Selective Oxidation of Toluene to Benzaldehyde by O_2 with Visible Light in Barium(2+)- and Calcium(2+)-Exchanged Zeolite Y

Hai Sun, Fritz Blatter, and Heinz Frei*

Laboratory of Chemical Biodynamics
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Received March 28, 1994

Selective oxidation of toluene to benzaldehyde by molecular oxygen is one of the current challenges in the field of environmentally benign chemical synthesis of important organic intermediates.[1] Photochemical means are attractive because reaction surfaces can be accessed selectively and the chemistry can be run at ambient temperature. The absence of a need for elevated temperatures is especially important for attaining high product selectivity as it minimizes the chance for loss of control by thermal reaction of the initial products. Photooxygenation by direct excitation of $C_6H_5CH_3{\cdot}O_2$ complexes in O_2-saturated solution is well established, but light of the UV region must be used in order to access the $C_6H_5CH_3{\cdot}O_2$ charge-transfer absorption. The consequence is that the selectivity is poor. A mixture of benzaldehyde and benzyl alcohol is obtained as final oxidation products.[2] The alcohol was determined to be formed from benzyl hydroperoxide intermediate by thermal homolytic O–O bond rupture and by secondary photolysis of the hydroperoxide.[2] Likewise, irradiation of the $C_6H_5CH_3{\cdot}O_2$ charge-transfer absorption in solid O_2 by UV light was found to cause oxidative cleavage of the aromatic ring to form dicarbonyl compounds and CO_2 as main products.[3] Selective photochemical conversion of toluene to benzaldehyde by O_2 would require the use of much longer wavelength photons in order to avoid secondary photochemistry. Furthermore, conditions have to be chosen so that random chemistry of transient radicals is suppressed. We report here the first selective photooxidation of toluene to benzaldehyde by O_2. It was accomplished by photoexcitation of $C_6H_5CH_3{\cdot}O_2$ complexes in the molecular-scale cages of alkaline earth exchanged faujasitic zeolites[4] with visible light.

Loading of toluene from the gas phase into dehydrated zeolite BaY[5–7] resulted in an infrared spectrum with absorptions at 1386, 1467, 1495, 1599, 2748, 2876, 2925, 2959, 2982, 3028, 3061, and 3084 cm^{-1}. Subsequent addition of 500 Torr of O_2 gas did not result in any new infrared spectral features, and no dark reaction was noticed when the matrix was kept at room temperature for several hours. However, chemical reaction was observed upon irradiation of the toluene and O_2-loaded zeolite pellet with visible light of a tungsten source ($\lambda > 390$ nm),[8] or the green or blue emission of a CW dye laser or an Ar ion laser ($\lambda < 515$ nm).[9] An FT-infrared difference spectrum in the regions 1900–1250 and 900–800 cm^{-1} taken before and after photolysis at 488 nm (400 mW cm^{-2} for 3 h) is shown in Figure 1. All toluene absorptions decrease, while product bands emerge at 832, 1317, 1394 (4), 1458 (2), 1580 (2), 1594, 1656 (20), and 1678 cm^{-1} (11) (numbers in parentheses indicate red shifts of the corresponding toluene + $^{18}O_2$ product absorptions). These bands agree well with the spectrum of an authentic sample of benzaldehyde in BaY. The well-established Fermi resonance of the C=O stretching mode with a C–H bending overtone is much more pronounced in the zeolite cage environment compared to conventional phases.[10] The two bands (1678 and 1656 cm^{-1}) have similar intensity, and each has a substantial ν(C=O) component as indicated by the ^{18}O frequency shifts. A very broad product band centered at 3300 cm^{-1} and a broad shoulder around 1640 cm^{-1} indicate concurrent generation of H_2O. No other absorption grew in, not even after prolonged photolysis. We conclude that toluene and O_2 react in zeolite BaY upon irradiation with blue or green light to produce benzaldehyde as the sole final oxidation product.

