# The Oxidative Dehydrogenation of Isobutyric Acid to Methacrylic Acid on Ion Exchange Modified 12-Heteropoly Oxometalates

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The oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA) has been studied over a series of 12-heteropoly oxometalate catalysts. $H_3PMo_{12}O_{40}$, $Cs_3PMo_{12}O_{40}$. $(NH_4)_3PMo_{12}O_{40}$, and a series of catalysts prepared using an ion exchange modification that resulted in the formation of mixed cation composition salts ($NH_4^+/Cs^+$) were studied to investigate the contribution of the cation in the IBA to MAA process. Whereas the product selectivities obtained with the parent acid and ammonium salt were similar, those obtained with the cesium salt were markedly different. Studies of the self exchanged salts provided insight into the role of protons in the process, while investigations of the $Cs^+/NH_4^+$ ion exchanged materials indicated that the cation can participate directly in the IBA to MAA reaction. The formation of MAA and acetone appears to involve a common intermediate, whereas propene forms through a different route.  © 1991 Academic Press, Inc.

## INTRODUCTION

The production of methacrylic acid, a precursor to methyl methacrylate, is an important step in the poly(methyl methacrylate) process. Conventional commercial technologies have utilized the acetone cyanohydrin reaction (1), but increased environmental concerns and reduced production of HCN have intensified the search for viable alternative routes to methyl methacrylate production.

Several methodologies based on $C_3$ and/or $C_4$ processes are currently being explored for the production of methyl methacrylate. Isobutene can be oxidized on $V_2O_5$–$P_2O_5$ catalysts to yield methacrylic acid and methacrolein (2), although significant quantities of acetic acid were also produced. It was found, however, that some 12-heteropoly oxometalate catalysts were also active for this process with considerably lower production of acetic acid (2).

Propylene has become an extremely important commodity chemical since the ad-

vent of bismuth–molybdenum catalysts, which are able to catalyze oxidation and ammoxidation reactions through an allylic intermediate (3). Isobutyric acid is obtained indirectly from propylene in a carbonylation process in which isobutyryl fluoride is an intermediate. The product is subsequently subjected to oxidative dehydrogenation to yield methacrylic acid followed by esterification to methyl methacrylate. This process has been shown to be catalyzed by $FePO_4$ (4, 5), Pb–$FePO_4$ (6), $V_2O_5$–$P_2O_5$ (7), as well as 12-heteropoly oxometalates with the $PMo_{12}O_{40}^{-3}$ anion or, alternatively, Keggin anions in which a portion of the Mo atoms have been replaced by vanadium atoms (8–13). Obviously the ideal catalyst will produce the unsaturated acid at high conversion with high selectivity.

Because of the fact that the oxidative dehydrogenation process can be accomplished using a redox type cycle (8–13), it is useful to consider the redox properties of heteropoly anions when the choice of the anion is being made. In his monograph, Pope has discussed the redox chemistry of several heteropoly anions in solution (14). Of the many

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families of heteropoly anions, only those with one terminal oxygen atom per octahedral unit are capable of accepting an electron without causing significant structural distortion. When an electron is added to the peripheral atom it enters a mainly non-bonding orbital which induces only small changes in the $M-O_t$ bond length (*14*). The 12-heteropoly anion or Keggin anion is one such heteropoly oxometalate which can undergo this type of redox process.

The solution redox behavior of the heteropoly anion was encouraging but did not prove that the same behavior would necessarily be observed in the solid state at elevated temperatures. Several investigations dealing with the reduction behavior of 12-heteropoly acids and salts in the solid state have been undertaken (*10b, 15–19*). Investigations have been concerned mainly with the behavior of the $PMo_{12}O_{40}^{-3}$ anion although the $PW_{12}O_{40}^{-3}$ species has also been studied. Many of the studies have considered heteropoly salts such as those of $Ag^+$ and $Cu^{2+}$, for which the cation exhibits a strong tendency to dissociate molecular hydrogen (*15*) or, alternatively, the acids have been mixed with hydrogen activators such as Pd/C (*17a*). It is believed that the metal centre facilitates hydrogen dissociation and the resulting H atoms can subsequently form protons and electrons which are active in the reduction mechanism. Other investigations have considered either the unsupported acids or salts which contain irreducible cations (*16b*). These materials were also found to undergo reduction but the rates were appreciably lower, probably a result of a decreased ability to dissociate the molecular hydrogen.

The participation of lattice oxygen atoms in the redox cycle has important connotations for catalytic processes involving Keggin anions. The evidence suggests that lattice oxygens may participate in oxidation type reactions involving organic molecules, with the Keggin anion able to be partially reduced and reoxidized during the process (if an oxygen source is available). Reactions

of this type include the oxidation of methacrolein to methacrylic acid and the oxidative dehydrogenation of isobutyric acid to methacrylic acid.

In the present work, ion exchanged 12-heteropoly salts have been examined for their catalytic properties in the isobutyric acid dehydrogenation process. It is well known that Keggin anions possessing molybdenum and/or vanadium peripheral atoms are more effective catalysts for the IBA to MAA process, and oxidation processes in general, than the corresponding 12-heteropoly tungstates (*20–23*). Therefore the catalytic studies deal mainly with 12-molybdophosphate salts. The $Cs^+/NH_4^+$ salt combinations have been chosen for this study in part because of previous studies of oxidation processes using $Cs^+$ salts of 12-heteropoly anions (*2, 11c, 23*). In addition, several studies of the catalytic (*24–28*) and diffusion (*29*) properties of ammonium salts of $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ have been undertaken in this laboratory. In the methanol to hydrocarbons process, $(NH_4)_3 PW_{12}O_{40}$ was found to produce larger amounts of saturated hydrocarbon species and a greater quantity of $C_4$ species than the parent acid or metal salts (*24*). The rather unique nature of the ammonium ion as compared to the alkali cations suggested that it may influence the catalytic behavior of the ion exchanged salts. The choice of these two cations should yield new information regarding these materials for the process, while at the same time allowing a comparison of the present results with those obtained previously. The purpose of the present work is to examine the effect of changing the cations present in the solid as well as the relative amounts of the cations. A recent publication from this laboratory has provided qualitative and quantitative information on the ion exchange capabilities of 12-molybdo- and 12-tungstophosphoric acid, particularly those of cesium and ammonium cations (*30*), and most recently it has been shown that the pore structures of these solids are invariant under the ion ex-

| Compound | $NH_4^+$ Cations/Anion | $Cs^+$ Cations/Anion |
|---|---|---|
| $H_3PMo_{12}O_{40}$ | — | — |
| $(NH_4)_3PMo_{12}O_{40}$ | 2.17 | — |
| $Cs_3PMo_{12}O_{40}$ | — | 2.78 |
| $NH_4PMoNH_41$ | 2.50 | — |
| $NH_4PMoNH_43$ | 2.51 | — |
| CsPMoCs1 | — | 2.82 |
| CsPMoCs3 | — | 3.08 |
| $NH_4PMoCs1$ | 1.75 | 1.15 |
| $NH_4PMoCs3$ | 1.30 | 1.53 |
| $CsPMoNH_41$ | 2.59 | 0.04 |
| $CsPMoNH_43$ | 2.44 | 0.14 |

change although, not surprisingly, lattice parameters shift as the interchange of two cations occurs (31).

