JOURNAL OF CATALYSIS **91**, 93–103 (1985)

Study of Heteropoly Compounds with the Keggin Structure by Temperature-Programmed Reduction and H–D Exchange

B. K. HODNETT AND J. B. MOFFAT[1]

Department of Chemistry, and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received December 13, 1983; revised May 7, 1984

Heteropoly acids and salts with the Keggin structure were studied using temperature-programmed reduction (TPR) and temperature-programmed hydrogen–deuterium exchange (TPE) techniques. $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ were characterized in TPR by peaks in identical positions to those observed in temperature-programmed desorption experiments. No distinct peaks due to reduction were observed for monovalent salts but continuous reduction occurred in TPR above 873°K. Behavior similar to that shown by the acids in reduction was observed for divalent salts. Exchange occurred at lower temperatures than reduction for $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ whereas the opposite behavior was noted for $H_3PMo_{12}O_{40}$. A reduction mechanism for the acids was proposed in which rearrangement of the secondary structure which involved localization of the protons on a single lattice oxygen anion released other lattice anions so that they could act as sites for dissociative sorption of hydrogen and partial reduction of the acids.

Heteropoly compounds are being examined as catalysts for such fundamentally different processes as selective oxidation reactions (*1–3*) and the conversion of methanol to hydrocarbons (*4–9*). Acidic and oxidizing powers seem to coexist in these compounds (*10, 11*) and considerable interest is being focused on the relationship between these two properties.

Infrared (*6*) and photoacoustic spectroscopic (*12, 13*) investigations indicate that these compounds can act as Brønsted acids toward basic probe molecules, such as pyridine or ammonia. In addition, many of the metallic salts of $H_3PW_{12}O_{40}$ (HPW) have recently been shown to be nonstoichiometric and possess considerable Brønsted acidity (*12*). That acidic and redox properties are not independent of one another was demonstrated in a recent temperature-programmed desorption (TPD) study which indicated that the acidic properties of HPW can be lost by the reaction of protons with lattice oxygen (*14*).

The reactivity of lattice oxygen in heteropoly acids and in some salts containing monovalent cations has been examined. A recent report shows that $H_3PMo_{12}O_{40}$ (HPMo) and HPW readily exchange lattice oxygen with $H_2{}^{18}O$ in relatively mild conditions (≈493°K) (*11*). This property has been associated with the ease with which water can penetrate through their structures. Terminal and bridging oxygens exchanged with equal ease but it has been postulated elsewhere (*15, 16*) that rapid exchange can occur between these two types of oxygen anions in the Keggin structure. Interestingly, exchange with the cesium salt of HPMo was much less extensive in spite of its higher surface area (*11*). Although no data is available for the reactivity of HPMo with $H_2{}^{18}O$ it is noteworthy that lattice oxygen of the corresponding silver salt does not exchange with $^{18}O_2$(g) even at 573°K (*15, 16*).

Considerable attention has been paid to

---

[1] To whom correspondence should be addressed.

0021-9517/85 $3.00

the mechanism of reduction of HPMo and some of its salts by hydrogen. Two general cases may be identified: (a) reduction of the free acid and salts containing nonreducible cations; (b) reduction of the free acid in the presence of activators of molecular hydrogen, such as Pd/C, and reduction of salts containing easily reducible cations. In the former cases reduction rates tend to be slow with temperatures in the range 553–593°K needed in static conditions to bring about measurable reaction rates (*11*). Eguchi *et al.* (*17, 18*) have shown that reduction of the potassium salt proceeds by preferential removal of bridging lattice oxygen; terminal oxygen anions were removed only after reduction had proceeded beyond about 4 electrons per Keggin unit (K.U.).

The second category listed above has received more attention. Reduction rates become measurable at 298°K when Pd/C was mechanically mixed with HPMo (*11*). In this case also reduction proceeded to 1–2 electrons per K.U. before any changes occurred in the infrared spectra. Yoshida *et al.* (*19*) have shown that the silver and copper salts of HPMo started to be reduced in TPR conditions 200°C lower than the free acid. It was postulated that activation of molecular hydrogen via the intermediary of the cations was responsible for the higher reactivity of these salts.

Some reservations must be expressed regarding experiments which monitor reductions according to the consumption of gas phase hydrogen. Misono *et al.* have shown that HPMo–Pd/C can sorb up to 1 hydrogen molecule per K.U. at 298°K without reduction of Mo^{6+} to Mo^{5+} (*11*). It was shown that extra protons could be generated in this process but that the electrons which were released did not become localized on the molybdenum ions until lattice oxygen was lost by the K.U. by reaction with the protons at 573°K (*11*).

