JOURNAL OF CATALYSIS 96, 242–250 (1985)

Stoichiometric and Nonstoichiometric Al–P–O Catalysts: Studies with the Probe Molecule 2-Methylcyclohexanol

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Received June 26, 1984; revised June 8, 1985

Stoichiometric and nonstoichiometric Al–P–O catalyze the dehydration of *cis*- and *trans*-2-methylcyclohexanol to 1-methylcyclohexene (1-MCH) and 3-methylcyclohexene (3-MCH). While the *cis* isomer is converted more extensively than the *trans* with all compositions, the relative amount of the two olefinic products (1-MCH/3-MCH) increases markedly on addition of phosphorus. The observations are consistent with an E1 mechanism for the *trans* form and an E2 *trans* elimination for the *cis* alcohol, the latter appearing to require the presence of catalytic sites related to both aluminum and phosphorus atoms.

INTRODUCTION

Interest in catalysts containing phosphorus as the common element has been evident for many years (*1, 2*). Although the first studies of aluminum phosphate may be traced to 1960 (*3–5*), a resurgence in activity has recently become evident. New and significant structural understanding has been provided by a group at Gulf (*6*), and workers in Spain continue to provide information on the catalytic properties of this solid (*7*). In spite of such work, our understanding of the catalytic sites and mechanisms on aluminum phosphate is still incomplete. While many techniques, based on a variety of principles, are available for the study of solid surfaces, chemisorbed species, and heterogeneous reactions, information in this area can often be advantageously obtained with the use of probe molecules and probe reactions. A number of workers, notably Pines (*8*), Hall (*9*), and more recently Davis (*10–16*) have demonstrated the utility of cyclic alcohols in such mechanistic studies.

A number of different reactions are in principle possible for alcohols on solid surfaces. These reactions include dehydration, dehydrogenation, *cis–trans* isomerization, and cracking, although the latter is usually less frequently observed on catalysts for which an alcohol is used as a probe. Such process selectivity can often provide useful information on the nature of the catalytic surface. In addition, a steric selectivity may exist. For example, with many homogeneous organic systems, elimination reactions are frequently found to occur by an antielimination process (*17*). Where such steric preference exists, the product distribution may also be a function of such selectivity.

Davis (*14*) has noted that the size of the base as well as the base strength will be factors in the elimination process (*18*). A larger base will favor the Hoffman (anti-Saytzeff) elimination. The imposition of a catalytic surface will contribute additional variables to the process. The catalytic surface may be unable to meet certain topological and energetic demands in order for the elimination process to follow routes with more stringent requirements. Finally, conformational changes of the probe molecule, particularly those brought about as a consequence of its interaction with the surface, although more restricted in the case of cy-

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0021-9517/85 $3.00

clic alcohols, may produce perturbations in the potential energy surface. Although it is generally difficult to disentangle all of these factors, often the results of experiments with probe molecules are sufficiently definitive to permit useful inferences to be drawn.

In the present work, *cis*- and *trans*-2-methylcyclohexanol are employed as probe molecules to examine their surface reactions on Al–P–O catalysts with stoichiometry varying from a P/Al molar ratio of 0 to 1.2.

EXPERIMENTAL

The Al–P–O catalysts were prepared by two different methods, that due to Kearby (*3*) and that due to Kehl (*19*), the former procedure being employed to prepare the stoichiometric $AlPO_4$ solids, and the latter for the nonstoichiometric materials. The Kearby-type Al–P–O catalysts were prepared from aluminum chloride (Baker Analyzed) and orthophosphoric acid (Fisher Certified) and a 10% solution of ammonium hydroxide for adjustment of the pH during preparation to either 3.5 or 7.3. The gels were repeatedly redispersed with isopropanol, filtered, and dried at room temperature for 48 h.

