

## Observation of Acetyl Radical in a Zeolite by Time-Resolved FT-IR Spectroscopy

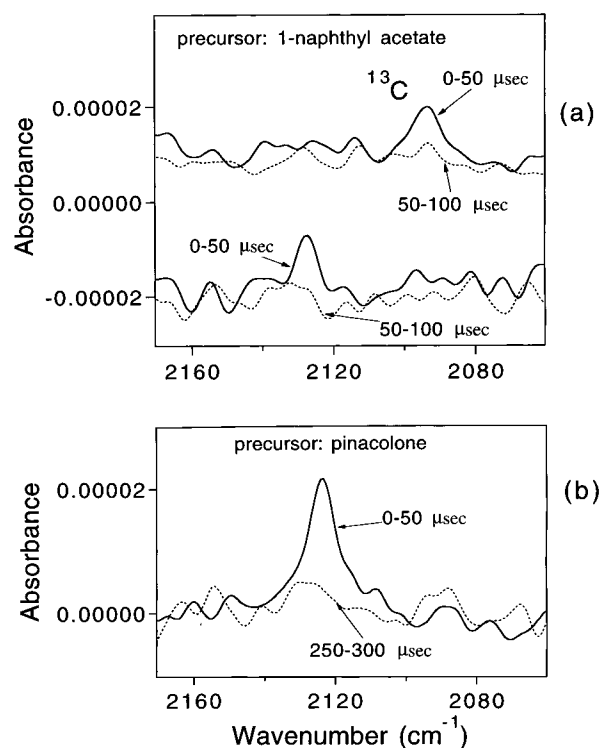
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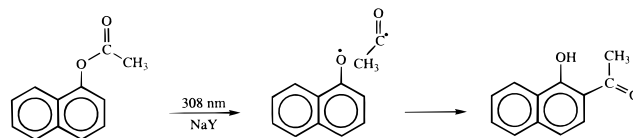
Monitoring of short-lived intermediates in zeolites is crucial for the elucidation of photochemical reaction mechanisms in these important microporous solids. Time-resolved studies of transients in zeolites have thus far been conducted on aromatic radicals<sup>1</sup> or radical cations<sup>2</sup> by nano- and microsecond UV/vis diffuse reflectance spectroscopy. The resonance Raman method has also been employed, but studies were again limited to aromatic systems.<sup>3</sup> Small radicals which lack aromatic moieties are not suitable for monitoring by UV/vis or Raman methods because they lack the chromophores for ready identification or resonance enhancement. Here, infrared spectroscopy is a most useful tool for detection and identification, especially if use of isotopic labeling is made. Time-resolved infrared work in zeolites has thus far been limited to photophysical systems. The groups of van Santen and Domen have conducted picosecond vibrational relaxation studies of adsorbates interacting with the zeolite environment,<sup>4</sup> which includes monitoring of infrared-induced conformational dynamics of methanol clusters in zeolites.<sup>5</sup> Sun and Frei have reported transient FT-IR spectra of triplet excited duroquinone occluded in NaY.<sup>6</sup> We wish to communicate the first observation of a small radical intermediate of a photochemical reaction in a zeolite. The result was obtained by step-scan FT-IR spectroscopy on the microsecond time scale. Systems studied were the photo-Fries rearrangement of 1-naphthyl acetate and the photodissociation of pinacolone.

Upon loading of naphthyl acetate into zeolite NaY,<sup>7,8</sup> the self-supporting solvent-free wafer was irradiated for 30 min at room temperature with 308 nm pulsed laser light (10 Hz, 6 mJ pulse<sup>-1</sup>). The difference of the infrared spectra before and after photolysis showed product growth at 1283, 1327, 1385, 1468, 1505, 1573, 1607, and 1635 cm<sup>-1</sup> under concurrent depletion of all naphthyl



**Figure 1.** (a) Step-scan FT-IR spectra of 1-naphthyl acetate photodissociation (<sup>12</sup>C and <sup>13</sup>C (carbonyl) species) representing the coaddition of the first ten 5 μs time slices (0–50 μs) and the second ten 5 μs time slices (50–100 μs), respectively. (b) Analogous step-scan FT-IR spectra of pinacolone photodissociation in NaY. A Bruker Model IFS 88 step-scan spectrometer equipped with an InSb PV detector (fwhm = 50 ns) and an optical filter with a 2400–1850 cm<sup>-1</sup> window was used. Resolution = 4 cm<sup>-1</sup>. The results represent the average of 80 step-scan experiments, each with 15 photolysis pulses per mirror position. Reactant depletion was about 1% per step-scan run, and no more than ten runs were conducted with each zeolite pellet. Details of the spectrometer and the measurement procedure are described in ref 6.

