Photooxidation of 1-Alkenes in Zeolites: A Study of the Factors that Influence Product Selectivity and Formation

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Abstract: Photochemical oxidation of hydrocarbons with molecular oxygen is potentially an environmentally benign method for the selective oxidation of hydrocarbons. In this study, in situ FT-IR spectroscopy and ex situ NMR spectroscopy were used to investigate the factors that influence product formation and selectivity in the room-temperature photooxidation of 1-alkenes in zeolites. Upon irradiation with broadband visible light, propylene, 1-butene, and 1-pentene loaded in BaY were photooxidized with molecular oxygen. As discussed in the literature, initial excitation of alkene and molecular complexes results in the selective formation of unsaturated aldehydes and ketones, proposed to occur through a hydroperoxide intermediate. In addition, epoxide and alcohol products are formed when the hydroperoxide intermediate reacts with an unreacted parent alkene molecule. Here it is shown that saturated aldehydes and ketones are formed as well through both a thermal ring-opening reaction of the epoxide in BaY and a second photochemical oxidation route involving a dioxetane intermediate. The yield of saturated aldehydes and ketones increased with decreasing wavelength, increasing temperature, and at a given temperature and wavelength, increasing chain length. Photooxidation of propylene in BaX, BaZSM-5, and BaBeta zeolites was also investigated. Photooxidation in BaX is very similar to that of BaY. In zeolites, BaZSM-5 and BaBeta, propylene polymerized upon adsorption. The polymer, polypropylene, also undergoes photooxidation with molecular oxygen to form an oxygenated polymer product. The results of this study show that product formation and selectivity in the photooxidation of 1-alkenes in zeolites depends on several factors. These factors include thermal reactions of the reactant and photoproduct molecules in the zeolite at ambient temperatures. Several reactions of 1-alkenes in cation-exchanged zeolites contribute to the loss of selectivity; they include: epoxide ring opening, double-bond migration, and alkene polymerization. Some of these reactions are proposed to occur at Brønsted acid sites that are present in various amounts in cation-exchanged zeolites.

Introduction

One of the most important applications of homogeneous catalysis is the oxidation of hydrocarbons to produce industrially important chemicals, such as terephthalic acid and adipic acid, which are used in the production of polymers.[1,2] Oxidation by O_2 with homogeneous catalysts exhibits very low selectivity because side reactions are difficult to control and intermediates are often more easily oxidized than the parent under thermal conditions.[1,2] The problem with autoxidation is that it is slow and nonselective.[3] One challenge is to find new, more efficient catalysts for the conversion of hydrocarbons into oxygenates. A second challenge is to develop processes that have a minimal environmental impact.

Recently, Frei and co-workers have demonstrated that hydrocarbons in zeolite Y can be selectively oxidized by visible light with relatively high quantum yields (∼0.3).[4−11] It has been demonstrated that upon irradiation with visible light, small hydrocarbons such as propylene and 2-butenes loaded in zeolites BaY and NaY, respectively, can be selectively oxidized to allyl hydroperoxide and 3-hydroperoxy-1-butene by molecular oxygen at low temperatures near −100 °C.[5,7] Upon warming to 0 °C, allyl hydroperoxide and 3-hydroperoxy-1-butene convert to acrolein and methyl vinyl ketone, respectively; water is also a product in the reaction. The mechanism for propylene photooxidation is outline in Scheme 1A. Photolysis of the hydrocarbon· O_2 complex with visible light results in a charge-transfer complex in the zeolite cage.[7] The hypothesis is that the electrostatic field of the cation-exchanged zeolite (on the order of several V nm^{-1}) stabilizes the excited charge-transfer state which otherwise can only be accessed by high-energy ultraviolet photons. The allyl hydroperoxide is produced from the charge transfer state which subsequently goes on to form acrolein. The use of visible rather than ultraviolet irradiation allows access to this low-energy pathway, eliminates many secondary photoprocesses, and leads to product selectivity. The geometric constraints of the zeolite framework are also thought to be important in achieving high reaction selectivity. The implications of this methodology for environmentally benign synthesis of chemicals are 2-fold. The increased selectivity of the oxidation reaction will decrease the production of unwanted side products.

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Scheme 1. Proposed Mechanism for the Formation of Unsaturated Carbonyl Compounds

A. Propylene

Acrolein

B. 1-Butene

Methyl Vinyl Ketone   Crotonaldehyde

C. 1-Pentene

Ethyl Vinyl Ketone   Trans-2-Pentenal
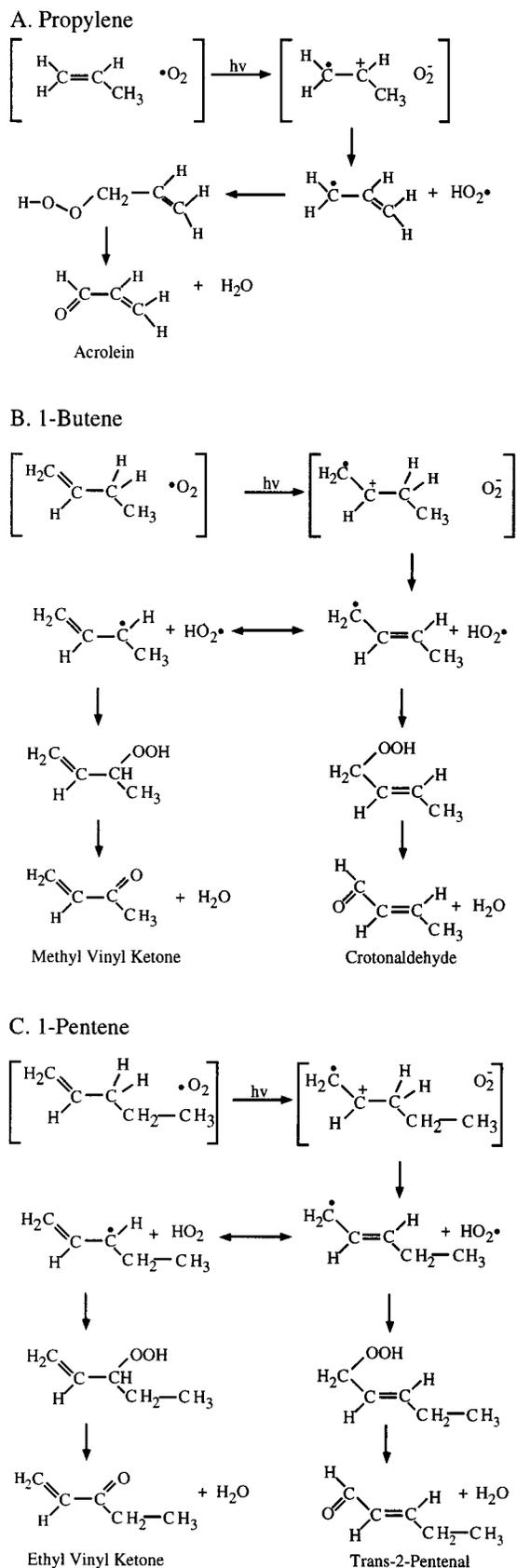
In addition, a zeolite catalyst and gas-phase reactants and products will eliminate the use of expensive and environmentally toxic solvents. From a practical point of view, these reactions

need to be done as close to ambient temperature as possible, rather than low temperatures, if they are to be of industrial use.

