JOURNAL OF CATALYSIS 75, 94–100 (1982)

The Dehydration of *cis*- and *trans*-2-Methylcyclopentanol on Stoichiometric and Nonstoichiometric B–P–O Catalysts

J. B. MOFFAT[1] AND S. S. JEWUR[2]

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

Received August 11, 1981; revised November 18, 1981

The dehydration of *cis*- and *trans*-2-methylcyclopentanol on B–P–O catalysts with P/B from 0.6 to 1.4, yields only 1-methylcyclopentene and 3-methylcyclopentene, with the relative amounts depending on the catalyst composition and the alcohol conformation. This data and that obtained from water-added catalysts and HMDS poisoning are interpreted to suggest a mixed mechanism involving a dominant E2 antielimination and an E1 2-methylcyclopentyl cation process.

INTRODUCTION

One of the most commonly occurring processes in chemistry involves the removal of adjacent groups or atoms from a molecule to produce a bond of order higher than found in the original molecule. Although considerable work has been done on such elimination reactions, the mechanisms are still not understood and the introduction of a catalytic surface adds a further degree of complexity. Elimination mechanisms in both the liquid state and on catalysts have been classified as E1, E1cB, and E2, referring to two step, two step with rupture of the C–H bond, and one step processes, respectively (*1*). Of course, a continuum of possibilities exists, depending on the relative heights of the activation barriers, so that such subdivisions are somewhat arbitrary, although convenient. Two stereochemical mechanisms are generally distinguished, the *cis*- or syn-elimination, involving removal of the groups from the same side of the host bond pair, and the *trans*- or antielimination, in which the groups leave from opposite sides.

Alcohols are probably the most common group of compounds which has been employed for the study of catalytic eliminations. To a large extent such selection may be due to the convenient nature of the eliminated molecule. Aliphatic alcohols have the disadvantage that relatively free rotation about the host bond pair is often possible so that stereochemical studies are difficult, if not impossible. However, with cyclic molecules where the groups to be eliminated are ring-attached, this problem is largely circumvented. Indeed, cyclic compounds have been used for a number of years for this purpose (*1*). One of the earliest reports is concerned with the dehydration of menthol and neomenthol on alumina, which Pines and Pillai (*2*) found to involve antielimination. The same stereochemistry was deduced for the dehydration of various alkyl- and phenyl-substituted cyclohexanols on alumina (*3, 4*), and for 2-methylcyclohexanol on thorium oxide (*5*).

The results of studies of the dehydration of butanol, and methyl- and dimethylbutanols on B–P–O catalysts of various P/B ratios have recently been reported (*6, 7*). However the stereochemical nature of the elimination could not be deduced. In the present work the dehydration of *cis*- and

---

[1] To whom correspondence should be addressed.

[2] Present address: Departamento de Quimica, U.F.R.N., Natal, RN 59,000 Brazil.

0021-9517/82/050094-07$02.00/0

trans-2-methylcyclopentanol (MCPA) has been studied on B–P–O catalysts with P/B molar ratios of 0.6, 0.8, 1.0, 1.2, and 1.4. Although elimination reactions with cyclopentanol have been explored, no heterogeneous catalytic studies with MCPA have been reported.

EXPERIMENTAL

Materials. The B–P–O catalysts were prepared from boric and orthophosphoric acids as previously described (7) with phosphorus to boron molar ratios (P/B) ranging from 0.6 to 1.4. Samples employed were of 100/200 mesh size and were pretreated at 10^{-3} Torr for 8 hr at 400°C. Catalysts were also prepared by adding 5 ml of water with the boric and phosphoric acid and were labeled as water-added (WA) samples. In some cases these were pretreated at 650°C for 12 hr.

Cis- and *trans*-2-methylcyclopentanol were obtained as 99% pure from Chemical Samples Co. and were used as received. 1-Methylcyclopentene (1MCP) was purchased from Aldrich Chemical Co., 3-methylcyclopentene (3MCP) and 4-methylcyclopentene (4MCP) from Pfaltz and Bauer, Inc., and methylenecyclopentane (MCP) was obtained from Fiuka. Less than 1% of impurity isomers was found in these samples, which were used as received. 1,1,1,3,3,3-Hexamethyl-disilazane (HMDS) was obtained 98% pure from Aldrich Chemical Co.

