

有机磷、砷、碲合钼聚多酸盐的研究

VIII. 3-硝基-4-羟基苯砷合钼聚多酸盐的制备和

解聚法制备有机砷合钼聚多酸盐的尝试

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为研究有机基团对有机砷合钼聚多酸盐类型的影响, 试验了 3-硝基-4-羟基苯砷酸与钼酸钠在 pH 为 3~5 条件下的反应, 制得了两种新化合物: (1) $(\text{NH}_4)_6[(3-\text{NO}_2-4-\text{OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$ (2) $(\text{CN}_3\text{H}_6)_6[(3-\text{NO}_2-4-\text{OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$. 报道和讨论了它们的红外、可见与紫外光谱、热分解性质和电化学氧化还原性质。它们与钼同系物类型相同。化合物 (1) 可用酸化聚合法及解聚法制得, 经过实验比较证实了以七钼酸铵为原料的解聚法具有产物纯化方便、得率高的优点。

关键词: 有机砷 聚多钼酸盐 聚多钼酸盐 解聚法

STUDIES ON ORGANO-PHOSPHORUS, -ARSENIC AND -ANTIMONY POLYTUNGSTATES AND POLYMOLYBDATES

VII. PREPARATION AND PROPERTIES OF 3-NITRO -4-HYDROXYPHENYLARSENIC POLYMOLYBDATES AND DEGRADATION METHOD FOR PREPARING ORGANOARSENIC POLYMOLYBDATES

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In order to investigate the effect of organic groups on the types of organoarsenic polymolybdates, the reaction of 3-nitro-4-hydroxyphenylarsonic acid with sodium molybdate has been tested at pH=3-5. Two salts have been prepared and characterized: (1) $(\text{NH}_4)_6[(3-\text{NO}_2-4-\text{OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$ (2) $(\text{CN}_3\text{H}_6)_6[(3-\text{NO}_2-4-\text{OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$. The IR, UV spectra, thermal properties and electrochemical behaviors have been reported and discussed. They belong to the same type as that of their tungsten congener. Single-crystal X-ray diffraction studies show that (2) and its tungsten congener have not only the same space group, but also very close cell dimensions. Compound (1) has been prepared by two different method: acidification building up method and degradation method. It is verified that the degradation

method starting with ammonium heptamolybdate has advantage in the simplification of reaction product, thus leading to its higher yield.

Keywords: organo-arsenic polymolybdate polytungstate degradation method

Introduction

The organo-phosphorus and organo-arsenic polymolybdates have been synthesized by Pope M.T. since 1975 and 1976 respectively.^(1,2) They are compounds consisting of a ring of some linked MoO₆ octahedra with two organic handles above and below the molybdenum ring. It is stated by Kwak et al. that only one type of organo-arsenic polymolybdates [(RAs)₂Mo₆O₂₄]⁴⁻ is formed at pH = 3–5 condition no matter which one R is: alkyl group or aryl group⁽²⁾. They only reported the crystal structural data for a double salt of the methyl derivative [CH₃]₄N]₂Na₂[(CH₃As)₂Mo₆O₂₄] · 6H₂O⁽²⁾ and took it for granted that all alkyl- or aryl-arsenic polyimolybdates belong to the same type. Matsumoto reported, however, the crystal and molecular structure of a guanidinium salt of the phenyl derivative (CN₃H₆)₄[(C₆H₅As)₂Mo₆O₂₄H₂] · 4H₂O⁽³⁾.