## EXPERIMENTAL

The materials chosen for the catalytic studies were selected from the ion exchanged series of 12-molybdophosphate salts which included $Cs^+$ and $NH_4^+$. The $Cs_3PMo_{12}O_{40}$ and $(NH_4)_3PMo_{12}O_{40}$ salts used as the starting materials for the exchanges were employed along with $H_3PMo_{12}O_{40}$ as benchmark materials. The ion exchanged salts selected were $NH_4PMoCs1$, $NH_4$ $PMoCs6$, $NH_4PMoNH_41$, $NH_4PMoNH_45$, $CsPMoNH_41$, $CsPMoNH_46$, $CsPMoCs1$, and $CsPMoCs5$ using a similar material designation as described in a previous publication (30). The notation describes the ions involved in the exchange procedure along with a label to indicate the number of exchange reactions used to modify the catalyst. For example, $NH_4PMoCs1$ indicates that the ammonium heteropoly salt was ion exchanged once with 0.1 $M$ $CsNO_3$. The cation compositions of the materials used in the present study are listed in Table 1. By choosing the self exchange series as well as the series in which different cations were exchanged, it was possible to study the effect of the concentration of cations and of protons as well as the surface area and pore structure of the catalysts. The first and last materials from the exchange series were

chosen so as to maximize the effect of the cation exchange.

The cation compositions ($NH_4^+$, $Cs^+$) as reported in Table 1 were determined by application of ion chromatography. Analyses were made with a Dionex Series 4500i ion chromatograph equipped with a conductivity detector using the Dionex Fastcation separation columns and an eluant consisting of 20 m$M$ HCl and 0.3 m$M$ DAP. Background conductivity suppression was achieved using a cation micromembrane suppressor column and the closed loop Autoregen system with 0.1 $M$ tetrabutylammonium hydroxide as the regenerant. Chromatograms were recorded on a Spectra-Physics ChromJet integrator. All reported results are the mean of at least two measurements. The samples were heated at 533K for 2h to remove any remaining adsorbed water. The details of the analytical procedure were recently described (30).

Catalytic reactions were carried out using a continuous flow microcatalytic reactor. The body of the reactor system was constructed from 1/8″ stainless steel tubing (0.02″ wall thickness). The reactor tubes were constructed from Pyrex tubing (6 mm OD, 4 mm ID) of length 20 cm. The catalyst bed of approximately 50 mg was supported between two Pyrex wool plugs.

The isobutyric acid was introduced into the reactor by passing helium gas through two thermostatted saturators connected in series. Oxygen was introduced downstream and its flow was again regulated using needle valves.

The exit flow from the reactor passed through two Valco 6-port sampling valves which were connected in series and equipped with 5-mL sample loops. The analyses were made using a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) and two injection ports. A 30-m DBFFAP capillary column (J and W Scientific) was connected to the FID detector and was used to separate propene, acetone, methacrylonitrile, isobu-

tyronitrile, acetic acid, isobutyric acid, and methacrylic acid. Detector responses were measured using an HP-3392 A integrator. A 10' × 1/8" Carbosieve S II packed column (100/120 mesh Supelco) was used for the separation of $O_2$, CO, and $CO_2$. Detector responses were measured using a Spectra-Physics ChromJet integrator. The water produced in the course of the reaction was not quantified. Analyses were made simultaneously by making concurrent switches of the two sampling valves. Satisfactory separations of the various components were obtained using the following temperature program: (i) 5.5 minutes 100°C; (ii) ramp at 25°C $min^{-1}$ to 175°C; and (iii) hold 8 minutes. All sections of the reactor system through which IBA or MAA flowed were heated to temperatures >170°C to preclude condensation of these high boiling materials.

Isobutyric acid purchased from Aldrich (Gold Label 99+ %) and from Fluka were both found to contain significant quantities of impurities when introduced into the reaction system from the saturators. The isobutyric acid was purified following the method of Khosla and Widom (32). Approximately 200 mL of IBA was placed in a 500-mL round bottomed flask with 8 KOH pellets and was swirled constantly for 3 min. The IBA was decanted from the KOH and transferred to a clean 500-mL flask. Anhydrous $Na_2SO_4$ was added and the mixture swirled periodically for 15 min. The IBA was filtered and placed in a distillation flask with a column approximately 1 m in length and 5 cm in diameter and an insulated vacuum jacket that was packed with glass rings of 1-cm diameter.

The IBA was heated slowly and small quantities of fractions at 63, 74, and 120°C were distilled over. No additional fractions were observed until the temperature reached 154.5°C and this material was collected until approximately 25 mL of material remained in the distillation flask.

Mass balances were calculated on a carbon account basis and were usually better than 90%. In most cases the mass balance

increased as the reaction time progressed. The imprecision is believed to arise from degradation of the reactant on the catalyst surface.

Following an initial pretreatment in flowing helium (35 mL $min^{-1}$) at 300°C for 1 h, the reaction temperature was 250 or 300°C. For reactions at 350°C a pretreatment temperature of 350°C was employed. Steady state was generally reached within 4 h. The conversion of IBA was calculated as

$$\text{Conv} = 100 \left( 1 - \left[ \frac{\text{moles of unreacted IBA}}{\text{moles of IBA introduced}} \right] \right),$$

in which the moles of IBA introduced was determined by measuring the quantity of IBA through the reactor bypass section.

Selectivities of the various products were determined as

$$\text{Sel} = 100 \left[ \frac{\text{moles of component } i}{\text{total moles of products}} \right].$$

The contact time, or apparent residence time, was defined as the weight of catalyst/total flow rate across the catalyst (mg min $mL^{-1}$). The $O_2$/IBA molar ratio of 2.65/1 avoided oxygen starvation conditions. Apparent residence times of approximately 0.85 and 1.45 mg min $mL^{-1}$ were employed at each of the three reaction temperatures, 250, 300, and 350°C.

