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Transformations of Cyclohexane Derivatives in Supercritical Water

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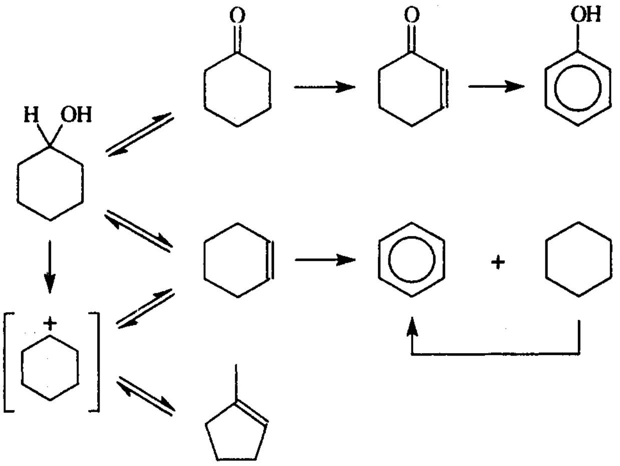
Functional group transformations in supercritical water were examined for a series of cyclohexane derivatives including cyclohexane, cyclohexene, cyclohexanol, cyclohexanone, benzene, and phenol. No reactions were observed in the absence of a catalyst, but hydration–dehydration, skeletal isomerization, and hydrogenation–dehydrogenation transformations did occur in the presence of an acid, base, or metal catalyst. Dehydrogenations included the ketonization of cyclohexanol and the aromatization of cyclohexanone, cyclohexene, and cyclohexane. The dehydrogenations required a late transition metal catalyst (e.g. PtO_2 or 10% Pt/C) and proceeded even in the absence of a sacrificial hydrogen acceptor. Cyclohexanol dehydration was catalyzed by either acid or base, while cyclohexene hydration was only observed in reactions involving both PtO_2 and an acid or base. Skeletal isomerization was an acid-catalyzed process. These reactions demonstrate that organic functional group transformations in supercritical water can be accessed through the selection of appropriate catalysts.

Introduction

Organic and organometallic reactions in supercritical water are gathering increasing interest, particularly in relation to the extraction of coal or wood products,[1] the destructive oxidation of organic wastes,[2] and hydrothermal systems.[3] Most studies of reactions in supercritical water have therefore been aimed at elucidating the processes which occur when model compounds are placed under representative conditions. Interest in the use of supercritical water as a solvent for targeted synthetic processes has also been growing and is primarily motivated by environmental concerns affecting the disposal of organic solvents. However, the development of synthetic processes requires an understanding of product control in addition to product elucidation. Reports of rate control in supercritical water are quite common; however, product control has not previously been extensively explored.

We are attempting to determine how catalysts and other additives influence functional group transformations in supercritical water. We report here the fundamental conversions and interconversions of several cyclohexane derivatives which are affected by various transition metal catalysts and pH conditions.

Scheme 1



Results and Discussion

Cyclohexane derivatives undergo a series of hydration–dehydration and hydrogenation–dehydrogenation interconversions in supercritical water which are different from those observed at lower temperatures. A major portion of this work has been concerned with elucidating these relationships, a general summary of which is shown in Scheme 1. The second objective of this work was to determine how these conversions could be controlled by the choice of catalyst or reaction conditions. Variations in the transition metal catalyst and pH were shown to access different portions of this scheme, as detailed below, while the substrates were recovered unchanged after heating alone in carefully neutralized water. (See Tables 1 and 2, experiments 1 and 13.) The effect of acid on reaction chemistry in supercritical water media has received some previous attention;[4,5] however, few reactions have been reported in supercritical water under basic conditions.[3a,4e,6]

Dehydration. The dehydration of alcohols to alkenes is generally a very facile process in supercritical water. Cyclohexanol is no exception and underwent facile dehydration to form cyclohexene in acidic supercritical water.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

[1] (a) Egiebor, N. O.; Li, L. *Energy Fuels* **1992,** *6,* 35. (b) Tsao, C. C.; Zhou, Y.; Liu, X.; Houser, T. J. *J. Supercrit. Fluids* **1992,** *5,* 107. (c) Funazukuri, T.; Wakao, N.; Smith, J. M. *Fuel* **1990,** *69,* 349. (d) Houser, T. J.; Dyla, J. E.; Van Atten, M. K.; Li, Z.; McCarville, M. E. *Coal Sci. Technol., 11 (Int. Conf. Coal Sci. 1987)* **1987,** 773.