When *n*-propylarsenic polymolybdates were prepared in our laboratory, we found a unique phenomenon that two types of crystals, containing different numbers of ring molybdenum atoms, are formed under same pH condition from same solution⁽⁴⁾. The six-molybdenum compound $(\text{CN}_3\text{H}_6)_4[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_6\text{O}_{24}]$ is consistent with Kwak's prediction, whereas the five-molybdenum compound $(\text{CN}_3\text{H}_6)_4[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_5\text{O}_{21}] \cdot 2\text{H}_2\text{O}$ is isostructural with organophosphorus polymolybdates. In the case of allyl arsonic acid, however, only five-molybdenum compound $(\text{CN}_3\text{H}_6)_4[(n\text{-C}_3\text{H}_5\text{As})_2\text{Mo}_5\text{O}_{21}] \cdot 2\text{H}_2\text{O}$ can be isolated⁽⁵⁾. When phenylarsenic polymolybdates were prepared in our laboratory, only $(\text{CN}_3\text{H}_6)_5[(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{25}\text{H}] \cdot \text{H}_2\text{O}$ can be isolated from the solution at pH = 3–5⁽⁶⁾. Single-crystal X-ray diffraction studies and elemental analyses show that this compound is different from that reported by Matsumoto, but is isostructural with its tungsten congener $(\text{CN}_3\text{H}_6)_5[(\text{C}_6\text{H}_5\text{As})_2\text{W}_6\text{O}_{25}\text{H}] \cdot 2\text{H}_2\text{O}$ reported by Wasfi et al.⁽⁷⁾. When mono-substituted phenylarsonic acid such as *o*-, *m*-, *p*-nitrophenylarsonic acid reacted with sodium molybdate, $[(\text{RAs})_2\text{Mo}_6\text{O}_{25}\text{H}]^{5-}$ type of complexes, not $[(\text{RAs})_2\text{Mo}_6\text{O}_{24}]^{4-}$ type, were formed⁽⁸⁾. When benzylarsonic acid, which is containing phenyl group not directly connected to the arsenic atom, reacted with sodium molybdate, the $[(\text{RAs})_2\text{Mo}_6\text{O}_{24}]^{4-}$ type of complexes, which is also consistent with Kwak's prediction, has been synthesized and characterized⁽⁹⁾.

In order to investigate the influence of organic groups on the types of organoarsenic polymolybdates, we tested the reactions of 3-nitro-4-hydroxyphenylarsonic acid with sodium molybdate at pH = 3-5. Here we wish to report another new type of arylarsenic polymolybdates: 3-nitro-4-hydroxyphenylarsenic polymolybdates.

Experimental

3-nitro-4-hydroxyphenylarsonic acid was purchased from E. Merck Corporation. Other reagents are domestic analytical reagents. IR measurement was made on a Nicolet FTIR-5DX instrument (KBr pellets). UV spectra were obtained on a Hitachi-557 instrument. Thermogravimetric curves were obtained on an LCT-2 analyzer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. Arsenic and molybdenum analyses were performed by ICP method on a Jarrell-Ash 2000 ICP instrument. The selected wavelengths are $\lambda = 202.3$ nm for Mo and $\lambda = 228.8$ nm for As. The cyclic voltammograms were performed on an F-78 pulse-polarograph (platinum electrode, area 2.5 mm^2 , reference electrode Ag / AgCl , supporting electrolyte $1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$, scan rate $50 \text{ mV} / \text{s}$.)

Preparation and properties of $(\text{NH}_4)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}](1)$ Ten mL of aqueous solution of 2.90 g (12 mmol) sodium molybdate dihydrate were mixed with 10 mL of hot aqueous solution of 1.05 g (4 mmol) 3-nitro-4-hydroxyphenylarsonic acid, then $6 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloride solution was added drop by drop until the pH value was adjusted from 6.3 to about 4.5. The color of solution was converted from orange-redish to orange. The mixture was refluxed for two hours. After it was cooled to room temperature, it was filtered to remove a small amount of insoluble redbrownish residue. An orange transparent solution was then obtained. Tests for cations show that sodium, potassium, cesium, tetramethylammonium, tetrabutylammonium, magnesium, calcium, strontium and even barium salts are very soluble in water, the ammonium and guanidinium salts can easily be separated from the solution. One mL of saturated ammonium acetate solution was added to the orange solution, neither precipitate nor crystal appeared. The solution was boiled and concentrated to about 8 mL and then was cooled to room temperature. Five or six hours later, orange-redish crystals grew gradually. The amount of crystal was no longer increased after two days. These crystals were filtered, washed with a small amount of cold water, and then sucked dry. 2.28 g of orange crystals (1) was obtained. The yield is 75.5%. $\text{C}_{12}\text{H}_{32}\text{N}_8\text{As}_2\text{Mo}_6\text{O}_{31}$ ($M = 1509.90$, calculated: C, 9.55%; H, 2.14%; N, 7.42%; As, 9.92%; Mo, 38.12%; found: C, 9.77%; H, 2.22%; N, 7.33%; As, 9.75%; Mo, 37.88%) $\lambda_{\text{max}}(\text{H}_2\text{O})$: 222, 336 nm. $\nu_{\text{max}}(\text{KBr})$: 3440(s, br.N-H), 3140(s, br.N-H), 1600(s, N-H), 1530-1500, 1395(vs, NH_4^+), 1350, 1325(Ar- NO_2), 1260-1240(s), 1153(s, C-N, Ar.), 1095(As-C), 935(sh.), 890(vs, Mo-O), 860, 830-815(s, As-O), 660(s, br., Mo-O), cm^{-1} . The thermogravimetric curve of (1) is shown in Figure 1. Below 240°C its weight remains unchanged. When it is heated from 240 to 300°C , it loses 15.0% of its weight (calcd. 14.6%). This is exothermic and corresponding to the decomposition of ammonium salt. When heated from 300 to 442°C , it loses its organo-arsenic groups (27.8% of its weight, calcd. 28.2%) and releases a great deal of heat. The final product is MoO_3 (57.2% of its weight, calcd. 57.2%). The cyclic voltammogram of $1.06 \text{ mmol} \cdot \text{dm}^{-3}$ solution of (1) shows there is a reduction shoulder at the potential -0.60 V . One obvious oxidation peak ($E_{\text{pa}} = -0.50 \text{ V}$, $I_{\text{pa}} = 18.0 \mu\text{A}$) and another oxidation shoulder at the potential -0.71 V can also be observed.