## RESULTS

*Unexchanged $(NH_4)_3PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$ and the Parent Acid, $H_3PMo_{12}O_{40}$*

To establish appropriate benchmarks for comparison purposes, the ammonium and cesium salts of 12-molybdophosphoric acid were prepared by a precipitation procedure from the parent acid and were employed in unexchanged form together with the parent acid as catalysts in the IBA conversion studies. The selectivities for MAA, propene, and acetone at three different temperatures are shown in Figs. 1 (a–c) for $W/F = 0.85$ and
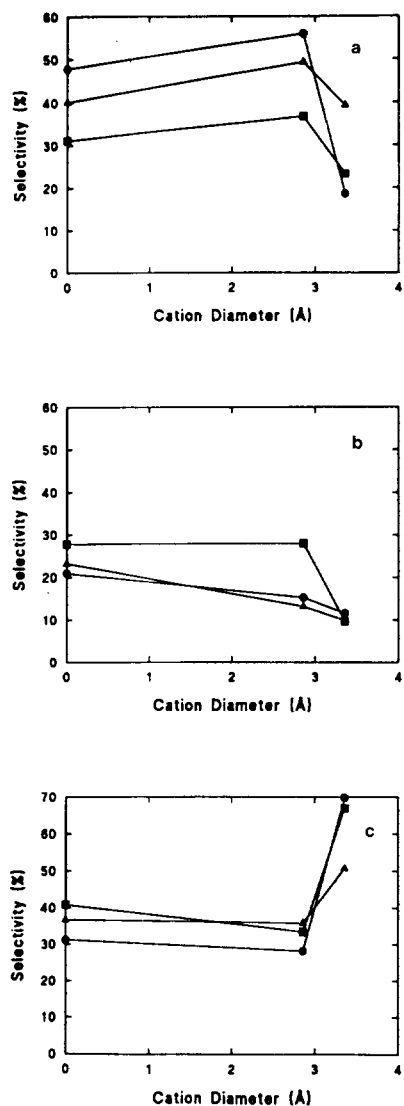
for $W/F$ = 1.45 in Table 2. It is evident that the cation associated with the $PMo_{12}O_{40}^{-3}$ anion affects the product selectivity considerably. At each temperature, the selectivity to MAA is highest for the ammonium salt (cation diameter = 2.86 Å), while the lowest selectivity for MAA is obtained for the ce-

sium salt (cation diameter = 3.34 Å). Interestingly, the MAA selectivity obtained with the unexchanged ammonium salt and the parent acid are quite similar. The differences between the three materials are also reflected in the selectivities to acetone, which show the cesium salt possesses the highest acetone selectivity and the ammonium salt the lowest. Propene selectivity was found to be highest for $H_3PMo_{12}O_{40}$ and lowest for $Cs_3PMo_{12}O_{40}$. While the selectivities to acetone and propene increase with increase in temperature from 250 to 350°C, those to MAA decrease. The cesium salt is evidently a less effective catalyst than either $H_3PMo_{12}O_{40}$ or its ammonium salt for the oxidative dehydrogenation of IBA.

It should also be noted that small quantities of nitriles, in particular isobutyronitrile and methacrylonitrile, were observed in the products from the ammonium salts, both as precipitated and in ion exchanged form, but not, of course, where the ammonium ion was absent.

## Cesium and Ammonium Self Exchanged Salts

Deviations from stoichiometry and the presence of residual protons have been observed in previous studies of 12-heteropoly salts (30, 33) and the Brønsted acidity was shown to be an important feature of the catalytic activity of 12-tungstophosphate salts for the methanol to hydrocarbons conversion process (33). To investigate the role of the proton in the oxidative dehydrogenation of IBA to MAA, the self exchanged salts were examined. Studies in which the residual protons are exchanged by cations of the same type as those in the unexchanged solid provide information on the effect of proton removal without the addition of a second cation.

Figures 2 and 3 show the selectivities to MAA, propene, and acetone at 300°C and $W/F$ = 0.85 for exchanges with the cesium and ammonium series of self exchanged materials, respectively. It is evident that the first exchange is the more important, consis-

TABLE 2

Selectivities[a] to Major Products over Various 12-Heteropoly Compounds

| Compound | $\sim W/F^b$ | 250°C | | | 300°C | | | 350°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | MAA | Propene | Acetone | MAA | Propene | Acetone | MAA | Propene | Acetone |
| $H_3PMo_{12}O_{40}$ | 1.45 | 49.8 | 20.3 | 29.3 | 43.8 | 21.2 | 34.6 | 36.4 | 24.6 | 38.7 |
| $(NH_4)_3PMo_{12}O_{40}$ | 1.45 | 58.1 | 14.4 | 26.8 | 55.8 | 10.4 | 32.1 | 42.6 | 20.6 | 36.0 |
| $Cs_3PMo_{12}O_{40}$ | 1.45 | 17.5 | 11.3 | 71.2 | 40.1 | 9.9 | 49.0 | 24.7 | 11.4 | 63.2 |

*Note.* Data for $W/F$ equal to 0.85 can be found in Fig. 1.

[a] mole %.

[b] mg min mL$^{-1}$.

tent with the recently reported observations concerning the changes in concentration of the entering and leaving cations (*30*). At all reaction temperatures studied, but particularly at 250 and 300°C, the selectivity to acetone increases markedly after one exchange of cesium into CsPMo, while that to MAA decreases proportionately (Tables 2 and 3). In contrast, there are little or no changes in the production of propene except at the highest reaction temperature. The results for the higher residence time (Table 3) are qualitatively similar with differences in the actual selectivities as would be expected. Inspection of the data for the CsPMoCs5 catalyst which had been ion exchanged five times shows a further decline in the MAA selectivity with a concomitant increase in acetone selectivity. At 250 and 300°C the selectivity to propene decreases marginally with increased exchange number, while at 350°C a maximum in the selectivity to propene is evident for the CsPMoCs1 salt.

The effect of the self exchange procedure on the selectivities to the three products with the ammonium salts is less dramatic.
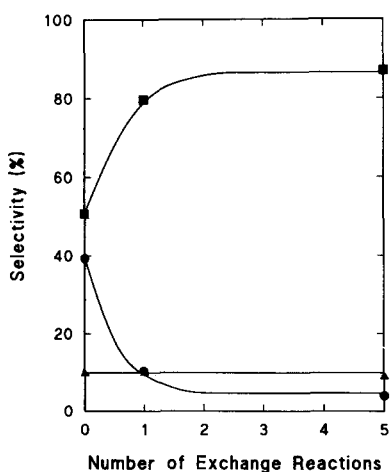


FIG. 2. Selectivities to methacrylic acid, propene, and acetone as a function of the number of exchange reactions for CsPMoCsn ($W/F = 0.85$ mg min mL$^{-1}$) at 300°C: ● methacrylic acid, ▲ propene, ■ acetone.
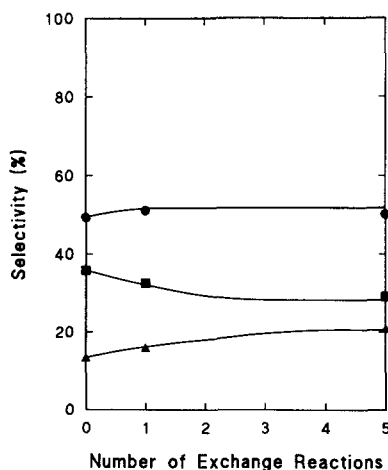


FIG. 3. Selectivities to methacrylic acid, propene, and acetone as a function of the number of exchange reactions for $NH_4PMoNH_4n$ ($W/F = 0.85$ mg min mL$^{-1}$) at 300°C: ● methacrylic acid, ▲ propene, ■ acetone.