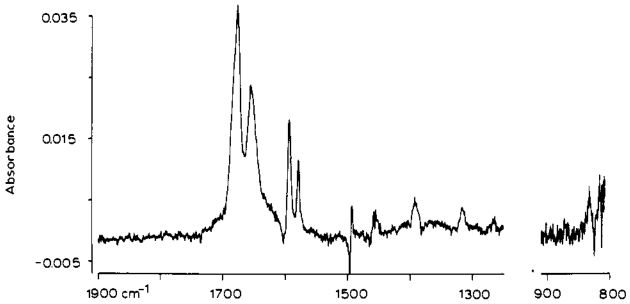

Figure 1. Infrared difference spectrum of the BaY pellet loaded with toluene and O_2 before and after photolysis with continuous-wave Ar ion laser light at 488 nm (400 mW cm^{-2}, 3 h) at room temperature.

Benzaldehyde was also the exclusive final oxidation product of the visible light induced reaction ($\lambda > 480$ nm) of toluene with O_2 in zeolite CaY (98% Na$^+$ replaced by Ca^{2+}). Reaction could be initiated by light extending into the orange spectral range (photolysis threshold 590 nm). Figure 2 shows the diffuse reflectance spectra of CaY (curve b) and BaY (curve a) loaded with toluene and O_2.[11] This absorption appears only when toluene and O_2 are simultaneously present in the zeolite matrix, and it can be reversibly removed by pumping off the oxygen. This indicates that the band originates from a $C_6H_5CH_3{\cdot}O_2$ complex. We can conceive of two possible assignments, namely, an O_2-enhanced triplet absorption of toluene and a $C_6H_5CH_3{\cdot}O_2$ charge-transfer absorption. The first can be ruled out because the lowest triplet state of toluene has its minimum at 28 900 cm^{-1} (346 nm) in conventional environments.[12] Phosphorescence studies by several research groups have shown that spectral shifts of triplet states of aromatics observed upon loading into zeolites are small.[13] By contrast, red shifts of the $C_6H_5CH_3{\cdot}O_2$ charge-transfer transition upon loading into alkali or alkaline earth zeolites may

---

(1) (a) Haber, J. In *Perspectives in Catalysis*; Thomas, J. M., Zamaraev, K. I., Eds.; IUPAC/Blackwell Scientific Publications: London, 1992; pp 371–385. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed., Wiley: New York, 1992; pp 237–268. (c) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; pp 315–339.

(2) (a) Wei, K. S.; Adelman, A. H. *Tetrahedron Lett.* **1969**, 3297–3300. (b) Slifkin, M. A.; Allison, A. C. *Nature* **1967**, *215*, 949–959.

(3) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1989**, *93*, 571–577.

(4) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; Wiley: New York, 1974.

(5) BaY was prepared by ion exchange of NaY in a 0.5 M $BaCl_2$ solution. Inductively-coupled plasma atomic emission spectroscopy showed that 95% of Na$^+$ was replaced by Ba^{2+}. Spectroscopic and vacuum instrumentation and experimental procedures were the same as described in previous reports.[6,7]

(6) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501–7502.

(7) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812–1820.

(8) A Corning filter No. 3–75 was used.

(9) A heating effect of the laser on the observed product growth is ruled out by our observation, in a separate experiment, that no toluene + O_2 reaction occurred upon elevating the zeolite temperature to 80 °C for 5 h. The absence of large heating effects (by laser or tungsten source light) is also evident from our previous work on alkene + O_2 systems in NaY.[6,7] In those cases, no rearrangement of the alkene hydroperoxide intermediate to the corresponding carbonyl product was observed during photolysis when the zeolite temperature was kept below −20 °C (the temperature above which the hydroperoxide rearranges thermally). From measurements of propylene desorption upon laser irradiation of propylene/O_2/BaY matrices, we infer an upper limit of 10 deg for the laser heating effect (488 nm, 500 mW cm^{-2}).

(10) Bellamy, L. J. *Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1980, Vol. 2, p 132.

(11) Experimental setup and procedure were similar to those described in a previous report: Blatter, F.; Moreau, F.; Frei, H. Submitted.

(12) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; p 256.

(13) For a leading reference, see: Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991; pp 429–493.