Less work has appeared for HPW and its salts. This acid does not appear to be susceptible to more facile reduction by spilled over hydrogen from Pd/C (*20*). However, Baba *et al.* (*21*) have shown that by treating the silver or copper salt of HPW with hydrogen, protons could be generated with concurrent reduction of the metal.

The importance of gaining an insight into the precise mechanism of reduction of heteropoly compounds can be gauged by some recent reports which show the benefits of activating these catalyst in hydrogen, particularly for the conversion of methanol to hydrocarbons. Hayashi and Moffat (*7*) have shown that HPW could be activated at much higher temperatures in hydrogen than in helium or oxygen without loss of catalytic activity.

This study was designed to further study the relationship between acidic and redox properties of heteropoly compounds. It concentrates on the reactivities of HPW, $H_4SiW_{12}O_{40}$ (HSiW), and HPMo and the sodium, magnesium, ammonium, and pyridinium salts of HPW in conditions where dissociation of molecular hydrogen on metallic sites, mechanically mixed with these compounds or generated *in situ* by reduction of the cation, does not occur. Reactivity toward hydrogen in TPR conditions and exchange between heteropoly compounds and $D_2(g)$ in temperature-programmed conditions (TPE) were used as probe reactions to examine these properties. The former technique yields information on the reactivity and lability of lattice oxygen, of potential interest in selective oxidation reactions, whereas the latter reaction can be expected to give an insight into the mobility of protons, of importance in methanol conversion to hydrocarbons.

EXPERIMENTAL

Apparatus and Procedures. TPR and TPE experiments were carried out in a flow apparatus which has been fully described elsewhere (*14*). Detection was with a katharometer and by mass spectrometric analysis. For TPR experiments, hydrogen, at 40 ml min^{-1}, was used as carrier gas and a fresh charge of 250 mg of catalyst was used for each run. Samples were pretreated in predried helium for 2 h at a temperature sufficiently high to produce anhydrous materials without loss of Brønsted acidity (*14*); this temperature was determined from the results of TPD experiments already reported and was 593°K for all except HPMo; the latter was pretreated at 473°K.

For TPE experiments a charge of 500 mg of catalyst was used for each run (250 mg was used for the ammonium salt of HPW). The carrier gas was a mixture of nitrogen and deuterium (cp. grade), flowing at 40 ml min^{-1} with P_{D_2} = 100 Torr. Pretreatments were the same as described for TPR experiments. Results are presented below as mole fractions of D_2, HD, and H_2 detected in the gas phase during temperature programming. X-Ray powder diffraction analysis and sorption of pyridine were examined by standard techniques previously described (*14*).

Materials. All the catalysts used in this study were as outlined in a previous publication (*14*) and the same shorthand notation will be used here such that $Na_3PW_{12}O_{40}$ will be referred to as NaPW and $(NH_4)_3PW_{12}O_{40}$ as NHPW.

RESULTS

TPR and TPE for HPW, HSiW, and HPMo. Figures 1–3 (a) present TPR profiles recorded for HPW, HSiW, and HPMo. All the observed peaks were due to water. A feature is the similarity in overall shape and positions of peaks to that found in analogous TPD experiments (*14*); the latter were performed in essentially identical conditions except that helium was used as carrier gas. For convenience TPR peaks will be referred to as 1, 2, or 3 as indicated in Figs. 1–3. Quantitative measurement of peaks 2 in TPR yield values of 8.6 water molecules produced per K.U. for HPW, 9.4 for HSiW, and 8.0 for peaks (2 + 3) for HPMo. The corresponding values measured from TPD experiments were 1.4, 1.9, and 1.5 water molecules per K.U., respectively, which correlated with the numbers of protons present initially in these acids.

