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Direct Observation of the Benzyl Radical and the Benzyl Anion within Cation-Exchanged Zeolites. A Nanosecond Laser Study

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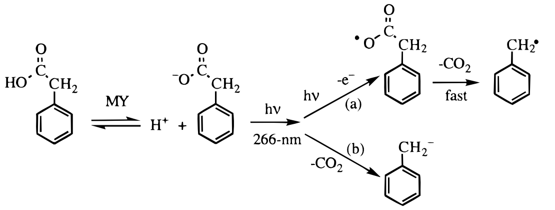
In recent years, there has been considerable interest in the generation and reactivity of simple monoaryl benzylic radicals within the cavities of zeolites.[1−5] The majority of these studies have determined the ratio of products upon steady-state photolysis of dibenzyl ketone and its methylated derivatives. Both the reactivity and mobility of the monoaryl radicals within the zeolite framework have been inferred from the yield and distribution of the product mixtures, with the conclusion that simple monoaryl benzyl radicals are highly mobile within the zeolite framework and that coupling reactions are very fast.[4]

The direct detection of reactive intermediates within the cavities of zeolites has given important information about the reactivity of transients species in the unique environment provided by the zeolite.[6−21] Surprisingly, however, no time-resolved studies of the benzyl radical produced upon photolysis of dibenzyl ketone within the cavities of zeolites have been reported. Presumably, the lack of time-resolved results is due to the ill-defined transient diffuse reflectance spectra generated upon laser excitation of dibenzyl ketone within zeolites.[22] We now report the direct observation of photogenerated benzyl radicals within cation-exchanged Y faujasites using nanosecond diffuse reflectance spectroscopy. Evidence is also presented for the simultaneous detection of the benzyl anion.

Our belief was that the ill-defined spectra generated upon photolysis of dibenzyl ketone within the cavities of zeolites was due, at least in part, to the initial generation of a radical pair within the supercage instead of a single "free" benzyl radical.[23,24] Thus, our approach was to utilize a precursor, phenylacetic acid,[20,25−27] that upon 266-nm laser photolysis would generate a zeolite supercage with only one radical species.

Figure 1 shows the transient diffuse reflectance spectrum generated upon 266-nm laser[28] excitation of phenylacetic acid incorporated into dry NaY under reduced pressure (10^{-3} Torr).[29] The spectrum shows a strong absorption band centered at 315-nm and a shoulder at 305-nm that coincide nicely with the known absorption spectrum for the benzyl radical in solution.[26] The transient species at 315-nm is completely quenched by the addition of oxygen to the sample, which is characteristic of radical species.[30,31] Consistent with the formation of the benzyl radical is that one of major products upon steady-state photolysis in NaY[32] in the absence of oxygen is bibenzyl,[33] the product from radical−radical coupling. The proposed mechanism for the generation of the benzyl radical is shown in eq 1, path a. Upon incorporation into the nonacidic Y zeolite, phenylacetic acid deprotonates to the phenylacetate anion,[34] which undergoes photoionization[20,25,35] upon 266-nm laser excitation to give the acyloxy radical that then rapidly loses CO_2 to yield the benzyl radical.



(1)

A second weaker absorption band at 350 nm is also clearly observed, (Figure 1). The decay rate constant for the 350-nm band, $k_{350} = 5 \times 10^5\ s^{-1}$, is significantly faster than that for the 315-nm band,[36] $k_{315} = 2 \times 10^5\ s^{-1}$, indicating that these absorption bands do not belong to the same transient species. The 350-nm

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(22) Laser photolysis of dibenzyl ketone in NaY in the absence of oxygen leads to a broad absorption located around 330−350-nm. This absorption hinders the observation of the photogenerated benzyl radicals.

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(33) Photolysis of phenylacetic acid in NaY (loading level of 1 molecule/2 cavities) under dry conditions with a stream of dry nitrogen purged over the sample throughout the photolysis time gave toluene (60%) and bibenzyl (20%) after 50% conversion of starting materials.

(34) IR spectra of phenylacetic acid within the cation-exchanged Y zeolite showed a strong carbonyl band centered at 1620 cm^{-1} and no signal above 1700 cm^{-1}, which is consistent with the carboxylate ion being the predominate species in the zeolite environment.

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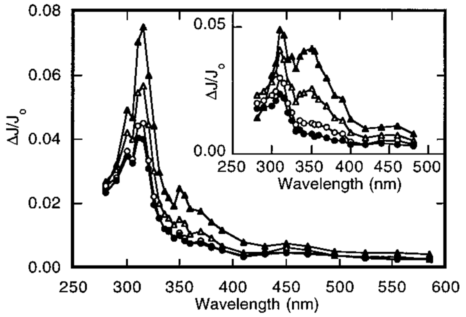

Figure 1. Transient diffuse reflectance spectrum generated upon 266-nm laser photolysis of phenylacetic acid in evacuated (10^{-3} Torr) NaY under dry conditions. The inset shows the transient spectrum after the sample was exposed to the atmosphere for a period of 10 s and then reevacuated (10^{-3} Torr). Spectra were recorded (▲) 0.20, (△) 0.74, (○) 1.76, and (●) 6.36 μs after the laser pulse.

band is also completely quenched by oxygen, indicating that the transient species is not due to a carbocation or radical cation intermediate.[37]

