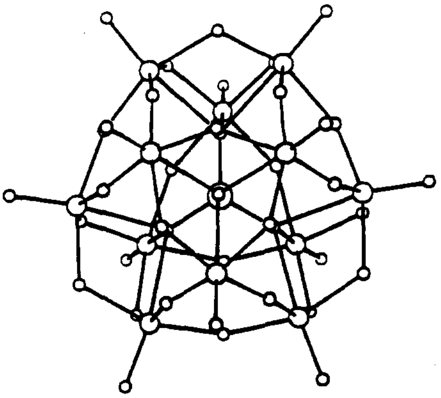

Fig. 1. Anion of 12-tungstophosphoric acid (bigger circles: central and peripheral atoms; smaller circles; oxygen atoms).

solid acids are formed and recent microcalorimetric studies on the adsorption of ammonia have provided evidence for the classification of these solids as superacids [4–7]. Not surprisingly, considering the large, rather complex, structure of the anions, their thermal stability, at least within the acidic forms, is less than desirable. Salts of these acids with monovalent cations prepared by precipitation from aqueous solution have been shown to be microporous as contrasted with the low surface area (<10 m^2 g^{-1}) parent acids [8–11]. Furthermore, the thermal stabilities as well as the catalytic properties in certain reactions of these salts have been shown to be superior to those of the parent acids [12–14].

The stability of the anions at various pH has been studied by a number of workers [2,15–21]. Some years ago Kepert and Kyle [15] investigated the decomposition of 12-tungstosilicate and noted that the reaction proceeds in three distinct stages with intermediates $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$. In the same year these authors also examined the Keggin anions containing phosphorus or boron as the central atoms and tungsten in the peripheral metal positions [16]. Five years later a report appeared on the stopped-flow kinetics of the formation and decomposition of 12-molybdophosphate [17]. The hydrolysis of 9-tungstophosphate $[PW_{12}O_{34}]^{9-}$, one of the intermediates in the decomposition of $[PW_{12}O_{40}]^{3-}$, has been studied in detail by Kyle [18]. Molybdophosphate complexes in aqueous solution have been identified by ^{31}P NMR spectroscopy [19] and recently the rate of exchange of structural units between anions containing tungsten and molybdenum has been measured with the same techniques [20]. Also recently, ^{31}P NMR spectroscopy has been applied to the study of species present in aqueous solutions of vanadate–phosphate, chromate–phosphate, molybdate–phosphate and tungstate–phosphate at values of pH from 0 to 12 [21].

Since the microporous salts are prepared by addition of aqueous solutions of an appropriate cation-carrying compound which are usually of pH greater than 7 to aqueous solutions of the parent acid, the stabilities of the acids in aqueous solutions of various pH is of considerable importance. In addition, an ion chromatographic method for the analysis of the MOCC which is based on the decomposition of the anions and analysis of the constituent ions has recently been developed in the laboratory for which stability data is a prerequisite for the generation of accurate elemental compositions [22]. Lastly, but not leastly, use of the aforementioned solid acids as homogeneous catalysts in aqueous solution necessitates the availability of data on their stabilities at a variety of values of pH.

2. Experimental

The solid acids 12-molybdophosphoric ($H_3PMo_{12}O_{40}$ abbreviated as HPMo), 12-tungstophosphoric ($H_3PW_{12}O_{40}$, abbreviated as HPW) and 12-tungstosilicic ($H_4SiW_{12}O_{40}$, abbreviated as HSiW) were AnalaR grade purchased from BDH, while 12-molybdosilicic ($H_4SiMo_{12}O_{40}$, abbreviated as HSiMo) was obtained from Pfaltz and Bauer. The solids were dried at 110°C to constant weight. Aqueous acidic solutions were prepared with distilled deionized water.

Lithium hydroxide was purchased from BDH. The concentrations of LiOH, prepared from distilled deionized water, were determined by titration with HCl solutions of known concentration.

Sodium molybdate, tungstate and silicate were obtained from BDH, Aldrich and Johnson Matthey, respectively.