The objective of this study is to further develop this methodology for the environmentally benign synthesis of industrially important chemicals as an alternative to conventional liquid-phase oxidation and to determine its limitations.[12] Here we report on the photooxidation of 1-alkenes in zeolites Y, X, ZSM-5, and Beta at room temperature. The Ba^{2+}-exchanged form of these zeolites was used to achieve high electrostatic field strengths on the order of $4-8$ V nm^{-1}. These zeolites were chosen because they differ in chemical composition and structure, i.e., Si/Al ratio and framework topography. If it can be shown that the photooxidation of hydrocarbons in zeolites is a general phenomenon, then the shape and size selective properties of these zeolites may potentially be used to impact further control the selectivity of these reactions. For example, ZSM-5 is an important shape-selective catalyst in many reactions, such as the disproportionation reaction of toluene.[13] *p*-Xylene is the dominant product because the transport of the other isomers, *o*- and *m*-xylene, is restricted due to the pore size of ZSM-5. Thus, stereochemical aspects of these reactions may also be influenced by the zeolite and may be used in the design of environmentally benign syntheses of industrially important molecules.

In this study, in situ FT-IR spectroscopy and ex situ NMR spectroscopy were used to analyze product formation and product yields. This combined approach allows for a more detailed analysis of the product distribution. As discussed here, several factors influence product selectivity and formation in these reactions. These factors include excitation wavelength, temperature, hydrocarbon chain length, and the parent zeolite.

Experimental Section

In situ FT-IR spectra were recorded with a Mattson RS-10000 infrared spectrometer equipped with a narrowband MCT detector. Each spectrum was taken by averaging 500 scans at an instrument resolution of 4 cm^{-1}. The infrared sample cell used in this study has been described previously.[14] Briefly, $50-70$ mg zeolite is sprayed from a water slurry onto a 3×2 cm^2 photoetched tungsten grid held at 40 °C. The tungsten grid coated with the zeolite is mounted onto nickel jaws that are attached to a copper feedthrough. The sample can be heated and cooled from 150 to 1200 K. The temperature of the sample is measured by a thermocouple wire spot-welded to the center of the grid. The entire assembly is mounted inside a 2.75-in. stainless steel cube with BaF_2 windows. The IR cell is then evacuated by a turbomolecular pump to a pressure of 1×10^{-7} Torr. Zeolites are heated under vacuum to 300 °C for BaY and BaX, 350 °C for BaZSM-5, and 450 °C for Beta and kept at the temperature overnight to remove adsorbed water.

Alkenes were loaded into the zeolite by adsorption under an equilibrium gas pressure of $15-16$ Torr at room temperature, lower temperatures for some experiments, for 45 min. The excess hydrocarbon was then pumped out for 5 min, and oxygen was added to the IR cell at a pressure of approximately 200 Torr. A 500-W mercury lamp (Oriel Corp.) with a water filter was used as the light source for photolysis. Broadband long pass filters were placed in front of the lamp (Oriel Corp., filter 59492, %$T = 0$ at 495 nm; filter 59472, %$T = 0$ at 400 nm; filter 59460, %$T = 0$ at 348 nm; and filter 59423, %$T = 0$ at 285 nm). The broadband light was then reflected off an aluminum coated mirror and turned by a 1-in. quartz prism onto the zeolite sample. The quartz prism is mounted inside the FT-IR sample compartment so that the dry air purge was not broken during irradiation. For room-

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temperature experiments, even with the water filter in place, the zeolite sample warmed to between 35 and 45 °C after several hours of irradiation.

Ex situ proton NMR spectra were recorded at room temperature on a Bruker NMR AC-300 spectrometer. Samples were prepared for ex situ analysis as follows. After photooxidation of the alkene in the IR cell at conversions on the order of 45%, the zeolite containing unreacted parent and product molecules was removed from the tungsten grid and suspended in CDCl$_3$. The suspension was placed in a sonic bath for 1 h, and then the zeolite powder was filtered from the suspension. The resulting solution was placed in a 5-mm NMR tube with TMS (tetramethylsilane) as an internal standard before acquisition of the ^{1}H NMR spectrum. Several control experiments were done to ensure that the extracted product distribution was representative of the reaction product distribution. Except for very volatile products and reactants, e.g., formaldehyde and propylene, the reported product distributions from ex situ NMR experiments are representative of the chemistry occurring in the zeolite. NMR experiments done after longer and shorter reaction times did not show an appreciable change in the product distribution.

The Ba^{2+}-forms of zeolites Y, X, ZSM-5, and Beta were used so that high electrostatic field strengths could be achieved. The shift in the CO stretching frequency upon adsorption in the zeolite was used to estimate the electrostatic field strength.[15−17] For BaY, BaX, BaZSM-5, and BaBeta the field strength is estimated to be 6.3, 4.8, 7.4, and 7.8 V nm^{-1}. Zeolites BaY, BaX, BaZSM-5, and BaBeta were prepared from NaY (Aldrich), NaX (Acros Organics), NaZSM-5 (Zeolyst), and NH$_4^+$ Beta (Zeolyst) by standard ion-exchange procedures at 90 °C with aqueous 0.5 M BaCl$_2$ (Aldrich) solutions. The Si/Al ratios for BaY, BaX, BaZSM-5, and BaBeta were determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy) to be 2.4, 1.4, 19, and 16.5, respectively. The Ba/Al ratios for BaY, BaX, BaZSM-5, and BaBeta were determined to be 0.39, 0.33, 0.26, and 0.49, respectively.

To qualitatively test for Brønsted acidity in these cation-exchanged zeolites, a colorimetric method was used. Approximately 50 mg of the zeolite sample was pretreated at 300 °C under vacuum for approximately 12 h. One milliliter of a dilute solution of retinol (Aldrich) or retinyl acetate (Aldrich) in dry hexane was injected onto the activated zeolite. A color change to blue indicated the presence of Brønsted acid sites.[18]

Propylene (Matheson, 99.6% purity), 1-butene (Matheson, 99.9% purity), and O$_2$ (Air Products, 99.6% purity) were used without further purification. 1-Pentene (99% purity) was purchased from Aldrich and subjected to several freeze−pump−thaw cycles prior to use. Standards of acrolein (97% purity), allyl alcohol (99% purity), 3-butene-2-ol (99% purity), butyraldehyde (99% purity), crotonaldehyde (99+% purity), crotyl alcohol (97% purity), epoxybutane ((99% purity), epoxypropane (99+% purity), ethyl vinyl ketone (97% purity), methyl vinyl ketone (99% purity), *trans* 2-pentenal (99+% purity), *cis* 2-pentene (99% purity), *trans*-2-pentenal (95% purity), and 3-penten-2-one and propionaldehyde (97% purity) were purchased from Aldrich and subjected to several freeze−pump−thaw cycles prior to use. Deuterated chloroform (Aldrich, CDCl$_3$, 99.8 atom % D) was used for the NMR experiments.

