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EFFECT OF CATIONS INTRODUCED INTO 12-MOLYBDOPHOSPHORIC ACID ON ITS CATALYTIC PROPERTIES IN DEHYDRATION OF 2-PROPANOL

II. Na⁺ - AND Zn²⁺ - SALTS

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The effect of the type and amount of cations introduced into 12-molybdophosphoric acid on its function as an acid-catalyst was studied for the conversion of 2-propanol under atmospheric pressure and at 300°. Thermal studies revealed that molybdophosphates lose a large part of its water content at about 250° and their decomposition begin around 500°. It was found that the salts are more active than the free acid and the dehydration reaction is more favourable than the dehydrogenation. Propylene is the most selective product whereas both ether and acetone were produced in low quantities.

Key words: Conversion, 2-Propanol, Molybdophosphoric acid.

Introduction

Several authors have investigated the origin of acidity in the salts of heteropoly acids. Niiyama *et al.* [1] assumed that the origin of acidity in these salts is due to the dissociation of the water coordinated to metal cation (Mn⁺), whereas Baba *et al.* [2] suggested that proton generation from H₂ or H is due to the reduction of metal cations like Ag⁺ and Cu²⁺. On the other hand, Okubara *et al.* [3] assumed that the protons are formed by the partial hydrolysis of anions in the preparation processes. Misono *et al.* [4] previously proposed the involvement of protons originating from dissociation of molecular hydrogen in the reduction of molybdophosphoric acid.

The effect of the counter cation on acidity was studied by many authors [5,6]. Tanaka *et al.* [6] studied the correlation between the acidity of some neutral salt catalysts by ammonia adsorption at 200° and the electronegativity of their metal ions. They found that the acidity of the salts of 12-molybdophosphoric acid is strongly affected by the electronegativity of the cation as well as its amount. Salts of cations with lower electronegativity are less acidic, whereas with acidic cations as Bi³⁺ and Fe³⁺ the acidity increased.

Hodnett *et al.* [7] have postulated, from their study on heteropoly compounds by temperature-programmed reduction and temperature-programmed hydrogen-deuterium exchange techniques, 2 explanations to rationalize the lower reactivity of salts of the monovalent cations:-

- (i). Monovalent cations can stabilize W-O bonds in the Keggin structure sufficiently to make them resistant to reduction below their decomposition temperatures,
- (ii). Cations occupy sites which are necessary for the activation of molecular hydrogen.

Okuhara *et al.* [8] found that the absorption of 2-propanol into the bulk of the copper salts was accelerated by the

presence of water. They ascribed the increase of the rate to the expansion of the effective reaction zone caused by water-promoted absorption of 2-propanol.

The aim of the present work is to show the effect of the counter cation content on the activity of sodium and zinc salts of 12-molybdophosphoric acid for dehydrating of 2-propanol at 300°.

Experimental

A series of salts of 12-molybdophosphoric acid were prepared by addition of different amounts of sodium and zinc carbonates to an aqueous solution of the free acid with vigorous stirring at room temperature according to the method of Tsigdinos [9]. The produced solutions were evaporated over a water bath and then dried at about 120° overnight. The molecular formulae and abbreviations of the catalysts used, MxH₃-xPMo₁₂O₄₀ (x = 1-3), are given in Table 1.

From each sample, 0.2g was heated at 300° for 3 hrs under a stream of nitrogen. The reaction conditions were: reaction temp. 300°, flow rate of nitrogen 57 x 10⁻³ mole/hr. and flow rate of 2-propanol (vapour) 3.47 x 10⁻³ mole/hr. and WWH = 1.04 h⁻¹.

The reaction products in wt. % are propylene (C³), diisopropyl ether (DIE) and acetone (CCOC) were analyzed chromatographically in the gas phase using a varian 3700 GLC with an FID. The separation column was packed with 10% squalene supported on chromosorb.

Results and Discussion

Thermal stability of heteropoly compounds (TGA & DTG): Heteropoly compounds are known to be highly hydrated. Various amounts of water of crystallization, n = 24 -30 for H₃PMo₁₂O₄₀ nH₂O at room temperature have been reported

TABLE 1. CATALYST FORMULA, ABBREVIATION, ACTIVITY AND PRODUCT DISTRIBUTION OF 2-PROPANOL OVER 12-MOLYBDOPHOSPHATES AT 300°.