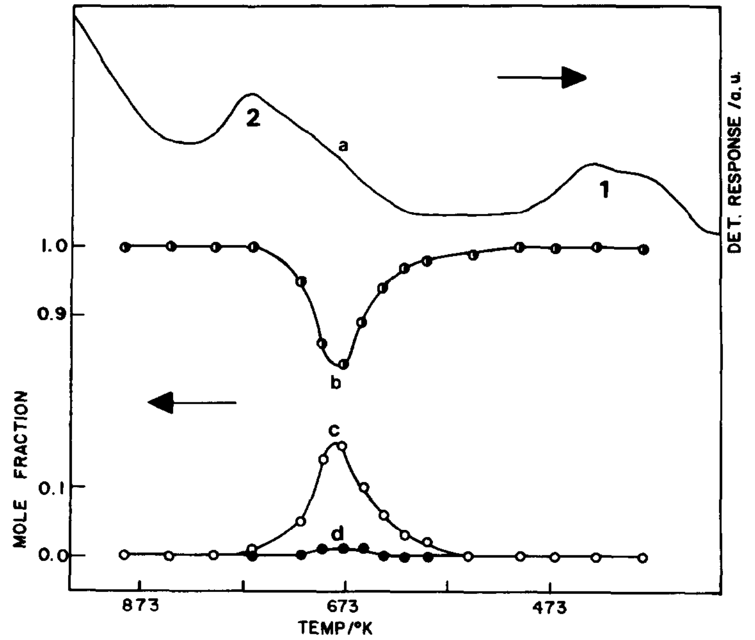

FIG. 1. (a) TPR profile for HPW. (b)–(d) Mole fractions D_2(g)(◑), HD(g)(○), and H_2(●) during TPE of HPW.

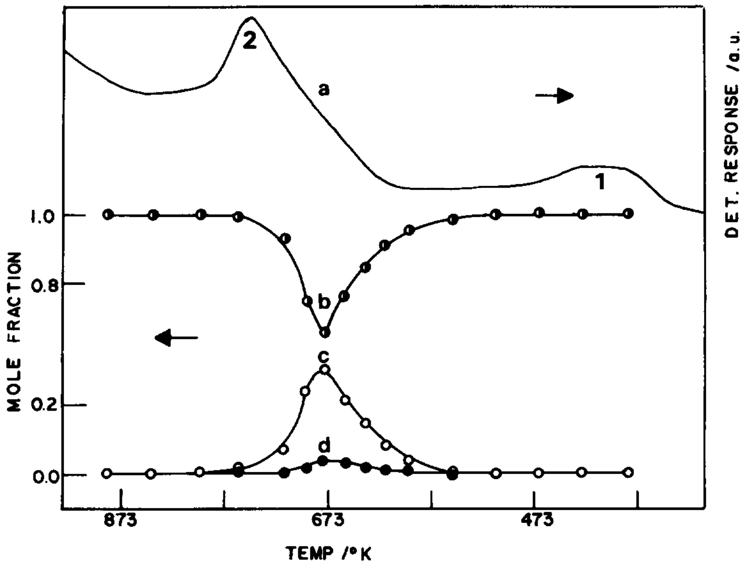

FIG. 2. (a) TPR profile for HSiW. (b)–(d) Mole fractions D_2(g)(◑), HD(g)(○), and H_2(g)(●) during TPE of HSiW.

On this basis peak 2 in TPD was assigned to deprotonation of the acids with concurrent nonreductive loss of lattice oxygen (*14*). In TPR conditions loss of lattice oxygen in the process corresponding to peak 2 was much more extensive but the coincidence of peak positions indicates some similarities in mechanism with the TPD process.

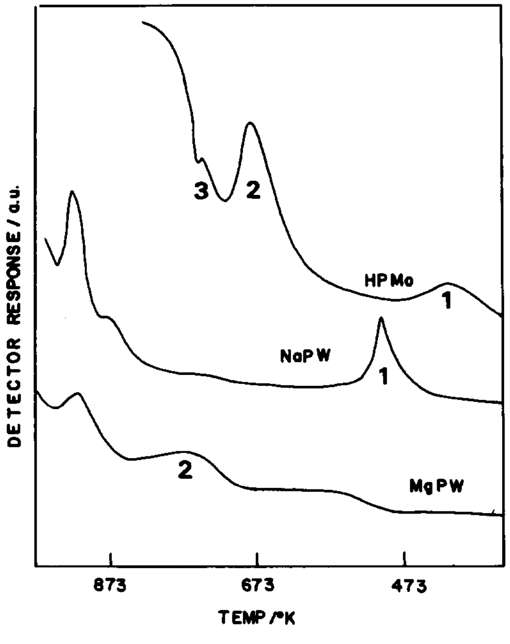

FIG. 3. TPR profiles for HPMo, NaPW, and MgPW.

By contrast peak 1 in TPR was much smaller than the corresponding peak measured in TPD experiments. The appearance of this peak in TPR was not surprising in view of the fact that these acids were pretreated at much higher temperatures than those at which peak 1 appeared. The presence of hydrogen as carrier gas would appear to be essential in forming the peak; when helium was used for this purpose (TPD conditions), no peaks appeared below the pretreatment temperature (*14*). This phenomenon may be associated with the low-temperature uptake of hydrogen reported previously by Misono *et al.* (*11, 20*).