[2] (a) Li, R.; Thornton, T. D.; Savage, P. E. *Environ. Sci. Technol.* **1992,** *26,* 2388. (b) Webley, P. A.; Tester, J. W.; Holgate, H. R. *Ind. Eng. Chem. Res.* **1991,** *30,* 1745. (c) Lee, D.-S.; Gloyna, E. F.; *Environ. Sci. Technol.* **1992,** *26,* 1587. (d) Barner, H. E.; Huang, C. Y.; Johnson, T.; Jacobs, G.; Martch, M. A.; Killilea, W. R. *J. Hazard. Mater.* **1992,** *31,* 1. (e) Kodra, D.; Balakotaiah, V.; *AIChE J.* **1992,** *38,* 988. (f) Torry, L. A.; Kaminsky, R.; Klein, M. T.; Klotz, M. R. *J. Supercrit. Fluids* **1992,** *5,* 163. (g) Klein, M. T.; Mentha, Y. G.; Torry, L. A. *Ind. Eng. Chem. Res.* **1992,** *31,* 182. (h) Modell, M. *Chem. Phys. Process Combust.* **1989,** E1. (i) Takahashi, Y.; Wydeven, T.; Koo, C. *Adv. Space Res.* **1989,** *9,* (8), 99. (j) Shaw, R. W.; Brill, T. B.; Clifford, A. A.; Eckert, C. A.; Franck, E. U. *Chem. Eng. News* **1991,** *Dec. 23,* 26 and references therein.

[3] (a) Katritzky, A. R.; Balasubramanian, M.; Siskin, M. *J. Chem. Soc., Chem. Commun.* **1992,** 1233. (b) Katritzky, A. R.; Lapucha, A. R.; Murugan, R.; Luxem, F. J.; Siskin, M.; Brons, G. *Energy Fuels* **1990,** *4,* 482 and following 18 papers (482–584).

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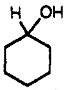
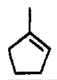
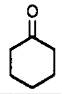
Table 1. Relative Product Distributions from Reactions of Cyclohexanol in Neutral, Acidic, or Basic Water

			rel % of products			
expt	catalyst[a]	T (°C)				
1		375	100			
2	HCl	375	2	93	4	
3	$MnCl_2$	375	2	98		
4	$CuCl_2$	375	3	90	7	
5	$SnCl_2$	375		38	62	
6	NH_4OH	375	16	84		
7	NH_4OH	140	100			
8	NH_4OH	25	100			
9	HCl	140	86	14		
10	HCl	25	100			
11	$CuCl_2$	140	98			2
12	$CuCl_2$	25	100			

[a] 1.0 mmol of substrate, 0.3 mmol of MCl_2, 0.6 mmol of HCl, 0.6 mmol of NH_4OH, 3.5 mL of H_2O; 20 min, 375 °C; 12 h, 140 °C; 24 h, 25 °C.

(See Table 1 for representative results.) This dehydration occurred in the presence of a variety of catalysts including mineral acids and acidic metal complexes. Among these were HCl (expt 2), HNO_3, H_2SO_4, V_2O_5, $RuCl_3$, $MnCl_2$ (expt 3), $CuCl_2$ (expt 4), $SnCl_2$ (expt 5), and $FeCl_3$. The dehydration has been suggested to occur via an acid-catalyzed E2 mechanism.[5]

Base-catalyzed dehydration of the cyclohexanol also occurred in the presence of NH_4OH (expt 6). This is noteworthy since the dehydration of alcohols in basic supercritical water has not been previously reported. The precise action of the base is not yet known, but it could accelerate proton removal in the second step of a conventional dehydration mechanism or it could induce alkoxide formation followed by deoxidation.[7]

Although dehydration was facile at 375 °C, the reverse hydration process was not observed at this temperature. No cyclohexanol was obtained from cyclohexene utilizing any of these simple acid or base catalysts under supercritical water conditions (expts 14–18) (Table 2). The addition of PtO_2 to the reactions of cyclohexene with either HCl (exp 29) or NH_4OH (expt 30) did yield small amounts of cyclohexanol, however (Table 3). The primary dehydrogenation function of the platinum catalyst is attenuated by both HCl and NH_4OH (see below), and it is likely that deactivation of the catalyst for dehydrogenation is linked to its activation toward hydration. Although it is still a very small component of the overall reaction profile, this is the first evidence of productive alkene hydration which we have observed in our supercritical water systems.