Formula	Abbrev	Activity, mol.h ⁻² , g ⁻¹ 10 ⁻⁴			Product selectivities (5 mins)			
		A _i	Ac	A _r	%X	%C	%Die	%CCOC
H ₃ PMo ₁₂ O ₄₀ .xH ₂ O	HPMO	160	157	0.98	100	92.1	3.9	3.9
NaH ₂ PMo ₁₂ O ₄₀	Na(1)PMo	172	178	~1.0	96.5	87.0	4.7	4.7
Na ₂ H ₂ PMo ₁₂ O ₄₀	Na((2)PMo	177	178	1.0	99.0	98.1	0.9	0.9
Na ₃ PMo ₁₂ O ₄₀	Na(3)PMo	178	178	1.0	99.8	99.6	—	0.2
Zn _{0.5} H ₂ PMo ₁₂ O ₄₀	Zn(1)PMo	162	148	0.9	100	90.9	2.1	7.0
ZnH ₂ PMo ₁₂ O ₄₀	Zn(2)PMo	155	160	~1.0	86.8	83.5	3.8	12.5
Zn _{1.5} PMo ₁₂ O ₄₀	Zn(3)PMo	178	152	0.86	99.9	99.0	—	0.9

Where Ar = Residual activity after 180 mins., A_i = Initial activity after 5 mins., A_r = Final activity after 180 mins., %x = total conversion.

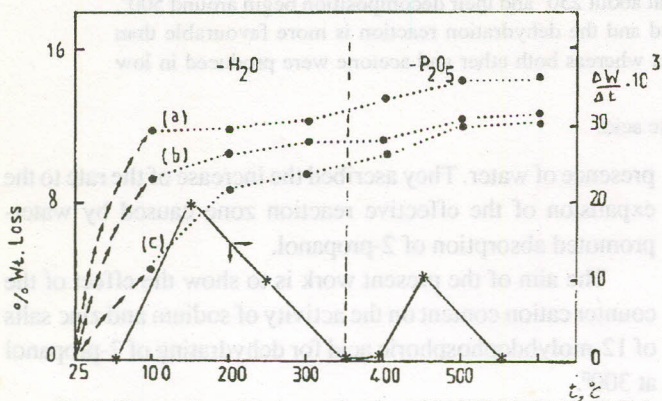


Fig. 1. Changes in weight loss on heating of (a) HPMO, (b) Na(3) PMo and (c) Zn(3) PMo in air for 3 hrs (static) and differential thermal gravimetric ($\Delta w/\Delta t$) as a function of temperature for Na(3) PMo.

[10]. Some of the differences in the reported thermograms and hydration numbers may be due to failure to attain equilibrium conditions. Figure 1 (TGA) shows the % of weight loss due to calcination of H₃PMo₁₂O₄₀.xH₂O and its sodium and zinc salts in air for 3 hrs (static). On heating to 300°, 12-molybdophosphoric acid and its salts are converted to the anhydrous solids, apparently through an endothermic process [9,11]. Weight loss was observed in 2 stages as shown in Fig. 1 (the relation between $\Delta w/\Delta t$ against mean temperature, DTG for Na₃PMo): (i) the removal of zeolitic water (~100°) to give the 4-5 hydrate and the formation of anhydrous salt at about 300-400° are in good agreement with the differential thermal analysis (DTA) reported by West and Audreith [11], and (ii) the decomposition starts as low as 500° to sublimate phosphorus pentoxide (P₂O₅). Decomposition, which takes place at 400-600° is believed to be according to the following equation:



It is also observed that during salt formation, elimination of a part of the water content occurs and thus resist the weight loss during higher temperature calcinations. The water desorbed

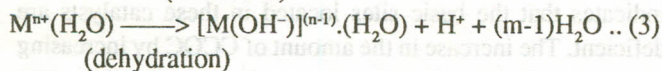
from 150-250° may be strongly bound to the heteropoly compound or may exist in the bulk of the compounds. The strong acidic sites will be formed by the interaction of the counteraction with the desorbed water. At higher temperature calcinations, the nature of the acidic sites will also be converted from Lewis acid to protonic ones.