The nonstoichiometric Al–P–O catalysts (P/Al from 0.1 to 1.2) were prepared from aluminum nitrate (BDH), orthophosphoric acid, and a 10% solution of ammonium hydroxide (*19*), and were treated as previously described. All catalyst samples were calcined in air at 650°C for 18 h, and were sieved to 100–140 mesh (150–106 μm) immediately prior to use.

cis-2-Methylcyclohexanol (*cis*-2-MCHOL) 97%, *trans*-2-methylcyclohexanol (*trans*-2-MCHOL) 98%, 1-methylcyclohexene (1-MCH) 95%, 3-methylcyclohexene (3-MCH) 98%, 4-methylcyclohexene (4-MCH), and methylene cyclohexane (MECH) 99%, were obtained from Aldrich. All chemicals were used as received.

A microcatalytic pulse reactor with a trapping coil and connected gas chromatograph (H.-P. 5880A) was employed for all reaction experiments. Preliminary tests were performed to determine suitable operating conditions for the various reactions. A 40-ft. × $\frac{1}{8}$-in. column of 25% β,β'-oxydipropionitrile on 80/100 mesh Chromosorb P (NAW) at 80°C was used to analyze the alkenes, while a 15-ft. × $\frac{1}{8}$-in. column of 20% diglycerol on 60/80 mesh Chromosorb W (AW) at 120°C was employed for the water and alcohols. Prior to operation of the reactor, the 50-mg catalyst samples contained therein were predried for 4 h in a flow of helium at the reaction temperature. Experiments were performed in helium as carrier gas with pulse size of 2.0 μl. A preheat zone of volume approximately three times that of the reactor preceded the catalyst sample.

X-Ray powder diffraction patterns were recorded with the aid of a Phillips Model PW-1011/60 diffractometer using nickel-filtered Cu$K\alpha$ radiation. All samples except that with a P/Al of 1.2 were found to be essentially amorphous.

Elemental analyses (Galbraith Laboratories) on selected samples after preparation and calcination agreed to ±2% or less with the aluminum and phosphorus concentrations as prepared.

RESULTS

The conversions of the *cis* alcohol are greater than those of the *trans* at 175°C and all P/Al (Fig. 1). Mass balances fall within the range 90 ± 10% at these temperatures, but were considerably lower by 550°C, at which temperature values as low as 10% were found with the Kearby-type catalysts. Consequently, the data reported here to illustrate the effect of changes in P/Al are restricted to 175°C, a temperature at which optimum mass balances were obtained. The conversions of both isomeric forms of the alcohols increase with P/Al, pass through a maximum at P/Al equal to 0.1, and then decrease to values of 5% or less with further increase in P/Al.

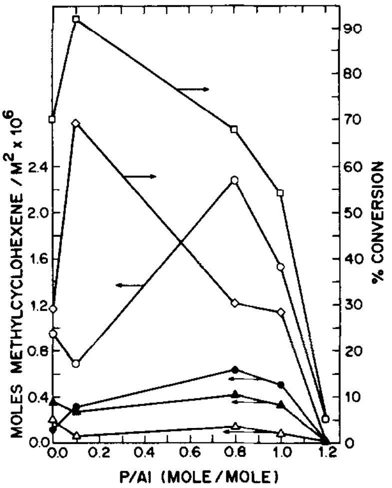

FIG. 1. Conversion (%) of *cis*-2-methylcyclohexanol (□) and *trans*-2-methylcyclohexanol (◇) for various molar P/Al ratios. Products formed (moles/area): 1-methylcyclohexene (○) and 3-methylcyclohexene (△) from *cis*-2-methylcyclohexanol; 1-methylcyclohexene (●) and 3-methylcylohexene (▲) from *trans*-2-methylcyclohexanol. Reaction temperature 175°C.

No *cis–trans* isomerization of the alcohols and no skeletal isomerization of either reactants or products were observed with any of the present catalysts. Only 1-MCH and 3-MCH were obtained as products, although four isomeric alkenes, 1-, 3-, and 4-methylcyclohexene, and methylenecyclohexane are possible in principle. Since the stabilities of these alkenes decreases in the order 1-MCH $\gg$ 4-MCH $>$ 3-MCH $\gg$ MECH (*20*) it is expected that any MECH formed would be rapidly isomerized.

