

An exceptionally stable carbocation from indene generated and trapped within Ca Y zeolite

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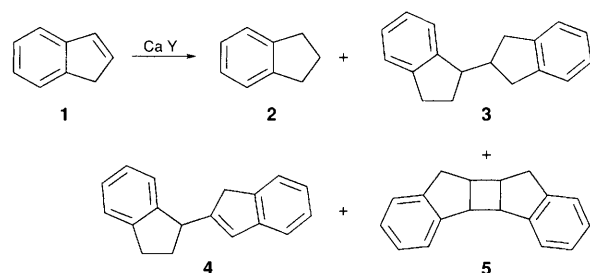
Inclusion of indene within activated Ca Y zeolite generates a persistent dimer carbocation; the chemistry that occurs within the supercages of Ca Y is controlled by the number of Brønsted acidic sites that are generated during the activation process.

Here, we show that with Ca Y as reagent, one can generate a carbocation which is persistent and inert under normal laboratory conditions. To our knowledge, such a long-lived carbocation has not previously been generated from alkenes within zeolites.¹ Indene was chosen for investigation because there are indications in the literature that cations derived from indene are relatively stable in solution under certain conditions.^{2,3} An aspect that we did not anticipate but which has come out of this study, is that by controlling the activation process one can influence the products resulting from proton transfer within a zeolite.

Ca Y, prepared by exchanging Na Y with Ca²⁺, was used.⁴ When Ca Y (250 mg), activated at 500 °C under aerated conditions, was added at room temp. to a hexane solution of indene (20 mg in 5 ml), a dark red colour developed immediately and persisted for several months. Extraction of the zeolite with dichloromethane gave products 2–5 (Scheme 1).

The products were identified by comparing their NMR and mass spectral data with authenticated samples.⁵ What was most remarkable was that extraction with dichloromethane did not remove the red colour of the zeolite which did not even fade after three months under laboratory conditions and persisted after refluxing in methanol or water for 24 h. Even addition of dilute HCl did not affect the stability of the 'red' zeolite. The zeolite lost its colour only when it was refluxed in dilute NaOH solution. The diffuse reflectance spectrum of the 'red' zeolite is shown in Fig. 1. We were indeed surprised to realize that the absorption in the region 400–600 nm was due to a carbocation derived from indene. The carbocation **8** (Scheme 2) derived from 2- α -indanylidene **4** is reported to display an absorption spectrum identical to that recorded here within Ca Y.³ In solution the cation is stable only under vacuum. We are in the process of characterizing and estimating the amount of **8** within Ca Y via MAS NMR.

Several novel features with respect to the product distribution have come out of this investigation. For the same loading level (1.2 molecules per supercage), depending on the activation process employed to prepare Ca Y, the product distribution varied. Also the loading level of **1** influences the product



Scheme 1

distribution. A few important observations are the following: (a) when the zeolite was activated at moderate temperatures (100–150 °C) or under vacuum at higher temperatures (400–500 °C) the major product was 2- α -indanylidene **4**, (b) when the zeolite was activated under aerated conditions in the temperature range 400–550 °C the major product was **3**, (c) indane **2** and product **3** were formed in equal amounts at very low loading levels (<0.1 molecule per supercage), (d) at very high loading levels (>4 molecules per supercage) the products **3** and **4** were formed in equal amounts, (e) at intermediate loading levels (0.5–2 molecules per supercage) **3** was the major product; both **2** and **4** were formed only in small amounts, (f) dimer **5** was formed in variable amounts depending on the activation condition of the zeolite but it never exceeded 15% of the total products.

Formation of products **2**, **3** and **4** can be understood on the basis of protonation of indene by Brønsted acid sites.⁶ We utilize Scheme 2, an exercise in acid–base chemistry, to qualitatively rationalize the observations on product distribution. The basic features are the following: (a) the protonation of indene leads to carbocations **6** and **7**, the precursors of products **2**, **3** and **4** [Scheme 2 eqns. (1)–(3)], (b) the product **4** is formed via the acid–base equilibrium shown in eqn. (3), (c) the persistent carbocation **8** is generated by a hydride transfer from **4** to either **6** or **7**.