Catalytic activity of molybdophosphates. Under the reaction conditions indicated above propylene and diisopropyl ether are formed as dehydration products from 2-propanol. The presence of acetone in the reaction products indicates that the dehydrogenation reaction occurs to a certain extent. The catalyst properties (activity, stability and selectivity) are connected with the type and amount of the cation introduced into the free acid.

Initial activity and stability of catalyst activity. From the results obtained in Table 1, it is obvious that all the samples are active in catalyzing this reaction. The values of the initial activities are in the range of (155-178). 10⁴ mol.h⁻¹.g⁻¹. The initial activity of the free acid (HPMo) was changed upon introducing the alkali-metal (Na⁺ and Zn²⁺) depending on the properties and amount of this cation. The initial activity increases in the following order, HPMO < Zn(2)PMo < Zn(1)PMo < Na(1)PMo < Na(2)PMo < Na(3)PMo ~ Zn(3)PMo. The higher initial activity of the neutral salts may be due to the participation of surface reactions besides the bulk reactions which occur in the pseudo-liquid phase. Under certain reaction conditions, heteropolymolybdophosphates behave like solutions and the catalytic reaction proceeds in the catalyst bulk depending on the polarity of the substrate [12]. Polar molecules such as alcohols and water are capable to penetrate into bulk and come out of it which results in expanding the reaction zone [13].

It is also observed that by increasing the reaction time, the catalyst activity is almost constant or slightly decreased as evidenced from the values of the residual activity, A_r, retained by the catalyst after 3 hrs (Table 1). This higher stability in the catalyst activity may be due to the decrease in the rate of coke

formation and regeneration of new active sites during the reaction. These sites results in the dissociation of H₂O of hydration and for water of crystallization as a result of cation electronegativity and its redox properties:

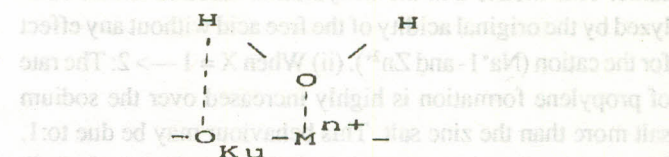


The decrease in the rate of coke formation over the used samples may be due to the reduction of the cations during the initial period. At this stage, the secondary structure of the heteropoly acid crystallites is rearranged by its reaction with water. This rearrangement allows the crystallites to be penetrated by alcohol which causes a controlled formation of the acidic sites, therefore high coking rates are avoided [14,15].

Product distribution and selectivities. The distribution of reaction products after 5 mins from the beginning is given in Table 1. It is observed that propylene is the most selective product obtained. Diisopropyl ether and acetone are produce in small percentages over most of the samples used. These results indicate that propylene formation is accelerated in the bulk due to the formation of a stable complex between the alcohol molecules and the oxygen of the Keggin structure. This behaviour also indicates that dehydration reaction takes place on certain active sites independent the kind of the cation.

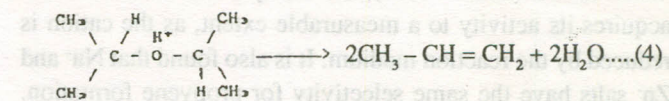
Selectivity for dehydration. In the dehydration reaction of 2-propanol 2 products are in competition, diisopropyl propylene and ether. It is observed in Fig. 2 that the percentage of DIE is slightly increased or approximately constant with increasing the reaction time. Its quantity does not exceed 5% which indicates that this product is unfavourable under our conditions and appears to be a side reaction. This poor selectivity for DIE formation may be due to the following reasons [16]: (i)

Ether formation is more strongly poisoned by water of dchydration than is the corresponding olefin formation. The water molecules of structural and/or dehydration are strongly adsorbed over the counter cation and the terminal oxygen of the Keggin structure. Thus, the selectivity changes in favour of propylene formation due to the creation of new active sites required for propylene formation.

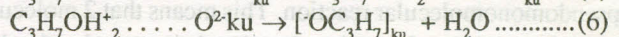
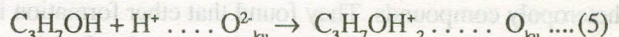


Both dehydration reaction products (C³ and DIE) may be produced via a common intermediate, C₃H₇OH₂+...Oku [16], species using the same active centres.

Because of the difficulties of diffusion of the bulky molecules, DIE, due to its greater kinetic diameter from the microporous structure [17]. At this point, the ether may be converted to propylene which has smaller kinetic diameter as a result of loosing two molecules of water.