TABLE 1

Surface Area of Al–P–O Catalysts

P/Al (mol/mol)	Surface area (m^2/g)
0	143
0.1	387
0.8	92
1.0	110
1.2	77

Since the values for conversion are influenced by the considerably different surface areas (Table 1) for the catalysts of various P/Al, it is instructive to examine the total alkenes produced per unit surface area. On an areal basis, the quantities of 1-MCH produced from *cis*-2-MCHOL can be seen to be considerably larger than those of 3-MCH for all P/Al (Fig. 1). Maximum amounts of either products per unit area are obtained with the catalysts of P/Al equal to 0.8.

The ratio of 1-MCH/3-MCH (1/3) is conveniently employed as a means of tracking product composition. The effect of reaction temperature on this ratio for the stoichiometric (P/Al = 1.0) Al–P–O catalyst is shown in Fig. 2, together with the relative quantities of these two olefins expected at equilibrium (*20*). It may readily be observed that the preparation pH for the Al–P–O has relatively little effect on the 1/3 ratio for all temperatures. Most noticeable, however, is the size of (1/3) from *cis*-2-MCHOL at 175°C compared to that for equilibrium (6.7). In contrast the (1/3) ratio from the

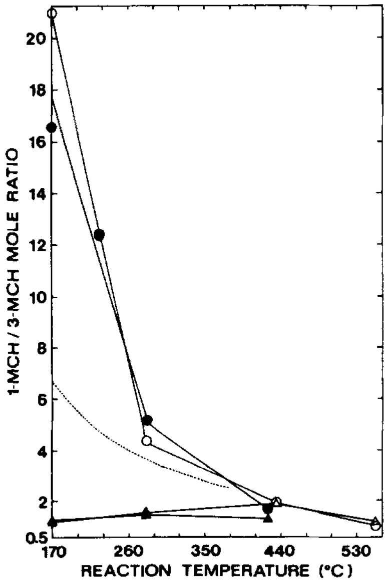

FIG. 2. Product ratios at various reaction temperatures for the dehydration of *cis*-2-methylcyclohexanol (○, ●) and *trans*-2-methylcyclohexanol (△, ▲) by Kearby-type (P/Al = 1.0) Al–P–O catalysts prepared at pH 3.5 and 7.3, respectively. Product ratios at equilibrium (-----).

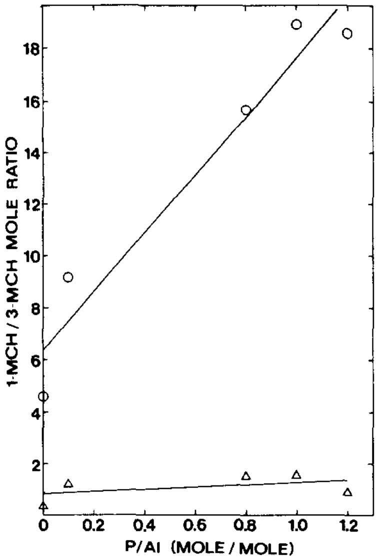

FIG. 3. Product ratios for the dehydration of *cis*-2-methylcyclohexanol (○) and *trans*-2-methylcyclohexanol (△) for various P/Al ratios at 175°C reaction temperatures.

trans alcohol falls well below that for equilibrium at this same temperature. Increase in the reaction temperature produces a precipitous drop in (1/3) from the *cis* form and the equilibrium value is approached at approximately 400°C, while that from the *trans* alcohol increases slightly to converge with the data from the *cis* isomer and that for equilibrium.

The manner in which the (1/3) ratios vary with P/Al for a reaction temperature of 175°C can be most clearly seen from Fig. 3. With the *cis* alcohol, the (1/3) is similar to the equilibrium value (6.7) for a P/Al value of zero (alumina), but increases markedly to a value of approximately 20 for P/Al equal to 1.2. In contrast, the (1/3) ratio with the *trans* isomer is approximately 1 for all catalyst compositions.