Procedures. The dehydration reactions were carried out in a microcatalytic pulse reactor (7) by injecting a known amount of reactant into the preheated helium carrier gas. Various helium flow rates, catalyst masses, and reaction temperatures were tested to determine the most suitable reaction conditions to minimize mass transfer effects and secondary reactions. The work reported here employed a helium flow-rate of 180 ml/min, 40 mg of catalyst, and 160°C reaction temperature. The products and unreacted alcohol were trapped in liquid nitrogen and subsequently flashed at 160°C to the gas chromatograph. An 18-ft × ¼-in. column of 20% carbowax 20M (TPA) on 60/80 mesh chromosorb W(AW) operated at 145°C and a 15-ft × ¼-in. column of 25% β,β-oxydipropionitrile on 80/100 mesh chromosorb P(NAW) at 70°C were used for the alcohols and alkenes, respectively.

The surface acidity was estimated from the chemisorption of ammonia. The samples of catalyst were evacuated at 200°C for 3 hr prior to equilibration with 150 Torr of ammonia at room temperature for 12 hr. The system was then evacuated to constant weight.

RESULTS

Dehydration of *cis-* and *trans*-2-methylcyclopentanol on all catalyst compositions employed in this work produced 1-methylcyclopentene (1MCP) and 3-methylcyclopentene (3MCP). No evidence for the presence of methylenecyclopentane (MCP) and 4-methylcyclopentene (4MCP) was found under any conditions of temperature and helium flow rate. The total amounts of alkenes produced per unit area from each of the alcohols as a function of P/B show a minimum near the stoichiometric composition for boron phosphate and maxima at P/B of approximately 0.8 and 1.2 (Fig. 1), with the highest value at the lower P/B. The quantity of ammonia chemisorbed at room temperature shows similar trends with the maximum at a P/B of 0.8 considerably larger than that at P/B equal to 1.2. The *cis*-conformation is the more reactive in all cases.

Dehydration of either *cis-* or *trans*-MCPA produces considerably larger quantities of 1MCP than 3MCP for all compositions of catalyst (Fig. 2). However catalysts of P/B equal to 0.8 and 1.2 produced the maximum amounts of 1MCP while catalysts of P/B equal to 0.9 and 1.0 produced minimum amounts. Amounts of 3MCP formed from either *cis-* or *trans*-MCPA were relatively small for all P/B and were almost constant from both the *cis-* and *trans*-alcohol.

In spite of the careful selection of reac-

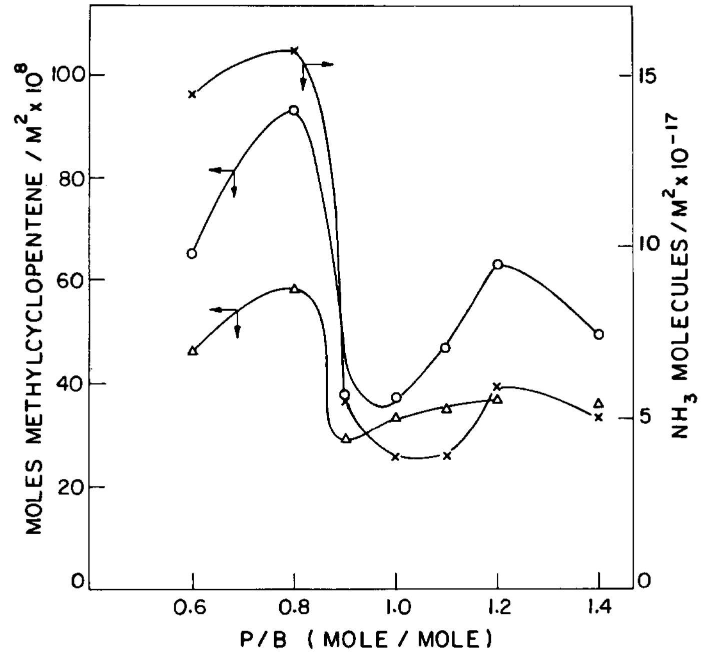


FIG. 1. Specific dehydration activities for *cis*-2-methylcyclopentanol (○) and *trans*-2-methylcyclopentanol (△) and ammonia chemisorbed (×) for various molar P/B ratios.