3. Procedure

The analyses were performed with a Dionex 4500i ion chromatograph. The eluents were 10 mmol/ℓ NaOH and 10 mmol/ℓ Na_2CO_3 mixed at a 4 : 6 ratio by volume. The anions were separated with a Dionex AS5 column after which the solution passed through an anion micromembrane suppressor column with a 30 mM H_2SO_4 regenerant. Detection employed conductivity measurements. Data were collected for 10 min and converted into ion concentrations with a Spectra Physics Chrom-Jet integrator. Retention times for the constituent anions under the operating conditions in the present work were 1.5, 3.1, 3.8 and 6.2 min for the silicate, tungstate, molybdate and phosphate ions, respectively.

The ion chromatograph was calibrated for each of the constituent anions resulting from decomposition of each of the acids. Thus, standard solutions were prepared from each of sodium molybdate, sodium phosphate, sodium silicate and sodium tungstate. The solutions used for calibration purposes were obtained by careful dilution of the standard solution. Tests of the calibrations were made with aqueous solutions of known concentrations of pairs of the anions. For the stability measurements, a measured quantity of LiOH aqueous solution of known concentration was added to a measured quantity of an aqueous solution of the acid of known concentration at room temperature. This was then diluted to 100.0 ml with

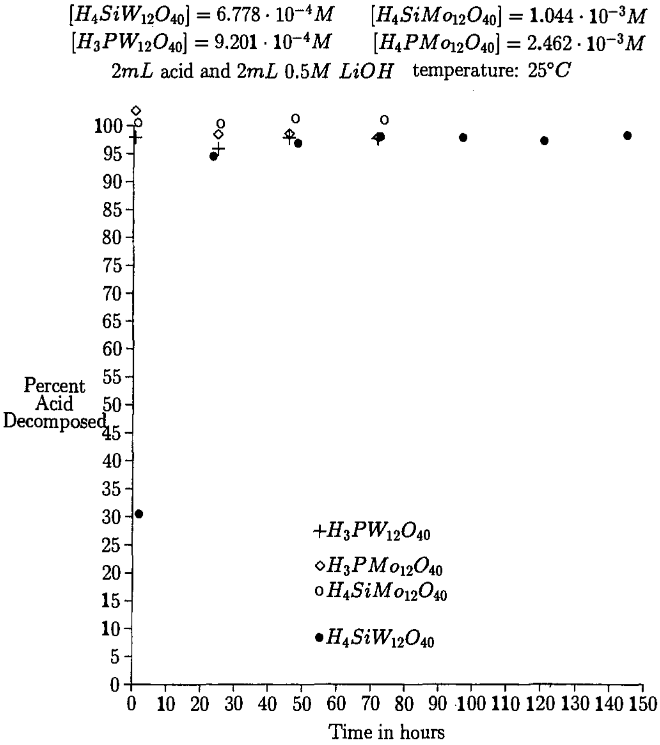

Fig. 2. Anion decomposition as a function of time.

distilled water. The solution was isolated from the atmosphere, periodically shaken and, after a period of time from 24 to 168 h, a 6 ml aliquot was analyzed by ion chromatography. The pH of the remaining solution was measured with a Fisher Accumet pH meter which was calibrated before each measurement with a solution of pH 7.0 and tested with a solution of pH 4.4.

4. Results and discussion

Since the effect of pH on the decomposition of the four acids required data obtained either at complete decomposition or at equilibrium with respect to the decomposition process, preliminary experiments were carried out to provide information on the length of time required to reach equilibrium. To 2.00 ml of aqueous solutions of each of the acids HSiW, HSiMo, HPW and HPMo of concentrations 0.678, 1.044, 0.920 and 2.462 mM, respectively, 2 ml of 0.5 M LiOH aqueous solution were added. The solutions were then diluted to 100.0 ml with distilled deionized water. The concentrations of the constituent anions were measured immediately after preparation and thereafter at approximately 24 h intervals to provide estimates of the decomposition rates of each of the acids. For all of the acids except HSiW equilibrium with respect to the decomposition process was attained within the length of time required to prepare the solutions (fig. 2). However, with HSiW, only approximately 30% of the acid had decomposed during the preparative time for the solutions and at least 50 h were required to reach equilibrium. Consequently, with HSiW, the results which follow were obtained after a minimum of 50 h following preparation of the solutions.