The isomerization of the products was studied in supplementary experiments. In the absence of a catalyst, none of the four alkenes, 1-MCH, 3-MCH, 4-MCH, and MECH, show any appreciable thermal isomerization at temperatures up to 435°C and other experimental conditions employed in the present work. However, MECH is catalytically converted to 1-MCH at temperatures as low as 120°C while 1-MCH is partially isomerized to 3-MCH at the higher reaction temperatures. Although the extents of the isomerization of MECH and 1-MCH at 120–435°C are considerably different, the product distributions are similar. Both 3- and 4-MCH partially isomerize to form 1-MCH and under the most severe conditions employed 48% (410°C) and 42% (435°C), respectively, were converted to 1-MCH. At 175°C the secondary isomerization processes for 1-, 3- and 4-MCH are estimated to convert less than approximately 3, 17, and 15%, respectively, of these alkene products. Although in the present experiments no evidence for 4-MCH or MECH was found, the analytical method used was incapable of completely resolving 4-MCH from 3-MCH. Blanc and Pines have reported the same difficulty (*8b*). In addition to the species previously noted, an unidentified product, estimated at no more than 4% was observed from *trans*-2-MCHOL and catalysts with P/Al ratios of 1.0.

DISCUSSION

The conversion of *cis*-2-MCHOL exceeds that of *trans*-2-MCHOL for all temperatures below approximately 500°C and for all catalyst P/Al compositions. Similar results have been reported for various catalytic systems, including alumina (*8b*), hydroxyapatite (*9*), gallia (*10*), hafnia (*12*), anatase (*13*), india, yttria, zirconia (*14*), and molybdena (*16*). In the present case, however, there is no evidence for *cis–trans* isomerization of the reactant nor of dehydrogenation of the alcohol to the corresponding ketone. While with a number of the aforementioned catalysts, *cis–trans* isomerization of *cis*- and *trans*-2-MCHOL is observed, little or no isomerization of the reactant alcohol occurs with alumina (*15*), gallium oxide (*10*), anatase (*13*), and molybdena (*16*). The present results with the Al–P–O catalysts suggest both a high degree of stereoselectivity as well as dehydration processes which are rapid relative to those of dehydrogenation and *cis–trans* isomerization.

It is of interest to note that the dehydration activity of the catalyst containing only aluminum and oxygen is considerably enhanced by the addition of a relatively small quantity of phosphorus. The conversion of the *trans* alcohol with the catalyst, where P/Al is equal to 0.1, is more than double that in the case where no phosphorus is present, while that of the *cis* alcohol is increased from approximately 70 to 90%.

As with cyclohexanes and monosubstituted cyclohexanes, disubstituted cyclohexanes may exist in two alternative chair conformations. A 1,2-disubstituted cyclohexane such as 2-methylcyclohexanol may exist in *cis* and *trans* configurations. The *trans* isomer (*dl* pair) will be either diequatorial (e,e) or diaxial (a,a) with the diequatorial conformation predominating. In contrast, the *cis* isomer will be either equatorial–axial or axial–equatorial. When the two substituents are different, as with 2-MCHOL, the conformation in which the larger substituent is equatorial will predominate. Thus with 2-MCHOL, the *trans* isomer (e,e) is expected to be more stable than the *cis* (e,a) because of the greater number of equatorial substituents (*21–23*). Recent ^{13}C NMR studies (*24*) have shown the (ea/ae) and the (ee/aa) equilibrium constants for 2-MCHOL to be 4.3 and ≥50.0, respectively, from measurements at 193 K. These correspond to conformational energies of 0.53 and ≥1.4 kcal/mol, respectively. Although thermodynamic data are incomplete, the heats of formation (ΔH_f°, 298 K) of the *trans* and *cis* alcohols have been reported as −99.6 and −93.3 kcal/mol, respectively (*25*).

