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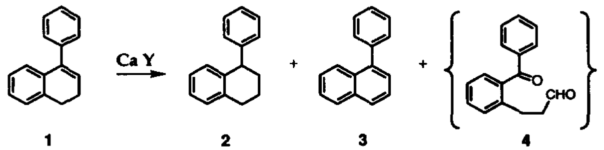
CATION RADICAL AND CARBOCATION MEDIATED REACTIONS WITHIN CA Y ZEOLITE: 1-PHENYL 3,4-DIHYDRONAPHTHALENE

K. PITCHUMANI, P. H. LAKSHMINARASIMHAN, G. TURNER,# M. G. BAKKER# AND V. RAMAMURTHY*
Department of Chemistry, Tulane University, New Orleans, LA 70118
Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487

Reactions of carbocations and radical cation of 1-phenyl 3,4-dihydronaphthalene have been investigated within Ca Y. Copyright © 1996 Elsevier Science Ltd

Phenyl substituted acyclic olefins (stilbenes, styrenes, 1,1-diarylethylenes), upon introduction into activated zeolite Ca Y, undergo spontaneous reduction to yield the corresponding aryl substituted hydrocarbons in near quantitative yield.[1] In this Letter we show that the behavior of aryl substituted cyclic olefin is slightly different from that of acyclic olefins reported earlier. The main difference between the cyclic and acyclic olefins is in the source of the hydride ion that completes the reduction process; in the cyclic systems the reactant itself serves as the hydride ion source and in acyclic systems the solvent is the hydride ion source.

Ca Y, prepared from Na Y by an exchange process, was used in this study. The normal activation procedure involved baking about 300 mg of Ca Y at 500 °C in an oven under aerated conditions for about 12 h. When such activated Ca Y, after cooling to room temperature, was dropped into a hexane solution of 1-phenyl 3,4-dihydronaphthalene (**1**, 20 mg/3 mL; 1 molecule per supercage) a bright yellow color developed which persisted for several hours. Extraction of the hexane-zeolite slurry with methylene chloride gave 1-phenyltetralin (**2**) and 1-phenylnaphthalene (**3**) in equal amounts; none of **1** was left unreacted (Scheme 1).[2] A surprising result was obtained at low loading levels of **1** within Ca Y (<1 molecule per 100 supercages). At low loading levels, the product **3** was obtained as the major product (~92%) along with minor amounts (<3%) of **4**. The product distributions obtained at various loading levels of **1** included in Ca Y are presented in Figure 1. It is important to note that when the loading level is above one molecule per two supercages both **2** and **3** were obtained in equal amounts; at lower loading levels, **3** is the major product. The unusual dependence of product distribution on the loading level prompted us to explore this reaction in some detail.



Scheme 1

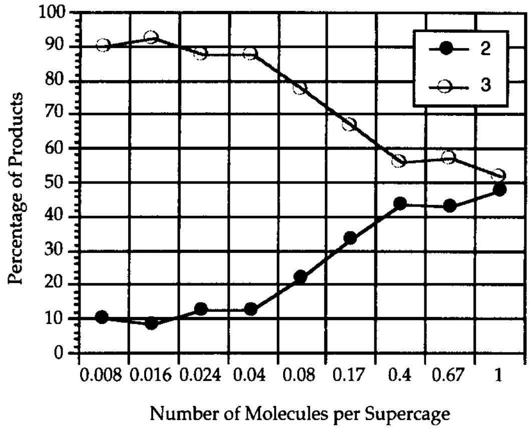
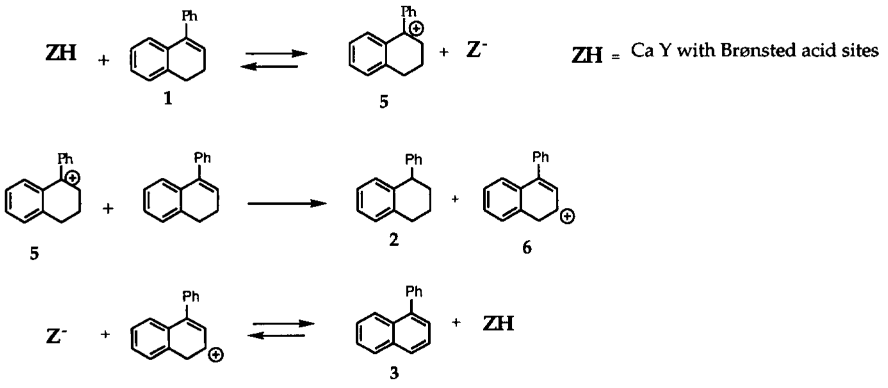


Figure 1: Dependence of product distribution on the loading level of 1-phenyl 3,4-dihydronaphthalene within Ca Y (activated at 500°C under aerated conditions.