tion conditions it was not found possible to eliminate net loss of reactant and/or product presumably by irreversible chemisorption and/or cracking on the catalyst. Coloration of the catalyst at the termination of an experiment was also observed. Mass balances were also found to differ from expected values. The amounts of reactant and/or product not accounted for in the mass balance and presumably remaining on the catalyst were calculated from the analytical results for the various catalyst compositions. Although, as a consequence of the method of calculation, relatively large errors can be expected, nevertheless two observations appear to be valid. The percentage of *cis*-MCPA held irreversibly on the catalyst is greater than that of the *trans*-conformer for all catalyst compositions. A maximum in the amount of irreversibly adsorbed material occurs at approximately the stoichiometric composition of boron phosphate in the case of both conformers.

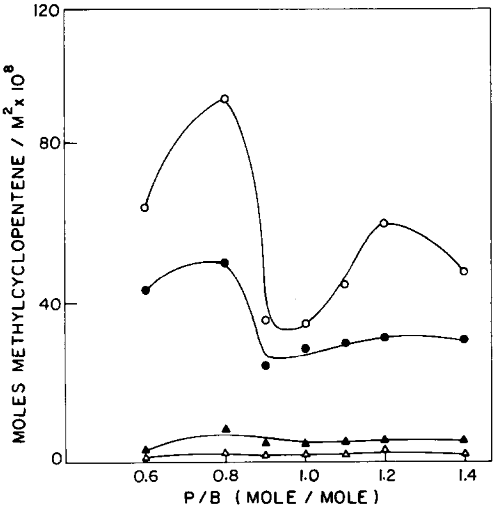


FIG. 2. Moles 1-methylcyclopentene (○,●) and 3-methylcyclopentene (△,▲) produced per unit area from *cis*- and *trans*-2-methylcyclopentanol, respectively.

With the catalysts prepared by addition of supplementary quantities of water, various differences may be noted (Fig. 3). For all compositions the activity of the catalysts for the dehydration has been decreased, and the trends observed previously (Fig. 1)

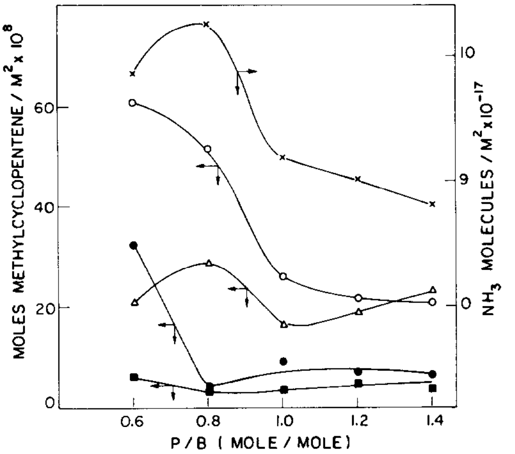


FIG. 3. Specific dehydration activities for *cis*-2-methylcyclopentanol (○,●) and *trans*-2-methylcyclopentanol (△,▲) on water-added catalysts and on water-added catalysts poisoned by HMDS, respectively, various molar P/B ratios. Ammonia chemisorbed (×) on water-added catalysts.

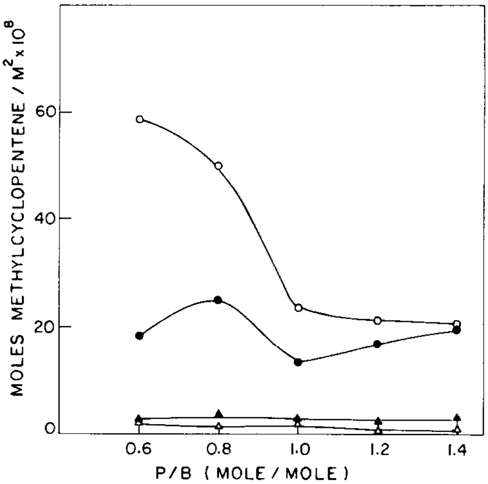


FIG. 4. Moles 1-methylcyclopentene (○,●) and 3-methylcyclopentene (△,▲) produced per unit area from *cis* and *trans*-2-methylcyclopentanol, respectively, on water-added catalysts.

