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Action of Salt Formation on the Bifunctional Nature of 12-Molybdophosphoric Acid and Their Relationship to the Catalytic Activity

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Acidic properties and the catalytic activity of 12-molybdophosphates ($M_{x/n}^{n+}H_{3-x}PMo_{12}O_{40}$; $M = Cu^{2+}$, Bi^{3+}, Cr^{3+} and $X = 1—3$) have been studied. The results are discussed as the effect of these catalyst components on the partial charge on oxygen atom which is in a relation with the acidity. It is shown that the oxygen-hydrogen bond is weakened as the value of partial charge on oxygen ($-\delta_0$) becomes more negative, while the vapor-phase dehydration activity of 2-propanol is explained on the basis of the reacting zone wideness taking into account the pseudo liquid phase nature of the heteropoly compounds. Correlation, the percentage conversion of 2-propanol with the fractional charge on molybdenum atom was successful to interpret the effect of the redox properties of these catalysts on their catalytic activity.

INTRODUCTION

Heteropoly acids have recently attracted much attention as catalysts for various industrial processes, such as oxidation, dehydration, esterification, and etheration.[1] It has been reported that metal salts of heteropoly acids are more active and selective than the acid form in some acid-catalyzed reactions.[2-4]

Relationships between catalytic activity and either the acidic or redox properties of these heteropoly compounds have been reported. Niiyama *et al.*[5] obtained a fair correlation between the activity for alcohol dehydration and electronegativity of metal cations. Hayashi and Moffat found that the activity for methanol conversion was related to the partial charge on oxygen atom,[6] while in considering the redox properties many schemes have been proposed[7-10]. Also, the participation of both the surface and bulk heteropoly salt molecules in the catalytic processes has been investigated by several workers.[4,11-13]

The present work, in an attempt to gain more insight into the bifunctional nature of the heteropoly salts (the acidic and redox properties), is concerned with an investigation of the acidity, dehydration activity and the electrical conductivity properties of the substituted 12-molybdophosphoric acid with Bi^{3+}, Cr^{3+} and Cu^{2+} cations.

EXPERIMENTAL

BDH 12-molybdophosphoric acid was incorporated with the nitrates of Cu(II), Cr(III), and Bi(III). An aqueous solution containing the required amounts of these cations to form a series of salts having the general formula $M^{n+}_{x/n}H_{3-x}PMo_{12}O_{40}$ (where $X = 1—3$) was added to a solution of 12-molybdophosphoric acid with vigorous strirring. The produced mixtures were dried over a water-bath, then the resultant solids were calcined at 300 °C for 4 h. in air stream.

The acidity of the samples was estimated by measuring the liberated amounts of acetic acid produced by the hydrolysis of ethyl acetate. The reaction was carried out in a water thermostate at 60 °C using a 5.0% aqueous solution of ethyl actate. The extent of hydrolysis of ethyl acetate was determined by conventional titrimetry with 0.1 N NaOH solution and phenolphthalein as an indicator.

The catalytic activity of the heteropoly compounds was measured via the dehydration reaction of 2-propanol, it was carried out using a conventional flow reactor. Purified air was used as carrier gas. The exit feed was analyzed using a 104 series PYE UNICAM gas Chromatograph with a polyethylene glycol 20% column coated on celite.

Electrical conductivity measurements were carried out with a conductivity cell described by Chapman *et al.*[14]. The temperature was controlled with a Gallenkamp temperature controller. Voltage was obtained via a 240A Keithley Instruments supply and the current was measured with a 410A picoammeter (Keithley Instruments).