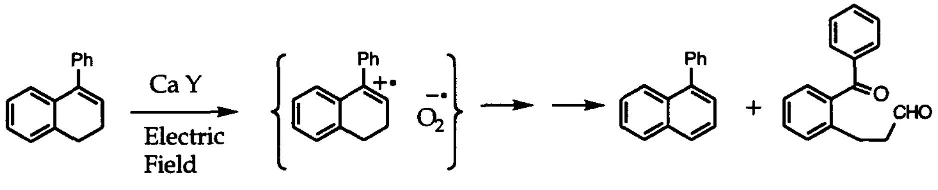
The diffuse reflectance spectrum of the bright yellow solid obtained upon stirring Ca Y with **1** showed two maxima at 435 and 540 nm. Both these absorptions disappeared upon extraction of the zeolite with methylene chloride indicating that the intermediate(s) responsible for these transitions react with the solvent methylene chloride. Based on the literature reports, the two maxima observed in diffuse reflectance spectrum are attributed to the carbocations **5** and **6** (Scheme 2). Although, the spectra of the carbocations **5** and **6** have not been reported, those for closely analogous $Ph_2C^+CH_3$ and $PhCH=CHCH_2^+$ are reported to have maxima at 425 and 500 nm, respectively.[3]



Scheme 2

It has been established previously that activation of Ca Y in the temperature range 200 to 500°C generates Brønsted acid sites.[4] We suggest that Brønsted acid sites generated within Ca Y during the activation process described above are responsible for the formation of the carbocation **5**. The proposed mechanism for the formation of the products **2** and **3** is outlined in Scheme 2. As per this mechanism, the carbocation **5** abstracts a hydride ion from the reactant **1**, instead of from the solvent. The final step involves the return of the proton by the carbocation **6** to the zeolite. In this overall process the zeolite serves as a true catalyst. Consistent with this postulate, when Ca Y exchanged with D_2O was used as the catalyst and the products were extracted with C_6D_{12}/CD_2Cl_2 mixture, the product **2** contained only one deuterium. Had the solvent been the hydride source, two deuteriums should have been incorporated.

The mechanism proposed in Scheme 2 demands that **2** and **3** be formed in equal amounts. But, at low loading levels of **1**, **3** is the major product. We believe that under such conditions the predominant pathway leading to products is not a proton transfer but an electron transfer process. At low loading levels, carbocation **5** is unlikely to react with another molecule of **1** and therefore the equilibrium shown in Scheme 1 may not lead to any permanent products. The diffuse reflectance spectrum of the yellow solid obtained upon stirring Ca Y with **1** did not contain any absorption corresponding to the cation radical. However, this solid showed a strong ESR signal with a g-value of 2.0019. The ESR spectrum was broad and structureless. We attribute the observed ESR signal to the radical cation of **1**. An indication of what might be important in this oxidation process came when the zeolite activated under nitrogen atmosphere was used. When Ca Y activated under nitrogen atmosphere was used, for the same loading level of **1**, the yield of **3**, reduced by an order of magnitude compared to that of Ca Y activated under aerated conditions. Based on this, we believe that oxygen is critical in the cation radical formation of **1** within Ca Y. A proposed mechanism is outlined in Scheme 3. The radical ion pair formed between **1** and oxygen collapses either by superoxide anion abstracting a hydrogen radical (or H^+) from the allylic position or by adding to the double bond. The latter pathway, we believe, leads to product **4**. This must only be a minor pathway since the relative ratio of **3**:**4** is > 20:1. The former one leads to **3** via several steps not elaborated here. The mechanism provided above serves as a good working hypothesis to plan further experiments and should not be considered to be final. We are in the process of establishing the role of oxygen in the electron transfer process within zeolites.