altered considerably. While the activity for the dehydration of the *cis*-conformer is again higher than that for the *trans* form, the activity for the former decreases as P/B increases, so that for P/B equal to 1.2 and 1.4, these values are nearly identical. Addition of hexamethyldisilazane (HMDS) considerably reduces the dehydration activity for both conformers and all catalyst compositions. The dependence of the quantity of ammonia chemisorbed on the composition of the water-added catalyst is now somewhat altered from that observed with the unmodified catalyst (Fig. 1). There is, however, as in the previous case, an approximate correspondence between the quantities of ammonia chemisorbed and the quantities of alkenes produced on the water-added catalyst. With the water-added catalysts the amounts of 1MCP are again greater than those of 3MCP for all compositions, as observed with the unmodified catalysts (Fig. 4), and the quantity of 1MCP produced from the *cis* conformer is considerably greater than that formed from the *trans*-alcohol for samples with P/B equal to 0.6 and 0.8. However as P/B increases the amounts of 1MCP from the *cis*- and *trans*-conformers become nearly equal, as expected from Fig. 3.

Poisoning of the WA catalysts almost eliminates any dependence of amounts of the various alkenes produced on the composition of the catalyst (Fig. 5). However, the amount of 1MCP from the *cis*-alcohol

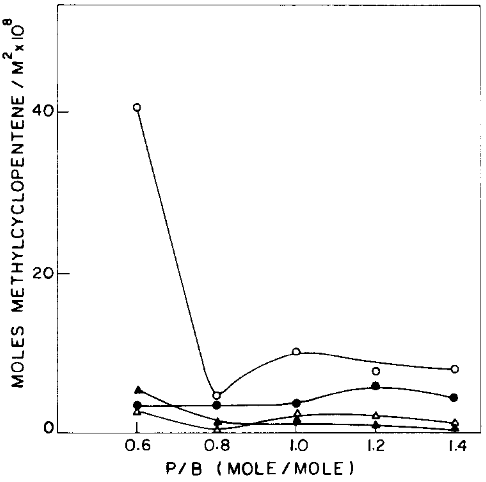
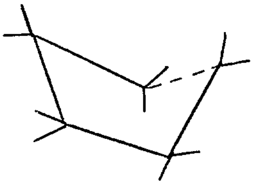
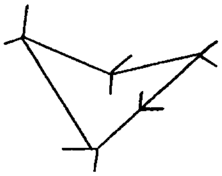


FIG. 5. Moles 1-methylcyclopentene (○,●) and 3-methylcyclopentene (△,▲) produced from *cis*- and *trans*-2-methylcyclopentanol on water-added catalysts, and on water-added catalysts, poisoned by HMDS, respectively.

remains relatively high for the catalyst with P/B equal to 0.6. The amount of irreversibly adsorbed material on the WA catalysts increases with P/B and that on the HMDS-poisoned catalysts decreases as P/B increases.


Envelope


Half-Chair

DISCUSSION

The approximate correlation between the acidity, as estimated from the amount of ammonia chemisorbed, and the total alkenes produced, demonstrates that the reaction is dependent on the number of acidic sites present. Earlier work (*8, 9*) has shown that catalysts with P/B greater than one have primarily Bronsted sites, while those with P/B less than one are predominantly Lewis acidic in nature. It thus appears that Bronsted and Lewis acid sites are equally effective in catalyzing the dehydration of 2-methylcyclopentanol. It is also evident that the stoichiometric catalyst (P/B = 1) possesses fewer acidic sites than those which are nonstoichiometric. This is in agreement with the results of previous work (*6, 7, 10, 11*).

