

# $^{13}\text{C}$ MAS NMR observation of photoproducts in zeolites and their further reaction on acid sites

Jinhua Zhang, Thomas R. Krawietz, Timothy W. Skloss and James F. Haw\*

Laboratory for Magnetic Resonance and Molecular Science, Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

## *In situ* $^{13}\text{C}$ MAS NMR characterization following UV irradiation of two FAU zeolites with adsorbed benzaldehyde or acetophenone and toluene allows observation of photoproducts and subsequent acid-catalysed chemistry.

Photochemistry of organic compounds included in zeolites and other constrained media is of continuing interest. Many previous investigations have focused on the influence of framework topology and the charge compensating cation of the zeolite on the resulting photoproduct yield and distribution.<sup>1–9</sup> The zeolite is typically selected so as to be otherwise unreactive toward the reactants or photoproducts. Procedures used in diverse, published reports naturally vary; however, in many of the previous studies, the zeolite was irradiated in a slurry of excess reactant, and the products identified *ex situ* following liberation by extraction or destruction of the framework. Here we report  $^{13}\text{C}$  MAS NMR characterization of the photoproducts of benzaldehyde or acetophenone with toluene in two FAU type zeolites, with topologies dominated by 13 Å supercages interconnected through 7.4 Å pore openings.

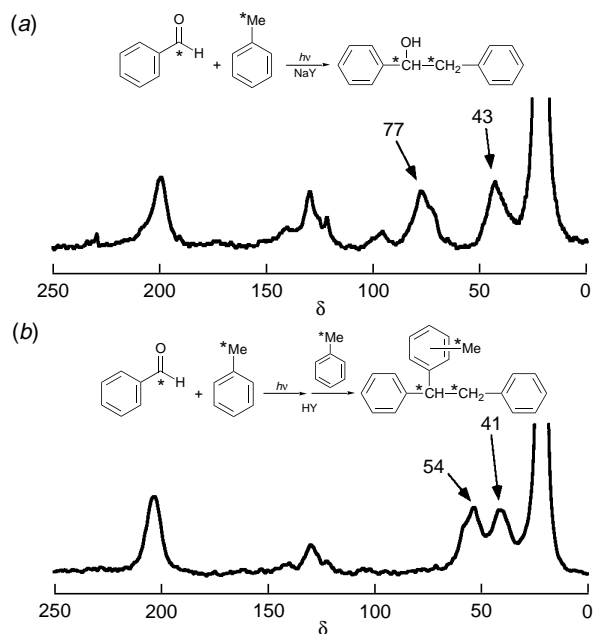
$[\alpha\text{-}^{13}\text{C}]$ Benzaldehyde and  $[\alpha,\beta\text{-}^{13}\text{C}_2]$ acetophenone were obtained from Isotec,  $[\alpha\text{-}^{13}\text{C}]$ toluene from Cambridge Isotope Labs and spectrophotometric grade toluene from Spectrum Chemicals. The zeolite catalysts, USY (ultrastable-Y in the acid form, UOP, Si/Al = 5.5) and NaY (Strem, Si/Al = 2.6), were loaded inside a quartz reaction tube (18 mm diameter, 250 mm length, with an axial valve on one end) and were activated using a previously described procedure.<sup>10</sup> The carbonyl-containing reagent was adsorbed at a loading of one molecule per zeolite supercage. The catalyst was then exposed to an excess of toluene vapour for 30 min to achieve saturation coverage (*ca.* 4 molecules per supercage). The sample container was then sealed, dismounted from the vacuum line, and set up for UV irradiation.

Ultraviolet light from a 500 W mercury vapour arc lamp system (Oriel, Stratford, CT) was filtered by a dichroic mirror to attenuate wavelengths longer than 400 nm then passed through a safety shutter and into a liquid filter (0.85 M aqueous  $\text{CoSO}_4$ ). Estimated filtered UV light intensity calculated from the Oriel optical handbook was 37 mW  $\text{nm}^{-1}$  near the peak at 254 nm, with a total intensity of 250 mW between 245 and 265 nm. The axis of the quartz reaction tube was placed normal to the path of filtered UV light and positioned with the sample in the centre of the beam. During UV exposure, the sample was rotated with one end angled down, at one revolution per second. No significant thermal heating was observed. Published NMR studies of benzaldehyde,<sup>11</sup> other ketones<sup>12</sup> and aldehydes<sup>13</sup> on zeolites suggest little or no thermal reactivity at 298 K for the species studied here.