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TABLE 3

Selectivities[a] with Self Exchanged 12-Heteropoly Oxometalate Salts

| Compound | $\sim W/F^{b}$ | 250°C | | | 300°C | | | 350°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | MAA | Propene | Acetone | MAA | Propene | Acetone | MAA | Propene | Acetone |
| $NH_4PMoNH_41$ | 0.85 | 55.2 | 17.2 | 27.5 | c | c | c | 38.1 | 27.8 | 33.5 |
| | 1.45 | 49.6 | 20.7 | 29.3 | 52.8 | 13.2 | 33.2 | 34.5 | 26.3 | 38.5 |
| $NH_4PMoNH_45$ | 0.85 | 53.4 | 20.4 | 26.2 | c | c | c | 36.9 | 28.3 | 34.2 |
| | 1.45 | 53.1 | 19.8 | 26.7 | 53.4 | 13.6 | 32.3 | 39.5 | 25.7 | 34.1 |
| CsPMoCs1 | 0.85 | 3.0 | 9.0 | 87.9 | c | c | c | 13.5 | 18.0 | 68.4 |
| | 1.45 | 3.6 | 9.3 | 87.0 | 10.4 | 11.5 | 78.0 | 13.1 | 19.0 | 67.4 |
| CsPMoCs5 | 0.85 | 11.6 | 8.2 | 80.1 | c | c | c | 10.0 | 11.8 | 78.1 |
| | 1.45 | 1.8 | 5.1 | 93.0 | 4.2 | 7.9 | 87.8 | 8.5 | 14.7 | 75.4 |

[a] mole %.
[b] mg min mL$^{-1}$.
[c] See Figs. 2–5.

As is illustrated in Fig. 3, the selectivities for the three products at 300°C change very little as the exchange process proceeds. This type of behavior was also observed at 250 and 350°C for each of the residence times that were studied. Unlike the Cs$^+$ self exchanged system for which the introduction of additional cesium ions led to significant changes in the product selectivities, the replacement of protons with ammonium ions does not significantly alter the quantities of the various products which form. However, it is important to note that, in contrast to the observations with the cesium self exchanged solids, with the ammonium salts the MAA and acetone increase and decrease, respectively.

## $NH_4^+/Cs^+PMo_{12}O_{40}^{-3}$ Ion Exchange Species

The oxidative dehydrogenation of isobutyric acid to methacrylic acid was studied on catalyst samples which were prepared via ion exchange modification of the unexchanged salts $(NH_4)_3PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$ with $CsNO_3$ and $NH_4NO_3$, respectively, to determine the effect of the two cations and their concentrations on the catalytic behavior of the salts. In order to assess the effects of the ion exchange modification, four catalysts were examined and

the results were compared with the corresponding unexchanged solids, NH$_4$PMo and CsPMo. NH$_4$PMoCs1 and NH$_4$PMoCs6 were prepared by exchanging NH$_4$PMo once and six times, respectively, with CsNO$_3$, while CsPMoNH$_4$1 and CsPMo NH$_4$6 were prepared by similarly exchanging CsPMo with NH$_4$NO$_3$ once and six times, respectively.

Figures 4 and 5 show the product selectivities for the NH$_4$PMoCs salts and the CsPMoNH$_4$ salts after successive ion exchange modifications for $W/F = 0.85$ mg min mL$^{-1}$ and a reaction temperature of 300°C. The results for the higher residence time employed in the present work displayed similar behavior as the number of exchange reactions increased (Table 4). As reported previously (30), significant quantities of cesium ions (40–50%) were exchanged into the ammonium salt after a single exchange reaction, while only small quantities of ammonium ions were capable of exchanging with the cesium ions of the unexchanged salt (30). At a given temperature an increase of the cesium content reduces the selectivity to MAA by less than 10% except for the investigations at 350°C, and the higher residence time where the decrease in MAA selectivity was approximately 20% (Table 4). At 250
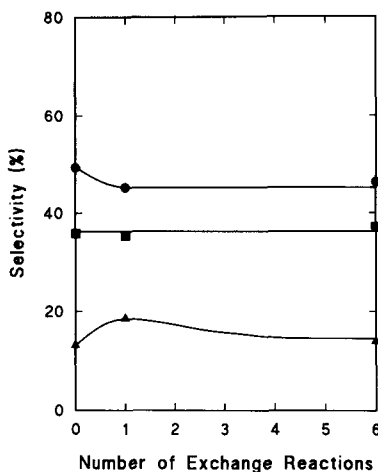
FIG. 4. Selectivities to methacrylic acid, propene, and acetone as a function of the number of exchange reactions for $NH_4PMoCsn$ ($W/F = 0.85$ mg min $mL^{-1}$) at 300°C: ● methacrylic acid, ▲ propene, ■ acetone.

and 300°C the acetone and propene selectivities were also quite constant as the number of exchanges with cesium increased. At 350°C, the decrease in the selectivity to MAA and acetone was accompanied by increases in the selectivity to propene. Interestingly, for this series of materials, the largest, albeit still quite small, selectivity to nitriles was observed at 350°C.

The changes in selectivities where $NH_4^+$ ions have been exchanged into the cesium salt are somewhat more significant. The exchange of ammonium ions into the cesium salt produces increases in the MAA selectivity while the acetone selectivity decreases approximately proportionately. The most significant effects were observed at 250 (Fig. 5) and 350°C, but similar behavior was observed for all of the conditions that were studied. The large differences in the behavior of the two exchange systems indicates that the ammonium ion, even in small quantities, has a beneficial or promotional effect as compared to the cesium ion. The selectivity to propene increases after one exchange for all temperatures, most significantly at 250°C, and either decreases slightly after six exchanges (reaction temperature of 250°C)

or increases slightly after the same number of exchanges for the two higher temperatures. The conversion data for the exchanged materials suggests that the presence of only small quantities of ammonium ions is sufficient to increase the activity of the catalysts (Table 5). The cesium salts exchanged with ammonium had conversions that were higher than for those which had been self exchanged with cesium. In addition, the ammonium salts which had been exchanged with cesium ions appeared to be more stable toward deactivation than those ammonium salts which had been self exchanged.

In order to assess the influence of oxygen in the reactant stream on the product distributions, experiments were carried out in which oxygen was excluded from the feed. Each of the catalysts displayed catalytic activity for the IBA to MAA process, as well as for the formation of side reaction products. The initial product selectivities are listed in Table 6. The formation of the same products both in the presence and absence of co-fed oxygen suggests that lattice oxygen atoms of the catalyst must participate in the process. As the duration of the experi-
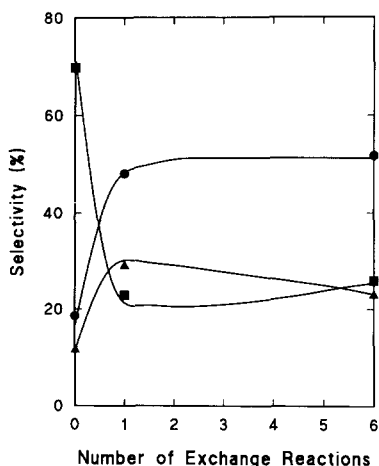


FIG. 5. Selectivities to methacrylic acid, propene, and acetone as a function of the number of exchange reactions for $CsPMoNH_4n$ ($W/F = 0.85$ mg min $mL^{-1}$) at 250°C: ● methacrylic acid, ▲ propene, ■ acetone.

