Highly Selective Formation of *tert*-Butyl Hydroperoxide from the Reaction of Isobutane and O_2 in a Zeolite under Visible Light

Fritz Blatter, Hai Sun, and Heinz Frei*

Abstract: Isobutane and oxygen gas loaded into zeolite BaY react upon irradiation with green or blue light to yield *tert*-butyl hydroperoxide in a single-photon process. This was discovered when monitoring the reaction at room temperature in situ by FT-infrared spectroscopy. Selectivity was 98%, even upon conversion of more than half of the reactants loaded into the zeolite. Diffuse reflectance spectra revealed a visible absorption tail which originates from an isobutane·O_2 collision complex. It is attributed to the isobutane·O_2 contact charge-transfer absorption, whose onset is shifted from the UV into the visible region by the high electrostatic field of the zeolite.

Keywords
hydroperoxides · isobutane · oxygen · photooxidations · zeolites

Introduction

Tertiary butyl hydroperoxide is a major industrial oxidant for the transformation of small olefins to epoxides.[1] For example, propylene oxide is produced on a large scale by metal-catalyzed oxygen transfer from *tert*-butyl hydroperoxide to propylene.[2] The hydroperoxide is generated by the reaction of isobutane with O_2 at 100–140 °C. Despite the vast research effort expended on this system, a selectivity of no more than 75% is achieved in the liquid-phase autoxidation at low conversion (8%) under practical conditions.[3, 4]

We report here a method that affords, for the first time, oxidation of isobutane to *tert*-butyl hydroperoxide by O_2 with nearly complete selectivity at high conversion. The approach takes advantage of a very large red shift of the alkane·O_2 charge-transfer absorption in Ba^{2+}-exchanged zeolite Y. This shift, which we observed previously in the case of alkene and toluene·O_2 complexes in alkali and alkaline earth zeolite Y[5] is attributed to an unprecedented stabilization of the excited charge-transfer state by the very high electrostatic field inside the zeolite cage. As a result, photoreaction of isobutane with O_2 can be induced by visible instead of UV light. Access to this low-energy excited state, coupled with the positional constraint imposed by the zeolite nanocage,[6] furnishes a new, selective reaction path for this important alkane oxidation. In addition, synthesis in the zeolite environment offers an opportunity for in-situ use of the hydroperoxide as an oxidizing agent, thus avoiding the necessity for accumulation of this hazardous reagent in bulk quantities.

Results and Discussion

Gaseous isobutane and O_2 were loaded into zeolite BaY at room temperature. The process was monitored in situ by Fourier-transform infrared spectroscopy. Figure 1a shows the infrared spectrum of the zeolite matrix after exposure to 5 Torr isobutane and 760 Torr O_2. While no thermal isobutane + O_2 reaction was observed at room temperature even 24 h after loading of the