### Scheme 1



acetate bands.<sup>9</sup> Frequencies and intensities were identical with those of an authentic sample of 2-acetyl-1-naphthol loaded into NaY, the established main product of the UV light-induced Fries rearrangement in solution<sup>10</sup> and in alkali Y or X in hexane slurry.<sup>11</sup> No other product absorptions grew in, indicating that the photo-Fries rearrangement in solvent-free NaY is completely regio-selective (Scheme 1).

Step-scan FT-IR spectroscopy of 1-naphthyl acetate photodissociation in the range 2400–1850 cm<sup>-1</sup> at 5 μs resolution (308 nm, 6 mJ pulse<sup>-1</sup>, fwhm = 9 ns) revealed a transient absorption at 2127 cm<sup>-1</sup>, shown in Figure 1a. When using 1-naphthyl acetate

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(7) Zeolite NaY was loaded with 1-naphthyl acetate by stirring dehydrated zeolite powder in a hexane solution of the ester (5 mg/mL). The loaded zeolite was washed with hexane, evacuated by a turbopump to remove the solvent, and pressed into a self-supporting wafer (6–8 mg cm<sup>-2</sup>). The latter was mounted inside a variable-temperature infrared vacuum cell described previously.<sup>8</sup>

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with a  $^{13}\text{C}$  labeled CO group, a  $34\text{ cm}^{-1}$  red shift was observed (Figure 1a).<sup>12</sup> The  $1/e$  decay time of the transient is  $75 \pm 11\ \mu\text{s}$  at  $21\text{ }^\circ\text{C}$ .<sup>13</sup>

It is well established from transient optical and CIDNP studies in solution that photo-Fries rearrangement of 1-naphthyl acetate involves homolytic C–O bond cleavage to yield transient acetyl radical and naphthoxy radical.<sup>10</sup> Indeed, the  $^{13}\text{C}$  shift of  $34\text{ cm}^{-1}$  of the observed transient infrared absorption (Figure 1a) indicates that the band originates from a CO stretch mode. Moreover, the isotope shift agrees with that reported for  $\text{CH}_3\dot{\text{C}}\text{O}$  radical in solid Ar.<sup>14</sup> However, the frequency of  $2127\text{ cm}^{-1}$  we observe in the solvent-free NaY zeolite lies  $270\text{ cm}^{-1}$  to the blue of the Ar matrix ( $1842\text{ cm}^{-1}$ )<sup>14</sup> or solution value of acetyl radical ( $1864\text{ cm}^{-1}$ ),<sup>15</sup> but fairly close to the triple bond CO stretch of acetylium ion ( $2200\text{ cm}^{-1}$ ).<sup>16</sup> Formylium cation ( $\text{H}-\text{C}^+=\text{O}$ ) has gas and solution phase absorptions ( $2184$  and  $2110\text{ cm}^{-1}$ , respectively, with a  $^{13}\text{C}$  shift of  $35\text{ cm}^{-1}$ )<sup>17–19</sup> that are also close to our frequency in NaY. This suggests that the observed transient in the zeolite is either acetylium ion or acetyl radical whose interaction with the poorly shielded  $\text{Na}^+$  ions results in an electronic structure resembling that of  $\text{CH}_3-\text{C}^+=\text{O}$ .