RESULTS AND DISCUSSION

Acidity measurements. — For the prepared catalysts, the acidity was estimated using the hydrolysis of ethyl acetate, since the reaction is known to be catalyzed by Brönsted acid sites.[15] Therefore, kinetic studies were made of this reaction over various catalysts as well as in different concentrations of hydrochloric acid solution for comparison. In all cases, the hydrolysis rate obeyed good first-order kinetics with respect to the concentration of ethyl acetate. The representative plots of the first-order kinetics over several catalysts are shown in Figure 1. During the hydrolysis in various concentrations of HCl solution, the first-order rate constant [k_{HCl} (min^{-1})] was proportional to the concentration of HCl and was expressed as

$$k_{HCl} = 3.72 \times 10^{-3}\, c_{HCl} \tag{1}$$

Hence, the acidities can be expressed as the amount of HCl required to attain the same reaction rates over the studied acid catalysts as appear in Table I.

TABLE I

The Specific Rata Constants of Ethyl Acetate Hydrolysis, Acidity of the Catalysts (Expressed in meq HCl), %Conversion of 2-Propanol at 150 °C, and the Calculated Fractional Charge on Oxygen (δ_0)

Catalyst	Suggested formulation	Rate constant $10^3 \times k$ (min$^{-1}\cdot$g^{-1})	% Conv.	Acidity meq·g^{-1}	δ_0
I	$H_3PMo_{12}O_{40}$	2.555	16.24	0.687	—0.1966
II	$Cu_3(PMo_{12}O_{40})_2$	2.531	24.10	0.680	—0.1968
III	$CuHPMo_{12}O_{40}$	2.464	21.07	0.662	—0.19675
IV	$Cu(H_2PMo_{12}O_{40})_2$	2.236	18.18	0.601	—0.1967
V	$CrPMo_{12}O_{40}$	1.750	14.2	0.470	—0.1954
VI	$Cr_2(HPMo_{12}O_{40})_3$	2.001	10.5	0.538	—0.1958
VII	$Cr(H_2PMo_{12}O_{40})_3$	2.200	8.2	0.59	—0.1962
VIII	$BiPMo_{12}O_{40}$	1.15	29.17	0.309	—0.1945
IX	$Bi_2(HPMo_{12}O_{40})$	1.640	30.77	0.441	—0.1952
X	$Bi(H_2PMo_{12}O_{40})_3$	2.156	36.9	0.579	—0.1959