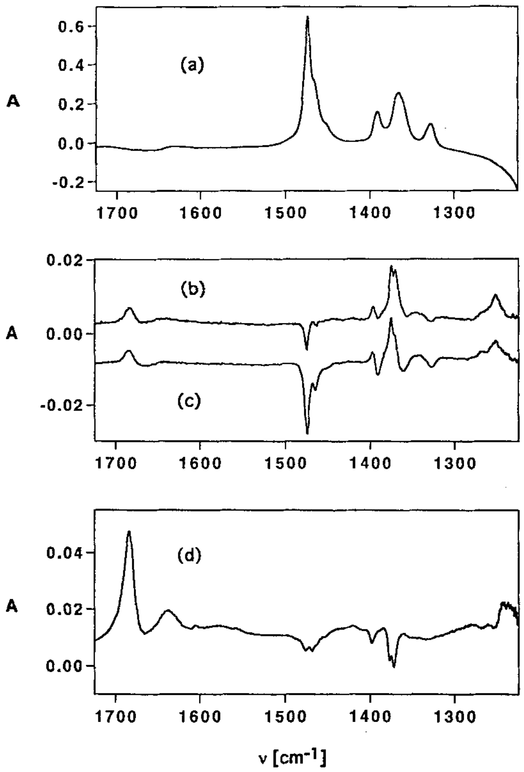

Fig. 1. a) FT-infrared difference spectrum before and after loading of isobutane and O_2 into zeolite BaY. b) IR difference spectrum before and after photolysis at 488 nm and 0 °C at 250 $mW cm^{-2}$ for 4 h; c) at 500 $mW cm^{-2}$ for 2 h. Note that the larger decrease of the isobutane band at this higher laser power is due to the loss of about 1% alkane by desorption from the zeolite into the gas phase. This desorption corresponds to a heating effect of approx. 10° [5]. d) IR difference spectrum following warming of the photolysis product *tert*-butyl hydroperoxide to 50 °C.

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zeolite, irradiation with the green or blue emission of an Ar ion laser (514 or 488 nm) resulted in product growth and concurrent loss of the alkane. Infrared difference spectra following irradiation with 488 nm light at 0 °C are shown by traces b and c of Figure 1. For a fixed number of photons absorbed, the product growth was independent of the photolysis power level, as can be seen from the two spectra. This shows that no thermal reaction that might be caused by a laser heating effect is detectable. From measurement of isobutane loss upon irradiation of loaded BaY matrices we infer an upper limit of 10° for laser heating effects at typical power levels used (500 mWcm^{-2}). Reaction could also be induced by the visible emission of a conventional tungsten lamp. Yields were independent of the light source and simply reflect the number of light quanta absorbed by the reactants. The use of the laser allowed us to determine the wavelengths responsible for the observed chemistry readily.

Except for the absorption at 1686 cm^{-1}, all infrared product bands originate from *tert*-butyl hydroperoxide. These bands, the corresponding ^{18}O isotope shifts, and the frequencies of an authentic sample of *tert*-butyl hydroperoxide loaded into zeolite BaY are presented in Table 1.

Table 1. Absorption frequencies of isobutane + O_2 reaction products and authentic samples in BaY (in cm^{-1}).

Reaction Product [a]	Authentic Samples [b]		
	TBHP [c]	Acetone	Methanol
829 [d]	*829*		
1243 (− 2)		*1243*	
1252 (−1)	*1252*		
1268 (− 6)	*1268*		
		1365	
1372 (−1)	*1372*	1375	
1376 (−1)	*1376*		
			1395 [e]
1398 (0)	*1398*		
1420		*1420*	
1452			*1452*
1468	*1468*		
1472	*1476*		
1686 (− 28)		*1686*	
2873	*2873*		
2938	*2938*		
2978	*2979*		
2988	*2988*		
3230 [e]	*3230*		
3440 [e]			*3440*

[a] ^{18}O frequency shifts (in parentheses) were obtained from isobutane + $^{18}O_2$ studies. For the CH_2 bending modes ($\tilde{\nu} > 1400$ cm^{-1}) and the CH_2 stretching modes the isotope shifts could not be determined because of strong overlap with decreasing product bands. [b] Spectra recorded in BaY. Italicized entries indicate assignment of the reaction product absorption of column 1. [c] TBHP = *tert*-Butyl hydroperoxide. [d] Absorption of the ^{18}O labeled product obscured by zeolite absorption (red shift > 20 cm^{-1}). [e] Very broad.

