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Stability of phospho-molybdc Wells–Dawson-type ion $P_2Mo_{18}O_{62}^{6-}$ in organic media

Graciela M. Valle, Laura E. Briand*

Centro de Investigación y Desarrollo en Ciencias Aplicadas, Dr. Jorge J. Ronco-CINDECA-Universidad Nacional de La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Calle 47, Number 257, C.C. Number 59, (B1900AJK) La Plata, Buenos Aires, Argentina

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Abstract

The stability of the ammonium phospho-molybdc Wells–Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ in various organic media was investigated at room temperature and 50 °C through infrared spectroscopy. The heteropoly-anion $P_2Mo_{18}O_{62}^{6-}$ is soluble and stable in methanol, ethanol, 2-propanol, ethyl ether, acetone and acetonitrile. The alcohols dissociatively chemisorb on the anion forming alkoxy (methoxy, ethoxy and isopropoxy) species. The interaction with acetone and acetonitrile is nondissociative.

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1. Introduction

A previous work was devoted to study the stability in aqueous medium of the ammonium phospho-molybdc Wells–Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ in order to obtain a stable solution of the heteropoly-anion $P_2Mo_{18}O_{62}^{6-}$. The study established that the anion is not stable in aqueous media, regardless of the concentration or pH conditions [1]. The phospho-molybdc Wells–Dawson-type anion decomposes to the Keggin-type anion $H_xPMo_{12}O_{40}^{(3-x)-}$, pentamolybdodiphosphate $H_xP_2Mo_5O_{23}^{(6-x)-}$ and heptamolybdate $Mo_7O_{24}^{6-}$ or molybdate MoO_4^{2-} species depending on the acidity. Moreover, the Keggin-type

anion decomposes to the lacunar anion $H_xPMo_{11}O_{39}^{(7-x)-}$ and molybdate species or precipitates as the ammonium phospho-molybdc salt $(NH_4)_3PMo_{12}O_{40} \cdot 4H_2O$ at high acidity values ($pH \leq 2$).

An indirect confirmation of the above-mentioned results are the studies published by Combs-Walker et al. [2]. The authors demonstrated that aqueous solutions of $H_3PMo_{12}O_{40}$ degrade on the lacunary Keggin heteropoly-anion $P_2Mo_{11}O_{39}^{7-}$, $P_2Mo_5O_{23}^{6-}$ and the Wells–Dawson heteropoly-anion $P_2Mo_{18}O_{62}^{6-}$.

Many publications show spectroscopic and voltametric analyses of the phospho-molybdc Wells–Dawson-type anion $P_2Mo_{18}O_{62}^{6-}$ in acetonitrile [3–6]. Studies of Pope [3] demonstrated that α/β - $P_2W_{18}O_{62}^{6-}$, $As_2W_{18}O_{62}^{6-}$, $P_2Mo_{18}O_{62}^{6-}$ and $As_2Mo_{18}O_{62}^{6-}$ are able to receive up to six electrons per anion both in neutral or acidic media ($pH < 3$). Reduced Wells–

* Corresponding author.

E-mail address: briand@quimica.unlp.edu.ar (L.E. Briand).

Dawson species such as $P_2W_{18}O_{62}^{n-}$, $As_2W_{18}O_{62}^{n-}$ ($n=7-9$) and the heteropoly blue (two-electron reduced anion) $[H_2P_2Mo_2^5+Mo_{16}O_{62}]^{6-}$ are more stable in basic solutions than nonreduced species. In fact, reduced species are stable up to $pH=13$ and fully oxidized species decompose at $pH=6$.

The photosensitivity upon exposure to visible light and UV radiation in organic liquid media is another important property of Wells–Dawson compounds. Under these conditions, the heteropolyanion is reduced to heteropoly-blue species and the organic molecules are oxidized. Papaconstantinou [7] and Papaconstantinou et al. [8] showed that $P_2Mo_{18}O_{62}^{6-}$ selectively oxidizes primary alcohols to aldehydes and secondary alcohols to ketones when exposed to a 254-nm radiation. Similarly to the electrochemical experiments, the photoreduction generates two, four and six electron blues and the HPC is suitable to be re-oxidized with molecular oxygen.