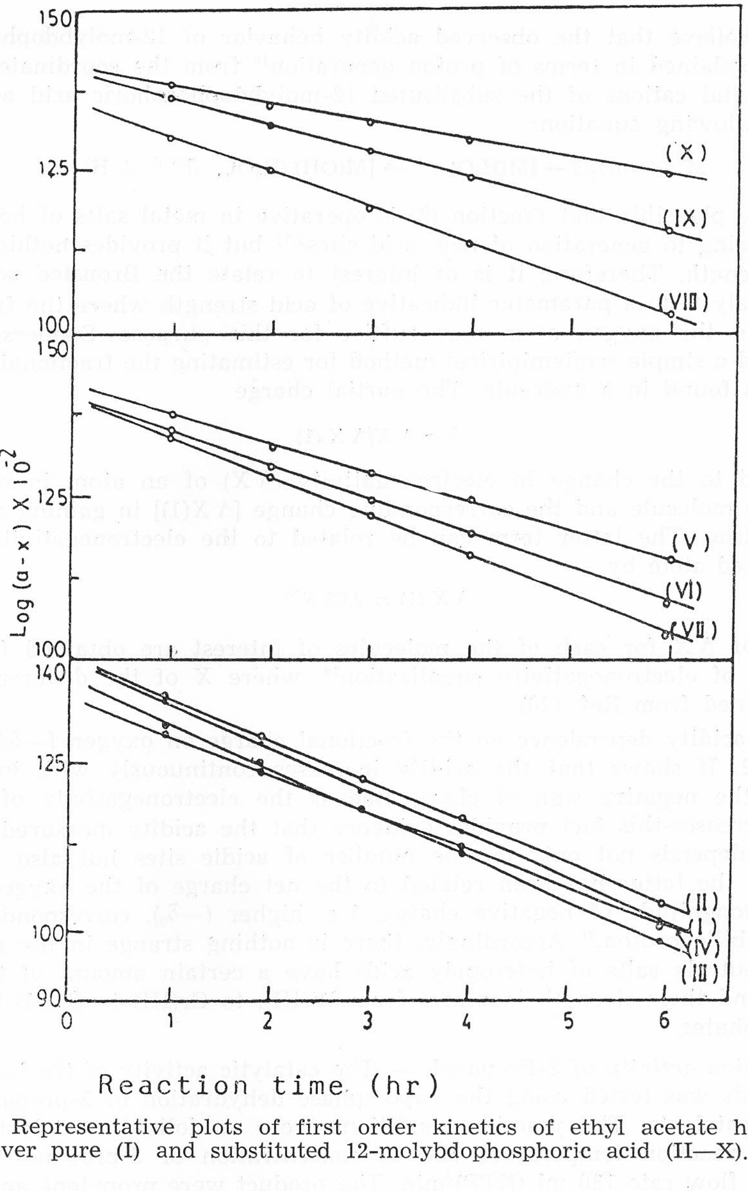

Figure 1. Representative plots of first order kinetics of ethyl acetate hydrolysis over pure (I) and substituted 12-molybdophosphoric acid (II—X).

The data illustrated in Table I show that: i — The acidity of $H_3PMo_{12}O_{40}$ continuously decreases by a stepwise replacement of H^+ by Bi^{3+} or Cr^+ cations. ii — Although substitution of one proton of the heteropoly acid with the equivalent amount of Cu^{2+} reduces the acidity, but it was found that an increase of Cu^{2+} content raises the acidity again. This means, that the number of available sites for reaction (protons) is higher than expected owing to the partial salt formation. Also, the acidic nature is still present even with the formation of »neutral« salts.

We believe that the observed acidity behavior of 12-molybdophosphates can be explained in terms of proton generation[16] from the coordinated water to the metal cations of the substituted 12-molybdophosphoric acid according to the following equation:

$$M^{n+} + mH_2O \rightarrow [M(H_2O)_m]^{n+} \rightarrow [M(OH)(H_2O)_{m-1}]^{(n-1)+} + H^+ \ldots \quad (2)$$

It is very plausible that reaction (2) is operative in metal salts of heteropoly acids leading to generation of new acid sites[5,17] but it provides nothing about their strength. Therefore, it is of interest to relate the Bronsted acidity of these catalysts to a parameter indicative of acid strength where the fractional charge on the oxygen atom may suffice for this purpose. Sanderson[18] has developed a simple semiemipirical method for estimating the fractional charges on atoms found in a molecule. The partial charge

$$\delta = \Delta X / \Delta X(1) \quad (3)$$

is related to the change in electronegativity (ΔX) of an atom in becoming part of a molecule and the corresponding change [$\Delta X(1)$] in gaining or losing one electron. The latter term can be related to the electronegativity, X, of the isolated atom by

$$\Delta X(1) = 2.08\, X^{1/2} \quad (4)$$

values for ΔX for each of the molecules of interest are obtained from the principle of electronegativity equalization[19], where X of the different atoms are obtained from Ref. (20).

The acidity dependence on the fractional charge on oxygen ($-\delta_0$) is seen in Fig. 2. It shows that the acidity increases continuously with increasing ($-\delta_0$)— the negative sign of charge means the electronegativity of oxygen atom decreases-this fact provides evidence that the acidity measured for our samples depends not only on the number of acidic sites but also on their strength; the latter has been related to the net charge of the oxygen where smaller magnitude of negative charge, i. e. higher ($-\delta_0$), corresponds to the more mobille proton.[21] Accordingly, there is nothing strange in the fact that even »neutral« salts of heteropoly acids have a certain amount of Brönsted acidity and their strength increases from Bi(III), to Cr(III) to Cu(II)-12-molybdophosphates.