The product absorption at 1686 cm^{-1} features a 28 cm^{-1} ^{18}O isotope frequency shift, indicating that it originates from a C=O stretching mode. The band coincides with ν(C=O) of an authentic sample of acetone recorded in BaY (but is not in agreement with the infrared absorption of other possible carbonyl products such as isobutyraldehyde or propionaldehyde). While the *tert*-butyl hydroperoxide absorptions follow first-order kinetics upon photolysis, the 1686 cm^{-1} feature showed an induction period. Speculating that acetone is produced by thermal rearrangement of the hydroperoxide, we removed the excess isobutane from the zeolite after photolysis by brief evacuation and then raised the temperature of the pellet to 50 °C. Figure 1 d shows the infrared difference spectrum after the matrix had been maintained at that temperature for 6 h. *Tert*-butyl hydroperoxide absorptions decreased, while the positive bands at 1686, 1420, and 1243 cm^{-1} indicate formation of acetone (Table 1). The intense OH stretching absorption at 3440 cm^{-1} and a very weak but reproducible band at 1452 cm^{-1} signal that methanol is also produced. We conclude that acetone and methanol are secondary thermal products of the hydroperoxide. Rearrangement of *tert*-butyl hydroperoxide to these products is a well-established process in solution.[7] However, in contrast to the behavior in fluid media, no concurrent O–O bond homolysis leading to *tert*-butanol was observed even at zeolite temperatures as high as 100 °C.

The selectivity for *tert*-butyl hydroperoxide is very high, namely 98 % even upon conversion of more than 50 % of the isobutane loaded into the zeolite, as shown in Figure 2. The result is based on the determination of the hydroperoxide-to-acetone branching ratio by the infrared measurements as described in the Experimental Procedure. This is very different from the thermal isobutane autoxidation in the gas or liquid phase, where secondary reactions degrade the selectivity at conversions as low as a few percent.[1] It is important to note that the depletion of isobutane in the experiment shown in Figure 2 corresponds to complete conversion of the reactants residing in the section of the pellet that is penetrated by visible light. The strong scattering of the photolysis light by the one-micron zeolite crystallites restricts penetration to the front section of the pellet (in contrast to infrared probe light, which is transmitted essentially without scattering).

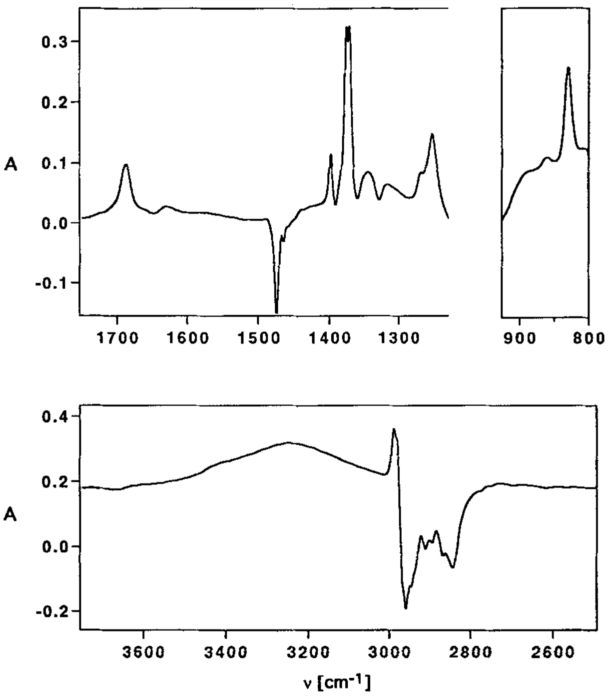


Fig. 2. FT-IR difference spectrum upon prolonged irradiation of an isobutane/O_2/BaY pellet. The loading pressure of isobutane was 1.6 Torr, that of oxygen was 900 Torr. Irradiation for 9 h at 488 nm (750 mWcm^{-2}) resulted in 57 % conversion of the initially loaded alkane.