Whether or not a catalytic surface is present, a number of factors deriving from properties intrinsic to the reactive molecule may be operative in reactions involving derivatives of cyclohexane. Inductive, steric, and ring deformation effects are evident in a number of homogeneous phase reactions. In the acetylation of the 2-substituted cyclohexanols, a *trans*-2-substituted methyl group produces a small acceleration, believed to be inductive in origin, while a *cis*-2-methyl substituent appears to yield a steric retardation (*26*). With homogeneous systems, it has been suggested that in the transition state the 1,2-substituted groups may relieve steric compression by bending away from other other, a process which is more facile in the *trans*-1,2- than in the *cis*-1, 2-disubstituted molecule (*27*). From inspection of models it has been found that the increasing separation of the *trans*-1,2 groups (or decreasing separation of the *cis*-1,2 groups) flattens the ring chain into the flexible form, a process associated with relatively little increase in energy, while increasing separation of the *cis*-1,2 groups (or decreasing separation of the *trans*-1,2 groups) would be associated with the more energetically difficult puckering of the chair. However, the more rapid oxidation of axial than equatorial forms of substituted cyclohexanols has been attributed to both steric and polar influences (*27*).

Recent mass spectrometric studies of the energy dependence of the fragmentation of stereoisomeric methylcyclohexanols (*28*) provide further information on the relative properties of the epimeric 2-methylcyclohexanols. In the $[C_6F_6]^{+\cdot}$ charge exchange mass spectra the $[M{-}H_2O]^{+\cdot}/[M]^{+\cdot}$ ratio is 1.4 for the *cis* epimer but only 0.44 for the *trans* epimer. This difference was attributed to both an enthalpic and a conformational effect, that is, the difference in the heats of formation of the two forms and the close proximity of the 4-H and the OH group in the boat conformation of the *cis* epimer, where the CH_3 group is in an equatorial position, in contrast to the *trans* epimer in which the methyl group is placed in a sterically more crowded position and as a consequence the aforementioned conformation is less favored.

While the enhanced conversion of *cis*-2-MCHOL as compared to the *trans* epimer observed in the present work may, in the light of the aforementioned studies, be attributed at least in part to the lower stability and more favorable position of the 4-H atom relative to the hydroxyl, which are found in the *cis* form, It will be apparent from examination of the product distributions that other factors must predominate. As has been noted earlier, of the four possible dehydration products from 2-MCHOL, only 1-MCH and 3-MCH are observed. With the *cis* alcohol, the amounts of 1-MCH are considerably larger than those of 3-MCH for all P/Al and all, except the highest, temperatures employed in this work. In contrast, for the *trans* alcohol such product distributions, but of diminished intensity, are only observed for the catalysts with P/Al of 0.8 and 1.0. With the stoichiometric catalyst (P/Al equal to 1.0) at temperatures below 250°C, the ratio of 1-MCH to 3-MCH produced from the *cis* alcohol is a factor of three times larger than that expected at equilibrium. This is indicative of a mechanism in which 1-MCH is produced as a primary product. 1-MCH could result as a primary product either from an E2 [1,2] elimination of water or through the formation of a secondary carbenium ion by extraction of the hydroxyl group followed by proton loss from the methyl-substituted carbon. However, as a consequence of the inductive effect of the methyl group, the secondary carbenium ion is more likely to suffer the loss of a proton from the C-3 position, thus generating 3-MCH.

Production of 1-MCH as a primary product through an E2 mechanism would appear to require an antielimination. While such an elimination may appear difficult to achieve on a solid surface, Knözinger and co-workers have demonstrated that effective contact of the *trans* leaving groups of an alcohol such as *cis*-2-MCHOL with the surface of the catalyst may be obtained by a tilted orientation of the molecule (*29, 30*). However, as is evident from aforementioned considerations of both steric and conformational effects, pseudorotation within the ring, partly surface-assisted, may render unnecessary any models invoking a rigid ring structure for cyclohexane. However, this is not to suggest the existence of a facile *cis–trans* process for the cyclic alcohol, particularly since no evidence for such has been observed in the present work.