TABLE 4

Selectivities[a] for Ion Exchanged 12-Heteropoly Oxometalate Salts

| Compound | $\sim W/F^b$ | 250°C | | | 300°C | | | 350°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | MAA | Propene | Acetone | MAA | Propene | Acetone | MAA | Propene | Acetone |
| NH$_4$PMoCs1 | 0.85 | 51.5 | 17.0 | 31.0 | c | c | c | 30.0 | 45.3 | 24.3 |
| | 1.45 | 60.7 | 13.6 | 25.1 | 47.4 | 13.4 | 36.7 | 35.5 | 37.3 | 26.5 |
| NH$_4$PMoCs6 | 0.85 | 54.1 | 17.8 | 27.6 | c | c | c | 30.4 | 46.0 | 21.4 |
| | 1.45 | 49.8 | 16.8 | 33.5 | 53.3 | 14.8 | 30.3 | 25.8 | 36.2 | 36.5 |
| CsPMoNH$_4$1 | 0.85 | c | c | c | 41.5 | 14.8 | 42.9 | 41.3 | 13.2 | 43.2 |
| | 1.45 | 48.1 | 32.2 | 19.1 | 48.1 | 15.1 | 35.5 | 43.4 | 11.0 | 42.2 |
| CsPMoNH$_4$6 | 0.85 | c | c | c | 48.8 | 17.8 | 32.5 | 42.0 | 17.5 | 37.8 |
| | 1.45 | 49.8 | 25.3 | 24.4 | 56.3 | 12.8 | 29.5 | 48.5 | 12.6 | 29.0 |

[a] mole %.
[b] mg min mL$^{-1}$.
[c] See Figs. 4, 5.

ments increased, changes were observed in the product distributions with the production of MAA decreasing to a negligible amount following four hours on stream. This is apparently a result of the depletion of lattice oxygens and the destruction of the Keggin anion. The gaseous oxygen in the feed stream apparently serves as an oxygen source for the reoxidation of the catalysts.

In contrast to the observations noted in the previous paragraph, ion chromatographic analysis, X-ray diffractometry, and infrared spectrometry showed no evidence of the decomposition of the heteropoly anion after either the ion exchange experiments or the reaction studies in the presence of oxygen.

DISCUSSION

The results of the present studies indicate that both the nature of the cations and their concentrations in the heteropoly salt play an important role in the catalyst selectivity.

The studies of the catalytic behavior of $H_3PMo_{12}O_{40}$, $(NH_4)_3PMo_{12}O_{40}$, $Cs_3PMo_{12}O_{40}$, the self exchanged, and the salts exchanged with other cations serve to indicate the strong role that is played by the cations in the IBA to MAA process. The stoichiometries of the ammonium and cesium unex-

TABLE 5

Conversions of IBA[a] for 12-Heteropoly Salts

| Compound | $\sim W/F^b$ | 250°C | 300°C | 350°C |
|---|---|---|---|---|
| $H_3PMo_{12}O_{40}$ | 0.85 | 11.7 | 43.0 | 88.3 |
| | 1.45 | 13.1 | 60.0 | 94.0 |
| $(NH_4)_3PMo_{12}O_{40}$ | 0.85 | 48.0 | 76.0 | 88.1 |
| | 1.45 | 48.5 | 71.0 | 83.4 |
| $Cs_3PMo_{12}O_{40}$ | 0.85 | 11.6 | 20.6 | 43.1 |
| | 1.45 | 5.7 | 23.5 | 35.6 |
| NH$_4$PMoNH$_4$1 | 0.85 | 40.9 | 65.0 | 74.4 |
| | 1.45 | 40.1 | 74.6 | 67.9 |
| NH$_4$PMoNH$_4$5 | 0.85 | 18.2 | 19.6 | 70.9 |
| | 1.45 | 28.8 | 59.0 | 79.7 |
| NH$_4$PMoCs1 | 0.85 | 65.5 | 89.6 | 96.8 |
| | 1.45 | 67.4 | 96.0 | 95.9 |
| NH$_4$PMoCs6 | 0.85 | 58.5 | 79.5 | 92.8 |
| | 1.45 | 91.3 | 84.9 | 99.0 |
| CsPMoCs1 | 0.85 | 3.9 | 21.4 | 25.6 |
| | 1.45 | 8.5 | 11.3 | 33.2 |
| CsPMoCs5 | 0.85 | 6.2 | 24.4 | 30.6 |
| | 1.45 | 7.6 | 22.7 | 40.6 |
| CsPMoNH$_4$1 | 0.85 | 43.4 | 75.0 | 99.6 |
| | 1.45 | 31.5 | 60.0 | 99.3 |
| CsPMoNH$_4$6 | 0.85 | 61.6 | 58.3 | 86.1 |
| | 1.45 | 40.2 | 94.8 | 98.7 |

[a] mole %.
[b] mg min mL$^{-1}$.

TABLE 6

Selectivities[a] to Products over 12-Heteropoly Compounds in the Absence of Oxygen

| Compound | MAA | Propene | Acetone | Nitriles |
|---|---|---|---|---|
| $H_3PMo_{12}O_{40}$ | 11.0 | 74.9 | 13.0 | — |
| $(NH_4)_3PMo_{12}O_{40}$ | 2.0 | 86.0 | 3.0 | 8.0 |
| $Cs_3PMo_{12}O_{40}$ | 11.0 | 4.0 | 86.5 | — |
| $NH_4PMoNH_41$ | 5.5 | 81.5 | 3.0 | 8.5 |
| $NH_4PMoNH_45$ | 17.5 | 54.0 | 5.0 | 22.0 |
| CsPMoCs1 | 23.5 | 6.0 | 70.0 | — |
| CsPMoCs5 | 8.8 | 5.8 | 84.3 | — |
| $NH_4PMoCs1$ | 10.0 | 78.0 | 4.0 | 5.5 |
| $NH_4PMoCs6$ | 1.0 | 91.0 | 3.0 | 5.0 |
| $CsPMoNH_41$ | 31.5 | 19.0 | 51.0 | — |
| $CsPMoNH_46$ | 10.0 | 84.5 | 5.0 | 1.0 |

Note. All experiments at 300°C and $W/F$ ~0.85 mg min mL$^{-1}$.