Results

Photooxidation of Propylene in BaY: The Effect of Wavelength. Propylene and molecular oxygen were added to the zeolite as described in the Experimental Section. After an initial spectrum of propylene and O$_2$ was recorded, the sample was irradiated with broadband light. A 495-nm broadband filter

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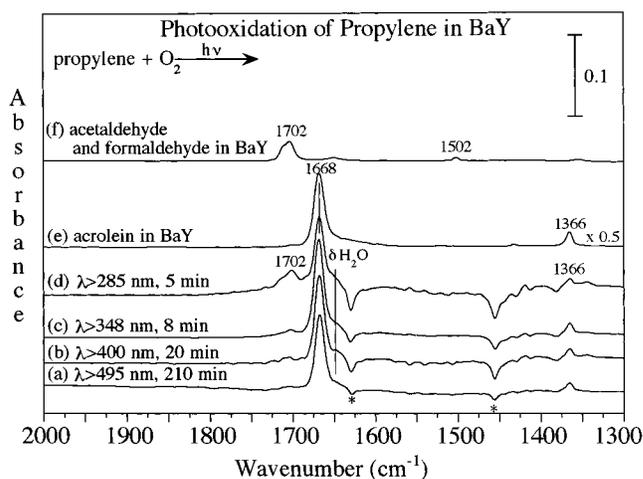
Figure 1. Difference infrared spectra before and after photolysis of propylene and oxygen in zeolite BaY near room temperature with (a) $\lambda > 495$ nm for 210 min, (b) $\lambda > 400$ nm for 20 min, (c) $\lambda > 348$ nm for 8 min, and (d) $\lambda > 285$ nm for 5 min. Propylene losses are indicated by asterisks. FT-IR spectra of (e) 1:1 acetaldehyde and formaldehyde in zeolite BaY.

was placed at the output of the lamp so that only wavelengths above 495 nm were incident on the sample. Figure 1a shows the difference spectrum, i.e., the spectrum recorded before irradiation subtracted from the spectrum recorded following irradiation for 210 min. The sample warmed to 45 °C during irradiation. The difference spectrum shows negative features due to the loss of propylene; these bands are marked by asterisks. The most intense positive features are observed at 1668 and 1366 cm^{-1} and are due to the formation of photoproduct molecules. These two absorption bands match the bands observed for an authentic spectrum of acrolein in zeolite BaY (see spectrum shown in Figure 1e).

The effect of wavelength on the photooxidation of propylene in BaY was examined. The same zeolite sample was used in these experiments, and the irradiation times were chosen so that the conversion at each wavelength was approximately the same. Before changing the wavelength of light for irradiation, the sample was heated under vacuum to 350 °C to remove adsorbed propylene and adsorbed photoproducts. The difference spectra upon irradiation at $\lambda > 400$ nm for 20 min, $\lambda > 348$ nm for 8 min, and $\lambda > 285$ nm for 5 min, are shown in Figure 1b−d. The conversion of propylene at each wavelength was estimated from the integrated absorbance of the 1467 cm^{-1} propylene band to be between 10 and 26% for each of the different wavelengths. It is seen from the FT-IR spectra that acrolein is not the only product observed in the IR spectra following the photooxidation of propylene in BaY. A band indicative of saturated aldehydes and ketones is observed near 1702 cm^{-1} as can be seen in the photoproduct spectra (Figure 1a−d) and in the spectrum of a 1:1 mixture of acetaldehyde and formaldehyde loaded in BaY (Figure 1f). A peak at 1502 cm^{-1} due to formaldehyde, not obvious in the difference spectra, was observed in other FT-IR experiments. Other saturated aldehydes, such as propionaldehyde, may also contribute to the band at 1702 cm^{-1}. In addition, the shoulder near 1645 cm^{-1}, labeled δ H$_2$O is due to the bending mode of water, another product of the reaction.

In two separate experiments, photoproducts and unreacted propylene in BaY were extracted in CDCl$_3$ after irradiation for several hours with broadband visible light at $\lambda > 400$ nm for 18 h and $\lambda > 285$ nm for 3.5 h. Room temperature proton NMR spectra recorded for each sample are shown in Figure 2. Peak assignments and integrated peak areas are presented in Table

Figure 2. Proton NMR spectra of the products extracted in CDCl₃ after photolysis of propylene and oxygen in BaY near room temperature with (a) $\lambda > 400$ nm, 18 h and (b) $\lambda > 285$ nm, 3.5 h. Spectra are referenced to an internal standard of TMS.

Table 1. Assignment of ¹H NMR Spectrum for Photooxidation of Propylene and Oxygen on BaY ($\lambda > 400$ nm)

peak position[a] (ppm)	multiplicity	relative integrated area	assignment
9.80	unresolved	0.2	acetaldehyde (1H) propionaldehyde (1H)
9.59	doublet (6.8Hz)	1.0	acrolein (1H)
6.40	multiplet	4.0	acrolein (3H)
3.00	unresolved	0.3	propylene oxide (1H)
2.76	unresolved	0.3	propylene oxide (1H)
2.46	unresolved	0.5	propylene oxide (1H) propionaldehyde (2H)
2.21	unresolved	0.3	acetaldehyde (3H)
2.17	unresolved	trace	acetone (3H)
1.32	unresolved	b	propylene oxide (3H)
1.25	broad peak	b	impurity
1.12	unresolved	b	propionaldehyde (3H)
0.90	singlet	b	impurity

ᵃ Chemical shifts are measured relative to an internal standard of TMS. ᵇ Integration unreliable due to broad background peak.

1. The products identified in Figure 2a after excitation with $\lambda > 400$ nm are acrolein, propylene oxide, acetaldehyde, propionaldehyde, and acetone. Through integration of the NMR spectrum (Table 1), the ratio of acrolein:propylene oxide:(acetaldehyde + propionaldehyde + acetone) is determined to be approximately 1.0:0.3:0.2.[19] The products identified in Figure 2b for excitation with $\lambda > 285$ nm are acrolein, propylene oxide, acetaldehyde, propionaldehyde, and acetone. Using the integrated areas in Table 2 the ratio of acrolein:propylene oxide:(acetaldehyde + propionaldehyde + acetone) was determined to be 1.0:0.5:0.3.

There are two conclusions that can be drawn from the wavelength dependence of propylene photooxidation in BaY. First, there is an increase in the rate of photoproduct formation using the shorter wavelength broadband filters. For example, the rate of formation of acrolein and propylene oxide is about 10 times higher at $\lambda > 400$ nm than at $\lambda > 495$ nm. Second, there is a decrease in product selectivity at shorter wavelengths as evidenced by the formation of nonselective saturated aldehydes, e.g., acetaldehyde, in the NMR spectrum. The appearance of a band at 1702 cm⁻¹ in the infrared spectrum is indicative of saturated aldehydes and ketones. This band is apparent, albeit

(19) Integrations shown in Table 1 for propylene oxide and the saturated aldehydes and ketone (propionaldehyde, acetaldehyde, and acetone) are highly uncertain because only trace quantities of these products are formed.

Table 2. Assignment of ¹H NMR Spectrum for Photooxidation of Propylene and Oxygen on BaY ($\lambda > 285$ nm)

peak position[a] (ppm)	multiplicity	relative integrated area	assignment
9.80	unresolved	0.3	acetaldehyde (1H) propionaldehyde (1H)
9.59	doublet (6.8Hz)	1.0	acrolein (1H)
6.40	multiplet	4.0	acrolein (3H)
3.00	unresolved	0.5	propylene oxide (1H)
2.76	triplet (4.5 Hz)	0.5	propylene oxide (1H)
2.46	unresolved	0.9	propylene oxide (1H) propionaldehyde (2H)
2.21	doublet (2.7 Hz)	0.7	acetaldehyde (3H)
2.17	singlet	0.1	acetone (3H)
1.32	doublet	1.1	propylene oxide (3H)
1.25	singlet	1.5	impurity
1.12	triplet (7.3 Hz)	0.9	propionaldehyde (3H)
0.90	singlet	0.8	impurity

ᵃ Chemical shifts are measured relative to an internal standard of TMS.

weak, even after irradiation with the longest wavelength broadband filters ($\lambda > 495$ nm and $\lambda > 400$ nm) used. However, the amount of saturated aldehydes and ketones (as indicated by the 1702 cm⁻¹ band in the FT-IR spectrum) relative to acrolein increases with excitation at the shorter wavelengths. The same conclusions can be drawn from the ex situ NMR data. Only very small amounts of saturated aldehydes and ketones are observed after excitation at $\lambda > 400$ nm. However, the ratio of acrolein to saturated aldehydes and ketones is approximately 1.0:0.3 after excitation at shorter wavelength, $\lambda > 285$ nm.