In contrast, the 1-MCH/3-MCH ratio obtained with *trans*-2-MCHOL on the stoichiometric catalyst at 170°C is considerably less than the equilibrium value, suggesting the 3-MCH is the primary product in the case. This alkene could be produced by either an *anti* or *syn* [2,3] elimination or alternatively through production of a secondary carbenium ion by loss of a hydroxyl group, that is by either an E2 or E1 mechanism. With the *trans* alcohol the product ratio changes very little with temperature, while with the *cis* alcohol this ratio decreases markedly with temperature until near 400°C these values from the two alcohols are approximately identical. Such an observation implies that with the *cis* alcohol 1- and 3-MCH are produced by different mechanisms with substantially different activation energies. On the other hand, it would appear that with the *trans* alcohol these two products may be produced by similar mechanisms.

The substantial increase in the amount of 1-MCH which is produced from the *cis* alcohol as the P/Al ratio increases up to 0.8, while the quantity of 3-MCH varies relatively little, suggests that the two-site process to which 1-MCH may be attributed requires both phosphorus and aluminum to be present. With the *cis* alcohol the ratio of products 1-MCH/3-MCH, exceeds the equilibrium value for all P/Al values except that corresponding to alumina, for which the 1-MCH/3-MCH ratio is similar to that expected at equilibrium. As with the stoichiometric catalyst at various temperatures, this observation suggests that for all catalysts containing both P and Al, with the *cis* alcohol 1-MCH is the primary product, apparently produced through a predominantly E2 mechanism. With the *trans* alcohol the 1-MCH/3-MCH ratio is less than the equilibrium value for all compositions of catalysts, thus suggesting that 3-MCH is the primary product with all catalyst com-

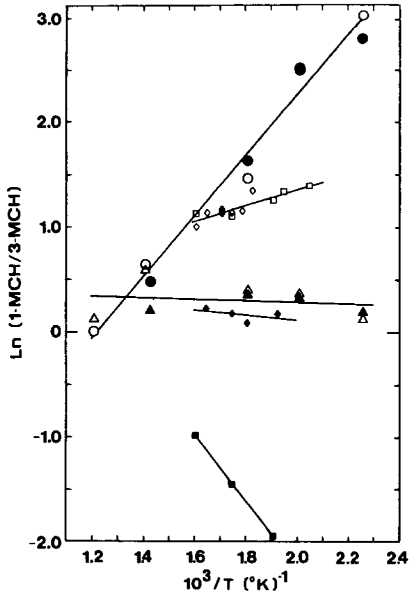

FIG. 4. Ln(1-MCH/3-MCH) vs reciprocal reaction temperature for the dehydration of *cis*- and *trans*-2-methylcyclohexanol by Kearby-type (P/Al = 1.0) Al–P–O catalysts [○ (pH 3.5), ● (pH 7.3); △ (pH 3.5), ▲ (pH 7.3)], alumina (*8b*) (□, ■), and hydroxyapatite (*9*) (◇, ◆) catalysts, respectively.

positions at 175°C. While it is possible for 3-MCH to be generated from either an E1 or E2 process, the former appears more likely in view of the relatively constant value for 1-MCH/3-MCH obtained with the *trans* alcohol. The partial generation of 1-MCH from the *trans* alcohol by secondary isomerization cannot be excluded. Earlier work (*8, 9*) has noted that the production of 1-MCH from the *trans* alcohol for hydroxyapatite and alumina catalysts cannot be adequately explained by a concerted *syn* elimination.