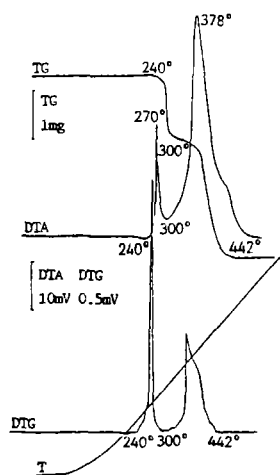


Fig. 1 Thermogravimetric curve of
 $(\text{NH}_4)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$

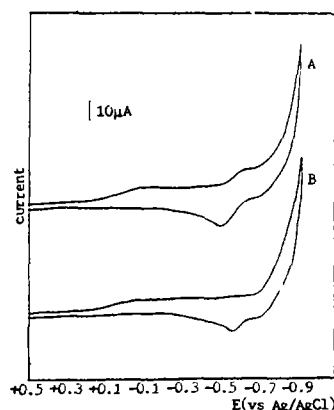


Fig. 2 Cyclic voltammograms of 0.96 and
 0.90 $\text{mmol} \cdot \text{dm}^{-3}$ solutions of
 compound A and B respectively in
 1 $\text{mol} \cdot \text{dm}^{-3}$ KNO_3 (scan
 initiated at 0.5 V versus Ag / AgCl in
 negative direction at 50 mV / s; platinum
 electrode, area 2.5mm^2)

A: $(\text{CN}_3\text{H}_6)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$

B: $(\text{CN}_3\text{H}_6)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{W}_6\text{O}_{25}]$

Preparation and properties of (1) by the "Degradation Method" 10 mL of aqueous solution of 2.40 g (1.71 mmol) ammonium heptamolybdate tetrahydrate were mixed with 10 mL of hot aqueous solution of 1.05 g (4 mmol) 3-nitro-4-hydroxyphenylarsonic acid. Neither acid nor alkali solution was added, the pH value was already about 5. The mixture was refluxed for one hour and concentrated to about 5 mL. Other operations are similar to those by "Acidification Building up Method". No crystals appeared after long time standing. Shortly afterwards 1 mL of saturated ammonium acetate solution was added to the orange solution, however, orange flocks accumulated more and more at the bottom of the vessel. Several hours later, these flocks converted to orange-redish crystals. 3.00 g of orange-redish crystals (1) was obtained. The yield is 99.3%. Because the elemental analyses and IR, UV spectra are the same as those prepared by "Acidification Building up Method", these two crystals obtained from two different methods are identical.

Preparation and properties of (2) The operations were similar to those for (1). 0.5 mL of 2 : 1 guanidinium hydrochloride solution was added to the above-mentioned hot orange solution. No precipitates appeared. The solution was boiled and concentrated to about 8 mL and was cooled to room temperature. Several hours later, orange-yellowish crystals appeared gradually. The amount of crystal was no longer increased after 24 hours. The crystals were filtered,