A third feature of the profiles presented in Fig. 1 was the continuous reduction which was observed above ca. 723°K for HPMo and 823°K for the tungsten acids which must correspond to extensive reduction of these compounds: this feature was not observed in TPD. Analysis by XRD after TPR experiments indicated that amorphous materials had been formed. However, the temperatures at which this process became important for each acid were close to their decomposition temperatures (*14*) and continued beyond this point; these features probably reflect the reaction of hydrogen with the constituent oxides of the decomposed acids.

Figures 1b–d and 2b–d show the results of TPE experiments between $D_2(g)$ and HPW or HSiW. No exchange was observed for HPMo but consumption of $D_2(g)$ and reduction of the acid were noted as with the corresponding TPR experiment. The temperature at which exchange began to be detected for each of the tungsten acids was ca. 623°K, which corresponds to the temperature at which peak 2 began to appear in TPR experiments (Figs. 1a and 2a). Maximum rates of exchange were observed between 675 and 700°K for both HPW and HSiW.

HD(g) was the principal product of this reaction; for each acid the HD: H_2 ratio was never less than 7 : 1. Quantitative measurements for the numbers of exchangeable protons were difficult to establish as this seems to depend markedly upon P_{D_2}. However, close to complete exchange was observed for both acids in these conditions indicating that all the original protons exchanged. An important point is that exchange was complete before the major portion of peak 2 had evolved. This excludes the possibility that exchange was occurring between $H_2O(g)$ and $D_2(g)$.

TPR and TPE for the salts of HPW. The TPR behavior of a number of salts of HPW are presented in Figs. 3b, c, 4a, and 5a. All peaks were due to desorption of water, except that which evolved from the pyridinium salt at ca. 823°K (Fig. 4a); this peak arose from a mixture of pyridine and water. Only the magnesium salt, which contained the only divalent cation, desorbed appreciable amounts of water around the position at which peak 2 for the corresponding tungsten acid was observed. The amount of water evolved in this case was 4 molecules per K.U. For all except the pyridinium salt small amounts of water were desorbed below the pretreatment temperatures.

Little variation was observed in the temperature at which extensive reduction began, but this probably reflects reduction of WO_3, formed after decomposition of individual heteropoly salts as with the free acids. With the sodium and magnesium salts strong peaks were observed at ca. 923°K. In the former case this feature may have been associated with the formation of a sodium tungsten bronze of formula $Na_{0.28}WO_3$, whose presence was detected by XRD at the end of the run (*22, 23*) and which may be cited as evidence that the primary structure of the NaPW was destroyed when the continuous reduction process occurred. The magnesium salt was X-ray amorphous after TPR.

Essentially no exchange was observed for the sodium and magnesium salts, which is consistent with their stoichiometric aprotic nature, as demonstrated in previous publications (*12, 14*).

The results of exchange experiments for the pyridinium and ammonium salts are presented in Figs. 4 and 5. The maximum exchange rate for the former coincided with the maximum for the peak due to desorption of water and pyridine in its TPR profile. This observation indicates that pyridine interacted very strongly with the protons and had to be removed before exchange could occur. A distinct exchange peak was also detected at lower temperatures, possibly due to the presence of some unreacted free acid.

By contrast, the ammonium salt exhibited behavior very similar to that shown by HPW and HSiW. Exchange was observed at the temperature at which reduction began and was complete long before this process was over. In this case exchange was the most extensive, of the order of 2–3 HD molecules per proton of the parent acid.

Influence of Pretreatment Conditions on the Acidity of HPW

The similarity in desorption temperature for peak 2 in TPD and TPR stimulated further experimentation to determine whether