Figure 3 shows the electronic absorption responsible for the photochemistry measured by the diffuse reflectance method. The continuous tail extends through the short-wavelength visible region to about 500 nm. The spectrum was obtained by first loading the zeolite pellet with the alkane by exposing it to 5 Torr

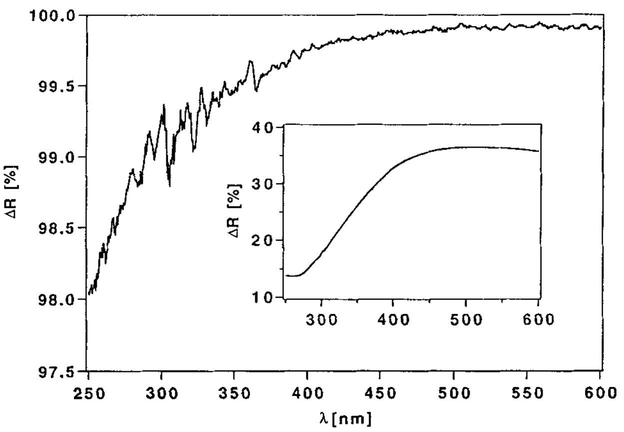
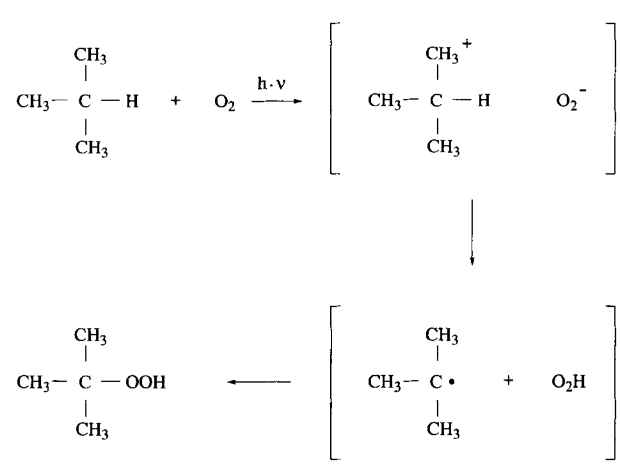


Fig. 3. Diffuse reflectance spectrum of isobutane·O_2 complex in BaY at room temperature. The curve shows the ratio of the reflectance of isobutane-loaded zeolite (5 Torr) after and before exposure to 700 Torr O_2 gas. The insert represents the diffuse reflectance spectrum of dehydrated zeolite BaY before loading of the reactants. $BaSO_4$ was used as a reference. For assignment, see text.

of the gas. No optical absorption caused by the isobutane was observed at $\lambda > 250$ nm. In a second step, 700 Torr O_2 gas was admitted to the UV/Vis cell. It is this difference in the spectra taken before and after adding O_2 to the NaY pellet that is shown in Figure 3. Since the small but significant absorption requires the simultaneous presence of isobutane and oxygen, we conclude that it originates from an isobutane·O_2 complex in the zeolite. It should be added that the diffuse reflectance band is weak because only a fraction of the isobutane·O_2 pairs are probed by visible light.

The only assignment we can conceive of is an isobutane·O_2 charge-transfer transition.[8] Corresponding absorptions of hydrocarbons with similar ionization potential (10.57 eV) in high-pressure O_2 gas or O_2-saturated liquid have an onset in the range 230–260 nm.[9] Hence, a red shift of the onset by the zeolite matrix by about 2.5 eV is implied. We attribute the shift to the stabilization of the excited state with its large dipole moment ($(CH_3)_3CH^+O_2^-$) by the high electrostatic field inside the zeolite cage. Measurement of the induced infrared O_2 and N_2 stretch fundamental in our laboratory signals cage fields in BaY of around 0.8 $VÅ^{-1}$.[10] The field has its origin in the fact that the supercage of zeolite Y carries a formal negative charge of 7. This charge resides mainly on the framework oxygen atoms and is counterbalanced by 3–4 Ba^{2+} inside the supercage. The poor electrical shielding of the cations by the framework oxygens is responsible for the high electrostatic fields. Assuming a separation of 4 Å of the alkane$^+$ and O_2^- charge centers, we calculate for a field of 0.8 $VÅ^{-1}$ a dipole stabilization ($-\mu \cdot E$) of 3 eV. This rough estimate shows that the stabilization by the cage field lies in the range of the observed red shift. The quantum efficiency of the isobutane + O_2 photoreaction with blue and green light is rather high, around 15%.