Dehydration activity of 2-Propanol. — The catalytic activity of the heteropoly compounds was tested using the vapor-phase dehydration of 2-propanol over various catalysts. The reaction conditions were as follows: catalyst weight 500 mg; reaction temperature 150 °C; concentration of 2-propanol 4.2% in air, total flow rate 180 ml (NTP)/min. The product were propylene and water. As shown in Table I, the percentage conversion of 2-propanol is inversely related to the acidity of both Bi(III) and Cr(III) heteropoly salts. On the other hand, there is a proportional relationship between the acidity and the dehydration activity for Cu(II) salts. These findings mean that when the kind of counter cation is changed the activity of the $M_{x/n}^{n+} H_{3-x} PMo_{12}O_{40}$ catalysts for dehydration of 2-propanol varies remerkably. Also, when the kind of counter cation is fixed and the amount of counter cation is changed, the dehydration activity varies in a way indicating that the activity is affected not only by the acidity of the catalysts, but also by other functions.

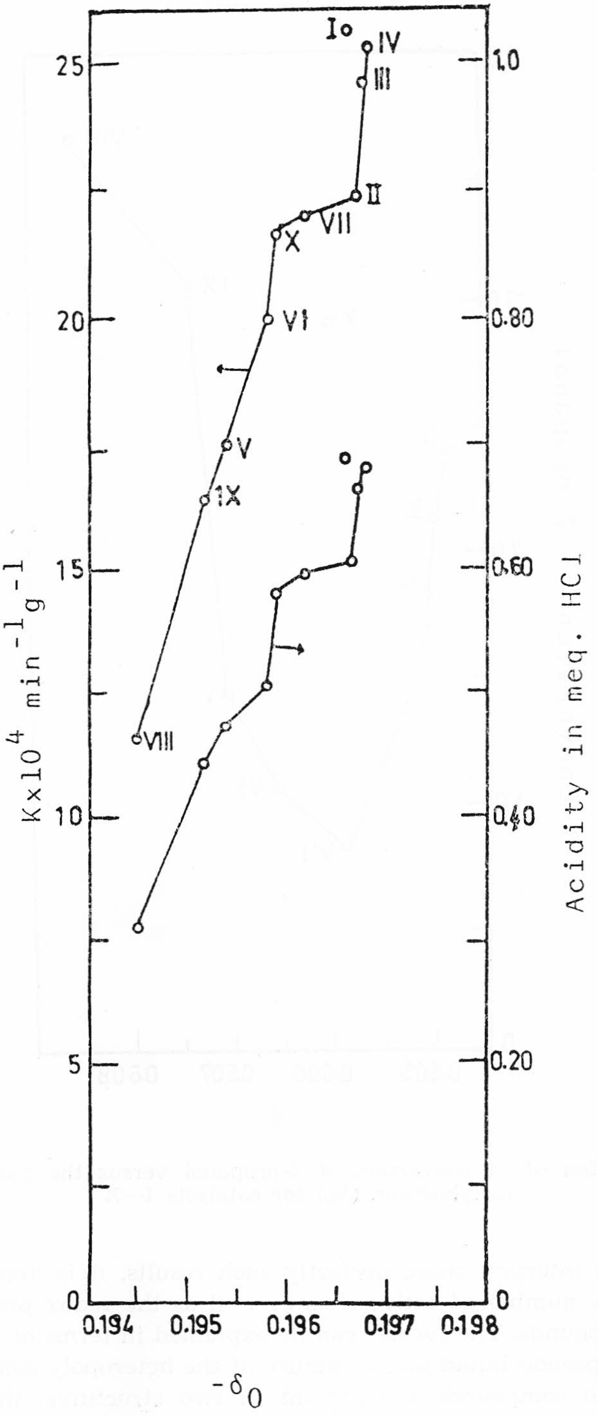

Figure 2. Specific rate constants of ethyl acetate hydrolysis and the acidity expressed in meq. HCl versus the partial charge on oxygen ($-\delta_0$) for catalysts I—X.