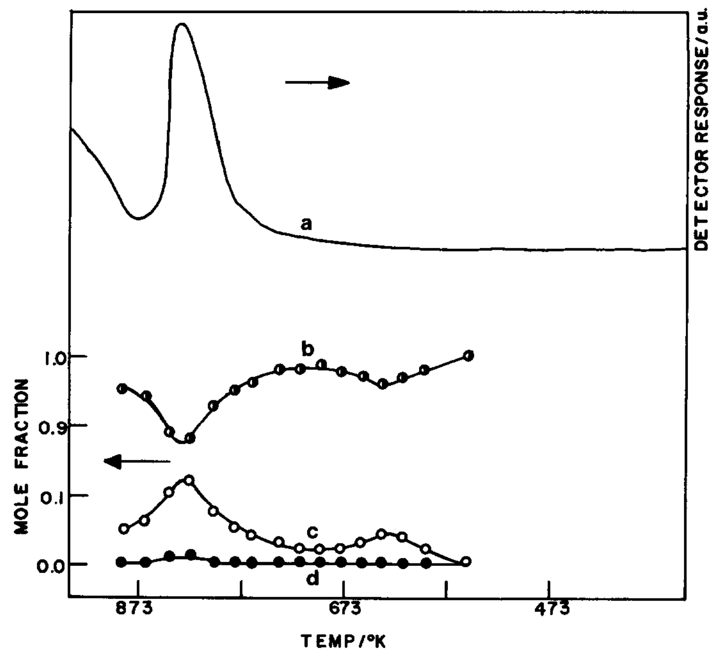

FIG. 4. (a) TPR profile for PyPW. (b)–(d) Mole fractions D_2(g)(◑), HD(g)(○), and H_2(g)(●) during TPE of PyPW.

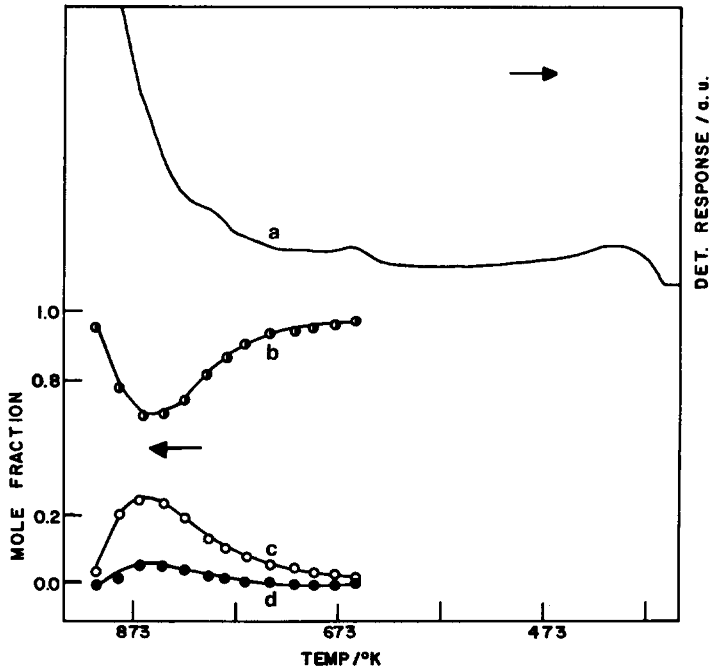

FIG. 5. (a) TPR profile for NHPW. (b)–(d) Mole fractions D_2(g)(◑), HD(g)(○), and H_2(g)(●) during TPE of NHPW.

TABLE 1

Sorption of Pyridine onto HPW at 298°K after Various Pretreatments

Pretreatment Temp. (°K)	Pretreatment (atm)	Amount irreversibly sorbed (molecules per K.U.)	
		298°K	473°K
673	O_2	6.2	2.6
573	O_2	6.2	2.8
593	*in vacuo*	6.5	2.4
593	H_2	5.9	2.7
723	*in vacuo*	2.3	0.7
723	H_2	0.75	0

the water which was produced in the latter arose exclusively from reaction with gas-phase hydrogen or whether some deprotonation of the acid also occurred in TPR conditions.

No significant differences were observed in the amounts of water desorbed from HPW during TPD experiments for which the acid was pretreated in oxygen, helium, or hydrogen. In addition no exchangeable protons were detected during TPE with HPW after pretreatment in flowing hydrogen at 450°C and cooled to room temperature. These findings were further verified by the data of Table 1 which shows the results for the sorption of pyridine onto HPW. No essential difference in sorptive capacities as a function of pretreatment atmosphere is evident. Thus pretreating HPW in hydrogen did not protect this acid from loss of protons and gas-phase oxygen did not significantly react with protons to cause deprotonation at temperatures lower than when pretreatment was carried out *in vacuo* or in helium.

XRD analysis of HPW pretreated at 723°K has already been described (*14*); some changes were indicated in secondary structure but the XRD pattern of the constituent oxides was not detected. Infrared evidence confirmed that the primary Keggin structure of HPW was intact (*12, 13*) after heating to 723°K.