From the results reported here, it is also apparent that, for all compositions of catalysts except that where P/B is equal to 1, the elimination of water occurs more readily with the *cis*-conformer than with the *trans*-alcohol. Although thermodynamic data do not appear to be available for 2-methylcyclopentanol, the evidence which is available suggests that the *trans*-conformer is slightly more stable than the *cis* structure (*12, 13*). However, cyclopentane itself has a puckered ring structure, together with an additional degree of freedom in the form of a rotation of the puckering around the ring, usually referred to as a pseudorotation (*14*). The ring puckering causes ring substituents to assume somewhat staggered positions, rather than the completely eclipsed positions expected for the planar form. At a puckering amplitude of 0.48 Å, the envelope and half-chair forms (C_s and C_2, respectively) have the lowest energy, with the former having an energy lower than the latter by 0.5 kcal/mole. Cyclopentane itself has been shown to be practically a free pseudorotator (*15*), but monosubstitution on the ring changes the potential barriers for rotation around the bonds adjacent to the altered center, thus reducing the pseudorotation. Unfortunately, no conformational analysis is yet available for 2-methylcyclopentanol. However it is believed that the complexities of molecules such as MCPA are manifestations of the five-membered ring (*14*). For example, it has been shown recently (*16*) that the oxidation of *cis*-MCPA by chromic acid in 90% acetic acid at 25°C occurs approximately twice as rapidly as that of the *trans*-conformer, while the acetylation by acetic anhydride in pyridine at 25°C occurs approximately three times more rapidly with the *trans* than with the *cis*. It has been postulated (*17*) that the rate of oxidation with chromic trioxide is directly related to the magnitude of ground state steric interactions involving the OH group of alcohols. However, it has also been shown (*18*) that transition state energy differences, probably the result of torsional angle effects, are important, and depend on the specific stereochemistry in the ground and transition states. Unfortunately, the mechanism of the acetylation reaction is unknown (*16*).

It is thus not possible to propose a unique rationalization for the difference in behavior of the *cis*- and *trans*-MCPA on the present catalysts. However, a number of possibilities can be proposed. The dehydration process may be one of antielimination, apparently occurring more readily with the *cis*- than the *trans*-alcohol. The *cis* form may be inherently more reactive because of the steric repulsive interaction between the hydroxyl and methyl groups. As has been mentioned, puckering of the cyclopentane ring can occur, but it may be anticipated that this would be more prevalent in the *cis*-conformer. However, torsion angle data for cyclopentane (*14*) suggests that, while the hydroxyl and methyl groups in the *cis* form will not be eclipsed, the staggering will probably amount to no more than 20°. The *cis*-alcohol may be able to interact with the solid surface more readily, by assuming the inclined orientation put forth by Knözinger *et al.* (*19*). However, the amounts of the *cis*- and *trans*-alcohols converted on the catalyst with P/B equal to 1 are quite similar, thus suggesting that the difference in behavior of the two conformations of MCPA are more a property of the solid surface than the molecules themselves.

The dehydration of MCPA can, at least in principle, yield four isomers of methylcyclopentene, namely, 1-methylcyclopentene, 3-methylcyclopentene, 4-methylcyclopentene, and methylenecyclopentene. In the present work only 1MCP and 3MCP are produced. No evidence for methylenecyclopentane or 4-methylcyclopentene was found under any reaction conditions. The stabilities of the isomers have been shown to decrease in the order 1MCP, 3MCP, 4MCP, and MCP (*20*). The quantities of 1MCP produced are greater than those of 3MCP for both the *cis*- and *trans*-alcohols and for all compositions of catalyst. However the ratio of 1MCP/3MCP from the *cis*-alcohol ranges from approximately 20 to 55, while that from the *trans*-MCP has values from 5 to 14. The equilibrium ratio of 1MCP/3MCP at 160°C is approximately 12. The significant difference in the compositions produced from the two isomeric alcohols suggests that a common intermediate is unlikely. The observation that the 1MCP/3MCP ratio produced from the *cis* dehydration is greater than the equilibrium value, while that from the *trans* dehydration is less, for all but one catalyst, can be interpreted as evidence for the production primarily of 1MCP and 3MCP from the *cis* and *trans* forms, respectively, a result consistent with antielimination. At the same time, however, the substantial amounts of 1MCP produced from the *trans*-alcohol may be the result of an additional mechanism or may be attributed to secondary isomerization of 3MCP to 1MCP.

It is also interesting to note that the ratio 1MCP/3MCP is highest (for either the *cis*- or *trans*-alcohol) for the catalyst with P/B equal to 0.6, and decreases as the proportion of phosphorus increases. In the case of the *cis*-alcohol the 1MCP/3MCP ratio is essentially constant for catalysts with P/B equal to or greater than 1.0 and for the *trans*-alcohol for all catalysts except that where P/B is equal to 0.6. Of course these ratios are strongly influenced by the changes in amounts of 3MCP produced.