0002-7863/94/1516-7951$04.50/0

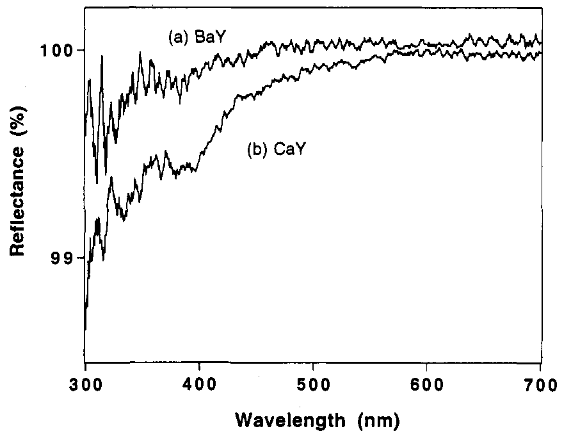

Figure 2. $C_6H_5CH_3{\cdot}O_2$ diffuse reflectance spectra in (a) BaY and (b) CaY.

be large due to Coulombic interactions of the excited reactants with Ca^{2+} (or Ba^{2+}) and the negatively charged cage walls.[4] According to the diffuse reflectance spectra, the onset of the absorption is at 600 nm in Ca^{2+}- and around 500 nm in Ba^{2+}-exchanged zeolite (Figure 2). The onset of the $C_6H_5CH_3{\cdot}O_2$ charge-transfer band in O_2-saturated solution, on the other hand, is around 370 nm.[14] We propose that the observed visible absorption tail of toluene/O_2/CaY and toluene/O_2/BaY samples originates from a hydrocarbon$\cdot O_2$ charge-transfer transition. In the case of zeolite CaY, this implies a more than 10 000 cm^{-1} stabilization of the excited charge-transfer state by the ionic cage environment. The red shift is similar to the one observed recently in the case of butene$\cdot O_2$ charge-transfer absorptions in zeolite NaY,[6,7,11] but an order of magnitude larger than for other types of charge-transfer systems (e.g., aromatic-pyridinium complexes in faujasitic zeolites reported recently by Kochi, or transition metal complexes studied by Dutta).[15] We attribute the stronger stabilization of the charge-transfer state in CaY as compared to BaY to the larger electrostatic field in the vicinity of Ca^{2+}.

We propose that the initial step following photoexcitation to the $C_6H_5CH_3^+/O_2^-$ excited charge-transfer state is proton transfer from toluene radical cation to O_2^- to form a $C_6H_5CH_2^{\bullet}/HO_2^{\bullet}$ cage radical pair. Toluene radical cation is known to be an extremely strong acid with an estimated pK_a of -10.[16] Benzyl and $HO_2^{\bullet}$ radicals so produced are expected to recombine to yield benzyl hydroperoxide analogous to the reaction path established in the case of alkene + O_2 photochemistry in NaY.[6,7] We have loaded benzyl hydroperoxide, which was synthesized by a published procedure,[17] into BaY and CaY matrices at room temperature and found that most of it rearranges to benzaldehyde and H_2O on the time scale of an FT-IR spectroscopic run (a few minutes). No byproducts were observed. This suggests that hydroperoxide rearranges according to the heterolytic mechanism[18] rather than homolytic O–O bond rupture since the latter often leads to radical chemistry with multiple products. Although the thermal rearrangement of the benzyl hydroperoxide and the low extinction coefficient of its infrared absorptions[19] all but prevent observation of the intermediate by infrared spectroscopoy, we have indirect kinetic evidence for its presence. Some thermal growth of benzaldehyde was observed when the BaY matrix was kept in the dark *after* toluene + O_2 photolysis. Such growth occurred even when O_2 was pumped off prior to the dark period. If the toluene + O_2 photolysis was conducted with $^{16}O_2$ and then replaced by $^{18}O_2$ prior to the dark period, no benzaldehyde-^{18}*O*, but only benzaldehyde-^{16}*O*, grew in. These observations are consistent with the intermediacy of the proposed benzyl hydroperoxide.