The mechanisms for the formation of acrolein and propylene oxide, taken from the low temperature work of Frei and co-workers, are shown in Schemes 1A and 2A.[5−7] In both cases, the allyl hydroperoxide is formed. At room temperature, inside of the zeolite cage, the allyl hydroperoxide either fragments to acrolein and water or reacts with an unreacted propylene molecule to yield propylene oxide and allyl alcohol. The allyl alcohol has been proven to be difficult to detect in ex situ NMR experiments and may be due to the volatility of this compound.

The formation of saturated aldehydes, in particular the nonselective, shorter chain ones at short wavelengths has been attributed to a photooxidation mechanism of the alkene to form a dioxetane intermediate that decomposes into shorter chain aldehydes. This mechanism for propylene photooxidation is shown in Scheme 3A. The other saturated aldehyde, propionaldehyde, identified unambiguously in the ex situ NMR experiments has not been previously detected in propylene photooxidation in zeolites, and its formation cannot be explained by the dioxetane mechanism. A mechanism for propionaldehdye formation which also accounts for the formation of acetone will be discussed (vide infra).

Photooxidation of 1-Butene in BaY: The Effect of Temperature. Photooxidation of 1-butene in BaY was investigated at two different temperatures and two different wavelengths using in situ FT-IR spectroscopy. The FT-IR spectra are shown in Figure 3. An experimental procedure similar to the one used for propylene was followed for 1-butene. The difference spectrum in Figure 3a was made by spectral subtraction of the spectrum recorded prior to irradiation and the spectrum recorded after warming the sample to 25 °C. The negative absorption bands are due to 1-butene depletion. The two most intense features at 1629 and 1465 cm⁻¹ are marked by asterisks. After photooxidation at −20 °C for 5 h with $\lambda > 400$ nm followed by warming to 24 °C, the intensity pattern of the bands in the difference spectrum (Figure 2a), particularly bands near 1615

Scheme 2. Proposed Mechanism for the Formation of Epoxides, Alcohols, Saturated Aldehydes, and Saturated Ketones

A. Propylene

B. 1-Butene

Figure 3. Difference infrared spectra before and after photolysis of 1-butene and oxygen in zeolite BaY with (a) $\lambda > 400$ nm at -20 °C for 5 h followed by warm-up at 24 °C without oxygen for 18 h and (b) $\lambda > 400$ nm near room temperature for 1.5 h, (c) $\lambda > 495$ nm at 45 °C for 14 h. Asterisks indicate the loss of 1-butene. FT-IR spectrum of (d) methyl vinyl ketone in zeolite BaY.

Scheme 3. Proposed Mechanism for the Formation of Saturated Aldehydes via a Dioxetane Intermediate

A. Propylene

B. 1-Butene

C. 1-Pentene

and 1584 cm^{-1}, match the characteristic bands observed for methyl vinyl ketone in BaY (Figure 3d). The shift of the strongest band from 1660 cm^{-1} for methyl vinyl ketone standard to 1653 cm^{-1} in the product spectrum is due to the coadsorption of water, another product in the reaction. Heating briefly to 175 °C removes the coadsorbed water and shifts the bands to within exact agreement with the authentic spectrum of methyl vinyl ketone. The weak shoulder near 1702 cm^{-1} is assigned to the formation of a small amount (~5%) of saturated aldehydes and ketones.

The difference spectrum shown in Figure 3 (b) was obtained by spectral subtraction of the spectrum recorded prior to irradiation and the spectrum recorded after irradiation with the sample initially at room temperature with $\lambda > 400$ nm. The sample warmed to ~45 °C during the course of the experiment. Note that the intensity pattern in the difference spectra shown Figure 3b does not match that of methyl vinyl ketone in BaY (Figure 3d). There are several additional bands in the spectrum, and broadening of some of the bands in the methyl vinyl ketone spectrum is observed, suggesting that other photooxidation products with similar infrared spectra are formed. The identity of these products can be more clearly determined by ex situ NMR spectroscopy as discussed below. The FT-IR difference spectrum obtained after irradiation with $\lambda > 495$ nm near room temperature is shown in Figure 3c and is qualitatively very

similar to the spectrum obtained in Figure 3b after irradiation of 1-butene with $\lambda > 400$ nm light. These data for the visible

Table 3. Assignment of ^{1}H NMR Spectrum for Photooxidation of 1-Butene and Oxygen on BaY ($\lambda > 400$ nm)

peak position[a] (ppm)	multiplicity	relative integrated area	assignment
9.80	singlet	0.7	acetaldehyde (1H) propionaldehyde (1H)
9.77	singlet	0.9	butyraldehyde (1H)
9.50	doublet	1.0	crotonaldehyde (1H)
6.89	multiplet (unresolved)	1.2	crotonaldehyde (1H)
6.27	multiplet	6.5	methyl vinyl ketone (2H)
5.92	doublet (9.8 Hz)	2.5	methyl vinyl ketone (1H)
4.50	broad peak (narrow peak at 4.52)		alcohol
4.09	unresolved		alcohol product
2.89	multiplet (unresolved)	0.2	epoxybutane (1H)
2.74	multiplet (unresolved)	0.9	epoxybutane (1H)
2.44	multiplet	6.7	epoxybutane (1H) propionaldehyde (2H) butyraldehyde (2H) 2-butanone (2H)
2.29	singlet	5.5	methyl vinyl ketone (3H)
2.21	doublet (unresolved)	0.6	acetaldehyde (3H)
2.14	singlet	2.1	2-butanone (3H)
2.04	doublet (6.6 Hz)	2.1	crotonaldehyde (3H)
1.69	multiplet (unresolved)	2.7	epoxybutane (2H) butyraldehyde (2H)
1.28	multiplet (unresolved)	7.1	impurity
1.03	multiplet (unresolved)	4.6	propionaldehyde (3H) butyraldehyde (3H) epoxybutane (3H) 2-butanone (3H)

[a] Chemical shifts are measured relative to an internal standard of TMS.

photooxidation of 1-butene suggest that in these experiments temperature, rather than wavelength is the more important factor in product selectivity.

Detailed product distributions were determined by ex situ NMR spectroscopy following irradiation of 1-butene and oxygen in BaY with $\lambda > 400$ nm light at 45 °C for 18 h. Products adsorbed in BaY were extracted in CDCl$_3$, and proton NMR spectra were recorded. Peak assignments and integrated peak areas are presented in Table 3. The reactant, 1-butene, and the following photoproducts, methyl vinyl ketone, crotonaldehyde, propionaldehyde, acetaldehyde, butyraldehyde, epoxybutane, and 2-butanone, are all observed in the proton NMR spectrum. There is also evidence of an alcohol product in the 4 ppm region of the proton NMR spectrum which is broadened, probably due to hydrogen bonding of the alcohol product. The relative ratios can be estimated from the integrated peak areas in Table 3. The relative ratio of unsaturated carbonyls (methyl vinyl ketone and crotonaldehyde):saturated aldehydes and ketones (propionaldehyde + acetaldehyde + butyraldehyde + 2-butananone) is approximately 3.5:2.3. The relative ratio of methyl vinyl ketone to crotonaldehyde is 2.5:1.0. Similar product ratios were obtained following irradiation of 1-butene and oxygen in BaY with $\lambda > 495$ nm light at 45 °C for 18 h. Again, this suggests that wavelength ($\lambda > 400$ vs $\lambda > 495$ nm) is not the factor that controls the selectivity and formation of saturated aldehydes and ketones in 1-butene photooxidation with visible light in BaY. As discussed below, thermal reactions of some of the products play a role in the formation of saturated aldehydes and ketones.