Two observations indicate that the transient species in the zeolite is an acetyl radical interacting with the extraframework  $\text{Na}^+$  ions, and not an acetylium ion. First, we expect on the basis of electronic structure considerations that interaction of the acetyl radical with a poorly shielded  $\text{Na}^+$  ion inside the zeolite results in a substantial increase of the carbonyl stretching frequency. Extension of the lone pair orbital of oxygen in the direction of  $\text{Na}^+$  would pull electron density from the highest, singly occupied carbon  $\sigma$  orbital toward oxygen.<sup>20</sup> As a result, the acetyl radical interacting with  $\text{Na}^+$  is assuming cation character with the CO group approaching the triple bond configuration. This is borne out in a recent ab initio calculation on formyl radical interacting with hydronium ion; the  $\text{H}\dot{\text{C}}\text{O}\cdot\text{H}_3\text{O}^+$  complex is predicted to have a CO stretching frequency  $220\text{ cm}^{-1}$  to the blue of the fundamental of  $\text{H}\dot{\text{C}}\text{O}$  free radical.<sup>21</sup> Second, photodissociation of pinacolone in zeolite NaY gave rise to the same transient absorption, shown in Figure 1b.<sup>22</sup> It is well established that the ketone undergoes homolytic  $\alpha\text{ C}-\text{C}$  bond cleavage in solution

upon excitation at  $290\text{ nm}$ .<sup>23</sup> Static infrared difference spectra upon prolonged irradiation showed growth at  $1354$ ,  $1403$ ,  $1429$ ,  $1721$ ,  $2768$ ,  $2855$ , and  $2905\text{ cm}^{-1}$ . Comparison with the spectra of authentic samples in NaY confirmed  $\text{CH}_3\text{CH}=\text{O}$  and isobutene as final products. While homolytic photodissociation followed by spontaneous electron transfer or even heterolytic photodissociation to acetylium ion and naphthoxy anion is conceivable in the strongly ionic zeolite, this path is not open for the ketone. The reason is that the *tert*-butyl radical is far too poor an electron acceptor. We conclude that the transient formed in zeolite NaY upon 1-naphthyl acetate or pinacolone photofragmentation is an acetyl radical interacting with  $\text{Na}^+$  ion.

According to ab initio work on infrared intensities of  $\text{H}\dot{\text{C}}\text{O}$  and  $\text{CH}_2=\text{O}$ , the extinction coefficient of the CO stretch absorption of formaldehyde is twice as high as that of the formyl radical.<sup>21,24</sup> Assuming that the extinction coefficient of  $\nu(\text{CO})$  of acetaldehyde in NaY is also twice that of the  $2127\text{ cm}^{-1}$  absorption of  $\text{CH}_3\text{CO}\cdot\text{Na}^+$ , we find from intensity measurements, within uncertainties, a 1:1 correspondence between the transient acetyl and the final product yield. This implies that the majority of acetyl radicals are located at  $\text{Na}^+$  sites.<sup>25</sup> Since in the case of the photo-Fries rearrangement the accompanying naphthoxy radical is expected to interact with  $\text{Na}^+$  as well, combination of the two radicals at the ortho position of the aromatic ring would be favored over para coupling. Our observation that most, probably even all, acetyl radicals form a complex with  $\text{Na}^+$  ions furnishes direct evidence for this mechanistic explanation of the complete regioselectivity of the Fries rearrangement in NaY. This explanation was previously proposed by Ramamurthy in the case of regioselective photo-Fries rearrangement of phenyl acetate in alkali zeolite Y and X.<sup>26</sup> The agreement between the concentration of acetyl radical and final product implies, moreover, that the bulk of the radicals live for tens of microseconds. This is an unexpectedly long lifetime at room temperature for a radical as small as  $\text{CH}_3\text{CO}$ , making step-scan FT-IR spectroscopy on the nano- and microsecond time scale a suitable tool for monitoring the fate of such reaction intermediates.

In summary, we have obtained the first infrared spectral record of a transient intermediate of an irreversible photoreaction in a zeolite. This opens up mechanistic studies of chemical reactions in microporous solids that can make use of detailed structural information on intermediates available from infrared spectroscopy.

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(13) Measurement of the rise kinetics of the final product 2-acetyl-1-naphthol is rendered difficult by the small (about one degree) thermal effect on its absorption bands, described in ref 6. This is caused by the fact that the final product accumulates during the step-scan run since it cannot be removed from the infrared probing zone between photolysis pulses.

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