The first step after excitation of the charge-transfer state is most probably proton transfer from the isobutane radical cation to O_2^- to form an isobutyl/O_2H radical pair (Scheme 1). The isobutane radical cation is a spectroscopically established transient.[11] Hydrocarbon radical cations are known to be highly acidic in general.[12] In the neat liquid at room temperature, typical lifetimes of light alkane radical cations with respect to deprotonation are below 10 ns.[13] It is expected that the proton transfer is even faster in the presence of a base like O_2^-. An additional factor that may favor the formation of isobutyl/O_2H radicals is the high exoergicity for electron back-transfer. It most likely places the transfer into the inverted Marcus region, with the implication that it would be slow. This, coupled with efficient proton transfer, would explain the rather high quantum yield of the reaction. Isobutyl and hydroperoxy radicals so produced are expected to undergo cage combination to yield the observed *tert*-butyl hydroperoxide without radical scrambling (Scheme 1).



Scheme 1.

In Figures 4 and 5, we demonstrate in-situ epoxidation of *trans* and *cis*-2-butene by the photogenerated *tert*-butyl hydroperoxide at room temperature. After the synthesis of the hydroperoxide shown in Figure 2, the oxygen and isobutane remaining in the zeolite were pumped off. Subsequently, *trans*-2-butene (1.5 Torr) was loaded from the gas phase into the zeolite, resulting in two molecules per supercage on average. Difference FT-infrared spectroscopy indicated formation of *trans*-2,3-epoxybutane and *tert*-butanol in the dark at room temperature just a few minutes after adsorption of the olefin. Figure 4 shows

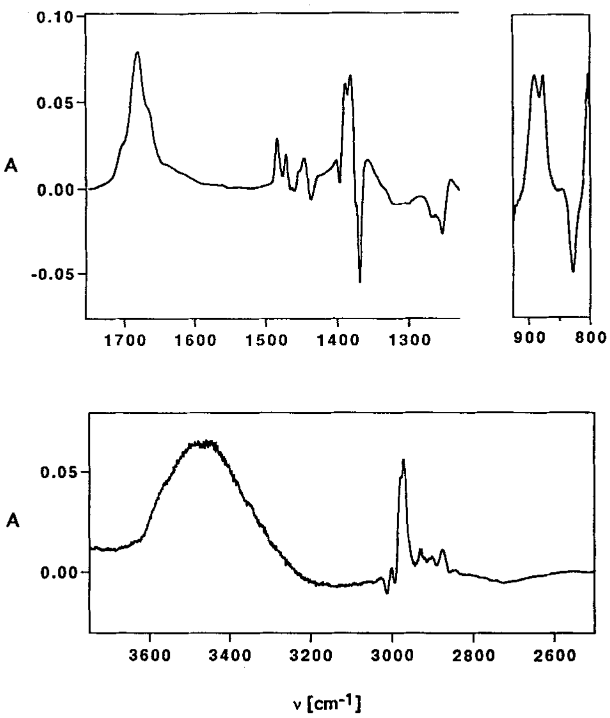


Fig. 4. Infrared difference spectrum upon in-situ thermal epoxidation of *trans*-2-butene by photochemically generated *tert*-butyl hydroperoxide in BaY. Reaction in the dark was recorded after 5 h, with 33% of the hydroperoxide converted.