It is of interest to compare the present results with those obtained for other catalysts by various workers. Product (1-MCH/3-MCH) ratios for the Kearby-type aluminum phosphate catalysts of the present work are compared with those for alumina (*8*) and hydroxyapatite (*9*) in Fig. 4. For *trans*-2-MCHOL on aluminum phosphate and on hydroxyapatite the plots are similar, and vary little with temperature, while with alumina a considerably different linear plot with negative slope is obtained. With the *cis* alcohol the data for alumina and hydroxyapatite lie on a common straight line, while those for aluminum phosphate fall on a separate linear plot with a more positive slope. While the mechanism for dehydration of the *trans* alcohol may be similar on hydroxyapatite and aluminum phosphate, that with the *cis* alcohol appears to be significantly different on aluminum phosphate from that observed with either hydroxyapatite or alumina.

The selectivities of alumina, gallium oxide, and anatase in the catalytic conversion of the *cis*-2-MCHOL are similar to those observed in the present work, 1-MCH being predominant in all cases (*10–16*). With alumina, the *trans* isomer produced relatively more 3-MCH than 1-MCH, while with gallia, hafnia, and molybdena approximately equal amounts of these two alkenes were formed. Davis has also compared the conversion of these alcohols over alpha and a transitional alumina (Al–N). With Al–N, the rate of dehydration is again signficantly higher than that of *cis–trans* isomerization, while the 1-MCH/3-MCH ratio was greater and less than 1 with the *cis* and *trans* isomers, respectively. With some oxides, zirconia, for example, a significant amount of *cis–trans* isomerization is observed, the conversions of *cis* and *trans* alcohols to alkenes are similar, and the 1-MCH/3-MCH ratios are approximately 1 with both isomeric forms. Davis (*16*) attributes the 1-alkene selectivity on various oxides with a variety of alcohols to an electronic effect (acidity or basicity) and arranges the oxides in order of increasing basicity: MoO_3, Al_2O_3, SiO_2, In_2O_3, Nd_2O_3, ZrO_2, ThO_2. Davis (*14–16*) suggests that the strong preference for antielimination with alumina is related to the size of the base (*18*). In the case of alumina the oxide ions surrounding the metal ion may constitute a basic anion.

The substantial increase with P/Al in the quantity of 1-MCH produced from *cis*-2-MCHOL suggests that the two-site process producing 1-MCH is dependent, at least partially, on the presence of both aluminum and phosphorus. There appear to be two possibilities: (1) phosphorus or group(s) attached to phosphorus serve as the second site in the two-site process, (2) the addition of phosphorus provides the electronic and/or geometric environment to induce appropriate second-site characteristics in adjacent species, for example, the oxide ions. Recent reports on the role of the phosphate anion in molybdena–alumina based catalysts suggest that this anion may be stabilizing strained Al–O–Al groups (*31*). In contrast the production of 3-MCH from either alcohol is little influenced by the presence of phosphorus atoms. This implies that 3-MCH results primarily from an E1 process, possible through a carbenium ion mechanism, which largely depends on the existence of sufficiently strongly acidic sites. The production of 1-MCH presumably requires an acidic and a basic site which may be provided directly or indirectly, by aluminum and phosphorus, respectively. The aluminum atoms may function as Lewis acidic sites or with hydroxyl groups attached, as Brønsted acidic sites. Hydroxyl groups or oxygen atoms bound to phosphorus atoms may serve as Brønsted and Lewis basic sites, respectively (*4*). However, Peri (*4*) has argued that P–O groups may not be suitable basic sites on aluminum phosphate, at least for cracking purposes. Of course, it must be kept in mind that the potential surface for the one-site process is continuous with that for the two-site mechanism, so that a continuum of possibilities exists, depending on the relative heights of the activation barriers.

In the present case, the enhanced activity for the dehydration of 2-methylcyclohexanol on addition of phosphorus may be attributed, in part, to the higher electronegativity possessed by phosphorus as compared with aluminum. This may produce a shift in electron density away from the aluminum atoms thus enhancing their (Lewis) acidic strength, while contributing to the production of both larger and more effective basic sites, presumably necessary for the two-site dehydration process.

ACKNOWLEDGMENTS

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

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