Scheme 3

Generation of radical cation within zeolite has been known for some time.[5] But its mechanistic origin has been under debate for a decade.[6] During the last few years, the stabilization of charge transfer complexes within zeolites has been reported by several groups.[7] The high electric field generated by cations is suggested to be responsible for this phenomenon.[8] Recently, Frei and co-workers have exploited the unique feature of divalent cation exchanged zeolites to stabilize charge transfer complexes between hydrocarbons and oxygen.[9] In these systems, electron transfer is achieved by activation of the charge transfer complex with light. Since the oxidation potential of **1** is expected to be much lower than that of the hydrocarbons used by Frei and co-workers, occurrence of spontaneous electron transfer is not surprising. Such reaction does not occur in isotropic solution. The role of dication exchanged Y zeolite must not be underestimated in this process.

We have shown above that reactions within Ca Y can be triggered by either H^+ or e^- transfer. The desired process can be achieved by properly activating the zeolite. The process described here is unique to divalent cation exchanged Y zeolite. Neither monovalent cation exchanged X and Y zeolites nor divalent cation exchanged X zeolites are active for the purposes described in this letter.

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References

1. Pitchumani, K.; Lakshminarasimhan, P. H.; Prevost,N.; Joy, A.; Ramamurthy, V. *J. Chem. Soc.,* Chem. Comm., in press.
2. The products were characterized by their NMR and mass spectral fragmentation data. The product **3** is commercially available and spectral data of the product was compared with an Aldrich sample. Spectral data for the product **2** have been reported in the literature and the data were compared with the report: Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.*, **1990**, *55*, 1338. Product **4** was characterized only by mass spectral data.
3. (a) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.*, **1988**, *110*, 6913. (b) Young, R. N.; Brocklehurst, B.; Booth, P. *J. Am. Chem. Soc.*, **1994**, *116*, 7885.
4. (a) Ward, J. W. in "*Zeolite Chemistry and Catalysis* ", Rabo, J. A. Ed., American Chemical Society: Washington, D. C., 1976, p. 118. (b) Poutsma, M. L. in "*Zeolite Chemistry and Catalysis* ", Rabo, J. A. Ed., American Chemical Society: Washington, D. C., 1976, p. 437.
5. Stamires, D. N.; Turkevich, J. *J. Am. Chem. Soc.*, **1964**, *86*, 749.
6. (a) Chen, F. R.; Fripiat, J. J. *J. Phys. Chem.*, **1992**, *96*, 819. (b) Liu,X.; Iu, K. K.; Thomas, J. K.; He, H.; Klinowski, J. *J. Am. Chem. Soc.*, **1994**, *116*, 11811. (c) Corma, A.; Fornes, V.; Garcia, H.; Marti, V.; Miranda, M. A. *Chem. Mater.*, **1995**, *7*, 2136.
7. (a) Kasai, P. H.; Bishop, R. J. *J. Phys. Chem.*, **1973**, *77*, 2308. (b) Kasa, P. H; Bishop, R. J. *J. Am. Chem. Soc.*, **1972**, *94*, 5560. (c) Yoon, K. B.; Huh, T. J.; Corbin, D. R.; Kochi, J. K. *J. Phys. Chem.*, **1993**, *97*, 6492.
8. (a) Rabo, J. A. *Catal. Rev. - Sci. Eng.*, **1981**, 23, 293. (b) Angell, C. L; Schaffer ,P. C., *J. Phys. Chem.*, **1966**, *70*, 1413. (c) Rabo, J. A.; Angell, C. L.; Kasai, P. H.; Schomaker, V. *Discuss. Faraday Soc.*, **1966**, *41*, 328. (d) Kasai, P. H.; Bishop, R. J. in "*Zeolite Chemistry and Catalysis*", Rabo, J. A. Ed., American Chemical Society, Washington, D. C., 1976, p. 350.
9. For recent publications see: (a) Blatter, F.; Sun, H.; Frei, H. *Chem. Eur. J.* **1996**, 2, 113. (b) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.*, **1996**, *118*, 6873.

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