Origin of the Band Near 1700 cm^{-1}: Epoxide Ring-Opening Reactions and Dioxetane Photooxidation Channels. The origin of the band near 1700 cm^{-1} in the infrared spectra is important since this band is indicative of the formation of additional products namely saturated aldehydes and ketones. At visible wavelengths, $\lambda > 400$ nm, the formation of saturated aldehydes and ketones appears to be more strongly dependent

on temperature rather than wavelength and, therefore, must be due in part to a thermal reaction. Using in situ FT-IR and ex situ NMR spectroscopy, we have observed that epoxides can react in BaY to form saturated aldehydes and ketones at room temperature. For example, when propylene oxide is adsorbed on BaY and then extracted into CDCl$_3$ for proton NMR experiments, propylene oxide, acetone, and propionaldehyde are observed in the NMR spectrum. In a parallel FT-IR experiment, growth of the band at 1702 cm^{-1} was observed when propylene oxide was adsorbed on BaY. Similarly, butyraldehyde and 2-butanone are observed when epoxybutane is adsorbed on BaY and then extracted and analyzed with NMR spectroscopy. Thus, ring opening and fragmentation of the epoxide product in the zeolite at ambient temperatures results in the formation of saturated aldehydes and ketones. These reactions for propylene oxide and epoxybutane are shown in Scheme 2 A and B as continued thermal chemistry of the epoxide. Similar epoxide ring-opening reactions have been previously observed in zeolites; it was determined that aliphatic epoxides rearrange to form saturated aldehydes and ketones in zeolites that only contain a few weakly acidic sites.[20]

As discussed in the case of propylene photooxidation, the formation of nonselective, shorter chain oxidation products increases when shorter wavelengths $\lambda < 400$ nm are used due to a photooxidation mechanism involving a dioxetane intermediate (Scheme 3). The NMR data show that this route also occurs for 1-butene and 1-pentene (vide infra) to some extent at $\lambda > 400$ nm as evidenced by the formation of propionaldehyde and butyraldehyde (Scheme 3 B and C). This mechanism involving a dioxetane intermediate is most likely the cause of the 1700 cm^{-1} shoulder observed in the low-temperature experiment as well.

In the case of room-temperature photooxidation of 1-butene, the NMR data also shows the formation of acetaldehyde. Acetaldehyde cannot be explained by any of the mechanisms outlined in any of the schemes presented thus far. One plausible mechanism for acetaldehyde production involves double bond migration of 1-butene to yield 2-butene via a thermal reaction, followed by photooxidation of 2-butene via a dioxetane mechanism. Additional evidence for double-bond migration is found in the product distribution for 1-pentene photooxidation.

Photooxidation of 1-Pentene in BaY: The Effect of Alkene Chain Length. The difference FT-IR spectra for the photooxidation of 1-pentene in BaY at ambient temperatures are shown in Figure 4. The more intense negative absorption bands of the parent molecule are at 1625 and 1467 cm^{-1} and are indicated by asterisks. The major product bands at 1700, 1688, 1669, 1650, 1613, and 1595 cm^{-1} in the FT-IR spectrum do not match the spectrum of any single standard, including those of ethyl vinyl ketone (not shown) and 2-pentenal (shown − Figure 4c) very well. The ^{1}H NMR results suggest that this is because there are a number of other products being formed during the photooxidation of 1-pentene in BaY at room temperature with visible light. The band near 1700 cm^{-1} is assigned to a mixture of saturated aldehydes and ketones that can be identified by ex situ NMR experiments as described below.

The ex situ NMR data recorded after irradiation of 1-pentene and oxygen in BaY with $\lambda > 400$ nm light at 45 °C for 12 h and extracted in CDCl$_3$ are presented in Table 4. Ethyl vinyl ketone, 2-pentenal, 3-penten-2-one, valeraldehyde, propionaldehyde, butyraldehyde, and acetaldehyde products are all

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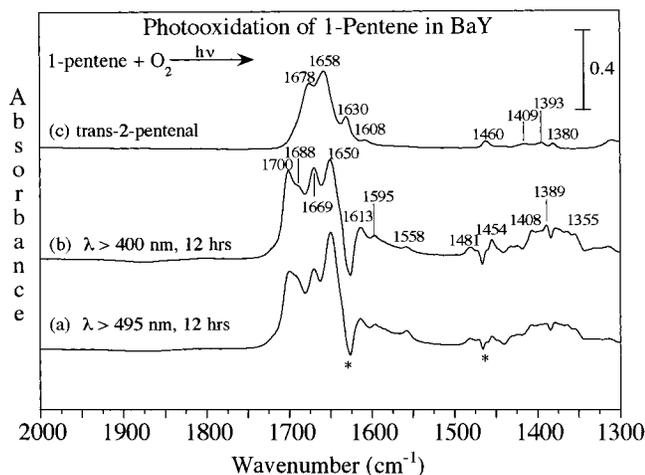
Figure 4. Difference infrared spectra before and after photolysis of 1-pentene and oxygen in BaY with (a) λ > 495 nm near room temperature for 12 h, (b) λ > 400 nm near room temperature for 12 h. Asterisks indicate the loss of 1-pentene. FT-IR spectrum of (c) *trans*-2-pentenal in BaY.

Table 4. Assignment of ^{1}H NMR Spectrum for Photooxidation of 1-Pentene and Oxygen on BaY (λ > 400 nm)

peak position[a] (ppm)	multiplicity	relative integrated area	assignment
9.80	singlet	0.2	acetaldehyde (1H) propionaldehyde (1H)
9.77	singlet	0.6	valeraldehyde (1H) butyraldehyde (1H)
9.52	doublet (8.1 Hz)	1.0	2-pentenal (1H)
6.87	multiplet	1.4	2-pentenal (1H) 3-pentene-2-one (1H)
6.24	multiplet	2.1	ethyl vinyl ketone (2H) 3-pentene-2-one (1H) 2-pentenal (1H)
5.82	doublet (9.5 Hz)	0.5	ethyl vinyl ketone (1H)
4.10	doublet (4.6 Hz)	0.3	alcohol product
2.62	quartet (7.32 Hz)	0.7	ethyl vinyl ketone (2H)
2.40	multiplet (unresolved)	5.3	2-pentenal (2H) valeraldehyde (2H) propionaldehyde (2H) butyraldehyde (2H)
2.24	singlet	0.5	3-pentene-2-one (2H)
2.22	doublet (2.7 Hz)	0.2	acetaldehyde (3H)
2.17	singlet	0.1	acetone (3H) pentanone (3H)
2.14	singlet	0.5	2-3-pentene-2-one (1H)
1.92	doublet (6.8 Hz)	0.7	3-pentene-2-one (3H)
1.62	multiplet (unresolved)	1.9	valeraldehyde (2H) butyraldehyde (2H)
1.37	multiplet (7.1 Hz)	1.8	valeraldehyde (2H)
1.28	triplet (unresolved)	1.6	impurity
1.13	multiplet	4.2	ethyl vinyl ketone (3H) 2-pentenal (3H)
0.93	multiplet	6.1	valeraldehyde (2H) propionaldehyde (3H) butyraldehyde (3H)