The reactivities of the various substrates which were observed under supercritical conditions were frequently different from those which occurred at lower temperatures. Although cyclohexanol underwent facile dehydration at 375 °C, it was essentially unreactive at both 25 °C and 140 °C (expts 7–12). Dehydration was observed in the presence of HCl at 140 °C (expt 9) but only to a minor extent.

Cyclohexene, on the other hand, was quite reactive at 25 °C. The alkene underwent complete hydration in the presence of HCl (expt 22) and near quantitative allylic oxidation in the presence of $CuCl_2$ (expt 24). At 140 °C this reactivity decreased, with no hydration and little oxidation observed from the reactions with HCl (expt 21) and $CuCl_2$ (expt 23), respectively, while at 375 °C neither hydration nor oxidation was observed.[8] The presence of NH_4OH alone had no apparent effect on the cyclohexene at any temperature (expts 18–20).

It is well-known that the hydration of alkenes to form alcohols is favored under acidic conditions at low temperatures, while this preference reverses at high temperatures, causing dehydration of the alcohol to be strongly favored at 375 °C.[5a] It is therefore not surprising that cyclohexene and cyclohexanol followed this trend in our system. Likewise, oxygenation, which was catalyzed by $CuCl_2$ at ambient temperature, was severely attenuated at the higher temperature. These differences in reactivity underscore the importance of reevaluating traditional reaction systems under supercritical water conditions.

Rearrangement. Reaction of either cyclohexanol or cyclohexene with HCl (expts 2, 14) or the more strongly acidic metal salts $CuCl_2$ (expts 4, 16) and $SnCl_2$ (expts 5, 17) in supercritical water resulted in the formation of methylcyclopentene. This ring contraction is believed to result from carbocation rearrangement and has been previously reported in acidic aqueous and organic systems.[9] The acid-catalyzed rearrangement could be halted by the addition of a base (^{-}OH, $CH_3CO_2^-$, CO_3^{2-}) to the reaction mixture and only occurred at high temperature; methylcyclopentene was not observed in any of the reactions carried out at 25 °C or 140 °C. The rearrangement was reversible, however, and methylcyclopentene isomerized to cyclohexene in acidic water at 375 °C.

A similar rearrangement has also been observed by Katrinsky and Siskin[6b] in near-critical water. In their experiment, cyclohexyl phenyl ether hydrolyzed in the presence of acid to yield phenol and methylcyclopentene. They propose that the rearrangement occurred by an E1 mechanism, in contrast to the E2 process reported for the dehydration.

Dehydrogenation. In addition to dehydrating the alcohol, late transition metal catalysts also promoted dehydrogenation processes in the supercritical water. This dehydrogenation was of two types: aromatization of the cyclohexyl ring and oxidation of the alcohol to the corresponding ketone. (See Scheme 1). Both alcohol and ring dehydrogenation processes occurred in the presence of a variety of complexes such as PtO_2, $Ru_3(CO)_{12}$, $Co(OAc)_2$, $IrCl_4$, and $Pt(PPh_3)_2Cl_2$. For purposes of comparison, each of the reactions reported here was carried out by combining the substrate with PtO_2 in supercritical water for 20 min, unless otherwise stated (Table 3). The

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(4) (a) Jerome, K.; Parsons, E. J. *Organometallics* **1993**, *8*, 2991. (b) Narayan, R.; Antal, M. J., Jr. In *Supercritical Fluid Science and Technology*; Johnson, K. P., Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989; p 226. (c) Penniger, J. M. L.; Kolmschate, J. M. M. In *Supercritical Fluid Science and Technology*; Johnson, K. P., Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989; p 242.

(5) (a) Xu, X.; De Almeida, C. P.; Antal, M. J., Jr. *Ind. Eng. Chem. Res.* **1991**, *30*, 1478. (b) Narayan, R.; Antal, M. J., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 1927. (c) Xu, X.; DeAlmedia, C.; Antal, J. J., Jr. *J. Supercrit. Fluids* **1990**, *3*, 228. (d) West, M. A. B.; Gray, M. R. *Can. J. Chem. Eng.* **1987**, *65*, 645.