More recently, Hu and Burns [9] showed that $PMo_{12}O_{40}^{3-}$ and $P_2Mo_{18}O_{62}^{6-}$, among other Keggin and Wells–Dawson heteropolyanions, are active in the homogeneous catalytic oxidation of isobutyraldehyde to isobutyric acid with H_2O_2 in acetonitrile at 50 °C. The phospho-molybdc Dawson anion suffered a minor degradation to peroxy-species under reaction conditions.

The thermal stability of the phospho-molybdc Wells–Dawson anion was investigated by Hu et al. [10]. The authors demonstrated that phospho-molybdc salts $M_6P_2Mo_{18}O_{62}$ ($M=K^+$, Rb^+ , Cs^+ , NH_4^+ and $(CH_3)_4N^+$) decomposes at 260 °C regardless of the nature of the counteranion.

The investigations concerning the structural stability of the phospho-molybdc Wells–Dawson anion are focused on the effect of the temperature in the solid state and the stability of ionic species formed upon reduction in acetonitrile. The literature does not address the effect of other organic solvents rather than acetonitrile, the time and temperature on the stability of the heteropoly-anion, and there are no spectroscopic studies on the interaction of organic substrates with the heteropolyanion (in solid or liquid media). This fundamental information is a key on the application of the heteropoly-anion in homogeneous or biphasic catalytic processes, the synthesis and characterization of $P_2Mo_{18}O_{62}^{6-}$ supported on metal oxides and the elucidation of reaction mechanisms in organic media.

The present work screens the stability of the phospho-molybdc Wells–Dawson anion in a series of polar and nonpolar organic solvents as a function of time and temperature through infrared spectroscopy.

2. Experimental

2.1. Synthesis of ammonium phospho-molybdc Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$

The Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ was synthesized according to the technique described by Wu [11]. Details of the method have been published before [1].

2.2. Spectroscopic analysis

2.2.1. Infrared analysis

Infrared analysis was performed with a FTIR Bruker IFS 66 equipment under ambient conditions. Solid samples were diluted with KBr and pressed in thin wafers. The solutions of the Dawson salt in organic solvents were analyzed by placing a drop of the liquid between KBr or CaF_2 crystals.

2.2.2. ^{31}P NMR analysis

Liquid NMR spectra were obtained with a Bruker AM500 spectrograph under ambient conditions. The

Table 1
Solubility of the ammonium phospho-molybdc Wells–Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ (20 mM) in organic solvents at room temperature

Solvent	Dielectric constant, ϵ^a (20 °C)	Soluble	Partially soluble	Nonsoluble
H_2O Water	78.5	•		
CH_3CN Acetonitrile	38.8 ^b		•	
CH_3OH Methanol	32.6	•		
C_2H_5OH Ethanol	24.3	•		
C_3H_6O Acetone	20.7		•	
C_3H_7OH 2-Propanol	18.3	•		
$C_4H_{10}O$ Ethyl ether	4.3			•
$CHCl_3$ Chloroform	4.8			•
Cl_4C Carbon tetrachloride	2.2			•
C_6H_{14} Hexane	1.9			•

^a Data from Ref. [12].

^b Data from Ref. [13].

equipment operates at a frequency of 202.459 MHz with 5–10 μs pulses. The analysis involved 8–800 pulse responses with a resolution of 0.25 Hz per point.

2.3. Stability experiments

The experiments were performed with solutions containing 20 mM of the $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ salt. The following high-purity solvents were used: methanol (Merck, 99.8%), ethanol (Merck, 99.8%), 2-propanol (Merck, 99.7%), acetone (Merck, 99.5%), chloroform (Merck, 99.4%), acetonitrile (J.T. Baker, HPLC grade 100.0%), *n*-hexane (J.T. Baker, 100.0%), ethyl ether (J.T. Baker, 99.0%) and carbon tetrachloride (U.V.E., 99.9%).

Two sets of experiments were performed on the solutions of Wells–Dawson anion in organic solvents: (1) infrared analysis immediately after the dissolution and as a function of time (up to 24 h) at room temperature and (2) spectroscopic analysis after maintaining the solutions at 50 °C for 2 h.

The remaining solution after all the analysis was allowed to dry and the solid residue was analyzed again to corroborate the identity of the species.