[a] Chemical shifts are measured relative to an internal standard of TMS.

observed as indicated in Table 4. A weak peak at 2.17 ppm has been assigned to a saturated ketone, most likely acetone or 2-pentanone. All other peaks expected for 2-pentanone overlap with other reaction products, valeraldehyde and 3-penten-2-one, and thus it is difficult to definitively assign the peak at 2.17 ppm. Using the integrated peak areas in Table 4, the relative ratio of unsaturated carbonyl compounds (ethyl vinyl ketone
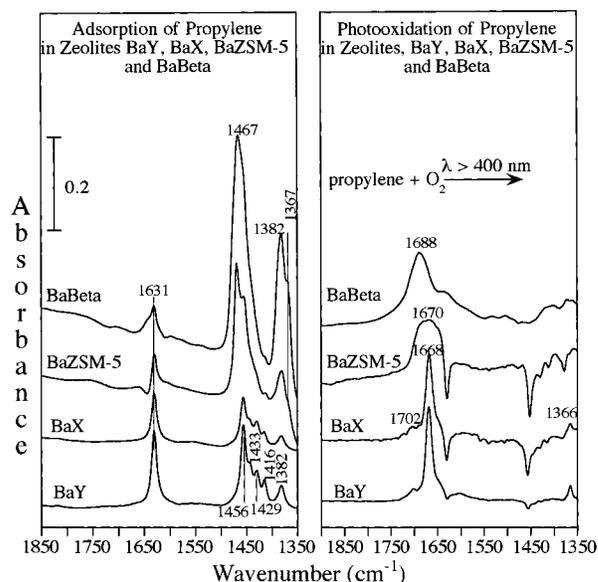
Figure 5. (Left panel). Infrared spectrum of propylene adsorbed in zeolites BaY, BaX, BaZSM-5, and BaBeta. (Right panel). Difference infared spectra before and after irradiation of propylene and oxygen in zeolites BaY, BaX, BaZSM-5, and BaBeta with λ > 400 nm near room temperature.

(0.5), 2-pentenal (1.0), 3-pentene-2-one (0.5)): saturated aldehydes (valeraldehyde, butyraldehyde, propionaldehyde, acetaldehyde) can be estimated to be 2:0.8. The product mixture observed after 1-pentene photooxidation is more complex than that observed after photooxidation of propylene or 1-butene. The reasons for this difference will be discussed further in the Discussion.

Photooxidation of Propylene in Zeolites X, Y, ZSM-5, and Beta: The Effect of the Parent Zeolite. In addition to investigating the effect of excitation wavelength, temperature, and alkene chain length on product selectivity, the role of the parent zeolite in photooxidation of alkenes was also investigated. The left panel of Figure 5 shows the infrared spectra of propylene adsorbed in BaY, BaX, BaZSM-5, and BaBeta. The infrared spectra of propylene in these four zeolites are very different. When propylene is adsorbed in BaY and BaX, there is an intense band in the infrared spectrum at 1631 cm^{-1} due to the C=C stretching mode of propylene.[21] When propylene is adsorbed at room temperature in BaZSM-5 and BaBeta, the intensity of the 1631 cm^{-1} band decreases substantially relative to other absorption bands in the spectrum. In addition, absorption bands between 1300 and 1500 cm^{-1} are broadened in the IR spectra of propylene adsorbed on BaZSM-5 and BaBeta compared to the IR spectra of propylene adsorbed in BaX and BaY. The most intense peak in the IR spectra of propylene adsorbed in BaZSM5 and BaBeta is at 1467 cm^{-1}. These changes in the propylene IR spectrum are consistent with the polymerization of propylene upon adsorption in BaZSM-5 and BaBeta. Polymerization of propylene at room temperature has previously been observed in the acid zeolites, HY, HZSM-5, and HMordenite using FT-IR spectroscopy.[21,22] Polymerization of propylene in HY, HZSM-5, and H Mordenite was detected by a substantial decrease in the intensity of the C=C peak at 1630 cm^{-1}. and the subsequent growth of a band due to -CH$_2$- at 1468 cm^{-1}.[21,22] The formation of propylene oligomers on BaZSM-5 and BaBeta is most likely due to the presence of residual Brønsted acid sites on these zeolites. For BaBeta, these

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(22) Gosh, A. K.; Kydd, R. A. *J. Catal.* **1986**, *100*, 185−195.

sites result from the incomplete exchange of the ammonium cation (NH_4^+) with Ba^{2+} as indicated by the ICP data (see Experimental Section). Upon heating, NH_4^+ is converted to Brønsted acid sites and ammonia, which desorbs at high temperature. The source of Brønsted acid sites is not as clear for BaZSM-5 which was prepared from NaZSM-5. In a recent study, Schiff bases were used to detect low levels of Brønsted acidity in NaY and NaX zeolites.[18] In the next section, the results of the colorimetric test for Brønsted acid sites in zeolites will be discussed.

Photooxidation following propylene adsorption in BaY, BaX, BaZSM-5, and BaBeta was then examined. The difference spectra following irradiation with broadband visible light ($\lambda > 400$ nm) at 318 K are shown in the right panel of Figure 5. Irradiation of propylene in BaY and BaX yielded primarily acrolein (1668 and 1366 cm^{-1}) at this wavelength with small amounts of saturated aldehydes and ketones (1702 cm^{-1}). New photoproduct bands are observed from adsorbed propylene in BaZSM-5 and BaBeta upon irradiation with visible light. These bands, however, are much broader and blue-shifted by ~12 cm^{-1} from the authentic acrolein infrared spectrum in the corresponding zeolite. We attribute these bands to the products from photooxidation of propylene oligomers and the remaining propylene. A broad band at 1683 cm^{-1} is observed in the spectrum that can be attributed to a carbonyl stretch of the oxidized species. In a previous FT-IR study, thermal reactions of propylene oligomers on acidic zeolites yielded IR peaks at 1590 cm^{-1} (HY) and 1510 cm^{-1} (HZSM-5 and HMordenite), attributed to coke and aromatics, respectively.[22] Intensity in the 1500 cm^{-1} region of FT-IR spectrum of BaBeta suggests that aromatic products could be formed and potentially be oxidized during irradiation.

Colorimetric Test for Brønsted Acid Sites in Na and Ba-Exchanged Zeolites X, Y, ZSM-5, and Beta. To clearly determine that Brønsted acid sites are present in the zeolites used in this study, the colorimetric test described by Ramamurthy and co-workers was utilized.[18] The colorimetric test is based on differences in the electronic absorption properties of neutral and cationic forms of probe molecules, such as retinol and retinol acetate. Both retinol and retinol acetate form a blue retinyl cation in an acid solution.[18] The zeolites were *activated* by heating to 300 °C under vacuum for approximately 12 h. Samples of BaZSM-5 and BaBeta both turned dark blue when a dilute solution of retinol was added to the activated zeolite, indicating the presence of Brønsted acid sites. Activated BaY zeolite turned light blue when retinol in hexane was added to the sample and activated samples of BaX, NaX, and NaY exhibited no color change when a dilute solution of retinol was added to the zeolite. These results suggest that, for the zeolites used in this study, the number and strength of Brønsted acid sites trend in the following way: BaZSM-5, BaBeta > BaY > BaX, NaY, NaX. This is qualitatively consistent with the observed oligomerization of propylene which is proposed to occur in BaZSM-5 and BaBeta, but not in BaY and BaX.