The results for the pH dependence of the decomposition of the four acids are shown in figs. 3–5. With HSiMo the decomposition is already 50% complete at a pH as low as 4.1 (fig. 3). As the pH is increased, the extent of the decomposition of the acid increases rapidly. At a pH of 5.2, the acid is essentially completely decomposed and further increase in the pH has no effect on the measured percent decomposition. To determine the influence, if any, of the concentration of the anions employed in the experiments various volumes between 1 and 5 ml of the original aqueous acid solutions were used. It is clear that the anion concentration has little or no effect on the extent of the decomposition at a given pH.

With HSiW, where the central atom in the anion remains the same as in HSiMo but the peripheral metal atoms are now tungsten rather than molybdenum, the dependence of decomposition on pH is markedly different (fig. 4). At values of pH in the basic range, the extent of the decomposition is 10% or less. At a pH of 8.9

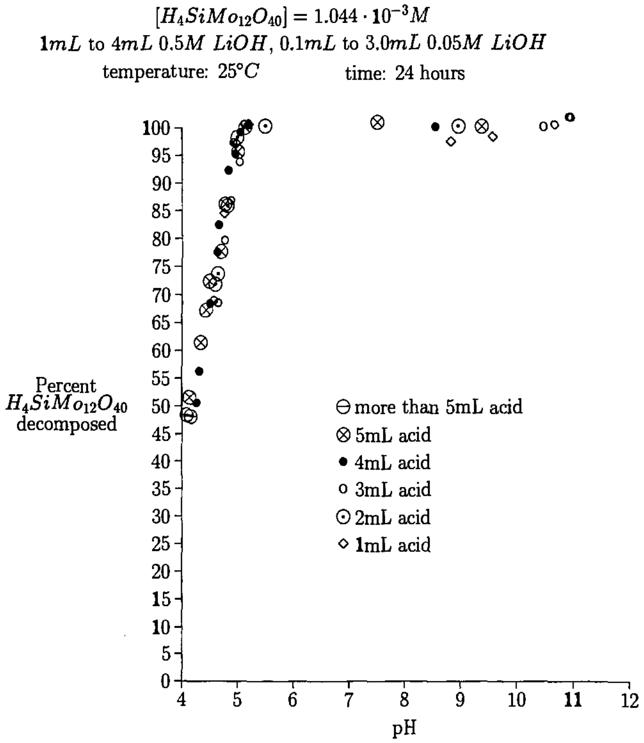

Fig. 3. Stability of $H_4SiMo_{12}O_{40}$ in aqueous solution as a function of pH.

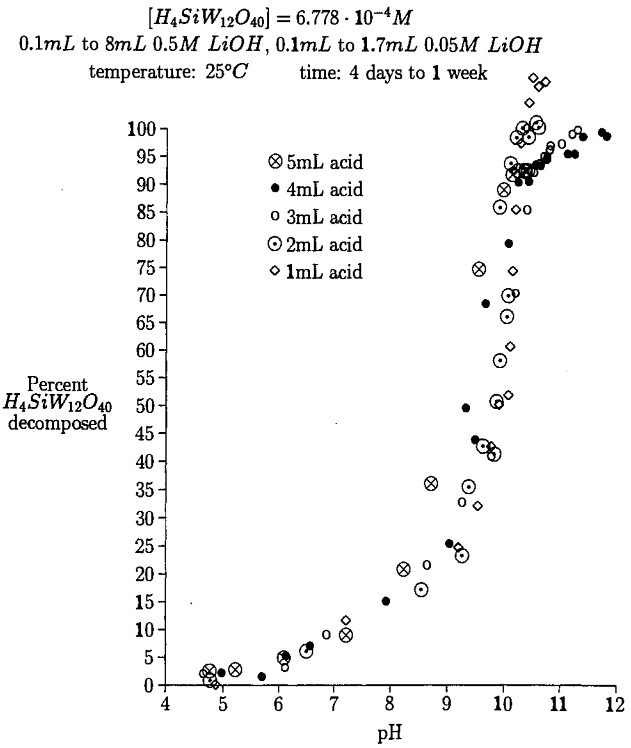

Fig. 4. Stability of $H_4SiW_{12}O_{40}$ in aqueous solution as a function of pH.