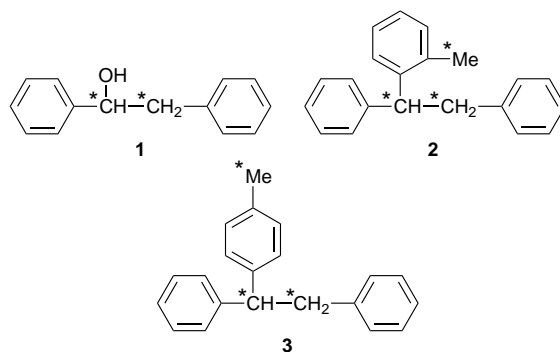
Fig. 1 reports the  $^{13}\text{C}$  MAS NMR spectra of  $[\alpha\text{-}^{13}\text{C}]$ benzaldehyde and  $[\alpha\text{-}^{13}\text{C}]$ toluene on zeolites NaY and USY after UV irradiation. On zeolite NaY, chemical shifts of  $\delta$  77 and 43 indicate that the major photoproduct is the asymmetric coupling product 1,2-diphenylethanol **1** which forms from hydrogen abstraction between benzaldehyde and toluene.<sup>14</sup> Compound **1** is not stable in an acidic environment, and on zeolite USY undergoes a Friedel–Crafts reaction with a second toluene

molecule, forming the isomeric triphenylethanes **2** and **3**, with resonances at  $\delta$  54 and 41, respectively.

Representative  $^{13}\text{C}$  MAS NMR spectra of  $[\alpha,\beta\text{-}^{13}\text{C}_2]$ acetophenone and natural abundance toluene on zeolites NaY and USY are shown in Fig. 2. In analogy to the benzaldehyde reaction, the major photoproduct of acetophenone and toluene on NaY was 1,2-diphenylpropan-2-ol **4** ( $\delta$  75). In the acidic zeolite, however, further reaction led not to Friedel–Crafts products analogous to **2** and **3**, but rather 1,2-diphenylpropane **5**, and other products by the reaction of a (formal) benzyl cation



**Fig. 1** 50.1 MHz  $^{13}\text{C}$  CPMAS NMR spectra of the products of  $[\alpha\text{-}^{13}\text{C}]$ benzaldehyde and  $[\alpha\text{-}^{13}\text{C}]$ toluene on FAU zeolites measured at 298 K following 4 h of UV irradiation (also at 298 K). (a) Spectrum of product on zeolite NaY acquired with 5000 transients at a spinning speed of 5000 Hz. (b) Spectrum of products on zeolite USY acquired with 4000 transients at a spinning speed for 5000 Hz. (★ Denotes  $^{13}\text{C}$  labelled atoms.)



with toluene. The latter included triphenylmethane as established by other experiments with labeled toluene.

For the cases studied here, the photoproducts observed in the zeolite by NMR were identical to those found *ex situ* in previous studies, but this need not be the case in future work where acid digestion of the zeolite might cause degradation of the photoproducts. Additionally, by matching the acid zeolites with non-acidic controls, we were able to characterize the combina-

tion of photochemistry and thermally-activated processes on acid sites. The possibility exists for using photochemistry to synthesize otherwise sterically-excluded adsorbates specifically for the study of carbenium ions or other intermediates<sup>15</sup> formed in a second thermal step.<sup>16</sup> Application of *in situ* NMR methodology to the emerging area of photocatalysis<sup>17,18</sup> should expand research of highly reactive photoproducts.

We acknowledge the National Science Foundation (Grant No. CHE-9528959) for financial support of this work.

