Generation, entrapment and reactivity of long-lived organic carbocations and radical cations within a supramolecular assembly: Ca Y zeolite

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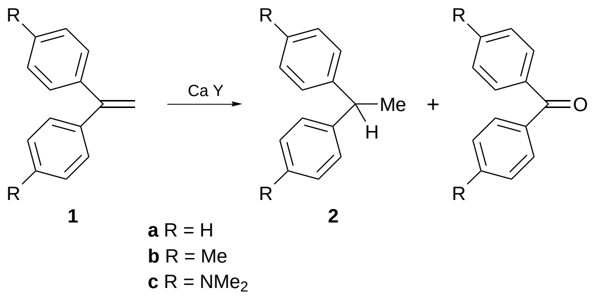
Diarylethenes spontaneously form the corresponding radical cations and carbocations upon inclusion within activated Ca Y zeolite; oxygen plays an important role in the generation of the radical cations.

By virtue of their ability to generate carbocations and radical cations, zeolites have been used in a number of catalytic processes.[1] Although the mechanism of carbocation formation is fairly well understood, the potential of such intermediates in routine organic transformations has not been fully realized. On the other hand, no agreement on the mechanism of cation radical generation within zeolites has been reached.[2] This communication addresses these concerns.

When Ca Y (300 mg) activated at 500 °C under aerated conditions for about 12 h, and cooled to room temperature, was dropped into a cyclohexane solution of 1,1-diphenylethene **1a**, (20 mg 3 ml) a bright green colour developed which, in the slurry, persisted for several weeks.† Extraction of the cyclohexane–zeolite slurry with dichloromethane gave 1,1-diphenylethane **2a** as the single product (Scheme 1). The zeolite residue after extraction was still coloured and remained so for at least 12 h under aerated conditions. When the zeolite turned colourless, it was extracted for a second time with dichloromethane to yield benzophenone. The overall yield of the two products was 90% diphenylethane and 10% benzophenone.

The diffuse reflectance spectra of the zeolite–**1a** complex as formed in cyclohexane, showed two strong absorptions with λ_{max} at 432 and 615 nm (Fig. 1). The zeolite residue after the first extraction with dichloromethane showed only a peak at 615 nm. On the basis of literature reports, we assign the 432 nm peak to the Ph_2C^+Me carbocation and the one at 615 nm to the radical cation of **1a**[3,4] The presence of a radical cation in the Ca Y sample is also indicated by EPR spectroscopy.[5] A strong EPR signal with a *g*-value of 2.00235 was obtained.

Ca Y activated in the temperature range 300–600 °C under aerated conditions was found to be ideal for carbocation generation. It has been established in the literature that such conditions of activation lead to the generation of Brønsted acid sites.[6] Through extensive deuteriation experiments, we have established that one of the hydrogens in diphenylethane **2a** (Scheme 1) comes from the water present within the zeolite and the other from dichloromethane which is used to extract the product from the zeolite. Results of the deuteriation experiments are summarized in Scheme 2.



Scheme 1

Of the various activation conditions we attempted, Ca Y activated > 400 °C on a vacuum line under reduced pressure (< 10^{-3} Torr) was found to be ideal for the generation of radical cations with minimum interference from carbocations. Two remarkable observations made by us in the case of 1,1-diarylethenes lead us to conclude that oxygen plays an important role in the generation of the radical cation within Ca Y. Inclusion of diphenylethene **1a** into Ca Y activated at 450 °C on a vacuum line and handled under nitrogen atmosphere generated only a very light green colour.‡ However, when oxygen was bubbled into such a solution, a dark green colour resulted and the benzophenone yield was enhanced from 1 to 10%. Enhancement of the yield of the radical cation was also confirmed by the diffuse reflectance spectral data. This observation suggested to us that oxygen is essential for radical cation generation. The following observation made with 4,4′-dimethylaminodiphenylethene **1c** further strengthened our view that oxygen plays a

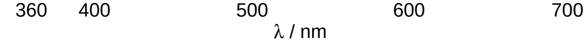
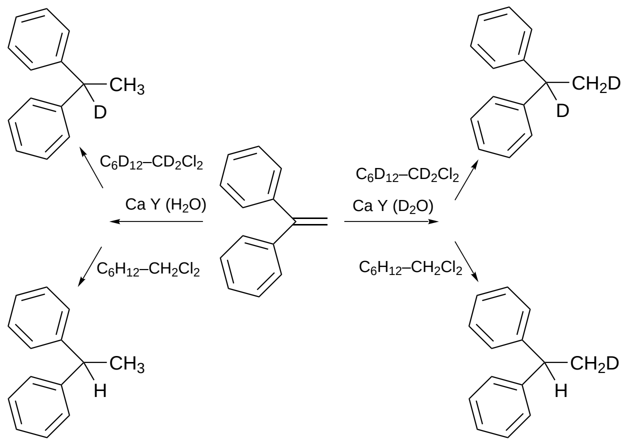


Fig. 1 Diffuse reflectance spectra of diphenylethene included within activated (500 °C aerated) Ca Y. (—) Soon after the addition of Ca Y to a cyclohexane solution of diphenylethene and (---) after extracting the above solution with CH_2Cl_2.