The diffuse reflectance signal is too weak for reliable quantum efficiency measurements in the case of BaY, but the visible charge-transfer absorption is sufficiently strong in CaY to allow us an estimate of the reaction quantum yield. While benzaldehyde is the final oxidation product in both BaY and CaY, an aromatic intermediate was trapped in the Ca^{2+}-exchanged zeolite that could readily be monitored by infrared spectroscopy. It interconverted photochemically to benzaldehyde at $\lambda < 515$ nm. Identification based on infrared analysis will be presented in a full report.[20] On the basis of the infrared absorbance growth of this intermediate, the quantum efficiency of the toluene + O_2 reaction upon 488 nm excitation in CaY was estimated to be on the order of 10%.[21] The rather high quantum yield implies that this photochemical toluene to benzaldehyde conversion could be used for practical synthesis. Note that the low value of the absorption in Figure 2 is due to strong light scattering of the pellet rather than a vanishing extinction coefficient of the $C_6H_5CH_3{\cdot}O_2$ charge-transfer absorption.[22] Particles in our pellets have sizes around 1 μm. Practical synthesis may require the use of zeolite powders made up of substantially larger crystals. Faujasite crystals of 100 μm diameter have been reported.[23]

In summary, high selectivity has been demonstrated upon visible light induced oxygenation of toluene to benzaldehyde in alkaline earth exchanged zeolite Y. We attribute the tight product control to mainly two factors. One is access to the $C_6H_5CH_3{\cdot}O_2$ excited charge-transfer state by light of sufficiently long wavelength to prevent loss of product control by photofragmentation of primary products or by homolysis of the proposed hydroperoxide intermediate. The second is confinement of benzyl/$HO_2^{\bullet}$ radical pairs to the zeolite matrix cage, which suppresses indiscriminate attack of these radicals and forces them to combine. The Co^{3+}-catalyzed radical oxidation of toluene by O_2 in solution used currently in an industrial process for benzaldehyde synthesis lacks this selectivity, mainly because of continued oxidation of the aldehyde to benzoic acid.[1b,c] This step is not observed with the photochemical method reported here, presumably in part because of the higher ionization potential (hence shorter wavelength charge-transfer absorption) of benzaldehyde compared to toluene.[24]

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

(14) Chien, J. C. W. *J. Phys. Chem.* **1965**, *69*, 4317–4325.

(15) (a) Sankararaman, S.; Yoon, K. B.; Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 1419–1421 and references therein. (b) Turbeville, W.; Robins, D. S.; Dutta, P. K. *J. Phys. Chem.* **1992**, *96*, 5024–5029.

(16) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165–2179.

(17) Walling, C.; Buckler, S. A. *J. Am. Chem. Soc.* **1955**, *77*, 6032–6038.

(18) March, *J. Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 1099.

(19) Spectra of authentic samples of $C_6H_5CH_2OOH$ in CD_3CN show that its absorptions at $\bar{\nu} > 1250$ cm^{-1} have much lower cross sections than those of benzaldehyde and/or overlap strongly with toluene bands.

(20) Sun, H.; Frei, H. To be submitted.

(21) The intermediate shows an aromatic C–H bending mode at 1415 cm^{-1}. The quantum yield estimate was based on the assumption that the extinction coefficient of this band is the same as that of the corresponding mode of benzaldehyde at 1458 cm^{-1}, which is 20 L mol^{-1} cm^{-1}.

(22) Absorptions in the infrared region (where there is very little scattering) of toluene loaded into these pellets are strong even for bands with a mere ϵ of 50 L mol^{-1} cm^{-1}.

(23) (a) Hamilton, K. E.; Coker, E. N.; Sacco, A., Jr.; Dixon, A. G.; Thompson, R. W. *Zeolites* **1993**, *13*, 645–653. (b) Charnell, J. F. *J. Cryst. Growth* **1971**, *8*, 291–294.

(24) *CRC Handbook of Chemistry and Physics*, 53rd ed.; Weast, R. C. *Ed.*; The Chemical Rubber Co.: Cleveland, 1972; p E-62.