3. Results and discussion

Table 1 shows the solubility of 20 mM of the ammonium phospho-molybdic Wells–Dawson salt $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ in water and organic sol-

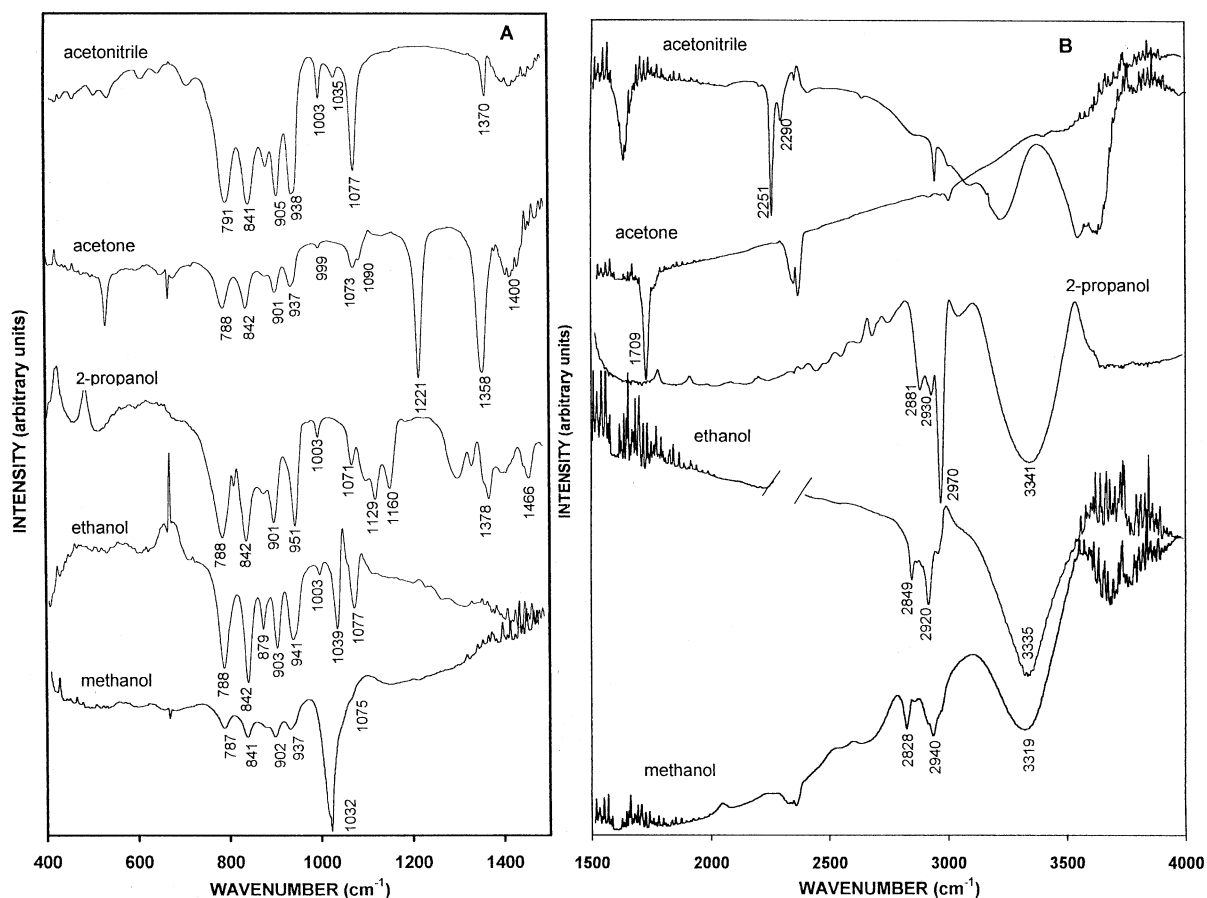


Fig. 1. Infrared spectra (transmittance mode) of solutions containing 20 mM of $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ in methanol, ethanol, 2-propanol, acetone and acetonitrile after 24 h (A) in the 400–1500 and (B) 1500–4000 cm^{-1} wavenumber ranges, respectively.

vents at room temperature. The series of solvents is organised in decreasing values of dielectric constant ϵ that is a measurement of the polarity of the substances. The salt is completely soluble in polar solvents (high dielectric constant) such as water, methanol, ethanol and 2-propanol, partially soluble in acetone and acetonitrile and non soluble in non polar solvents ($\epsilon \leq 4$) such as, ethyl ether, chloroform, CCl_4 and hexane.

Although the salt is highly soluble in aqueous medium ($1.3 \times 10^3 \text{ g l}^{-1}$), previous studies established that the Wells–Dawson anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ decomposes in aqueous medium to the Keggin-type anion $\text{H}_x\text{PMo}_{12}\text{O}_{40}^{(3-x)-}$, pentamolybdodiphosphate $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$, molybdate and phosphate species [1]. On line with that study, the speciation of the solutions of the Wells–Dawson salt in organic solvents was determined through infrared spectroscopy.