The selectivity towards propylene formation as a function of reaction time is shown in Fig. 3a. It is found that the selectivity for propylene formation over most of the used samples is changed by about ± 5% with the reaction time. This result indicates that propylene is formed according to the facil character of step (7) as follows [18];



From these reactions it is clear that the water produced during the reaction plays an important role in production of H⁺

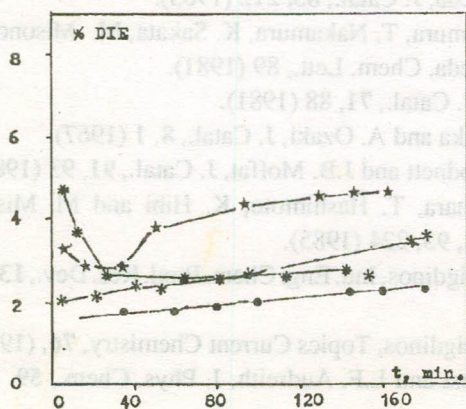


Fig. 2. Yield of Die formation as a function of reaction time over: • HPmo, * Na (1) PMo, * Zn (1) PMo and *Zn (2) PMo.

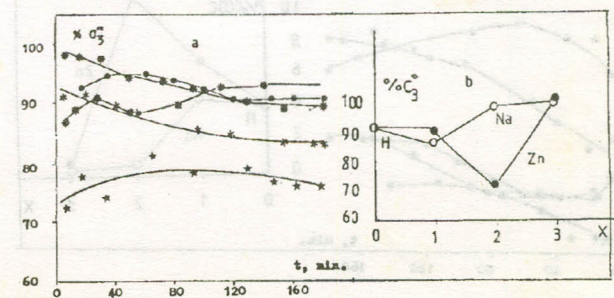


Fig. 3ab. Yield of propylene formation as a function of (a) reaction time over: • HPmo, * Na (1) PMo, * Na (2) PMo, * Zn (1) PMo and * Zn (2) PMo and (b) cation content (% X)..

necessary for propylene formation. The gradual formation of H^+ during the reaction causes the continuous formation of propylene at any time of the reaction.

To show the effect of the counter cation introduced into the free acid on the selectivity towards propylene formation, the amount of cation (X) was plotted against (%) of C_3 as shown in Fig. 3b. It is found that: (i) When X was increased from 0 to 1, the rate of propylene formation approx. is the same. This means that the dehydration reaction is still catalyzed by the original acidity of the free acid without any effect for the cation (Na^+ and Zn^{2+}). (ii) When $X = 1 \rightarrow 2$: The rate of propylene formation is highly increased over the sodium salt more than the zinc salt. This behaviour may be due to: 1. The decrease in penetration of alcohol molecules into the bulk of the sodium salt. 2- The full reduction of Na^+ -cations located at the external crystallites. Mc Monagle *et al.* [19] assumed that the valency and size of the counter cation affect critically the bulk secondary structure. These results show that at $X = 2$ polyvalent cations are less active than the monovalent cations. The study also indicates that molybdenum ions may be effective cations inside the bulk and play a role in the reaction mechanism as a result of its reduction from Mo^{6+} to Mo^{5+} . (iii) When $X = 3$ (neutral salts), the catalyst has no acidic sites acquires its activity to a measurable extent, as the cation is reduced by the reaction medium. It is also found that Na^+ and Zn^{2+} salts have the same selectivity for propylene formation. This means that over neutral salts the reaction occurs on the same active sites, Lewis acids and the water of dehydration. This water creates acidic sites on the surface or in the bulk near the surface catalyzing propylene formation.

To give some light on the molecularity of DIE, P.A. Jacobs *et al.* [20] carried out similar studies for conversion of 2-propanol over zeolites which are similar in their structure to heteropoly compounds. They found that ether formation is a pseudomonomolecular reaction. This means that 2 molecules participate in ether formation, 1 molecule is strongly adsorbed and the other is weakly adsorbed in the gas phase, in agreement