the decomposition amounts to only 25%. However, for further increase in pH the decomposition increases substantially and at pH values of 10.4 and 11.0, 95 and 100% decomposition, respectively, has occurred. Any further increase in the pH of the solution has no effect on the percent decomposition of the anion. As with the molybdenum–silicon acid the extent of the decomposition at a given pH is essentially independent of the anion concentration of the solution in which the decomposition is occurring.

It is clear that for the acids with Si at the centres of their anions, that containing tungsten is at any given value of pH up to approximately pH 10 considerably more stable than its molybdenum counterpart.

The results of similar experiments for HPMo and HPW are shown in fig. 5. As with the anions containing silicon, it was found that the latter anions were more stable in basic solution than the former. Comparison of the silicates with the phosphates showed that the former anions are more stable than the latter for a given peripheral metal atom, HPMo was already 100% decomposed at a pH less then 4.0 and further increase in pH had no effect on the percent decomposition. The tungstophosphoric acid was 10% decomposed at a pH of 5.0, but increased to 95% decomposition at a pH of 6.8. Further increases in pH had little or no effect on the decomposition.

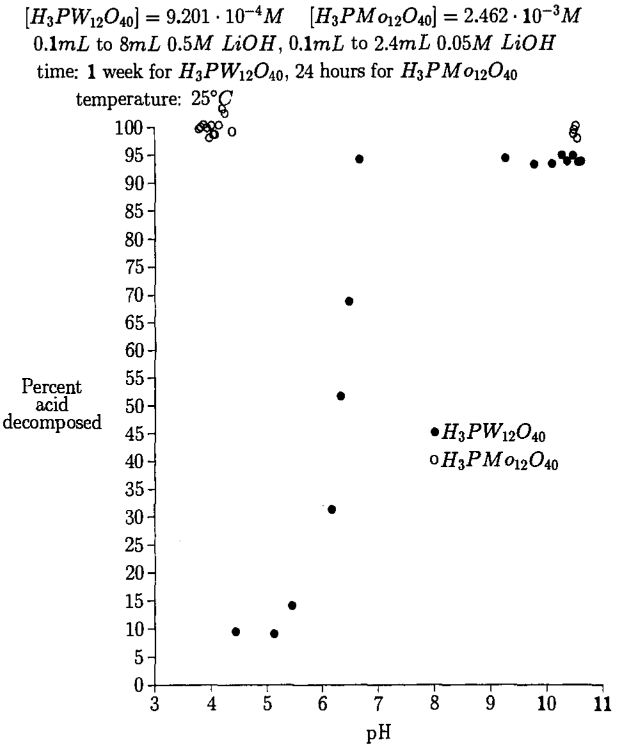

Fig. 5. Stabilities of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ in aqueous solutions as a function of pH.

It is important to emphasize that the method of analysis employed in the present work measures the quantities of complete decomposition products, SiO_4^{4-}, PO_4^{3-}, MoO_4^{3-} and WO_4^{2-}, of the heteropoly acids and consequently provides no evidence for multiple steps in the decomposition process nor of the existence of intermediates which may have formed in these steps, if they exist. For example, earlier work from this laboratory employing ^{31}P NMR has shown that the $PW_{11}O_{39}^{7-}$ anion exists over the pH range from 2.5 to 7.5 [21]. The present data indicate that substantial decomposition of $PW_{12}O_{40}^{3-}$ to the aforementioned constituent ions occurs only as the pH approaches 7, but are unable to show the presence of intermediates which exist, together with the ions resulting from decomposition, in the range of pH in which complete decomposition has occurred.

In conclusion, the stabilities with respect to pH of the four solid acids in aqueous solution follow the order HSiW > HPW > HSiMo > HPMo.

Acknowledgement

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