Discussion

Reaction Mechanism of 1-Alkene Photooxidation and Product Selectivity in Zeolite Y. Frei and co-workers previously suggested that the photooxidation of hydrocarbons in cation-exchanged zeolite Y proceeds through an intermolecular hydrocarbon·O_2 charge-transfer state.[5-7] The second step in the proposed mechanism involves tranfer of a proton to O_2^- to form an allyl/HO_2• radical pair that reacts further to yield the selective formation of a hydroperoxide at low temperatures near −100

°C. In the case of alkenes, the hydroperoxide fragments upon warming to room temperature to form the corresponding aldehyde and/or ketone products and water. The mechanism for the photooxidation of propylene to yield acrolein is shown in Scheme 1A. This mechanism is based on the mechanism proposed by Frei and co-workers.[5-7] A proposed reaction mechanism for the photooxidation of 1-butene and 1-pentene is presented in Scheme 1B and C. The mechanisms for the photooxidation of 1-butene and 1-pentene in Scheme 1 B and C are similar except for the resonance stabilization of the allyl radical formed after hydrogen abstraction from the hydrocarbon· O_2 charge-transfer state. The two resonance forms of the allyl radical intermediate lead to the formation of two different products.

For 1-butene, the two possible products resulting from this scheme are methyl vinyl ketone and crotonaldehyde. In the FT-IR spectrum after low-temperature irradiation of 1-butene in BaY followed by warming to room temperature (shown in Figure 2a), the spectrum is resolved, and there appears to be one major product, methyl vinyl ketone. Methyl vinyl ketone is the preferred product since it is formed from the more stable secondary radical cation in Scheme 1 B. Broadening of the FT-IR spectrum acquired after room-temperature irradiation of 1-butene with visible light suggests that a mixture of products is present. The FT-IR spectra of methyl vinyl ketone and crotonaldehyde are similar and therefore difficult to resolve. However, the formation of crotonaldehyde is observed in the proton NMR spectrum after room-temperature irradiation of 1-butene ($\lambda > 400$ nm, 18 h).

For 1-pentene photooxidation, the two possible products resulting from Scheme 1 C are ethyl vinyl ketone and 2-pentenal. Both products are clearly observed in the proton NMR spectra of the extracted products. In addition, 3-pentene-2-one and saturated aldehydes such as valeraldehyde, butyraldehyde, propionaldehyde, and acetaldehyde are identified in the proton NMR spectrum.

The most likely mechanism for the formation of 3-pentene-2-one is through the isomerization of 1-pentene to 2-pentene in the zeolite at room temperature, followed by photooxidation of 2-pentene to ethyl vinyl ketone and 3-pentene-2-one as depicted in Scheme 4. The isomerization of alkenes in zeolites has been previously documented.[23,24] There is evidence of 1-butene to 2-butene isomerization and 1-pentene to 2-pentene isomerization in some of the FT-IR and NMR experiments (not shown). The formation of small quantities of acetaldehyde from 2-butene photooxidation and acetaldehyde and propionaldehyde from 2-pentene oxidation also suggests that double-bond migration occurs in BaY, followed by dioxetane chemistry.

Schemes 1 and 4 account for all of the unsaturated aldehyde and ketone photoproducts formed from the photooxidation of 1-alkenes. However, epoxides are observed in the ex situ NMR experiments after photooxidation of 1-alkenes. The epoxides are proposed to be formed from the thermal reaction of the hydroperoxide intermediate with parent hydrocarbon as shown in Scheme 2.[4-7,9] In the case of propylene, the other product, allyl alcohol, should also be formed. It may be that the alcohol product is not observed because of its high volatility. The samples for NMR analysis were exposed to air during the extraction process, and some of the more volatile products were most likely lost. In general, the alcohols appear to be difficult to observe in proton NMR experiments due to hydrogen bonding

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(24) Alvarez-Idaboy, J. R.; Eriksson, L. A.; Lunell, S. *J. Phys. Chem* **1993**, *97*, 12742−12744.

Scheme 4. Proposed Mechanism for the Formation of 3-Pentene-2-one

Ethyl Vinyl Ketone   3-Pentene-2-one
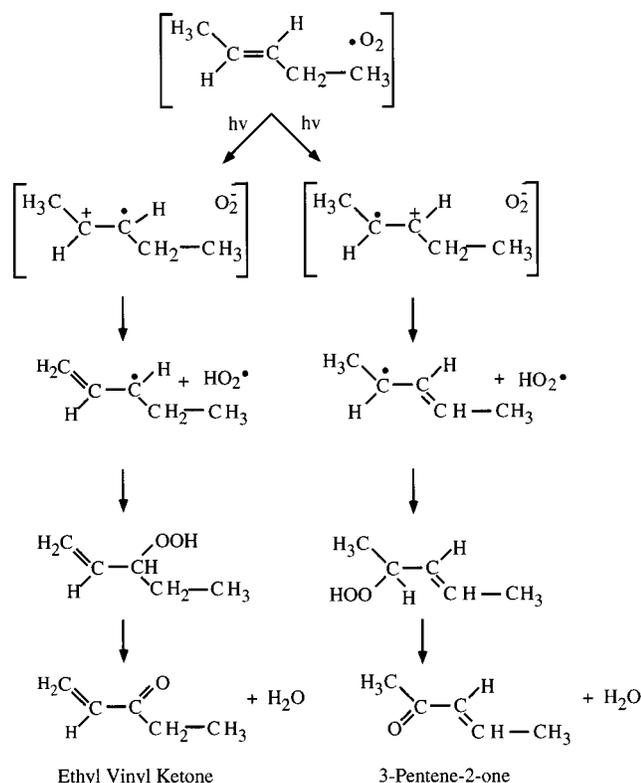
effects which cause spectral broadening. For 1-butene photo-oxidation, evidence of the alcohol and the epoxide products has been observed in the ex situ NMR experiments. For 1-pentene, the alcohol product is observed in the NMR spectrum; however, the epoxide is not. Instead a substantial amount of saturated aldehydes are detected. As discussed here, epoxides can react on BaY to form saturated aldehydes and ketones. Propylene oxide and epoxybutane both react on BaY to form the saturated aldehydes, propionaldehyde, and butyraldehyde and the saturated ketones, acetone and 2-butanone, respectively. This suggests that the presence of saturated aldehydes and ketones after photooxidation of 1-alkenes with visible light at room temperature is due in part to epoxide ring-opening reactions. The rearrangement of aliphatic epoxides in zeolites has been observed previously.[20]

Effect of Wavelength and Temperature on Product Selectivity. The wavelength dependence of the photooxidation of propylene in BaY was examined. It was found that the rate of photoproduct formation increased as the wavelength of light decreased. In addition, the results suggested that the formation of nonselective, short-chain saturated aldehyde and ketone products (acetaldehyde, formaldehyde, and propionaldehyde) increased when short wavelength light ($\lambda > 285$ nm) was used for photolysis of propylene and oxygen in BaY. The wavelength dependence of the formation of saturated aldehydes is most likely due to the increase in dioxetane chemistry (Scheme 2) when the shorter wavelengths of light were used for photolysis. Similar effects were observed in corresponding experiments of 1-butene and 1-pentene photooxidation in BaY. Frei and co-workers previously observed that when 2,3-dimethyl-2-butene (DMB) and oxygen were photooxidized in BaY at 223 K, hydroperoxide formation increased and the formation of acetone (by dioxetane chemistry) increased as the wavelength of photolysis decreased from 633 to 458 nm.[5] By using the longest possible wavelength of light that will form the hydrocarbon—

oxygen charge-transfer complex, the selectivity to the unsaturated aldehyde or ketone is maximized, but the rate of product formation is substantially decreased.