DISCUSSION

The equations

$$\begin{array}{llll}
D_2(g) + H(s) \rightleftharpoons HD(g) + D(s) & (a) & & \\
HD(g) + H(s) \rightleftharpoons H_2(g) + D(s) & (b) & R' & (1) \\
D_2(g) + 2H(s) \rightleftharpoons H_2(g) + 2D(s) & (a) & & \\
HD(g) + 2H(s) \rightleftharpoons H_2(g) + D_2(s) + H(s) & (b) & R'' & (2) \\
HD(g) + 2D(s) \rightleftharpoons D_2(g) + D(s) + H(s) & (c) & & \\
D_2(g) + H_2(g) \rightleftharpoons 2HD(g) & (a) & & (3)
\end{array}$$

are often evoked to describe the exchange processes which can occur between gas-phase deuterium and surface hydrogen species (*24*). To date these reactions have been studied largely in closed static systems which allow, not only accumulation of deuterated surface species such as those produced in Eqs. 1(a) and 2(a), but accumulation of intermediate products in the gas phase. Further reactions of these intermediates, as 1(b), 2(b), and 2(c) can complicate the initial product distribution. However, by operating in a suitable flow system the latter complication can be removed and the actual product distribution observed can be more easily extrapolated to reflect the initial reactivity. In such a system HD(g) would appear in the gas phase if an R′ mechanism prevailed whereas H_2(g) would result from an R″ mechanism. More complicated product distributions would result in flow conditions after these systems had experienced large degrees of exchange. Large-scale accumulations of D(s) species could result in the appearance of some HD in the gas phase with the R″ mechanism but in dynamic conditions this complication should manifest itself by a change in product distribution as a function of time on stream.

On the basis of the foregoing analysis it can be concluded that an R′ exchange mechanism was operative for HPW and HSiW since HD(g) was the principal reaction product and only trace amounts of $H_2(g)$ were produced irrespective of the extent to which the reaction has progressed. The precise exchange mechanism cannot be determined with certainty on the basis of the results of the exchange experiments alone but some correlations may be noted with TPD and TPR results which may be useful in pointing toward a possible reduction mechanism.

Peak 1 does not correlate with the exchange activity but it appeared at the same temperature as in TPD. It must be related to reactions between hydrogen and extremely labile lattice oxygen. The water which resulted remained in the structure to the temperature at which desorption of water as the result of decomposition of $(H_5O_2)^+$ ions occurred in TPD (*14*).

The coincidence of peak positions for TPD and TPR and the occurrence of the exchange at the temperature at which deprotonation or partial reduction began to occur in the former processes implies that exchange, reduction and deprotonation may have some steps in common. Misono *et al.* (*11, 20*) have already proposed the involvement of protons originating from dissociation of $H_2(g)$ in the reduction of HPMo.

The inability of HPW to sorb pyridine after pretreatment in $H_2(g)$ at 723°K and the absence of exchangeable protons in these conditions suggests that thermally induced deprotonation of this acid was not inhibited by reaction with hydrogen. Thus protons present in the HPW structure at the temperature at which peak 2 appeared were at least as reactive toward lattice oxygen as gas-phase hydrogen. In TPR peak 2 must have comprised water formed by reaction of lattice oxygen with the original protons of the acid (1.5 water molecules were produced per K.U. from HPW in TPD) and the balance formed by reaction of $H_2(g)$ with lattice oxygen. From this correlation it can be hypothesized that gas-phase hydrogen forms protons upon dissociation which in turn

$$H_2(g) \xrightarrow{2W^{6+}} 2H^+(Ads) \xrightarrow{O^{2-}(e)} H_2O \qquad (4)$$

react with lattice oxygen in a similar manner to the original protons of the free acid (Eq. (4)). The exchange process could be envisaged as proceeding via a related mechanism whereby each dissociated deuterium molecule reacted via

$$\begin{aligned} &D_2(g) + H^+(s) \xrightarrow{-2e} \\ &2D^+(Ads) + H^+(s) \rightarrow HD(g) + D^+(s). \qquad (5) \end{aligned}$$

In accordance with this mechanism surface or bulk protonic species are common intermediates in the exchange, reduction, and deprotonation processes.

Since exchange could occur at a slightly lower temperature than reduction for HPW and HSiW it must follow that dissociative sorption of $H_2(g)$ also occurred at lower temperatures than reduction. The fact that essentially complete exchange occurred before peak 2 had fully evolved points to the reaction between protons and lattice oxygen as the slow step.

For HPMo the situation seems somewhat different. No exchange was observed in TPE conditions. In this case it may be postulated that reduction began by reaction of those protons, which were present initially, with lattice oxygen, as occurred in TPD. The temperature at which this process began was the minimum at which lattice oxygen could react with protons. At a slightly higher temperature dissociation of $H_2(g)$, with formation of protons, may have begun, with extensive reduction of the acid to produce peaks 2 and 3. In this situation the reduction pathway, outlined in Eq. (4), would be preferred over the exchange, outlined in Eq. (5) for HPMo. The results presented above show a difference in reactivity of the acids to that of the salts containing monovalent cations. The latter do not exhibit reduction in the temperature region corresponding to peak 2 and NaPW showed very low reactivity toward hydrogen below its decomposition temperature (*14*).