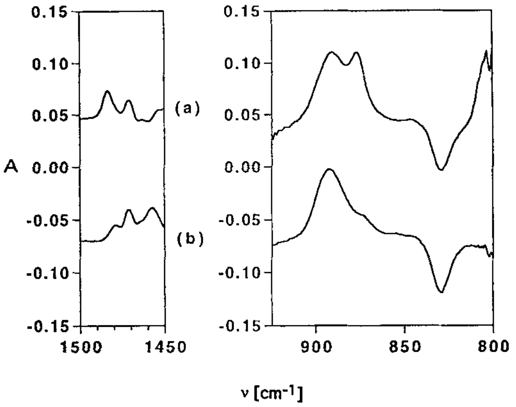


Fig. 5. Infrared difference spectra showing the diastereospecificity of the thermal 2-butene epoxidation. The reaction was recorded 5 h after loading of 2-butene into the *tert*-butyl hydroperoxide-containing zeolite pellet: a) *trans*-2-butene epoxidation, b) *cis*-2-butene epoxidation.

the product growth after reaction of 33% of the *tert*-butyl hydroperoxide, which took 5 h. As can be seen from Figure 4 and Table 2, all product bands can be assigned to *trans*-2,3-epoxybutane, *tert*-butanol and a small amount of acetone. The latter presumably originates from rearrangement of some *tert*-butyl hydroperoxide during the epoxidation reaction. No *cis* diastereomer of the epoxide was observed. Thermal epoxidation of *cis*-2-butene in BaY by photogenerated *tert*-butyl hydroperoxide gave exclusively the *cis* form of 2,3-epoxybutane. Spectral data showing the complete diastereospecificity of the 2-butene epoxidation reactions are presented in Figure 5. Trace a is the infrared difference spectrum before and after epoxidation of *trans*-2-butene, trace b the corresponding infrared spectrum of the *cis*-2-butene epoxidation. The characteristic *trans*-2,3-epoxybutane bands at 1485, 877, and 805 cm^{-1} are absent in the *cis*-2-butene product spectrum. In contrast, *cis*-2,3-epoxybutane absorptions at 1481, 1459, and 875 cm^{-1} are missing in the *trans*-2-butene product spectrum. We conclude that the thermal epoxidation of *cis* or *trans*-2-butene by *tert*-butyl hydroperoxide in BaY at room temperature is completely stereospecific.

Table 2. Absorption frequencies of *tert*-butyl hydroperoxide + *trans*-2-butene reaction products and authentic samples in BaY (in cm^{-1}).

Reaction Product	Authentic Samples [a]		
	TBOH [b]	2,3-epoxybutane	
		trans	*cis*
805		*805*	
			860 (shoulder)
			875
877		*877*	
890	*890*		
1248	*1248*	*1250*	
			1281
1332		*1332*	
			1355
1358	*1358*		
		1362	
1374 [c]		*1374*	
1377	*1377*		
			1384
1388		*1388*	
			1399
			1432
1444		*1444*	
1455		*1455*	
			1459
1472	*1473*	*1472*	
			1481
1485		*1485*	
1682 [d]			
2876	*2876*		
2932		*2932*	2933
[e]	*2940*		
2973		*2973*	2973
			2999
3002		*3002*	
3450 [f]	*3450*		

[a] Spectra recorded in BaY. Entries in italic indicate assignment of the reaction product absorption of column 1. [b] TBOH = *tert*-Butyl alcohol. [c] Overlaps with decreasing *tert*-butyl hydroperoxide absorption. [d] C=O stretching absorption consistent with acetone. The fact that no other infrared band of this species appears in the product spectrum is consistent with the very large extinction coefficient of the ν(C=O) mode. Integrated absorbance measurements indicate an acetone-to-*trans*-2,3-epoxybutane branching ratio of 0.09. [e] Overlaps with decreasing *trans*-2-butene absorption. [f] Very broad.