It is known that Ca Y activated at 500 °C under aerated conditions contains a large number of Brønsted acid sites.⁷ While a high loading level will ensure that **6** is entirely converted to **7**, the presence of a large number of acidic sites will keep **7** in the protonated form rather than in its conjugate basic form **4**. Thus high acidity and high loading will convert all indene molecules into the precursor of **3**, i.e. **7**. The neutral product **3** is the result of hydride-ion abstraction by **7** from the solvent hexane–dichloromethane during the extraction process. This model predicts that of the two hydrogens that are added to **3**, one comes from Ca Y/H₂O and the other from the solvent. Indeed, when a combination of Ca Y/D₂O and C₆H₁₂–CH₂Cl₂ was used, mass spectral analysis of the product **3** indicated that it contains one deuterium. Similarly, use of Ca Y/D₂O and C₆D₁₂/CD₂Cl₂ gave **3** with two deuterium atoms.

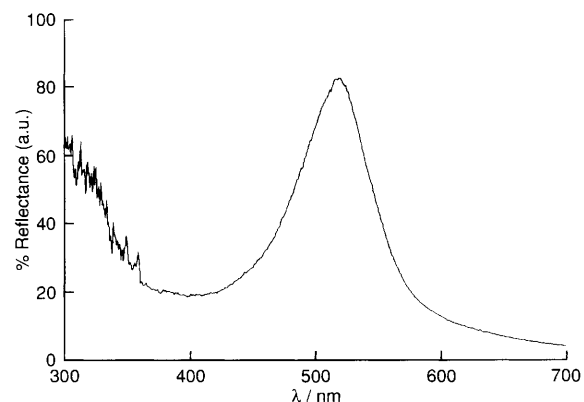
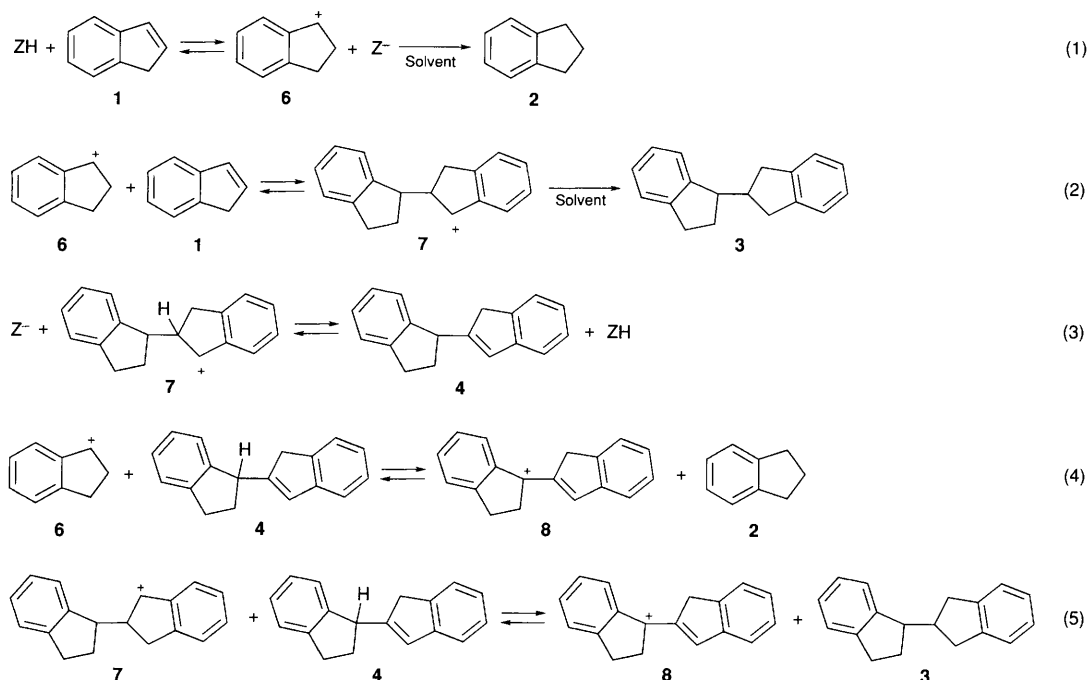


Fig. 1 Diffuse reflectance spectrum of persistent carbocation **8** within Ca Y



Scheme 2 ZH = Ca Y with Brønsted acid sites

It is known that Ca Y activated at *ca.* 100 °C under aerated conditions or at > 500 °C under vacuum contains only very few Brønsted acid sites.⁷ While higher loading of indene will result in the conversion of **6** into **7**, the presence of very few acidic sites will maintain only a very low steady-state concentration of **7**. In competition with that established by indene the carbocation **7** will establish an acid–base equilibrium of its own [eqn. (3)]. A high concentration of indene and the presence of a small number of acidic sites will drive the equilibrium represented in eqn. (3) towards the product **4**. It is indeed remarkable that by controlling the number of acidic sites present within Ca Y, one can obtain different products from indene.

