Direct Observation of Cumyl Cations in Nonacidic Zeolites. Absolute Lifetime and Reactivity with Coabsorbed Alcohols

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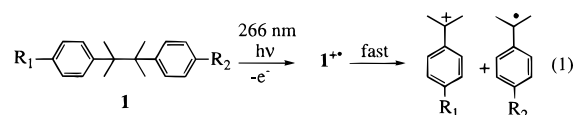*Halifax, Nova Scotia, Canada B3H 4J3*

An important property of acid zeolites[1] used as industrial catalysts is their ability to promote and support the formation of unstable and highly reactive carbocation intermediates. As a result, significant effort is currently being directed toward understanding the mechanisms by which zeolites influence the reactivity of incorporated carbocations, especially with respect to the stabilizing influence of zeolite cavities.[2−6] Several of these studies have shown that various carbocations are sufficiently long-lived in acid zeolites to be observed by diffuse reflectance spectroscopy and, in some cases, solid-state NMR. On the other hand, little information is currently available concerning the formation and behavior of reactive carbocations within zeolites containing no Brönsted acid sites.[7] It is therefore difficult to establish if the long lifetimes of carbocations in proton exchanged zeolites are due primarily to the presence of the strong Brönsted acid sites,[6] or if other factors are also important, such as electrostatic interactions[8] in which the negatively charged zeolite framework acts as a non-nucleophilic counteranion, or the confined environment[6] that protects the carbocation from nucleophilic quenchers. In the present work, we describe results concerning the generation and absolute reactivity of cumyl cations within cavities of the nonacidic zeolite NaY. These results represent the first direct observation of reactive carbocations in NaY, and provide novel information about the reactivity of the carbocations in the absence and presence of coadsorbed alcohol nucleophiles.

The transient diffuse reflectance spectrum obtained upon 266-nm laser irradiation (Nd:YAG laser, ≤10 mJ/pulse, ≤8 ns pulse width) of 4,4′-dimethoxybicumene incorporated into NaY,[9] Figure 1 (open circles), reveals the formation of a transient species with strong absorption centered at 360 nm. The transient was not affected by the addition of oxygen into the zeolite sample, but its decay did increase in the presence of nucleophiles (*vide infra*). In addition, the maximum at 360 nm and the nice symmetrical shape of the band match closely those for the 4-methoxycumyl cation previously observed in solution.[10] The
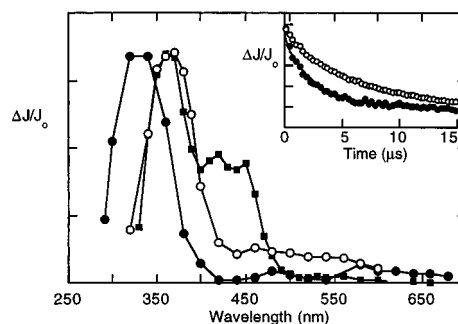
Figure 1. Transient reflectance spectra obtained 0.5 μs after 266-nm excitation of bicumene (closed circles) and 4,4′-dimethoxybicumene (open circles) encapsulated within the cavities of NaY, and 0.5 μs after 308-nm excitation of chloranil co-incorporated with 4,4′-dimethoxybicumene (squares) in NaY. The insert shows the decay of cumyl cation at 330 nm (closed circles) and the 4-methoxycumyl cation at 360 nm (open circles) generated within the cavities of NaY.

transient species is therefore identified as the 4-methoxycumyl cation formed upon laser photolysis of the incorporated neutral bicumene derivative, eq 1 ($R_1 = R_2 = OCH_3$).

$$R_1 \text{—} \underset{\textbf{1}}{\text{—}} \text{—} R_2 \xrightarrow[-e^-]{\substack{266 \text{ nm} \\ h\nu}} \textbf{1}^{\cdot+} \xrightarrow{\text{fast}} \overset{+}{\text{—}}_{R_1} + \overset{\cdot}{\text{—}}_{R_2} \quad (1)$$