Extraction of small polar product molecules like epoxides or *tert*-butanol from zeolite Y is routinely performed with a polar organic solvent.[14] However, solvent-free extraction methods would be preferable. We will explore conditions for desorption with the aid of an inert carrier gas, perhaps at modestly elevated temperature.[15]

Conclusion

The work reported here demonstrates that isobutane can be oxidized by O_2 to *tert*-butyl hydroperoxide with very high selectivity at high conversion. Partial oxidation by O_2 in a zeolite with this photochemical method opens up a new approach for selective alkane C–H activation at ambient temperature.[16] In order to scale the reaction up from the micromolar scale shown here to practical quantities, important issues to be addressed are optically translucent zeolite membranes and optimization of the conditions for desorption of the products from the zeolite.

Experimental Procedure

Zeolite BaY was prepared by repeated ion exchange of NaY (Aldrich, Lot No. 04724PZ) at 90 °C in a 0.5 M solution of $BaCl_2$. The degree of ion exchange was determined by dissolution of the zeolite in 40% hydrofluoric acid and recording of the Na, Ba, and Al content by inductively-coupled plasma atomic emission spectroscopy. Ninety-seven percent of the sodium ions were exchanged. Self-supporting zeolite wafers of 10 mg (1.2 cm diameter) were placed in a miniature infrared or UV/Vis vacuum cell described previously [5]. For infrared measurements, the cell was mounted inside a variable temperature vacuum system [5a–c]. To dehydrate the zeolite, the cell was heated to 200 °C for 12–15 h while being evacuated with a turbomolecular pump. The loading level of the reactants depended on the gas pressure and zeolite temperature. At room temperature and the pressures used (see results) there were 1–2 isobutane molecules per supercage and one O_2 per 5 supercages.

The photochemistry was monitored in situ by Fourier-transform infrared spectroscopy with a Bruker Model IFS 113 instrument. For photolysis, a prism-tuned Ar ion laser Coherent Model Innova 90-6 or the visible emission of a tungsten lamp was used. The output of the tungsten source was limited to $\lambda > 430$ nm by a Corning glass filter no. 3-72. Experiments were conducted at temperatures between −50 °C and 21 °C. Diffuse reflectance spectra in the UV–visible region were recorded with a Shimadzu Model 2100 spectrometer with an integrated sphere set-up Model ISR-260. Alkali or alkaline-earth-exchanged zeolites Y do not absorb in the visible spectral region [17], but diffuse reflectance spectra exhibit decreasing reflectance at the onset of the UV range, with a minimum around 250 nm (see insert of Fig. 3). While there is probably optical absorption by the zeolite at $\lambda < 300$ nm [17], the deviation of the reflectance curve from a horizontal line in the range 300–1000 nm originates from the wavelength-dependence of the scattering coefficient that cannot be compensated for by the reference scatterer ($BaSO_4$).

For determination of the product ratio *tert*-butyl hydroperoxide to acetone, known amounts of authentic samples of the hydroperoxide and the ketone were loaded into BaY in separate experiments. Quantities adsorbed were measured by manometric methods. Together with the known dimensions of the zeolite pellet, this allowed us to calculate the infrared extinction coefficients of the two products in the zeolite pellet within five percent. For quantum yield determinations the total number of product molecules generated was measured by the infrared absorbance growth, while the number of photolysis quanta absorbed by the charge-transfer band was obtained from the spectrum of Figure 3. We estimate an uncertainty of a factor of 2 for the quantum efficiency because of the very small signal of the diffuse reflectance spectrum.

Isobutane (Aldrich, 99%), *trans*-2-butene (Matheson, 99%), and *cis*-2-butene (Matheson, 95%) were purified by multiple freeze–pump–thaw cycles before use. Oxygen (Matheson, 99.997%) was used as received. Likewise, compounds needed for recording of authentic spectra in the zeolite (*tert*-butanol (Aldrich, 99%), *tert*-butyl hydroperoxide (90%, with 10% water), *cis* and *trans*-2,3-epoxybutane (97%), acetone (Aldrich, 99.9%), and methanol (Aldrich, 99.9%)) were subjected to vacuum distillation before use.

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