Fig. 1A and B show the infrared spectra of the $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ species after 24 h in the 400–1500 and 1500–4000 cm^{-1} wavenumbers, respectively (the spectra before 24 h are similar to those presented in the Fig. 1, therefore, they are not shown for simplicity). The contributions of the pure solvents have been subtracted.

Table 2 summarizes the infrared signals of pure Wells–Dawson anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ in the solid state and liquid media. The assignments of the infrared signals to the vibration of a certain bond are based on the spectroscopic studies of the Wells–Dawson

$\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ and Keggin anions $\text{PMo}_{12}\text{O}_{40}^{3-}$ reported in the literature [14–16]. The spectra show an important shifting and splitting of the infrared vibrations at ~ 1077 and $\sim 900 \text{ cm}^{-1}$ belonging to P–O species do not show modifications regardless of the nature of the solvent or time (see Table 2). This observation indicates that the molybdenum framework of the anion remains intact inhibiting any interaction of the central phosphorous anion with the solvent.

Further investigation through ^{31}P NMR analysis gave additional evidences of the stability of the phosphomolybdic anion. The spectra showed a single signal at -2.0 ppm characteristic of the central phosphorous species of the heteropolyanion anion [10] (spectra not shown).

The molybdenum–oxygen bonds Mo–O–Mo of the external molybdenum cage of the Wells–Dawson unit interact with the solvent, therefore, their infrared bands are greatly modified as can be expected. Additionally, a new band at $\sim 1032 \text{ cm}^{-1}$ belonging to the symmetric stretching of the C–O bond of metal alkoxides species $\text{M}(\text{OR})_n$ is observed in the solution containing methanol and ethanol (see Fig. 1) [17,18].

Additionally, the spectra of the Dawson anion in 2-propanol possesses the characteristic bands of 2-propoxy species. The signals at 1466 and 1378 cm^{-1} belong to the asymmetric and symmetric bending modes of CH_3 species, 1160 and 1129 cm^{-1} to the C–C and C–O stretching modes, respectively, and 951 cm^{-1} to the methyl rocking mode [19].

Moreover, additional bands of adsorbed species are observed in the 1500–4000 cm^{-1} region (Fig. 2). The bands at $\sim 2800 \text{ cm}^{-1}$ (CH_3 symmetric stretching), $\sim 2900 \text{ cm}^{-1}$ (CH_3 asymmetric stretching) and $\sim 3300 \text{ cm}^{-1}$ (OH stretching) are characteristic of alkoxy species RO^- (CH_3O^- , $\text{CH}_3\text{CH}_2\text{O}^-$, $(\text{CH}_3)_2\text{CHO}^-$) due to the dissociative chemisorption of alcohols on oxide surfaces [18,20].

However, the interaction is weak in the particular case of acetone and acetonitrile. The bands at 1709 cm^{-1} ($\nu\text{C}=\text{O}$), 1400, 1358, 1221 and 1093 cm^{-1} indicate a molecular adsorption of acetone on the Wells–Dawson anion [19,21,22]. Similarly, the bands belonging to the cyanide stretching vibration $\nu(\text{CN})$ at 2290 and 2251 cm^{-1} are characteristic of the molecular adsorption of acetonitrile on oxide surfaces [22]. The weak bands in the 400–500 cm^{-1} range are

Table 2
Summary of the characteristic signals of the phospho-molybdic Dawson-type anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ in the solid state and organic liquid media

Sample/ solvent	Wavenumber (cm^{-1})/assignment				
	ν_{as} (P–O)	ν_{as} (Mo–O)	ν_{as} (Mo–O– Mo) edge sharing	δ (O–P–O)	ν_{as} (Mo–O– Mo) corner sharing
Solid state ^a	1075	1001–985	938	905	865–761
Methanol	1075 sh	–	937	902	841, 787
Ethanol	1077	1003	941	903	879, 842, 788
2-propanol	1071	1003	951	901	842, 788
Acetone	~ 1073	999	937	901	842, 788
Acetonitrile	1077	1003	938	905	841, 791

sh, shoulder.

^a Data from Ref. [1].