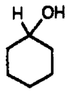
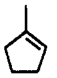
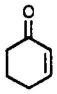
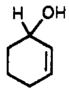
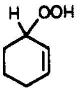
(6) (a) Thomason, T. B.; Modell, M. *Hazard. Waste* **1984**, *1*, 453. (b) Siskin, M.; Katritzky, A. R. *Energy Fuels* **1990**, *4*, 482.

(7) Skell, P. S.; Starer, I. *J. Am. Chem. Soc.* **1959**, *81*, 4117.

(8) It should be noted that these reactions at lower temperatures may be considered neat reactions of the organic substrate, since the solubility of these species is minimal in liquid water.

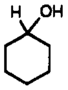
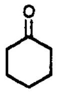
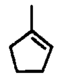
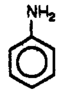
(9) For example, see: (a) Campelo, J. M.; Garcia, A.; Gutierrez, J. M.; Luna, D.; Marinas, J. M. *Can. J. Chem.* **1984**, *62*, 1455. (b) Werstiuk, N. H.; Timmins, G. *Can. J. Chem.* **1985**, *63*, 530. (c) Evers, J. Th. M.; Macker, A. *Tetrahedron Lett.* **1978**, *26*, 2321.

Table 2. Relative Product Distributions from Reactions of Cyclohexene in Neutral, Acidic, or Basic Water

			rel % of products					
expt	catalyst[a]	T (°C)						
13		375		100				
14	HCl	375		93	7			
15	$MnCl_2$	375		100				
16	$CuCl_2$	375		92	8			
17	$SnCl_2$	375		35	65			
18	NH_4OH	375		100				
19	NH_4OH	140		100				
20	NH_4OH	25		100				
21	HCl	140		100				
22	HCl	25	100					
23	$CuCl_2$	140		83		14	3	
24	$CuCl_2$	25		6		34	9	51

[a] 1.0 mmol of substrate, 0.3 mmol of MCl_2, 0.6 mmol of HCl, 0.6 mmol of NH_4OH, 3.5 mL of H_2O; 20 min, 375 °C; 12 h, 140 °C; 24 h, 25 °C.

Table 3. Products Obtained from the Reactions of Cyclohexanol, Cyclohexene, and Cyclohexane with PtO_2 in Supercritical Water

				rel % of products					
expt	catalyst								
				Cyclohexanol[a]					
25	PtO_2	25	44	9	6	11	5		
26	PtO_2 + HCl	76	<1	<1	9	9			6
27	PtO_2 + NH_4OH		11	2	26	56	3[b]	2	
				Cyclohexene[a]					
28	PtO_2	8	54	38					
29	PtO_2 + HCl	92			5				3
30	PtO_2 + NH_4OH	40	39	19	2				
				Cyclohexane[a,c]					
31	PtO_2		27	73					

[a] 1.0 mmol of substrate, 0.1 mmol of PtO_2, 0.6 mmol of HCl, 0.6 mmol of NH_4OH, 3.5 mL of H_2O, 375 °C, 20 min. [b] Obtained as the conjugate base. [c] No sacrificial olefin added.

reaction was not complete within this time period, however, and continuation of the reaction for longer periods of time resulted in continued dehydrogenation.[10]

Oxidation of the Alcohol. In the presence of late transition metal catalysts, ketone formation was competitive with the dehydration of cyclohexanol, leading to partial retention of the oxygen functionality. Platinum oxide was not a particularly efficient oxidant at 375 °C, however, and dehydration of the alcohol dominated over oxidation to the ketone at this temperature (expt 25). This balance was reversed at lower temperatures such that the reaction of cyclohexanol with PtO_2 at 140 °C gave good selectivity toward cyclohexanone.