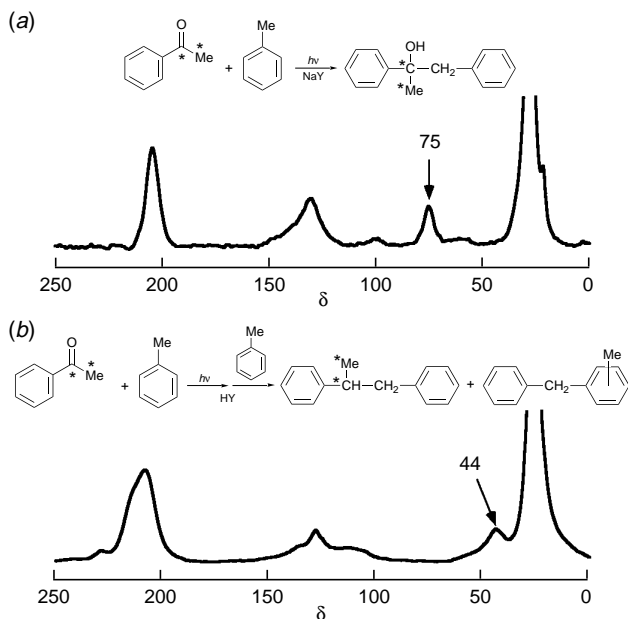
### Footnote

\* E-mail: haw@chemvx.tamu.edu

### References

- 1 V. Ramamurthy, *Photochemistry in Organized and Constrained Media*, VCH, New York, 1991.
- 2 N. J. Turro, A. L. Buchachenko and V. F. Tarasov, *Acc. Chem. Res.*, 1995, **28**, 69.
- 3 V. Ramamurthy, D. F. Eaton and J. V. Caspar, *Acc. Chem. Res.*, 1992, **25**, 299.
- 4 R. G. Weiss, V. Ramamurthy and G. S. Hammond, *Acc. Chem. Res.*, 1993, **26**, 530.
- 5 N. J. Turro, N. Han, X.-G. Lei, J. R. Fehlner and L. Abrahms, *J. Am. Chem. Soc.*, 1995, **117**, 4881.
- 6 V. Ramamurthy, *J. Am. Chem. Soc.*, 1994, **116**, 1345.
- 7 N. J. Turro, C.-C. Cheng, X.-G. Lei and E. M. Flanigen, *J. Am. Chem. Soc.*, 1985, **107**, 3739.
- 8 F. L. Cozens, H. Garcia and J. C. Scaiano, *J. Am. Chem. Soc.*, 1993, **115**, 11 134.
- 9 V. Ramamurthy, D. R. Corbin, C. V. Kumar and N. J. Turro, *Tetrahedron Lett.*, 1990, **31**, 47.
- 10 J. F. Haw, B. R. Richardson, I. S. Oshiro, N. L. Lazo and J. A. Speed, *J. Am. Chem. Soc.*, 1989, **111**, 2052.
- 11 T. Xu, J. Zhang and J. F. Haw, *J. Am. Chem. Soc.*, 1995, **117**, 3171.
- 12 T. Xu, E. J. Munson and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 1962.
- 13 E. J. Munson and J. F. Haw, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 615.
- 14 X. Lei and N. J. Turro, *J. Photochem. Photobiol. A: Chem.*, 1992, **69**, 53.
- 15 J. F. Haw, J. B. Nicholas, T. Xu, L. W. Beck and D. B. Ferguson, *Acc. Chem. Res.*, 1996, **29**, 259.
- 16 T. Xu and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 10 188.
- 17 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735.
- 18 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341.

Received in Corvallis, OR, USA, 20th December 1996; Com. 6/08523G



**Fig. 2** 50.1 MHz  $^{13}\text{C}$  CP MAS NMR spectra of  $[\alpha, \beta\text{-}^{13}\text{C}_2]$ acetophenone and natural abundance toluene on FAU zeolites measured at 298 K after 4 h of UV irradiation (also at 298 K). (a) Spectrum of product on zeolite NaY acquired with 1200 transients at a spinning speed of 3600 Hz. (b) Spectrum of product on zeolite USY acquired with 1200 transients at a spinning speed of 4500 Hz. The resonance at  $\delta$  44 did not survive 50  $\mu\text{s}$  of dipolar dephasing (not shown) supporting the assignment indicated. (★ Denotes  $^{13}\text{C}$  labeled atoms.)