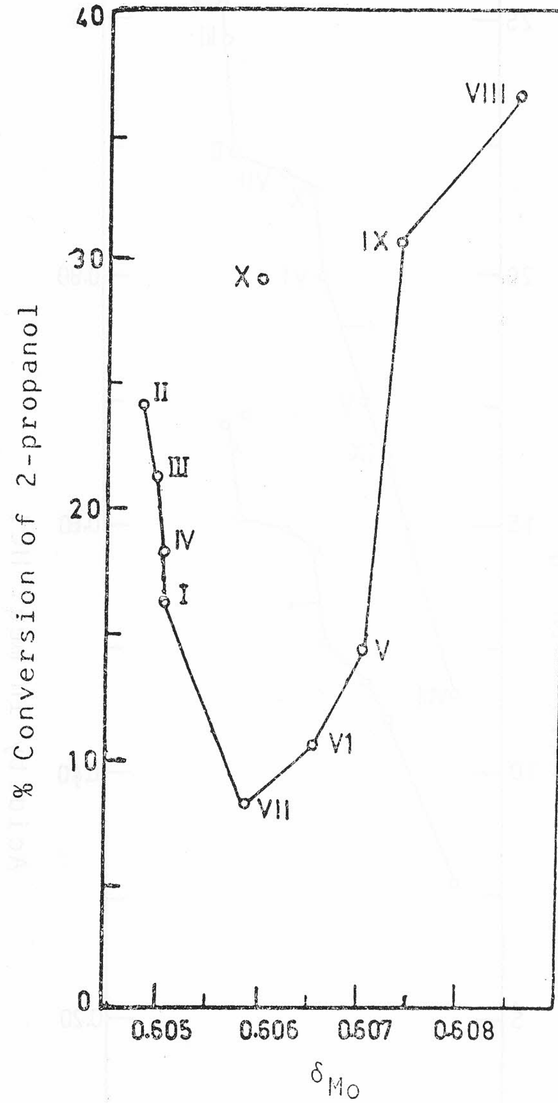

Figure 3. Variation of % conversion of 2-propanol versus the partial charge on molybdenum (δ_{Mo}) for catalysts I—X

In order to interpret more perfectly such results, it is necessary to take into account the number of active sites as well as the redox properties of the heteropoly compounds. The former can be explained in terms of Misono *et al.*[22] description of »pseudo liquid phase« nature of the heteropoly compounds. They stated that such compounds are present in two structures, the first is the stable »primary structure« (the Keggin unit, $PMo_{12}O_{40}^{3-}$) and the second is subjected to easy rearrangement and is called the »secondary structure« (the three-dimensional arrangement of the heteropoly anion, water and the counter cation). These characteristics make heteropoly compounds behave like a solution, and in some cases the catalytic reactions proceed in the interstitial space of the bulk[13]. Accordingly, the higher activity of Bi(III) salts may be attributed to an increase of the reacting zone wideness available for the catalytic reaction, more than takes place for the other salts. This opinion will be confirmed by electrical conductivity measurements.

A second explanation based on the redox properties[23,24] of 12-molybdophosphates is obtained by correlating the percentage conversion of 2-propanol with the fractional charge on molybdenum cation as the effective component. The results presented graphically in Figure 3, show that: i — Substitution with unreducible cations increases the dehydration activity with increasing δ_{Mo}, ii — An inverse situation is obtained in case of the substitution with reducible cations. Taking into account that increasing δ_{Mo} means increasing the electron affinity of Mo^{6+} and we suggest that the reaction proceeds according to the following steps: i — Attacking the Mo^{6+} cations by alcoholic OH groups, simultaneously C—OH bond becomes weaker and Mo^{6+} will be in a slightly reduced state ($Mo^{n+<6+}$), ii — Complete separation of alcoholic OH^- group, leaving the alcohol molecule as a carbonium ion to be attached to Mo^{6+} in a reduced state, Mo^{5+}. iii — Reoxidation of Mo^{5+} accompanied by separation of the hydroxyl ion to form with the released hydrogen ion a molecule of water.