The introduction of additional water in the preparation of the catalysts apparently poisons a number of the Lewis sites and may also reduce the effectiveness of some of the Bronsted sites. The irreversible adsorption appears to take place preferentially on those catalysts with smaller numbers of acidic sites and is least favored by Lewis acid sites. Although addition of water to catalysts with P/B greater than 1 reduces their dehydration activity, their ability to irreversibly adsorb either reactant or products is considerably enhanced. HMDS appears to be capable of poisoning both Lewis and Bronsted sites.

While it is not possible to interpret the present evidence in favor of a unique mechanism for the dehydration of 2-methylcyclopentenols, nevertheless it does appear that an E2 antielimination reaction is occurring. However it is not possible to rule out the participation of an E1 mechanism involving the 2-methylcyclopentyl cation. There is evidence in the present work to suggest that such a mechanism is more probable on catalysts with smaller numbers of acidic sites, preferably of Bronsted type, and that such a mechanism may be conducive to the formation of irreversibly adsorbed materials. It is also not possible to draw conclusions as to the influence of such irreversibly adsorbed materials on the reaction mechanism.

ACKNOWLEDGMENTS

The authors are grateful to the Natural Science and Engineering Research Council of Canada for an operating grant to one of us (JBM) and subsistence allowance to one of us while on leave from Brazil (SSJ), and to the Conselho Nacional De Desenvolvimento Cientifico E Tecnologico (Brasil) for their financial support of one of us (SSJ).

REFERENCES

1. Noller, H., and Kladnig, W., *Catal. Rev. -Sci. Eng.* **13,** 149 (1976).
2. Pines, H., and Pillai, C. N. *J. Amer. Chem. Soc.* **83,** 3270 (1961).
3. Blanc, E. J., and Pines, H., *J. Org. Chem.* **33,** 2035 (1968).
4. Pines, H., and Manassen, J., *Adv. Catal.* **16,** 49 (1966).
5. Blanchard, M., and Canesson, P., 2 ème Colloque Franco-Polonaise sur la Catalyse, Poitiers, 1969.
6. Jewur, S. S., and Moffat, J. B., *J.C.S. Chem. Commun.* 801 (1978).
7. Jewur, S. S., and Moffat, J. B., *J. Catal.* **57,** 167 (1979).
8. Miyata, H., and Moffat, J. B., *J. Catal.* **62,** 357 (1980).
9. Moffat, J. B., and Neeleman, J. F., *J. Catal.* **39,** 419 (1975).
10. Moffat, J. B., and Chao, E., *J. Catal.* **46,** 151 (1977).
11. Moffat, J. B., Chao, E., and Nott, B., *J. Colloid Interface Sci.* **67,** 240 (1978).
12. Umland, J. B., and Williams, B. W., *J. Org. Chem.* **21,** 1302 (1956).
13. Ouannès, C., and Jacques, J., *Acad. Sci. Compt. R.* **257,** 2118 (1963).
14. Fuchs, B., *in* "Topics in Stereochem" (E. L. Eliel and N. J. Allinger, Eds.), Vol. 10, Chap. 1, p. 1. Interscience-Wiley, New York, 1978.
15. Pitzer, K., and Donath, W. E., *J. Amer. Chem. Soc.* **81,** 3213 (1959).
16. Hach, V., *J. Org. Chem.* **42,** 1616 (1977).
17. Eliel, E. L., Allinger, N. L., Angyal, S. J., and Morrison, G. A., "Conformational Analysis." Interscience, New York, 1965; Wilcox, C. F., Sexton, M., and Wilcox, M. F., *J. Org. Chem.* **28,** 1079 (1963); Eliel, E. L., Schroeter, S. H., Brett, T. J., Biros, F. J., and Richer, J. C., *J. Amer. Chem. Soc.* **88,** 3327 (1966); Baker, R., and Mason, T. J., *J. Chem. Soc. B* 988 (1971).
18. Pasto, D. J., and Rao, D. R., *J. Amer. Chem. Soc.* **92,** 5151 (1970).
19. Knözinger, H., Bühl, H., and Kochloefl, K., *J. Catal.* **24,** 57 (1972).
20. Yursha, I. A., and Kabo, G. Ya., *Zhur. Fiz. Khim.* **49,** 1302 (1975).