The platinum-catalyzed oxidation of alcohols to ketones in water has been previously shown to occur readily at mild temperatures (25°–80 °C),[11] and these low temperature ketonizations proceeded independently of pH. This independence was also observed at 375 °C in either neutral (expt 25) or acidic (expt 26) water. However, the addition of NH_4OH to the PtO_2 (expt 27) at 375 °C enhanced the alcohol dehydrogenation, resulting in the formation of cyclohexanone as the major product. This preference is unlikely to result from simple inhibition of the competing dehydration pathway since NH_4OH catalyzed the dehydration in the absence of platinum (expt 6). Ammonium alkoxide formation may play a role in the reaction, although dissociation of a hydroxyl proton on transition metal surfaces is generally rapid even without added base.[12]

Platinum(0) has been previously shown to be the species responsible for oxidizing alcohols to their carbonyl products at lower temperatures.[13] This suggests that platinum(0) formed by *in situ* reduction of the PtO_2 in the supercritical water system may be the species responsible for ketone formation. X-ray diffraction on the insoluble powder resulting from each of the reactions (PtO_2, PtO_2 + NH_4OH, and PtO_2 + HCl) confirmed that the platinum's final state was indeed platinum metal by comparison with the JCPDS powder diffraction file (Figures S1 and S2 and Table S1 (supplementary material)). The reaction of cyclohexanol at 375 °C was therefore reexamined with metallic platinum in the form of 10% Pt/C (expt 32) (Table 4). Ketone formation was favored with this catalyst at the expense of both dehydration and aromatization, supporting the attribution of ketonization to a platinum(0) species. The role of the NH_4OH may therefore be to assist in the reduction of the platinum. The formation of

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(10) We previously reported cessation of the reaction after 2 min as observed by Raman spectroscopy. However, this observation is inconsistent with subsequent product analysis studies and may be an artifact of the reaction conditions or the spectroscopic setup: Myrick, M. L.; Kolis, J.; Parsons, E.; Chilke, K.; Lovelace, M.; Holliday, R.; Williams, M. *J. Raman Spectrosc.* **1994**, *25*, 59.

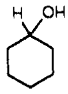
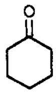
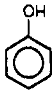
(11) (a) Nicoletti, J. W.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 759. (b) Heyns, K.; Blazejewicz, L. *Tetrahedron* **1960**, *9*, 67.

(12) (a) McKee, D. W. *Trans. Faraday Soc.* **1968**, *64*, 2200.

(13) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

(14) Powder Diffraction File: Inorganic Phases; JCPDS, International Center for Diffraction Data, 1985.

Table 4. Products Obtained from the Reactions of Cyclohexanol, Cyclohexene, and Cyclohexane with 10% Platinum on Carbon in Supercritical Water

		rel % of products					
expt	substrate[a]						
32	cyclohexanol		1	<1	59	39	
33	cyclohexene	4	62	35			
34	cyclohexane[b]		2	98			

[a] 1.0 mmol of substrate, 0.01 mmol of Pt as 10% Pt/C, 3.5 mL of H_2O, 375 °C, 20 min. [b] No sacrificial olefin added.

small amounts of aniline from the reaction of cyclohexanol with PtO_2 and NH_4OH (expt 27) further supports this idea by indicating that NH_3 is available and accessible for reaction in the supercritical water.

Controlled oxidation is desirable as a means of enhancing the utilization of alcohols in general and aqueous methanol and ethanol in particular. Few reports have appeared concerning the metal-catalyzed oxidation of alcohols to aldehydes or ketones in supercritical water, however.[1a,15] Oxidations of ethanol, methanol, and other alcohols have primarily been carried out in oxygen atmospheres at very high temperatures (400–550 °C), where further oxidation to CO and CO_2 becomes competitive. The reactions described here demonstrate that appropriate selection of the catalyst and reaction conditions can have a major impact on promoting and controlling the desired oxidation reaction.

Aromatization of the Cyclohexyl Ring. Ring dehydrogenation of cyclohexene to form benzene occurred readily at 375 °C in the presence of late transition metal catalysts, regardless of whether the substrate was directly added to the reaction mixture or was formed *in situ* (expts 28 and 25, respectively). Less facile dehydrogenation of cyclohexanone also occurred to form phenol (for example, see expts 25 and 27). Small amounts of cyclohexen-3-one were also occasionally observed from the cyclohexanone reactions, and this compound was independently shown to form phenol under the reaction conditions. Aromatization was clearly the driving force for the dehydrogenation; for example, the reaction of ethylcyclohexane yielded ethylbenzene but did not further dehydrogenate to styrene. Dehydrogenation of the cyclohexyl ring was severely attenuated at 140 °C and did not occur at 25 °C.