From this proposed mechanism two contradicitive steps appear to be involved, the first depends on the reducibility of Mo^{6+}, while the second depends on the reoxidizability of Mo^{5+}. As regards the relationship between δ_{Mo} and the dehydration activity (Figure 3) it is easy to decide that the reaction is predominantly affected by step 1 which is enhanced by increasing δ_{Mo} as found for Cr(III), and Bi(III)-molybdophosphates. On the other hand, an additional factor for the activation of step 1 is obtained from the observable higher catalytic activity for Cu(II) salts, which show a higher $^0/_0$ conversion of 2-propanol than corresponding to δ_{Mo} of these salts. This reflects a certain role of the presence of a reducible cation on the catalytic activity. The two explanation mentioned above may be supported by electrical conductivity measurements.

Electrical Conductivity Measurement. — It was carried out on the three »neutral« salts (compounds II, V, VIII) as well as on the free heteropoly acid (comp. 1); the initial conductivities at 150 °C in a flow of air were 1.26×10^{-10}, 0.59×10^{-10}, 1.20×10^{-10} and 43.48×10^{-10} Ω^{-1} cm^{-1}, respectively. When 2-propanol vapor was introduced the conductivity increased and attained constant values of 3.02×10^{-10}, 0.91×10^{-10}, 3.80×10^{-10}, and 87.1×10^{-10} Ω^{-1} cm^{-1}, respectively, after 2 h. The data illustrated above are represented as ($\sigma_i/\sigma_o - 1$) — where σ_o is the conductivity before admission of 2-propanol and σ_i is that measured at time t_i after admission of alcohol-versus time, as shown in Figure 4.

From Figure 4, complete agreement between our opinion on the effect of the reacting zone wideness on the catalytic activity and the conductivity behavior can be seen from the order of increase of the relative conductivity σ_i/σ_o which has the same sequence of increasing the catalytic activity. This result provides evidence of the parallel relationship between the conductivity

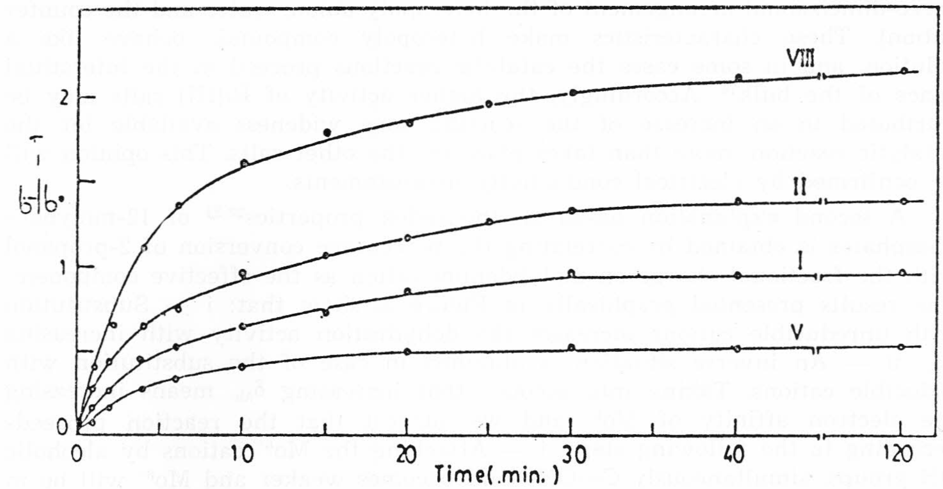

Figure 4. Relative change of electrical conductivity versus time of amdission of 2-propanol over catalysts I, II, V, and VIII.

and the number of active sites which increase with an increase of the reacting zone wideness, showing more current carriers available for conduction. Further support can be obtained from the activation energy calculations using equation (5).

$$\sigma = \sigma_0 \exp(-E/RT) \qquad (5)$$

where Log σ values have been plotted against the reciprocal absolute temperature (Figure 5); the slope of the obtained lines was considered to give the activation energy, E^{25}.