A reasonable mechanism for the formation of the 4-methoxycumyl cation is rapid fragmentation of the radical cation[11,12] produced by photoionization of the precursor, eq 1. This agrees with formation of the 4-methoxycumyl cation, together with the chloranil radical anion ($\lambda_{max} = 420$ and 450 nm)[13] upon photoinduced electron transfer with co-incorporated[14] chloranil as the sensitizer, Figure 1 (squares).[15−17] Our inability to observe the intermediate radical cation, which should have an absorption band similar to that of the 4-methoxytoluene radical cation at 420 nm,[18] is consistent with the rapid (ca. 10^8 s^{-1}) fragmentation of the 4,4′-dimethoxybicumene radical cation in solution,[19] and indicates that fragmentation is also rapid in NaY.[20]

Photoionization of the unsymmetrical 4-methoxybicumene (eq 1, $R_1 = OCH_3$; $R_2 = H$), which might have resulted in the formation of either the 4-methoxycumyl cation or the parent cumyl cation, led only to the formation of the 4-methoxycumyl cation. The parent cumyl cation was generated upon 266-nm irradiation of bicumene (eq 1, $R_1 = R_2 = H$) in NaY as indicated by the formation of a strong absorption band centered at 330

(1) Corma, A. *Chem. Rev.* **1995**, *95*, 559−614.
(2) (a) Cano, M. L.; Cozens, F. L.; Garcia, H.; Vicente, M.; Scaiano, J. C. *J. Phys. Chem.* **1996**, 18152−18157. (b) Cano, M. L.; Cozens, F. L.; Vicente, F.; Garcia, H.; Scaiano, J. C. *J. Phys. Chem.* **1996**, 18145−18151. (c) Cozens, F. L.; Garcia, H.; Scaiano, J. C. *Langmuir* **1994**, *10*, 2246−2249. (d) Cozens, F. L.; Garcia, H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 11134−11140.
(3) (a) Xu, T.; Zhang, J.; Munson, E. J.; Haw, J. F. *J. Chem. Soc., Chem. Commun.* **1994**, 2733−2735. (b) Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 10188−10195. (c) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1995**, *29*, 259−267.
(4) Pitchumani, K.; Corbin, D. R.; Ramamurthy, V. *J. Am. Chem. Soc.* **1996**, *118*, 8152−8153.
(5) Tao, T.; Maciel, G. E. *J. Am. Chem. Soc.* **1995**, *117*, 12889−12890.
(6) Cano, M. L.; Corma, A.; Fornés, V.; García, H. *J. Phys. Chem.* **1995**, *99*, 4241−4246.
(7) Pitchumani, K.; Lakshminarasimhan, P. H.; Turner, G.; Bakker, M. G.; Ramamurthy, V. *Tetrahedron Lett.* **1997**, *38*, 371−374.
(8) Spackman, M. A.; Weber, H. P. *J. Phys. Chem.* **1988**, *92*, 794−796.
(9) Incorporation of the bicumenes was carried out by mixing 10 mg of the organic compound dissolved in 20 mL of hexane and 800 mg of activated (500 °C) NaY (Aldrich, Si/Al = 2.4) for 1 h. The suspension was centrifuged and the isolated zeolite was then washed with hexane and dried under vacuum.
(10) McClelland, R. A.; Chan, C.; Cozens, F. L.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337−1339.

(11) Okamato, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175−6178.
(12) Maslak, P. *Top. Curr. Chem.* **1993**, *168*, 1−65.
(13) Andre, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97−99.
(14) These samples were prepared by first incorporating 10 mg of chloranil into 800 mg of NaY, followed by co-incorporation of the bicumene.
(15) Maslak, P.; Chapman, W. H. *J. Org. Chem.* **1996**, *61*, 2647−2656.
(16) Sankararaman, S.; Yoon, K. B.; Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 1419−1421.
(17) Yoon, K. B.; Hubig, S. M.; Kochi, J. K. *J. Phys. Chem.* **1994**, *98*, 3865−3871.
(18) Liu, A.; Sauer, M. C. J.; Loffredo, D. M.; Trifunac, A. D. *J. Photochem. Photobiol. A: Chem.* **1992**, *67*, 197−208.
(19) Maslak, P.; Chapman, W. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1809−1811.
(20) The radical is a necessary product upon fragmentation of the radical cation. Under ideal conditions where the strong absorption due to the 4-methoxycumyl cation was removed by quenching with methanol, a weak transient with an absorption maximum at wavelengths <320 nm and that is quenched by oxygen was observed and is tentatively assigned to the 4-methoxycumyl radical.[21]
(21) Tokumura, K.; Ozaki, T.; Nosaka, H.; Saigusa, Y.; Itoh, M. *J. Am. Chem. Soc.* **1991**, *113*, 4974−4980.