The reason why peak 2 was absent in TPD conditions for all the stoichiometric salts is self-evident; these salts did not possess any Brønsted acidity, hence no protons to cause reaction. However, consideration of the mechanism proposed above suggests that most of the water molecules which constituted peak 2 of HPW, (i.e., 8.6 in TPR–1.5 in TPD) 7.1 per KU arose from reaction of $H_2(g)$ with lattice oxygen. A priori considerations imply that at least this amount of reduction should also be possible with the monovalent salts of HPW. Some water did desorb from the divalent magnesium salt at the temperature characteristic of peak 2.

Two possible explanations may be evoked to rationalize the lower reactivity of the monovalent salts: (i) that monovalent cations can stabilize W–O bonds in the Keggin structure sufficiently to make them resistant to reduction below their decomposition temperatures, (ii) that cations occupy sites which are necessary for the activation of gas-phase hydrogen.

Two phenomena have been reported which can influence the stability of metal–oxygen bonds in the K.U. Hydrogen-bonding between water molecules or NH_4^+ ions has a destabilizing effect (*26*). Anion–anion interactions stabilize the metal–oxygen bonds; as cation size decreases, the K.U.'s can approach each other and their interactions intensify (*27*). These two phenomena explain why the metal–oxygen bonds in the anhydrous sodium salt of HPW should be less reactive toward hydrogen than in the hexahydrate. The sodium cation is smaller than $(H_5O_2)^+$ and does not hydrogen-bond.

These hypotheses do not explain the difference in reactivity between NaPW and HPW in their anhydrous forms. All water had been eliminated from both materials before peak 2 began to emerge in the latter so that the former had the larger cation.

The hypothesis that cations occupy sites which are necessary for the activation of $H_2(g)$, offers a rationale for the properties of MgPW. Its cation charge implies the presence of some unoccupied sites, vis-à-vis the monovalent salts.

Examination of the published structures of heteropoly acids and monovalent cation salts with the Keggin structure indicates that the diaquahydrogen ion, i.e., $H_5O_2^+$, in $H_3PW_{12}O_{40} \cdot 6H_2O$, or monovalent cations are located in central positions between 4 protruding oxygen anions in a cubic secondary structure (*25*). On the basis of a crystallographic study of $H_3PW_{12}O_{40} \cdot 6H_2O$, Brown *et al.* (*25*) have proposed that other hexahydrate acids with nonhydrated protons, such as $(H_5O_2^+)HSiW_{12}O_{40}^{3-}$ and $(H_5O_2^+)_3H_2BW_{12}O_{40}^{3-}$, accommodate these extra protons close to the protruding oxygen anions (O(4) in Brown's notation) of the Keggin unit. It has been demonstrated that when tungsten heteropoly acids are heated above 573°K, anhydrous materials result and changes in secondary structure follow (*14*). Although no precise data are available, it may be hypothesized that protons become localized adjacent to oxygen(4) anions as outlined in Fig. 6 or are free to move through the structure, but make ensembles of oxygen(4) anions available for reception and dissociative chemisorption of hydrogen molecules. After displacement of the protons in this way, sorption, dissociation, and reduction could proceed to produce peak 2 for as long as suitable arrangements of protons and O(4) sites remained in the acid. It is assumed that these sites facilitate reduc-

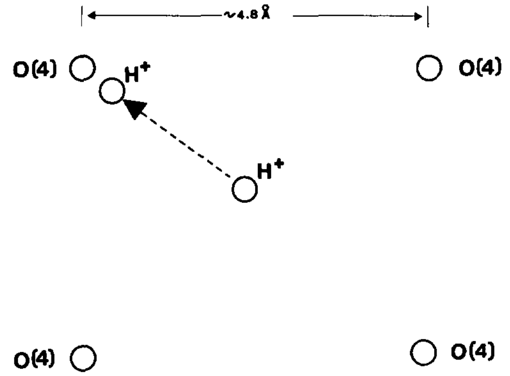

FIG. 6. Structure of the local environment of the protons in HPW in its anhydrous form; the arrow indicates the movement of the proton necessary for localization close to an O(4) oxygen (Brown's notation) to occur.

tion by molecular hydrogen at lower temperatures than can occur with lattice oxygen of the constituent oxides. For the purposes of this hypothesis it is assumed that the larger sodium ions in NaPW cannot be displaced in the way that protons can so that O(4) sites do not become available for the reduction process.