In addition, as the temperature is increased at a given wavelength (Figure 3a and b), the amount of unsaturated aldehyde and ketone being formed increased. In fact, all of the observed chemistry once the initial hydroperoxide is formed is thermal chemistry including the rearrangement of the hydroperoxide to the corresponding unsaturated ketone and aldehyde and epoxide formation from the reaction of the hydroperoxide and an unreacted parent molecule. Thermal chemistry also contributes to the formation of nonselective, short-chain saturated aldehydes and ketones when the photooxidation experiments are conducted at room temperature. As shown here, a thermal reaction involving ring opening of the epoxide yields both saturated aldehydes and saturated ketones on BaY. In addition, a thermal reaction involving double-bond migration followed by photooxidation of the 2-alkene gives rise to other unsaturated carbonyls (e.g., 3-pentene-2-one) and saturated carbonyls (e.g., acetaldehyde). However, it is important to point out that although there are other products in the reaction, there is a rather high selectivity for the formation of unsaturated carbonyl compounds. It is seen for all of these compounds that greater than 60% of the reacted parent alkene goes on to form an unsaturated carbonyl compound and that the selectivity increases as the carbon chain length decreases.

The Effect of Prereaction in Zeolites ZSM-5 and Beta on the Photooxidation Product. Our efforts to exploit the shape-selective properties of zeolites for the photooxidation of hydrocarbons in zeolites have been complicated by prereaction of alkenes to form polymers. The polymerization of alkenes has been extensively studied on the acid form of zeolites, such as HZSM-5.[21,22,25,26] Prereaction in ZSM-5 and Beta involves polymerization of the parent alkene which most likely occurs on acid sites.

The source of Brønsted acid sites in BaZSM-5 is due to the following reaction that occurs during pretreatment or activation of a divalent cation-exchanged zeolite at elevated temperature:

$$M^{2+} + H_2O + Si-O-Al \rightarrow M(OH)^+ + Si-O(H^+)-Al \quad (1)$$

where $Si-O-Al$ represents a part of the zeolite framework.[27] It has been shown that Brønsted acid sites can be present in low concentrations in alkali—metal zeolites. For example, Jayathurthe et al. have established the presence of low levels of Brønsted acidity in NaY and NaX zeolites using the color change of a base indicator.[18] The cationic forms of retinyl acetate, retinol, and retinyl Schiff bases are colored and easily identified by both visual inspection and spectrophotometrically. Using these bases they were able to determine whether Brønsted acids were present in low concentrations and the relative differences in acid strength for the Brønsted acid sites in the different zeolites. Importantly, these studies showed that the presence of small quantities of acid sites can alter the reactivity of various alkenic substrates. In another study using solid-state NMR spectroscopy, the presence of Brønsted acid sites, as well as other types of sites, were identified in the alkaline earth zeolite CaY.[27] The presence and concentration of sites was found to depend on whether the zeolite was activated in air or under

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vacuum. These studies indicate that the reactivity and properties of cation-exchanged zeolites can change from source to source and from different pretreatment conditions. The zeolite samples used in this study contained various quantities of Brønsted acid sites. Using the colorimetric method with retinol as a probe molecule, the activated forms BaZSM-5 and BaBeta were both found to contain Brønsted acid sites. BaY contained much fewer Brønsted acid sites than BaZSM-5 and BaBeta, and no Brønsted acid sites were detected colorimetrically in BaX. These results are qualitatively consistent with the observed oligomerization of propylene which occurs on BaZSM-5 and BaBeta, but not on BaY or BaX.

Photooxidation of the propylene oligomers and unreacted propylene in BaZSM-5 and BaBeta results in broad, unresolved FT-IR spectra, particularly in the $1550-1700$ cm^{-1} range. The observed broadening in the FT-IR spectra suggests a mixture of oxygenated products. Loss of propylene was also observed as indicated by the peaks with asterisks.

Hydrocarbon Photooxidation Reactions in Cation-Exchanged Zeolites: A Comparison to Other Studies. Recent studies using zeolites as hosts for photooxidation reactions of hydrocarbons show that selectivity is significantly enhanced, compared to solution studies. Ramamurthy and co-workers have shown remarkable selectivity in the formation of hydroperoxides from alkenic systems through a singlet oxygen mechanism using dye-exchanged zeolites in hexane solution.[28,29] However, in terms of the challenges for industrial oxidation processes outlined in the Introduction, the use of hexane solvent is nonideal for environmentally benign synthesis. The approach developed by Frei and co-workers using gas-phase reactants and a host zeolite is very promising in terms of minimal environmental impact. However, most of the reactions have been done at low temperatures near -100 °C, not very practical from an industrial standpoint. As shown here, when reactions are run near -20 °C, they remain fairly selective; however, thermal reactions near ambient temperatures can lead to loss of selectivity.[30]

Conclusions

The photooxidation of a homologous series of 1-alkenes in zeolites was investigated by using in situ FT-IR spectroscopy and ex situ NMR spectroscopy. Propylene, 1-butene, and 1-pentene were photooxidized in BaY with excess oxygen. One important factor in the photooxidation of hydrocarbons in zeolites is the wavelength dependence. Higher energy UV photons open up reaction pathways, e.g., dioxetane chemistry, that do not occur with lower energy visible photons. However, as shown here, selectivity can also be lost when visible photons are used. Although these reactions are initiated with light, thermal reactions at ambient temperatures can result in a loss of product selectivity. At room temperature, mixtures of aldehydes, ketones, epoxides, and alcohols were observed by FT-IR and NMR spectroscopy after visible excitation of hydrocarbon·O$_2$ complexes with visible light. Studies of the photooxidation of propylene in other zeolites, BaX, BaZSM-5, and BaBeta, were also investigated to determine if the methodology was of general use and if shape selectivity through the use of zeolites ZSM-5 and Beta on the reactant and product molecules could be imposed. Prereaction on residual acid sites in the zeolite leads to polymerization of the alkene. These results illustrate that the selectivity of the overall oxidation process is controlled by a number of factors including thermal chemistry at ambient temperatures. Several room temperature reactions of reactants and products in Ba-exchanged Y, X, ZSM-5, and Beta give rise to the loss of selectivity. These include: (i) epoxide ring opening, (ii) alkene double bond migration, and (iii) alkene polymerization. Therefore, if 100% selectivity for the formation of a single oxygenated hydrocarbon product is to be realized through the photooxidation reaction of a parent hydrocarbon molecule in cation-exchanged zeolites, a careful choice of chemical systems, such as those that are nonalkenic, is necessary. In addition, the choice of zeolite host may also be important in these systems. Further studies are currently underway in developing and extending this methodology in environmentally benign synthesis of partial oxidation products.[31]

Supporting Information Available: ^{1}H NMR spectra showing the photoproducts extracted in CDCl$_3$ after the photooxidation of 1-butene and 1-pentene in BaY (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA984477A

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(30) Blatter et al. have also observed a loss of selectivity at room temperature during photooxidation of propylene in BaY at room temperature (Figure 2 of ref 7). They observed an FT-IR band at ∼1700 cm^{-1} that they attributed to formaldehyde and acetaldehyde. In addition, in ref 5 during the photooxidation of 2-butene, Blatter and Frei mention the appearance of a band at 1720 cm^{-1}. The band is attributed to acetaldehyde, and the growth of the band was not reproducible.

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