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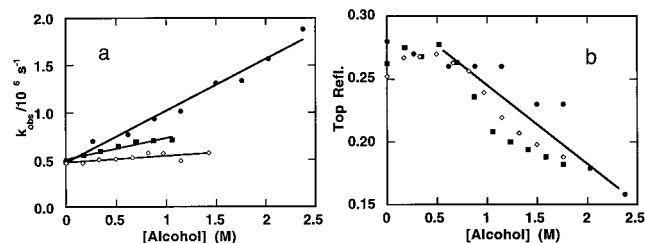
Figure 2. Effect of adsorbed methanol (circles), ethanol (squares), and 2-propanol (diamonds) on (a) the observed rate constant for the decay and (b) the top reflectance at 360 nm of the 4-methoxycumyl cation generated in NaY.

nm, Figure 1 (closed circles), identical to that observed for the cumyl cation in solution.[10]

The observed first-order rate constants for the decay of the carbocations in NaY, Figure 1 (inset), $k_{obs} = 3.8 \times 10^5$ s^{-1} for the 4-methoxycumyl cation and 5.9×10^5 s^{-1} for the unsubstituted cumyl cation, are significantly slower than for the same carbocations in solution such as in water or acetonitrile. In fact, highly nonnucleophilic solvents such as 2,2,2-trifluoroethanol (TFE) for the 4-methoxycumyl cation or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for the parent cumyl cation are required to stabilize kinetically the carbocations[10,22] to the same degree as observed in NaY. Thus, the environment within the cavities of a nonacid zeolite is capable of sustaining a significant carbocation lifetime, even in the absence of strong Brönsted acid sites. The relatively long lifetimes in NaY are consistent with the notion that the zeolite cavity kinetically stabilizes the carbocation, with the negatively charged framework possessing low nucleophilicity and acting instead as a nonnucleophilic counteranion. It is also likely that the high electrostatic field present within the NaY cavities plays an important role in stabilizing the cumyl cations.[8]

In NaY, the parent cumyl cation is only about 1.5 times more reactive than the 4-methoxy derivative. This small difference in reactivity contrasts sharply with that observed in nonnucleophilic solvents such as TFE where the cumyl cation is about 10 000 times more reactive toward addition of the solvent than the 4-methoxy derivative.[23] Thus, whereas reactivity in solution is largely determined by the thermodynamic stability of the carbocation, thermodynamic stability does not seem to play a significant role when the carbocations are embedded within the zeolite cavities.

As shown in Figure 2a, coadsorption of methanol, ethanol, or 2-propanol within the zeolite cavities[2d] results in an increase in the observed rate constant for the decay of the 4-methoxy-cumyl cation.[24] This increase indicates that the carbocation and alcohol react by a *dynamic* quenching process involving diffusion of the alcohol into the cavity containing the carboca-tion, Scheme 1. The slopes of the plots represent second-order rate constants, k_q, for the reaction of the alcohol and the carbocation. The rate constant for quenching by methanol, $k_q = (5.5 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, is significantly greater than that for quenching by ethanol, $k_q = (2.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, which in turn is larger than that by 2-propanol, $k_q = (0.8 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. In addition to dynamic quenching, the amount of the 4-methoxycumyl cation remaining after the 10-