The intensity of the 350-nm band was found to be highly dependent on the amount of water coadsorbed into the zeolite framework. Exposure of the sample to the atmosphere for 10 s and reevacuation to remove oxygen significantly enhanced the production of the 350-nm band (Figure 1, inset). We assign the 350-nm transient species to the benzyl anion generated upon photolysis of phenylacetate,[27] eq 1, path b, on the basis of the following information. The benzyl anion is known to be a photoproduct upon photolysis of phenylacetate in polar environments.[25,38] The benzyl anion is also known to have a strong absorption in the 350-nm region and to be rapidly quenched by oxygen.[39,40] In addition, the second major product generated upon steady-state photolysis of phenylacetic acid within NaY in the absence of oxygen is toluene, which is the product expected from the benzyl anion. Furthermore, when phenylacetic-α,α-d_2 acid was irradiated in NaY in the absence of oxygen, toluene-α,α-d_2, produced by protonation of the benzyl-α,α-d_2 anion, was obtained as a major product in addition to bibenzyl-α,α-d_4. No toluene-α,α,α-d_3 was produced, indicating that toluene is not generated by reaction of the benzyl radical with the precursor. In addition, when unlabeled phenylacetic acid was photolyzed within NaY, also in the absence of oxygen after the co-incorporation of methanol-*d* (CH_3OD), the products obtained were toluene, toluene-α-*d*, and bibenzyl.

The decay kinetics at 315-nm for the benzyl radical in LiY, NaY, KY, RbY, and CsY[41,42] are shown in Figure 2 (left). The decay of the benzyl radical is fastest in LiY and slowest in CsY. This suggests that the benzyl radical decays in a fast manner by a coupling reaction with a second benzyl radical and that the mobility decreases along the series from LiY to CsY. In addition, the end absorption, which indicates the number of radicals remaining after the fast decay, increases significantly along the series toward the larger counterions. These radicals associated with the end absorption are very long-lived and do not decay over 1 ms, the longest time scale of our laser system. The slow-decaying radicals are thought to be generated within local domains, where diffusion is restricted and less efficient, whereas the fast-decaying radicals are generated in open void spaces and are sufficiently mobile to cavity-jump into neighboring cavities.

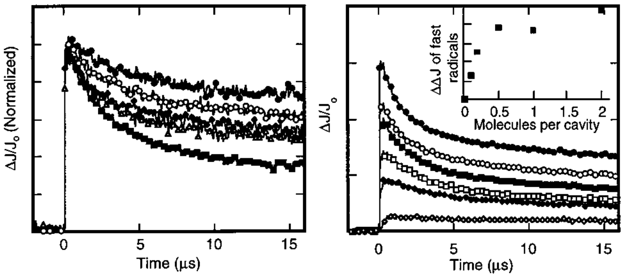

Figure 2. Transient decay traces at 315 nm for the benzyl radical generated upon 266-nm laser excitation of phenylacetic acid in (left) dry, evacuated (10^{-3} Torr) LiY (■), NaY (△), KY (◆), RbY (○), and CsY (●) and (right) dry, evacuated (10^{-3} Torr) NaY with loading levels (phenylacetic acid:number of NaY cavities) of 2:1 (●), 1:1 (○), 1:2 (■) and 1:5 (□), 1:10 (◆), 1:100 (◇). The inset shows the amount ($\Delta\Delta J = \Delta J_{t=16\mu s}$) of the fast-decaying benzyl radicals as a function of loading level.

The differences observed in the decay kinetics are presumed to be due to the variations in the mobility of the benzyl radical. With the larger cations, such as Cs^+, the mobility of the radicals is considerably reduced due to the cations partially blocking the movement of the radicals through the pores connecting neighboring cavities. In addition, the relatively high concentration of precursor molecules produces a secondary cage that inhibits the mobility of radicals,[4] and this effect increases as a function of cation size.

In contrast, the decay of the anion was found not to be dependent on the zeolite counterion.[43] In each case, the benzyl anion decayed with closely similar kinetics, $k \approx 5 \times 10^5$ s^{-1}. The decay traces return close to the baseline, indicating that mobility of the anion is not an important factor in the reaction of the benzyl anion. The coadsorption of water into the zeolite framework had little influence on the decay kinetics.

The decay traces at 315-nm upon laser photolysis of phenylacetate within NaY as a function of loading level are shown in Figure 2 (right). Clearly, the fraction of radicals that decay rapidly over the first 15 μs increases significantly as the total yield of radical increases. Thus, as more radicals are produced, the probability of finding a neighboring cavity containing another benzyl radical is higher than that at low loading levels.

In conclusion, we have shown clearly that the benzyl radical can be readily generated and observed within the cavities of alkali-exchanged Y faujasites. The benzyl anion is also generated upon photolysis of phenylacetate, and its yield is highly dependent on the hydration state of the zeolite. Our investigations into the behavior of photogenerated simple radicals and anions within the three-dimensional lattice of zeolites continue.

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[36] The decay of the 315-nm band over long time scales of 1 ms was distinctly nonexponential. Over a short time scale of 10−20 μs, the decay fit reasonably well to a first-order expression, but the calculated rate constant is qualitative. The band at 350 nm decayed completely over 20 μs, with reasonably good first-order kinetics.

[37] Cationic species typically do not react with oxygen.

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[41] The exchanged zeolites were prepared by stirring the NaY (Aldrich, LZY52 molecular sieves, Si/Al = 2.4) zeolite with 1 M aqueous solutions of the corresponding chlorides (LiCl, KCl, RbCl, CsCl) at 80 °C for 1 h. The zeolites were then washed until no chlorides appeared in the washing water and dried under vacuum. This procedure was repeated three times, and the zeolite was calcinated between washings. The percent exchange was 54% for LiY, 97% for KY, 44% for RbY, and 47% for CsY.

[42] The samples were prepared in the glovebox and sealed under vacuum to ensure dry conditions. The loading level was kept constant at 1 molecule/2 cavities.

[43] The benzyl anion was observed only upon laser photolysis in the exchanged zeolite samples that were briefly exposed to atmospheric moisture and then reevacuated at 0.001 Torr for 10 h. The amount of anion generated under hydrated conditions decreased significantly along the series LiY to CsY.