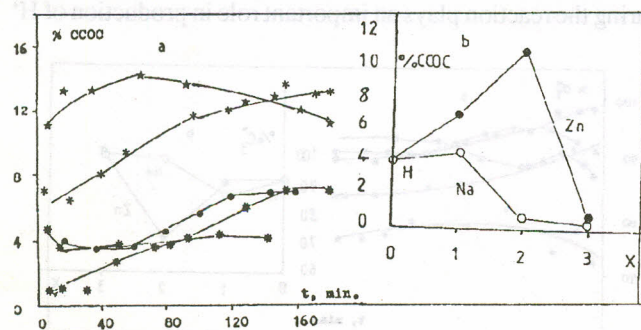
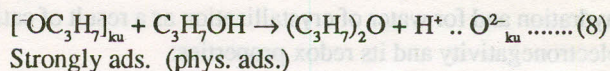
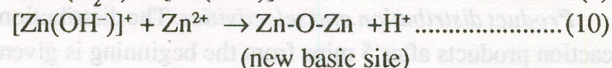
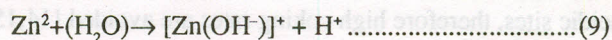


Fig. 4. Yield of acetone formation as a function of (a) reaction time over: • HPMo, * Na (1) PMo, * Na (2) PMo, * Zn (1) PMo and * Zn (2) PMo and (b) cation content (%X).

with R-E mechanism. This mechanism can be proposed as follows [18].



Selectivity for dehydrogenation. The small selectivity towards acetone formation over these molybdophosphates indicates that the basic sites located in these catalysts are deficient. The increase in the amount of CCOC by increasing the reaction time may be due to the continuous reduction of the cations and molybdenum by the alcohol vapour (Fig. 4a). It is found that zinc salts ($X = 1,2$) are much more selective toward acetone formation than the other samples (Fig. 4b). This result can be explained by assuming that zinc may create new basic sites required for acetone formation according to the following scheme;



The adjacent acid-base pair sites cause the increase in the rate of acetone formation over Zn-salt more than the monovalent Na-salt. At $X = 3$ (neutral salts) the selectivity towards acetone formation is highly decreased but the selectivity towards C_3 is highly increased which means that dehydration and dehydrogenation reactions are consecutive reactions. Hall *et al.* [21] and Mastsuda *et al.* [22] proposed that acetone is produced by the participation of both acidic and basic sites.

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The reactions of semicarbazide hydrochloride and hydrazine monohydrate with ethyl acetoacetate, acetylacetonate, benzoylacetonate and dibenzoylacetonate leading to the formation of pyrazole and pyrazolone derivatives have been intensively studied in the aqueous as well as in the nonaqueous medium under various sets of conditions. This has resulted in the development of simple and convenient methods for the synthesis of pure ethyl acetoacetate semicarbazone (I), 3-methylpyrazol-2-one-1-carboxamide (II), 3-methylpyrazol-2-one (III), 3,5-dimethylpyrazol-1-carboxamide (V), 3,5-dimethylpyrazole (VI), 3-phenyl-2-methylpyrazol-1-carboxamide (VII), 3-phenyl-2-methylpyrazole (VIII) and 3,5-dimethylpyrazole (IX). It has been suggested that the reaction of semicarbazide hydrochloride with β -diketo compounds proceeds through four stages. A reaction scheme has been proposed to explain the formation of different products.

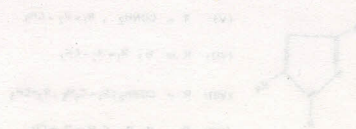
Key words: Synthetic Pyrazole and Pyrazolone derivatives.

Introduction

Hydrazine and hydrazine derivatives react with β -diketo compounds to form pyrazole, pyrazolone and pyrazolone derivatives. It has been reported [4-6] that many β - γ -disubstituted pyrazoles possess hypoglycemic and antimicrobial activity. They are used as corrosion inhibitors, antiloggic agents in photographic systems, and their metal complexes are useful as chemical reagents [7]. The reactions of hydrazine and semicarbazide hydrochloride with β -keto esters and β -diketones leading to the formation of heterocyclic compounds in the pyrazole and pyrazolone series and their methods of preparation have been reported in the literature. The present literature methods [8-16, 18, 21] for the preparation of pyrazole and pyrazolone derivatives involve different steps and are lengthy and tedious. It was considered appropriate to investigate the reactions of hydrazine and semicarbazide with 1,3-diketo compounds in an attempt to obtain their pyrazole and pyrazolone derivatives particularly in the aqueous medium. The



Structure (VI)



Structure (VII)