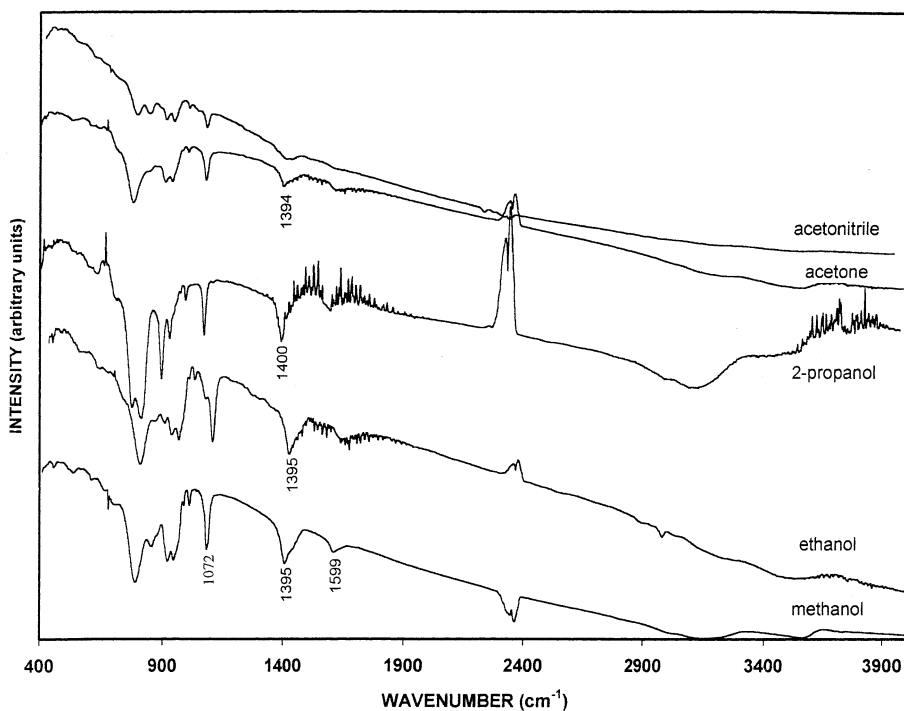


Fig. 2. Infrared spectra (transmittance mode) of solutions containing 20 mM of $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ in organic media after heating at 50 °C for 2 h.

assigned to Mo–CN bond stretches according to the investigations on octacyanide and hepacyno-molybdate complexes [23]. The remaining solids after the evaporation of the solvents (methanol, ethanol, 2-propanol, acetone and acetonitrile) were also analyzed through infrared spectroscopy (data not shown). The spectra demonstrated that the structure of the ammonium phospho-molybdc Dawson salt $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ was intact regardless of the organic solvent.

The infrared signals belonging to alkoxy species and molecular adsorbed acetone disappeared upon heating the solutions to 50 °C. Nevertheless, the characteristic infrared signals of the Wells–Dawson heteropoly-anion remain unaltered (see the signal of P–O bond at 1072 cm^{-1} in Fig. 2).

The new bands observed at ~ 1395 and 1599 cm^{-1} in the alcohols and acetone solutions are assigned to the symmetric and asymmetric stretching of the O–C–O bond of adsorbed formate and acetate species [18,19,24,25]. According to studies of the reaction pathway of the oxidation of alcohols and ketones on redox catalysts, alkoxy species are the intermediates of

the production aldehydes that are further oxidized to CO_2 through formate/acetate species [19].

4. Conclusions

Previous studies demonstrated that the phospho-molybdc Wells–Dawson-type anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ decomposes in aqueous media regardless of the concentration or pH conditions. This problem is overcome upon dissolution in organic media that avoids the decomposition of the anion towards Keggin-type species. The present study demonstrates that the heteropoly structure is stable for extended periods of time at room temperature or upon heating to 50 °C and is recovered intact after evaporation.

This information possess important applications in the synthesis of supported heteropoly anions through impregnation methods and the use of the phospho-molybdc Wells–Dawson anion as catalytic material in liquid media reactions. In fact, current studies demonstrate that a high surface area TiO_2 support is

suitable to be covered with a stable surface layer of $P_2Mo_{18}O_{62}^{6-}$ species through impregnation until dryness of an organic solution of the anion.

For the first time in the literature, the spectroscopic analysis demonstrates that the alcohols dissociatively chemisorb through intermediate alkoxy species on the heteropoly structure. Those species are oxidized on the redox sites of the anion to formate or acetate species.

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