[a] mole %.

changed salts used for the ion exchange modification were reported, and the cesium salt was found to be a more nearly stoichiometric material than the ammonium salt (Table 1). The similarity in the selectivities of the parent acid and ammonium salt suggest that either the ammonium ion and proton perform similar functions in the oxidative dehydrogenation of IBA, or the number (or distribution of strengths) of residual protons in the ammonium salt is sufficiently similar to the number of protons in the parent acid that the catalytic behavior is similar. The cesium salt behaves in a somewhat different manner which may reflect the difference in the number or distribution of acidic protons. It is also possible that the Cs$^+$ cations exert an influence on the reactivity of the 12-molybdophosphate anion. The conversion of IBA on the salts also points out differences between the materials. For each of the salts, the conversion increases with increasing temperatures (Table 5). The similarity between the ammonium salt and parent acid in contrast with the cesium salt is again evident from a comparison of the conversions. Regardless of the temperature, the conversion on the cesium salt is lower than the conversion over the acid or ammonium salt by a factor of approximately two.

The studies of the self exchanged materials provide information regarding the role of protons in the IBA to MAA process. For the cesium series of self exchanged salts it can be argued that the observed changes in the product selectivities result from the removal of the protons from the system through the ion exchange modification process. For the cesium salts, the number of cesium ions per Keggin unit was found to increase as the number of exchange reactions increased (30). If the number of associated protons is estimated to be the difference between the number of cations and the expected quantity of three cations per anion for a stoichiometric salt, then the proton content can be envisioned as being lower for the species that have undergone the self exchange process than for the unexchanged salt. Evidently the presence of protons, at least in certain quantities, has a positive effect on the conversion of IBA to MAA.

The self exchanged ammonium salts displayed a reduced dependence on the number of exchange reactions. A number of explanations are available for the similarities in the selectivities to MAA, propene, and acetone. It may be proposed that the nature of the cation has no effect on the catalytic behavior of the 12-molybdophosphate anion toward the oxidative dehydrogenation of IBA to MAA. This can be discounted based on the differences in the product distributions and selectivities over the ammonium and cesium catalysts. The cesium results indicate that the mode of participation of H$^+$ and Cs$^+$ in the IBA to MAA process is significantly different. Further, relatively large numbers of residual protons may remain even following several self exchange reactions with ammonium ions. Analytical data have shown that the ammonium salt of the 12-molybdophosphate anion had a stoichiometry that deviated from the expected three cations per anion to a greater extent than the corresponding potassium and cesium salts (30).
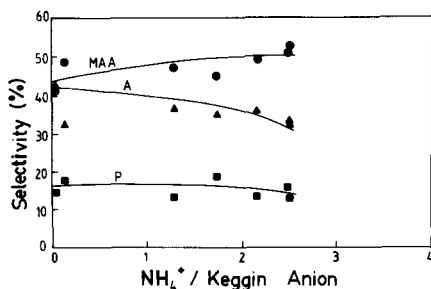
FIG. 6. Selectivity to methacrylic acid (●), propene (■), and acetone (▲) as a function of the number of $NH_4^+$ cations per Keggin anion ($W/F$ = 0.85 mg min mL$^{-1}$) at 300°C.

If the deactivation of the catalyst is related to the change in the conversion of the reactant molecules, then some interesting observations can be made. The participation of the ammonium ion does not appear to result in significantly higher catalyst deactivation for the NH$_4$PMo salt as compared to the parent acid. The apparent deactivation of these materials is, however, somewhat greater than for the cesium salt. This could be attributed to either an enhanced thermal stability for the cesium salt or the fact that there are fewer protons in the Cs$^+$ salt to participate in reactions.

It is instructive to examine the dependence of the selectivities to the major products, MAA, propene and acetone on the concentrations of cations (Cs$^+$ or NH$_4^+$) that exist in the solid (Figs. 6, 7). At 250 and 300°C the selectivity towards MAA is in general constant and apparently, relatively independent of the NH$_4^+$ content (Fig. 6). The negative effect of temperature for MAA selectivity is not observed until a reaction temperature of 350°C is reached, and slight decreases in the MAA selectivity are evident particularly at higher ammonium ion contents.

The selectivities to propene show a stronger dependence on the reaction temperature. At 250°C the selectivity to propene decreases marginally as the ammonium content of the salt is increased, while at 300°C

little if any dependence is observed as the ammonium content of the salts is changed (Fig. 6). The propene selectivity at 350°C passes through a maximum for the samples with approximately 1.5 NH$_4^+$ cations per anion. The maximum coincides with a minimum in the selectivity toward acetone, suggesting that the production of propene occurs at the expense of acetone. Conversely, the trend toward lower propene selectivity as the ammonium content increases at 250°C is mirrored by slight increases in the acetone selectivity. Similar to both the MAA and propene selectivities at 300°C, the acetone selectivity is essentially independent of the ammonium ion content (Fig. 6).

The MAA selectivity shows a strong dependence on the concentration of cesium cations in the 12-heteropoly salts. At 250 and 300°C, the introduction of NH$_4^+$ cations and concurrent removal of cesium ions leads to dramatic increases in the MAA selectivity (Fig. 7). At 350°C there is an initial increase in the MAA selectivity as the cesium content decreases, followed by a subsequent decrease in the MAA selectivity as the cesium content is further decreased. The increase in the selectivity to MAA at 300°C is apparently strongly related to the decrease in the selectivity to acetone (Fig. 7) as the
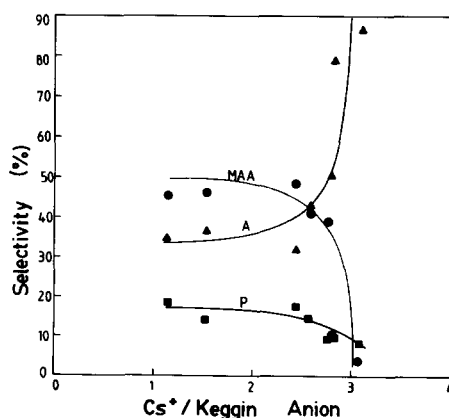


FIG. 7. Selectivity to methacrylic acid (●), propene (■), and acetone (▲) as a function of the number of Cs$^+$ cations per Keggin anion ($W/F$ = 0.85 mg min mL$^{-1}$) at 300°C.

cesium content decreases, since at this temperature the propene selectivity is relatively constant (Fig. 7). The initial increase in the MAA selectivity at 350°C can again be related to the decrease in the acetone selectivity. No obvious explanation for the trend in propene selectivity is apparent, as the MAA and acetone selectivities show rather regular increases and decreases, respectively.

The correlations between the selectivities to products and the cation composition of the catalysts serve to underscore the importance of the cation in the process. While it is obvious that the Keggin anion is necessary for the IBA process to proceed, the results indicate that the cations also play a very important role. The effect may result from the interaction of the cationic species with the Keggin anion. The cesium ion can be considered to be a stable species that apparently stabilizes the salt and leads to an enhanced thermal stability. Protons and ammonium ions, on the other hand, are more reactive species, and as such, are presumably able to interact with both the anion and the IBA to a greater extent. The direct interaction of the ammonium ions with the IBA is of interest as DTA studies indicated that $(NH_4)_3PMo_{12}O_{40}$ is stable up to 450°C (25, 34). In addition, studies of the reactions of methanol and ethanol over $NH_4PMo$ and the corresponding 12-tungstophosphate salts did not report the direct interaction of the ammonium ion (25). The correlations of the MAA selectivity as a function of the cesium content clearly show the enhancing effect of the incorporation of ammonium cations into the salts (Fig. 7). The MAA selectivity when considered as a function of the ammonium content is much less dependent on the cation composition, indicating that only relatively few ammonium ions appear to be required to enhance the process.