An increase in the yield of **3** at the expense of **2** (until a loading level of 1) is the result of efficient trapping of the carbocation **6** by **1**. After a certain loading level, when almost all of **6** is trapped, the product distribution is dictated by the equilibrium in eqn. (3). At high loading levels one would expect the product distribution to be 1 : 1 (**3** : **4**) which is indeed the case.

Independent of the loading level, the red colour develops and persists. However, the intensity of the colour depends on the loading level, with higher loading levels giving greater intensities. We propose that the carbocations **6** and **7** abstract a hydride ion from **4** to yield **8**. Generation of **8** depends on the buildup of **4**. Since the red colour develops almost instantaneously, we believe that the formation of **4** must be quite rapid. Why is the carbocation **8** persistent within a zeolite? Cation **8** has been generated in solution from indene using titanium tetrachloride and trichloroacetic acid as reagents and found to be stable for several days as long as the solution is kept under vacuum.² In our case, we found that the cation is indefinitely stable under aerated conditions in the laboratory at room temperature. The extraordinary stability of the carbocation **8** within zeolites derives partly from the π -conjugation with the aromatic substituents. This kinetic stability must be augmented by the highly polar supercages of Ca Y. The unusual stability does not derive from the inability of **8** to escape from the cage. Both **3** and **4**, molecules of the same size as **8**, can be easily included and extracted from Ca Y indicating that it is not the size of the cage that is restricting the removal of **8**. It is noteworthy that three carbocations, **6**, **7** and **8**, are generated upon inclusion of indene within Ca Y, and of these only **8** is persistent.

The observation that under certain conditions reactive intermediates prefer to stay within zeolites provides an opportunity to expand the number of reactive intermediates that can be stabilized within zeolites without resorting to a more demanding 'ship in a bottle' strategies.⁸

The authors thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy and USF-EPSCOR-LBR Center for Photoinduced Processes, Tulane University, for support of this program.

References

- Cyclopentenyl carbenium ions have been trapped within zeolites and have been shown to be stable under vacuum: T. Xu and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 7753. Xanthenium ion has been generated from 9-xanthenol within a number of zeolites: F. L. Cozens, H. Garcia and J. C. Scaiano, *Langmuir*, 1994, **10**, 2246.
- The cation derived from 2- α -indanylindene is reported to be stable in solution under vacuum for several days: H. J. Prosser and R. N. Young, *Eur. Polym. J.*, 1972, **3**, 879.
- It has been shown that 3-methyl-1-phenylindanyl cation is stable within HY zeolite up to 323 K: T. Xu and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 10188.
- ICP analysis indicated the zeolite has a composition of Si_{138.7}Al_{53.3}Na_{7.5}Ca_{23.3}O₃₈₄. We thank D. R. Corbin, Du Pont for performing this analysis.
- Spectral data for products, **2**, **4** and **5** are reported in the literature. The spectral data for all other isomers of **3** are reported. By comparison with the reported data for the other isomers, the structure **3** was assigned. K. Suga, S. Watanabe and T. Fujita, *Aust. J. Chem.*, 1972, **25**, 1583; P. H. Ruehle, T. K. Dobbs, L. L. Ansell, D. Helm and E. J. Eisenbraun, *J. Org. Chem.*, 1977, **42**, 1098; W. E. Noland, L. L. Landucci and J. C. Darling, *J. Org. Chem.*, 1979, **44**, 1358; R. N. Warrenner, I. G. Pitt and R. A. Russell, *Aust. J. Chem.*, 1993, **46**, 1845.
- W. E. Farneth and R. J. Gorte, *Chem. Rev.*, 1995, **95**, 615; A. Corma, *Chem. Rev.*, 1995, **95**, 559.
- J. W. Ward, in *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, American Chemical Society, Washington, DC, 1976, p. 118; M. L. Poutsma, in *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, American Chemical Society, Washington, DC, 1976, p. 437.
- K. J. Balkus and A. G. Gabrielov, in *Inclusion Chemistry with Zeolites: Nanoscale Materials by Design*, ed. N. Herron and D. R. Corbin, Kluwer Academic, Boston, 1995, p. 159; D. K. De Vos, *et al.*, in *Inclusion Chemistry with Zeolites: Nanoscale Materials by Design*, ed. N. Herron and D. R. Corbin, Kluwer Academic, Boston, 1995, p. 185.

Received, 30th August 1996; Com. 6/05988K