washed with cold water, and were recrystallized from 5 mL of hot water (pH = 4–5). 3.34 g of large orange–yellowish blocks (2) were obtained. The yield is 94.8%. $C_{18}H_{44}N_{20}As_2Mo_6O_{31}$ (2) (M = 1762.168 calculated: C, 12.27%; H, 2.52%; N, 15.89%; As, 8.50%; Mo, 32.67%; found: C, 12.49%; H, 2.61%; N, 15.27%; As, 8.76%; Mo, 33.02%) $\lambda_{max}(H_2O)$: 222, 336nm. $\nu_{max}(KBr)$: 3600–2400(vs,br.), 1660–1640(vs,C=N), 1530–1500, 1350(sh.), 1320(s,Ar–NO₂), 1260–1245(br.), 1150(C–N,Ar.), 1095(As–C), 880(vs,Mo–O_l), 860(sh.), 820(vs,As–O), 640(s,br.,Mo–O_b) cm^{-1} . The cyclic voltammogram of 0.96 mmol · dm⁻³ solution of (2) shows that there is a reduction shoulder at the potential -0.61 V. A strong oxidation peak ($E_{pa} = -0.495$ V, $I_{pa} = 12\mu A$) and another oxidation shoulder at the potential -0.68 V can also be observed.

Discussion

When two substituted groups 3–nitro, 4–hydroxy are introduced to the benzene ring, most of organoarsenic polymolybdates are very soluble, even the barium salt. Besides the guanidinium salt, the ammonium can also be easily isolated from the solution in high yield. Because the solubility of ammonium salt is relatively large, its recrystallization from water is somewhat difficult. It is surprising that the solubilities of some larger organo–ammonium salts (Me₄N⁺, Et₄N⁺) are much larger than that of ammonium salt, so they have not been isolated yet. This makes an exception to the general principle “the large anions can be precipitated by large cations”.

In our previous investigation we found that the degradation method using sodium metatungstate as a starting material has the advantages in the simplification of reaction product, thus leading to their higher yields⁽¹⁰⁾. Here we see these advantages again in the preparation of organoarsenic polymolybdates by the degradation method using ammonium heptamolybdate as a starting material. When the aqueous solutions of sodium molybdate are acidified by mineral acid solution, a lot of unnecessary anions have inevitably been added to the solution. It is more important that the fast formation of isopolymolybdate is superior to the formation of the organoarsenic polymolybdate. On the other hand, ammonium heptamolybdate is a widely–used commercialized reagents. As we see from the experimental, no acid solution is needed to adjust the pH value, and the desired organic derivative is rapidly formed. The yield of (1) is enhanced from 75.5% to 99.3%. It is verified that the degradation method has similar advantages in synthesizing the organoarsenic polymolybdate.

In the IR spectra of (1), the broad strong absorption peak at 3440, 3140 cm^{-1} have been assigned to the N–H stretching frequencies, and the sharp strong peaks at 1600 and 1395 cm^{-1} have been assigned to the N–H scissoring frequencies. The positions of other main absorption peaks are consistent with those of (2). It is verified that the anions of (1) and (2) have the same structure.

Single–crystal X–ray diffraction studies show that (2) and its tungsten congener have not only the same space group, but also very close cell dimensions (see Table 1). The differences be-

tween a , b , c are less than 0.1 \AA , and the difference between β is less than 0.5° . This is a strong evidence for the conclusion that these two guanidinium salts have not only the same numbers of guanidinium cations, but very close Mo—O or W—O bond lengths.

The cyclic voltammograms of (1) and (2) have similar shape. It is therefore concluded that the large anions are responsible for these electrochemical behavior. Figure 2 shows the cyclic voltammograms of $0.96 \text{ mmol} \cdot \text{dm}^{-3}$ and $0.90 \text{ mmol} \cdot \text{dm}^{-3}$ solutions of $(\text{CN}_3\text{H}_6)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{Mo}_6\text{O}_{25}]$ and $(\text{CN}_3\text{H}_6)_6[(3\text{-NO}_2\text{-4-OHC}_6\text{H}_3\text{As})_2\text{W}_6\text{O}_{25}]$ in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ respectively. The shoulders at -0.05 V are contributed by the supporting electrolyte, so we can take no account of them. There is a reduction shoulder at the potential -0.61 V for the molybdenum derivative, whereas no obvious reduction shoulder can be observed for the tungsten derivative. Furthermore, the anodic peak potential for the molybdenum derivative is more positive than that for the tungsten derivative. The difference between them is 0.05 V . From these facts it seems that the anion of the molybdenum derivative is more difficult to be oxidized than the anion of the tungsten derivative.

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