Consideration of the acetone and propene selectivities also emphasizes the effect of the cation content on the formation of these products. The dependence of the acetone and propene selectivities is much greater if the cesium content is considered rather than

the ammonium content (Fig. 7 as compared with Fig. 6). The correlations as a function of the ammonium content once again show that the presence of ammonium ions, in almost any amount, leads to catalysts with very similar catalytic behavior. The selectivity for propene and acetone show much stronger dependencies on the $Cs^+$ content as shown in Fig. 7. In essence, the acetone selectivity is inversely related to the MAA selectivity, i.e., increases in MAA selectivity are accompanied by concurrent decreases in the acetone selectivity. These strong correlations indicate that a common intermediate exists in the formation of these two species. The correlations also suggest that cesium ions promote the formation of the reactive species that interacts with the IBA intermediate to yield acetone. Ammonium ions appear to suppress this reaction or alternatively, enhance a competing reaction.

Since cesium incorporation in the ammonium salt has only a small effect (Fig. 4), even when the $Cs^+$ concentration is on the order of 1.5 per Keggin anion, the positive effect of the remaining ammonium ions must be considered to be significant. Interestingly, the selectivities to MAA for the $NH_4PMoCs6$ and $CsPMoNH_46$ samples at 250 and 300°C are quite similar (Table 4). This suggests that at these temperatures only small quantities of ammonium ions are required to maximize the selectivities for the $Cs^+/NH_4^+$ exchange system. At 350°C the MAA selectivity is higher for the $CsPMoNH_46$ sample than the $NH_4PMoCs6$ sample, indicating that the additional cesium ions in the former may assist in thermal stabilization of the salt. Finally, it may be noted that the exchange of $NH_4^+$ ions into the cesium salt results in MAA selectivities which are very similar to those for the self exchanged ammonium salts. Once again, this suggests that only small quantities of the ammonium ions are required to maximize the MAA selectivity for the $NH_4^+/Cs^+$ cation salts.

Studies of 12-heteropoly oxometalate

salts have shown that sample homogeneity can depend on the method of preparation of the samples. Precipitation reactions have been used extensively for the formation of such salts which have been found to consist of a single phase by powder X-ray diffraction (24, 35). Other studies which investigated the effect of proton content on the oxidation of acrolein to acrylic acid over $K_{3-x}H_x PMo_{12}O_{40}$ samples found that some samples behaved as if a layer of the heteropoly acid coated the insoluble heteropoly salt like a support (21). The samples in the present study were examined using powder X-ray diffraction measurements (31). Each of the samples was found to consist of a single phase with no evidence of addition heteropoly compounds. It should be noted that a single crystal X-ray diffraction study of ion exchanged $K^+/NH_4^+/PMo_{12}O_{40}^{-3}$ salts reported only a single phase (36).

As discussed previously, the 12-heteropoly salts are often found to contain significant numbers of residual protons even when prepared with stoichiometric quantities of the cation (31, 33, 37). The influence of the protons has also been observed in oxidation processes over heteropoly oxometalate salts. Studies of the oxidation of acrolein to acrylic acid over a series of $K_xH_{3-x}PMo_{12}O_{40}$ salts have indicated that neither the parent acid nor the stoichiometric salt is the most selective catalyst (21b, d). Instead, the salts which are substoichiometric showed higher selectivity, with the $K_{2.5}H_{0.5}PMo_{12}O_{40}$ salt the most selective catalyst. A similar investigation of the cesium salts of the $PMo_{10}V_2O_{40}^{-5}$ anion also showed that while the parent acid was not the most selective catalyst towards MAA production, neither was the stoichiometric salt (11c). This reaffirms the involvement of protons in the IBA oxydehydrogenation process.

Kasztelan and Moffat have proposed the involvement of protons in the partial oxidation of methane over silica supported 12-molybdophosphoric acid and salts (23c, d). Their studies showed that as the number of cesium cations per Keggin unit increased, up to a cesium loading of approximately 3.5 per anion, there were concurrent decreases in the selectivity to formaldehyde, oxidant ($N_2O$) turnover rate, and amount of oxygen consumed in reoxidation processes. Little variation in these quantities was observed at successively higher cation loadings. The cesium content after which no further changes took place, corresponded well with the formation of a stoichiometric heteropoly salt. It was proposed that, for materials containing protons, a mechanism whereby oxygen vacancies formed was possible through the dehydration mechanism

$$2 \text{ KUOH} \rightarrow \text{KUO} + \text{KU} \square + \text{H}_2\text{O},$$
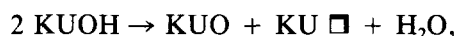
in which protons extract oxygen atoms from the heteropoly anion to release water and form one anion deficient of one proton and a second anion containing a vacancy or empty site. The role of the vacancy can be envisioned as functioning as a participant in one or more of several processes. Dissociation of a gas phase oxidant to replace the oxygen atom removed from the Keggin anion is one possibility that certainly exists. Alternatively, reactant molecules may find the vacancy to be a favorable adsorption site on the catalyst surface. A third mechanism, proposed by Goodenough and co-workers, suggests that oxygen molecules may adsorb in the vacancy as a peroxide species, which may lead to deep oxidation products because of the expected higher activity of such a species (21c).

While the self exchange process does increase the number of cesium cations in the structure, the uptake may result from the filling of empty cation sites or, alternatively, the uptake may not result in a 1 : 1 removal of residual protons. It has been established that heteropoly acids and salts possess distributions of acid strengths (24, 26, 37). The distributions of acid strengths for different materials have been found to depend on the cation and the pretreatment temperature. In addition to changes in the number of acid sites (protons) it is conceivable that the dis-

TABLE 7

Surface Areas of Catalysts Used for the Oxidative
Dehydrogenation of Isobutyric Acid

| Compound | Surface Area ($m^2g^{-1}$) |
|---|---|
| $H_3PMo_{12}O_{40}$ | ~5.0 |
| $(NH_4)_3PMo_{12}O_{40}$ | 88.5 |
| $Cs_3PMo_{12}O_{40}$ | 144.1 |
| $NH_4PMoNH_41$ | 88.0 |
| $NH_4PMoNH_45$ | 75.7 |
| $NH_4PMoCs1$ | 137.5 |
| $NH_4PMoCs6$ | 85.7 |
| $CsPMoCs1$ | 88.5 |
| $CsPMoCs5$ | 41.3 |
| $CsPMoNH_41$ | 110.0 |
| $CsPMoNH_46$ | 60.2 |

tribution of such sites shifts in such a way that a detrimental or negative effect is introduced as the self exchange with cesium proceeds.