Scheme 1

Slow "dynamic" quenching   Fast "static" quenching
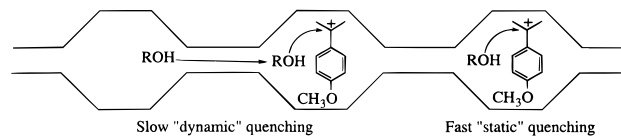
ns laser pulse decreases significantly as the alcohol content increases, Figure 2b. This represents a *static* quenching process involving rapid ($>10^8$ s^{-1}) reaction of an alcohol molecule that is in close proximity to (i.e. in the same cavity as) the photogenerated carbocationic center, Scheme 1. It is noteworthy that the decrease in the amount of observed carbocation is the same regardless of which alcohol is coadsorbed into the sample, as expected for a fast static quenching process in which the quencher and the carbocation reside in the same cavity.

Observation of static quenching is significant because it leads to the conclusion that a rapid intracavity reaction occurs each time an alcohol molecule enters a zeolite cavity containing a 4-methoxycumyl cation. Therefore, it can also be assumed that dynamic quenching represents a diffusion controlled process. This is consistent with the observation that the magnitude of the dynamic quenching rate constant is highly dependent on the size of the alcohol. Diffusion coefficients ranging from 2.6 $\times 10^{-9}$ cm^2 s^{-1} for methanol, 1.3×10^{-9} cm^2 s^{-1} for ethanol, and 0.67×10^{-9} cm^2 s^{-1} for 2-propanol can be calculated by using values of k_q obtained from the slopes of the quenching plots and a modified version of the Smoluchowski equation.[25,26] These values are in the range expected for diffusion coefficients in NaY,[27] and reinforce the conclusion that dynamic quenching represents a diffusion controlled process.

The static quenching observed in the present work suggests that the "encounter-complex" generated when an alcohol diffuses into a cavity containing a carbocation rapidly collapses to give product. On the other hand, the reaction of the 4-methoxycumyl cation with methanol in solvents such as TFE is activation controlled, taking place with a second-order rate constant of ca. 1×10^6 M^{-1} s^{-1} that is 10^3 times smaller than the diffusion limit. Thus, the intracavity reaction of the carbocation with the alcohol appears to occur more rapidly than collapse of an encounter-complex generated in solution. One consequence of the zeolite environment is therefore to actually *increase* the reactivity of the alcohol toward the carbocation once it has entered the carbocation containing cavity. This may be an in-cage effect caused by the presence of both reactants within the same restricted space, or a catalytic effect whereby the weakly basic oxygens of the active sites remove a proton from the oxygen of the alcohol as it reacts with the cumyl cation. At the same time, dynamic quenching is slower in NaY than in solution. Thus, because the alcohols must first navigate the channels and pores of the zeolite in order to find a cavity containing a carbocation, a second consequence of the zeolite is to *decrease* the overall dynamic quenching efficiency of the nucleophile by reducing the rate of diffusion of the alcohol.

(22) The crystal structure of a cumyl cation salt has recently been obtained. Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087−3092

(23) The rate constant of 2×10^8 s^{-1} for the decay of the cumyl cation in TFE can be estimated from a σ^{C+} plot for cumyl cations in TFE.

(24) One hundred milligrams of NaY has an internal volume of 0.070 mL as calculated from the molar mass of a NaY unit cell, 12 700 g/mol, and a unit cell volume of 1.5×10^4 Å^3. The concentration of added alcohols can then be calculated from the moles of alcohol per 100 mg of dry NaY.

(25) The diffusional coefficients were calculated by using the following equation, $k_q = p\pi R_c{}^2 D_q N_{Av}/1000 R_q$ where $p = 1$, $R_c = 3.5 \times 10^{-8}$ cm, $R_q = 2.0 \times 10^{-8}$ cm for iPrOH, 1.4×10^{-8} cm for EtOH, and 1.1×10^{-8} cm for MeOH, and N_{Av} is Avogadro's constant.

(26) Kim, Y. I.; Mallouk, T. E. *J. Phys. Chem.* **1992**, *96*, 2879−2885.

(27) Karger, J.; Pfeifer, H. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Ed.; Marcel Dekker, Inc.: New York, 1994; pp 69−138.