The dehydrogenation of cyclohexene to form benzene was accompanied by a transfer hydrogenation which produced cyclohexane (expt 28). This reaction was further complicated by subsequent dehydrogenation of the cyclohexane which also formed benzene. Dehydrogenation of the unactivated cyclohexane was confirmed by its independent reaction with PtO_2 and was much less facile than the dehydrogenation of cyclohexene (expt 31).

Late transition metal catalyzed dehydrogenations of cyclohexene and cyclohexane are well-known in both heterogeneous[16] and homogeneous systems.[17,18] Thermodynamics dictates that the hydrogen produced during the dehydrogenation must be removed from the reaction mixture, since the reverse hydrogenation is more favorable. In previously reported thermal systems this removal has been accomplished either by physical means[17] or by the provision of a sacrificial hydrogen acceptor, usually in the form of the weakly-coordinating olefin 3,3-dimethylbutene.[18] Both of these processes operated effectively in our supercritical water system.

Physical removal of the hydrogen occurred unintentionally from the stainless steel vessels in which the supercritical water reactions were run. The hydrogen from these reactions diffused into the steel, resulting in rapid flawing of the bombs used for these reactions.[19] When a suitable acceptor was provided (for example, cyclohexene or 3,3-dimethylbutene), both hydrogen transfer and diffusion competed to remove hydrogen from the reaction mixture. 3,3-Dimethybutene was hydrogenated to form 2,2-dimethylbutane concurrently with the dehydrogenation of cyclohexane to form benzene. Curiously, the products were obtained in a 1:1 ratio, regardless of the amount of excess dimethylbutene provided. Likewise, the reaction of cyclohexene with PtO_2 in the absence of 3,3-dimethylbutene yielded one cyclohexane per benzene, once the corresponding conversion of cyclohexane to benzene was accounted for. This stoichiometric outcome appears to be dictated by the diffusion of hydrogen from the system since sealing the reactions in quartz tubes halted the diffusion and increased the yield of the hydrogenated acceptor.

Supported platinum metal has been reported to be the most active of the heterogeneous dehydrogenation catalysts in nonsupercritical water systems. Since the PtO_2 is recovered as platinum metal at the end of the supercritical water reactions (see above), this metal may be the active aromatization catalyst in this system as well. To probe this possibility, cyclohexene and cyclohexane were each reacted with 10% Pt/C. The benzene yield from the reaction of cyclohexene with Pt/C (expt 33) was very similar to the yield obtained using PtO_2 (expt 28). However, significantly less benzene was obtained from cyclohexane with Pt/C (expt 34) than with PtO_2 (expt 31). Dehydrogenation of the unactivated substrate is therefore apparently more sensitive to the form or amount of the catalyst than is the activated cyclohexene. This may be due to slower reaction of the cyclohexane which allows deactivation processes to successfully interfere with the dehydrogenation.

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(15) For example, see (a) Helling, R. K.; Tester, J. W. *Environ. Sci. Technol.* **1988,** *22,* 1319. (b) Webley, P. A.; Tester, J. W. In *Supercritical Fluid Science and Technology*; Johnson, K. P., Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989; p 259.

(16) (a) Yukawa, K.; Fujii, T.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1991,** 1548. (b) Fujii, T.; Yukawa, K.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1991,** *64,* 938. (c) Sinfelt, J. H.; Hurwitz, H.; Rohrer, J. C. *J. Catal.* **1962,** *1,* 481. (d) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Boston, MA, 1984.

(17) (a) Aoka, T.; Crabtree, R. H. *Organometallics,* **1993,** *12,* 294. (b) Fujii, T.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1990,** 757.

(18) (a) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987,** *109,* 8025. (b) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Yingrui, L. *Tetrahedron Lett.* **1985,** *26,* 1999.

(19) Seward, T. M.; Kishima, N. In *Hydrothermal Experimental Techiques*; Ulmer, G. C., Barnes, H. L., Eds.; Wiley-Interscience: New York, 1987; p 141.

Although the pH of the PtO_2 reactions did not affect the final state of the platinum, it did affect the facility with which the aromatization reaction occurred. Ring dehydrogenation was partially inhibited in the presence of base (expts 27, 30) and was completely halted in acid (expts 26, 29). The acid was at first thought to act as a hydrogen source for the reverse hydrogenation reaction, as has been observed in some palladium catalyzed reactions.[20] However, no cyclohexane was obtained from the reaction of cyclohexene with HCl and PtO_2 (expt 29). In fact, very little reaction was observed at all, with only small amounts of cyclohexanol and methylcyclopentene obtained. This suggests that the acid, and to a lesser extent the base, are involved in catalyst deactivation processes (such as surface fouling) which interfere with the dehydrogenation reaction but which do not significantly alter the identity of the bulk platinum.