Although it is not possible to apply the cubic structures of hydrated acids and monovalent salts to salts with multivalent cations it is nevertheless reasonable to hypothesize that the concentration of charge on a single cation can lead to the release of ensembles of protruding oxygen(4) anions which might be suitable for activation of molecular hydrogen.

The behavior of the pyridinium salt may also be rationalized on the basis of the foregoing discussion. Measurements of the ratio of water to pyridine contributing to its TPR peak indicate that it was ca. 4 times greater than for the same sample in TPD conditions. These data indicate that desorption of pyridine was accompanied by release of sites for the activation of molecular hydrogen for exchange or reaction with lattice oxygen and subsequent production of additional quantities of water. The higher temperature at which these processes occur with this salt (i.e., 823°K) is a result of the strength of interaction of pyridine with protons and not any inherent difference in reactivity of material (presumably free acid) which is formed after desorption.

The behavior of the ammonium salt in TPR and TPE was closely analogous to that of the tungsten acids, in that exchange began and was complete shortly after water began to be evolved in TPR; no $NH_3(g)$ was detected at this temperature. These findings, considered with the fact that exchange seemed to far exceed 1 HD(g) molecule produced per proton of the parent acid, imply that the 4 hydrogen atoms of the NH_4^+ ion can exchange with $D_2(g)$ at this temperature.

ACKNOWLEDGMENT

The financial support of the National Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1980).
2. Misono, M., Komaya, T., Sekiguchi, H., and Yoneda, Y., *Chem. Lett.* 53, (1982).
3. Al, M., *J. Catal.* **27,** 88 (1981).
4. Baba, T., Sakai, J., and Ono, Y., *Bull. Chem. Soc. Jpn.* **55,** 2657 (1982).
5. Baba, T., Sakai, J., Watanabe, H., and Ono, Y., *Bull Chem. Soc. Jpn.* **55,** 400 (1982).
6. Misono, M., Mizuno, N., Katamura, K., Kasai, A., Konishi, Y., Sakata, K., Okuhara, T., and Yoneda, Y., *Bull Chem. Soc. Jpn.* **55,** 400 (1982).
7. Hayashi, H., and Moffat, J. B., *J. Catal.* **77,** 473 (1982).
8. Hayashi, H., and Moffat, J. B., *J. Catal.* **81,** 61 (1983).
9. Hayashi, H., and Moffat, J. B., *J. Catal.* **83,** 192 (1983).
10. Misono, M., Sakata, K., Yoneda, Y., and Lee, W. Y., *New Horiz. Catal., Proc. 7th Int. Congr. Catal.* 1047 (1980).
11. Mizuno, N., Katamura, K., Yoneda, Y., and Misono, M., *J. Catal.* **83,** 384 (1983).
12. Highfield, J. G., and Moffat, J. B., *J. Catal.* **88,** 177 (1984).
13. Highfield, J. G., and Moffat, J. B., *J. Catal.* **89,** 185 (1984).
14. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **88,** 253 (1984).
15. Tsuneki, H., Niiyama, H., and Echigoya, E., *Chem. Lett.* 645 (1978).

16. Tsuneki, H., Niiyama, H., and Echigoya, E., *Chem. Lett.* 1183 (1978).

17. Eguchi, R., Toyozawa, Y., Yamazoe, N., and Seiyama, T., *J. Catal.* **83,** 32 (1983).

18. Eguchi, K., Toyozawa, Y., and Furuta, K., *Chem. Lett.* 1253 (1981).

19. Yoshida, S., Niiyama, H., and Echigoya, E., *J. Phys. Chem.* **86,** 3150 (1982).

20. Katumara, K., Nakamura, T., Sakata, K., Misono, M., and Yoneda, Y., *Chem. Lett.* 89 (1981).

21. Baba, T., Watanabe, H., and Ono, Y., *J. Phys. Chem.* **87,** 2406 (1983).

22. ASTM 5-D361.

23. Magneli, A., and A. Blomberg, B., *Acta. Chem. Scand.* **5,** 572 (1951).

24. Heylen, C. F., Jacobs, P. A., and Uytterhoeven, J. B., *J. Catal.* **43,** 99 (1976).

25. Brown, G. M., Noe-Spirlet, M.-R., Busing, W. R., and Levy, H. A., *Acta Crystallogr. Sect. B* **33,** 1038 (1977).

26. Boeyens, J. C. A., McDougal, G. J., and Van R. Smit, J., *J. Solid State Chem.* **18,** 191 (1976).

27. Rocchiccioli-Deltcheff, C., Fournier, M., Franck, R., and Thouvenot, R., *Inorg. Chem.* **22,** 207 (1983).