Scheme 2

crucial role in the generation of radical cations within zeolites. When 4,4′-dimethylaminodiphenylethene was included within activated Ca Y the corresponding radical cation was generated. The diffuse reflectance spectrum of **1c** within Ca Y is shown in Fig. 2. The blue coloured solid, when degassed on a vacuum line ($< 10^{-3}$ Torr) turned colourless and the diffuse reflectance spectrum no longer contained the peak due to the radical cation at 620 nm. Introduction of air into this sample, most surprisingly, regenerated the blue colour and the peak at 620 nm reappeared in the diffuse reflectance spectrum. This process was reversible for at least six cycles. This remarkable observation lead us to suggest that oxygen is most likely the electron acceptor at least in the case of 4,4′-dimethylaminodiphenylethene. The alkene **1c** was unique in its behaviour in several ways: (*a*) no other alkenes including **1a** and **1b** above showed the reversible behaviour exhibited by **1c**; (*b*) the radical cation from **1c** was generated even in monovalent cation-exchanged (Li, Na, K, Rb and Cs) Y zeolite. All other alkenes gave radical cations only in divalent cation-exchanged Y and in ZSM-5 zeolites.

Recently, Frei and coworkers have exploited the unique feature of divalent cation-exchanged zeolites to stabilize charge-transfer complexes between hydrocarbons and oxygen.[7] In the case of the alkenes used by Frei and coworkers, the permanent charge separation occurs only upon activation by light. However, the alkenes we have investigated, all possessing much lower oxidation potentials[8] than those studied by Frei and coworkers, are oxidized even in the absence of light. Most surprisingly, 4,4’-dimethylaminodiphenylethene, possessing a very low oxidation potential (0.66 V), establishes a reversible oxidation process with oxygen as the acceptor.[9] Absence of such a process with either diphenylethene (1.88 V) or 4,4′-dimethoxydiphenylethene (1.32 V) suggests to us that the acceptor for these alkenes may not be the free oxygen. Further work, in progress, with a series of alkenes with oxidation potential varying between 0.6 and 2.0 V is expected to clarify this aspect of the oxidation of alkenes within Ca Y.

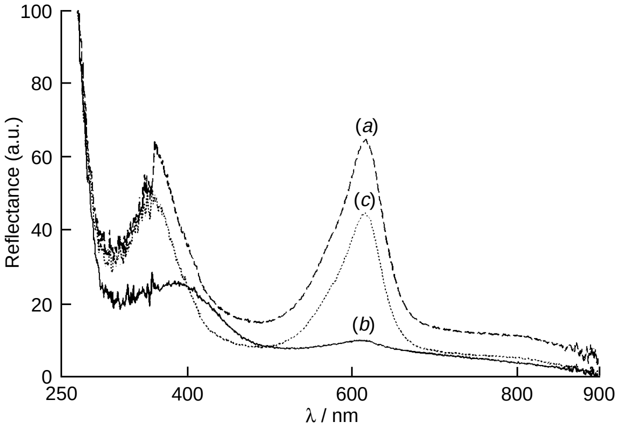


Fig. 2 Diffuse reflectance spectra of 4,4′-dimethylaminodiphenylethene **1c** included in Ca Y. (*a*) (---) Sample after extraction with dichloromethane under aerated conditions. (*b*) (—) The above sample degassed on a vacuum line and under reduced pressure (10^{-3} Torr). (*c*) (···) Sample (*b*) exposed to air.

The conditions under which radical cations and carbocations can be generated, independent of each other, within Ca Y zeolite have been established. Using this technique we have been able to generate long-lived radical cations and carbocations from a number of alkenes. We are in the process of characterizing the persistent carbocations and radical cations by CP MAS NMR and by EPR respectively. The mechanism of radical cation formation within activated zeolites is also being pursued.

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Footnotes

[†] ICP analysis indicated the zeolite used had the composition $Si_{138.7}Al_{53.3}Na_{7.5}Ca_{23.3}O_{384}$.

[‡] Ca Y was placed in a quartz tube and heated at 450 °C under reduced pressure (5×10^{-4} Torr). Nitrogen was adsorbed onto this sample at room temp. and degassed. This process was repeated four times and finally the sample was left under nitrogen overnight. Further handling was done under nitrogen atmosphere. Very light colour formation is consistent with a report [ref. 2(*b*)] that it is difficult to remove strongly adsorbed oxygen from Ca Y.

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