Conclusions

Supercritical water has the potential to replace organic solvents as the reaction medium for organic syntheses. In order to exploit this potential, the scope of organic transformations which are possible in supercritical water must be delineated. This paper addresses a series of simple transformations which were carried out under relatively mild conditions. A number of different catalyzed processes were observed, although no reaction of the various substrates was observed in the absence of a catalyst. The catalyzed processes were not necessarily identical to their analogous low-temperature reactions.

The primary importance of the observed reactions is that they demonstrate control of organic functional group transformations in supercritical water through the selection of appropriate catalysts. The formation of cyclohexane was highly favored at 375 °C, with cyclohexanol undergoing both acid and base catalyzed dehydration. Hydration of the alkene was observed only in the combined presence of acid or base and platinum catalyst. Acid also induced the rearrangement of cyclohexene and cyclohexanol to methylcyclopentene. Dehydrogenation processes occurred in the presence of late transition metal catalysts such as PtO_2 and 10% Pt/C. Ring dehydrogenation resulted in the aromatization of both cyclohexane and cyclohexene to form benzene and of cyclohexanone to form phenol. In addition, dehydrogenation of the alcohol yielded cyclohexanone, with this pathway becoming dominant in the presence of platinum metal.

The selectivities reported here are frequently low; nevertheless, the reaction control that is demonstrated makes it clear the targeted transformations are attainable. These controlled transformations will become increasingly accessible as our understanding of synthetic organic processes in supercritical water continues to expand.

Experimental Section

Water was distilled from basic potassium permanganate and then neutralized by vigorous boiling under a stream of purified argon. The 10.5-mL reaction vessels consisted of coned and threaded 316SS tubes each fitted with an end cap and a valve. All parts are rated to 20 000 psi or greater and are commercially available from HiP.

Powder X-ray diffraction spectra were measured over the range 2–70° at a rate of 1°/min on a Scintag XDS/2000 θ–θ diffractometer using Cu Kα radiation.

Reactions in Steel Bombs. Substrate (1.0 mmol) and water (3.5 mL) were placed in the reactor along with any metal catalyst (0.3 mmol MCl_2, 0.1 mmol PtO_2, 0.01 mmol Pt as 10% Pt/C), acid (0.6 mmol HCl), base (0.6 mmol NH_4OH), or 3,3-dimethylbutene (1.0–3.0 mmol). The reactor was then sealed and placed in a tube furnace at 375 °C for 20 min. Following the reaction, the bomb was cooled under a stream of water and the contents were removed. The mixture was placed in a separatory funnel, and the organic layer was separated and dissolved in $CDCl_3$. The water layer was extracted with $CDCl_3$, and NMR spectra of both the water extract and the organic layer were obtained. Further analysis of these samples was obtained via GC/MS. Occasional reactions were run in D_2O, and the water layer was analyzed directly.

Reactions in Quartz Tubes. Cyclohexane (100 μL, 0.9 mmol), 3,3-dimethylbutene (116 μL, 0.9 mmol), PtO_2 (0.3 mmol), and water (300 μL) were sealed in a quartz tube having a total volume of 1.5 mL. Up to 10 tubes were then placed in a Parr bomb, which was counterpressured to 3000 psi with argon. The bomb was placed in a tube furnace and heated to 375 °C for 2 h. Following the reaction, the tubes were cracked and the organic layer was separated and analyzed as above.

Low-Temperature Reactions. Reactions at 140 and 25 °C were run on the same scale as the reactions in steel bombs. The reactions at 140 °C were run for 12 h in sealed glass tubes which were immersed in an oil bath. Reactions at 25 °C were run for 24 h in stoppered round-bottom flasks.

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Supplementary Material Available: Figures showing powder patterns and a table providing a comparison of 2-θ values for reaction samples and the platinum metal standard (3 pages). Ordering information is given on any current masthead page.

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[20] Unpublished results from palladium coupling reactions in supercritical water carried out in our laboratory.