It has been shown that the surface area and pore structure of the 12-heteropoly oxometalate salts is strongly affected by the choice of the cation (34, 38) as well as the exchange of different cations into and out of the secondary structure (31). The surface areas of the catalysts used in the study of the oxidative dehydrogenation of IBA are listed in Table 7. Inspection of these quantities and consideration of the results of the catalytic tests indicate that the nature of the pore structure is less important for this process than the nature of the cation composition. By considering the behavior of the parent acid, $H_3PMo_{12}O_{40}$, and the cesium and ammonium salts (unexchanged, self exchanged, and exchanged with the other of the two cations) some interesting conclusions can be drawn regarding the IBA interaction with the catalyst.

The surface area of HPMo and the two virgin monovalent salts differ by approximately one order of magnitude (Table 7). In contrast to this observation, however, the selectivities to MAA, acetone, and propene over the parent acid and the ammonium salt are remarkably similar. This is in marked contrast to the differences reported for the methanol to hydrocarbon process (24) over

the acid and ammonium forms of the 12-tungstophosphate anions, where the methanol has been shown to interact with both the bulk and surface protons. On the former catalyst, the total yield of hydrocarbons was 32% as opposed to 77% over the latter salt. Since conversions were high over both materials, the lower yield was attributed to carbonization over the more highly acidic surface of the parent acid. Additionally, the ammonium salt was shown to possess a high surface area and significant micropore volume, while the parent acid was found to be nonporous (35). The product distribution over the ammonium salt showed a higher proportion of saturated species and species of higher carbon number, indicating the better hydrogen transfer capabilities of the catalyst.

The apparent lack of dependence of the oxidative dehydrogenation process on the surface area of the catalyst serves to show the largely different requirements for the two types of reactions. Whereas the pore structure is expected to be an important controlling factor in chain growth processes, it is not necessarily so for processes such as the one under discussion. Polar molecules such as alcohols have been shown to diffuse into the bulk of the heteropoly compounds (29, 33, 39), as have some carboxylic acids (39). This suggests that the isobutyric acid can react on the surface or in the bulk of the catalyst. From the similarities in the selectivities of the parent acid and ammonium salts, it is evident that the oxidative dehydrogenation reaction is not a shape selective process.

Conceptually the oxidative dehydrogenation of IBA to MAA is a simple process, and in the presence of oxygen the stoichiometric equation can be written

$$(CH_3)_2CHCOH + \tfrac{1}{2}O_2 \rightarrow CH_2$$
$$= \underset{\overset{|}{CH_3}}{C}COH + H_2O.$$
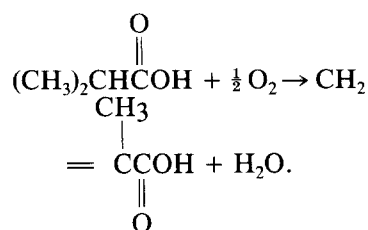
The present and earlier studies have shown that lattice oxygen atoms of the Keggin anion are direct participants in the reaction. The current study has shown that, even in the absence of co-fed oxygen, MAA is produced over the 12-molybdophosphate anion. Other studies have shown that gas phase oxygen is able to replace the lattice oxygen that was removed following reduction processes (*15b*).

Otake and Onoda have proposed a heterolytic process in which lattice oxygen atoms are not removed from the surface of the anion but participate nonetheless (*8a*). A second mechanism for the IBA oxidative dehydrogenation was proposed by Echigoya and co-workers to involve a homolytic process (*9a, b, c*).
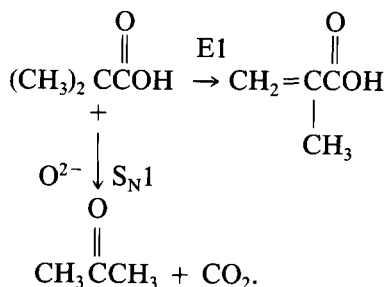
Ai has also studied the process over the $H_5PMo_{10}V_2O_{40}$ heteropoly acid and a $V_2O_5$–$P_2O_5$ catalyst (*7*). He proposed that the selectivity in this process can be explained on the basis of the acid–base properties of the catalyst. The MAA reaction was proposed to be accelerated by acidic and basic sites of intermediate strength, while propene formation was enhanced by acidic sites, and acetone formation by basic sites. Ai also suggests that IBA must be activated on acidic sites in order to produce MAA and that the oxidizing function of the basic sites is not rate controlling.

Throughout the course of discussion of the mechanism of MAA production from IBA, there has been no mention of a carbocation intermediate in the process. Such a mechanism would involve the initial abstraction of a hydride ion to yield the following species:

$$(CH_3)_2CHCOH \xrightarrow{-H^-} (CH_3)_2\overset{+}{C}COH.$$
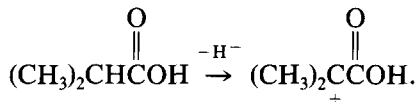
The possibility then exists for either an E1 mechanism, whereby the elimination of a proton will yield the desired MAA molecule, or a nucleophilic $S_N1$ attack of oxygen (either from the lattice or otherwise) can lead

to elimination of the carboxylate group to form $CO_2$ and acetone:

$$(CH_3)_2\overset{O}{\overset{\|}{C}}COH \xrightarrow{E1} CH_2{=}\overset{O}{\overset{\|}{C}}COH \\ + \\ \underset{O^{2-}}{\big\downarrow} S_N1 \quad\quad CH_3 \\ O \\ \| \\ CH_3CCH_3 + CO_2.$$

It appears that acetone formation results from degradation of the IBA intermediate and not from MAA as suggested by Echigoya to explain the higher acetone/MAA yields ratios over $Cs^+$ and $Rb^+$ salts. Acetone formation from MAA, in addition to the nucleophilic attack, would require subsequent rehydrogenation of the $CH_2$ group.

Evidence for carbocation formation in the $\alpha$-position to a carbonyl group has appeared recently in both experimental (*40*) and theoretical studies (*41*). Therefore, it seems difficult to rule out the existence of such a mechanism as it is essentially the reverse of the carbanion mechanism in that there is initial hydride abstraction followed by proton abstraction.

It is obvious from the preceeding discussion that the mechanism for the oxidative dehydrogenation of IBA over 12-heteropoly oxometalates has yet to be fully resolved. The presence of propene and acetone over virtually every heteropoly catalyst suggests that Ai's proposal that acidic and basic sites are participating, and that the best catalyst possesses a balance of these sites, is probably the best interpretation to date (*7*). The inference from this suggestion is that the removal of either all of the acidic or basic sites is not advantageous. It may be speculated, however, that modification of the strengths of the acidic and basic sites may enhance and reduce the positive and negative effects, respectively.

The present study has shown that ammonium salts (even partial salts) have positive

influences on the selectivity to IBA. This may result from a shift in the acid strength distribution as has been shown to occur with the 12-tungstophosphate salts (26, 37) or the ability of the ammonium ion to participate directly in the reaction through a dissociation type of mechanism. The choice of the second (alkali metal) cation that makes up the exchange pair may also play an important role in the IBA to MAA process by modifying the numbers and strengths of basic sites.

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