As appears in Table II, the order of decreasing ΔE have the sequence compound II < VIII < I < V, exhibiting the same order of decreasing the catalytic activity, where compound VIII > I > V the only exception is sample II. It shows the lowest value of ΔE confirming the acceleration role of the reducible cations on the electrons mobility.

TABLE II

Activation Energy Values for 12-Molybdophosphoric Acid and its Neutral Salts With Bi(III), Cr(III), and Cu(II).

Catalyst	E/ev in air flow	E/ev after admission of 2-propanol	ΔE/ev
$H_3PMo_{12}O_{40}$	0.586	0.688	0.102
$BiPMo_{12}O_{40}$	0.639	0.700	0.061
$CrPMo_{12}O_{40}$	0.527	0.791	0.264
$Cu_3(PMo_{12}O_{40})_2$	0.688	0.703	0.015

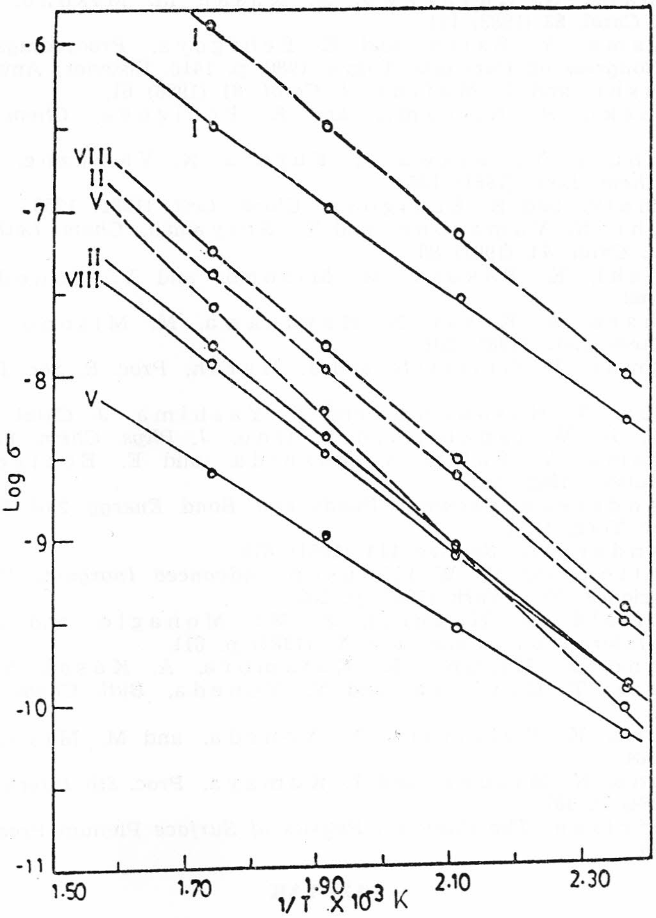

Figure 5. Variation of log σ versus 1/T for catalysts I, II, V, and VII in air (solid lines), and with admission of 2-propanol (dotted lines).

Finally, our conclusion is that the dehydration reaction of 2-propanol over 12-molybdophosphates is affected by the reacting zone wideness, *i. e.* the number of active sites, and the activity of these sites is essentially dependent on the acidic nature of the catalyst and the redox properties of Mo^{6+}, the former is related to the δ_0 while the latter is related to δ_{Mo}.

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SAŽETAK

Katalitička aktivnost 12-molibdofosfornih kiselina

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Ispitivani su 12-molibdofosfati općeg sastava $M^{n+}_{x/n} H_{3-x} PMo_{12}O_{40}$ gdje je $M = Cu^{2+}$, Bi^{3+}, Cr^{3+} i $x = 1 — 3$. U radu se objašnjava utjecaj različitih fizičko-kemijskih osebina tih spojeva kao što je na primjer parcijalni naboj na kisikovom atomu, redoks potencijal itd. na katalitičku sposobnost proučavanih spojeva.