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Cyclohexanone from Cyclohexane and O_2 in a Zeolite under Visible Light with Complete Selectivity

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Abstract: Irradiation of a cyclohexane and O_2-loaded zeolite NaY with green or blue light resulted in oxidation of the alkane to cyclohexyl hydroperoxide and cyclohexanone (plus water) as the sole products. The hydroperoxide was found to rearrange thermally to cyclohexanone without side reaction. Complete selectivity in terms of the final oxidation product cyclohexanone persists even at high (>40%) conversion of cyclohexane. The chemistry was monitored by in-situ FT-infrared spectroscopy and the visible reactant absorption by diffuse reflectance spectroscopy. The absorption is attributed to the cyclohexane·O_2 charge-transfer transition, which is shifted from the UV into the visible by the very high electrostatic field of the zeolite matrix cage. At elevated temperature, cyclohexane is thermally oxidized by O_2 to the same products.

I. Introduction

Selective partial oxidation of alkanes by O_2 is a key challenge in the manufacture of organic building blocks and industrial intermediates.[1] The reason is that for such large-volume chemicals, the choice of the oxidant is limited to molecular oxygen, mainly because of economics. Yet, as radical chain processes, autoxidations are inherently unselective. The oxidation of cyclohexane by O_2 plays a central role in the production of nylons.[1c] Moreover, cyclohexanone, one of the two main products of partial cyclohexane autoxidation (the other is cyclohexanol), is an intermediate in the synthesis of a variety of fine chemicals.[2] Despite extensive research and development in cyclohexane autoxidation, the selectivity of current liquid phase reactions under practical conditions is limited to 70% (combined cyclohexanone plus cyclohexanol yield) at low conversion (9%).[1a,c] The main problem that prevents selective synthesis at higher cyclohexane conversion is the overoxidation of the alcohol and carbonyl products.[3]

Various new catalytic routes have been explored for cyclohexane-to-cyclohexanol and cyclohexanone oxidation by O_2, and remarkable selectivities in terms of the combined products have been reported.[1b,e] However, most of these methods either require stoichiometric coreactants (most often a reducing agent) or photosensitization with a UV source,[4−6] which may constitute serious economical impediments for large-scale applications. Only very few attempts have been made thus far to overcome these obstacles. Sheldon has achieved autoxidation of liquid cyclohexane to cyclohexanone, cyclohexyl hydroperoxide, and cyclohexanol at high (>90%) selectivity for the combined products at low (3.4%) conversion.[7] The catalyst used was chromium-substituted aluminophosphate-5. Jacobs found that the cobalt-substituted version of this molecular sieve catalyst gives high yields of the same products at 4% conversion of the cyclohexane.[8] Ellis and Lyons have reported a general method for alkane oxidation by O_2 that uses a transition metal complex of perfluorotetraphenylporphyrin as catalyst.[9] For isobutane-to-*tert*-butyl alcohol autoxidation in benzene solution, for example, selectivities as high as 95% were achieved.

In this paper we report, for the first time, oxidation of cyclohexane by O_2 to cyclohexanone and its precursor, cyclohexyl hydroperoxide, without side reaction at high conversion of the alkane. The approach is based on a very large red shift of the cyclohexane·O_2 charge-transfer absorption in zeolite NaY which moves the absorption tail from the UV into the visible region. Access to this low-energy reactant state with visible photons, coupled with the inhibition of indiscriminate reactions of primary transients by the constraints of the zeolite nanocage[10] opens up a highly selective oxidation path. The large red shift of the cyclohexane·O_2 contact complex is attributed to a 2-eV stabilization of the excited charge-transfer state by the very high electrostatic field inside the zeolite cage. We have discovered this effect recently with toluene·O_2 and olefin·O_2 complexes in alkali and alkaline-earth exchanged zeolite Y[11a−e] and applied it to the selective oxidation of a tertiary alkane C−H group.[11f]

II. Experimental Section

Spectroscopic instrumentation, vacuum equipment, and experimental procedures were the same as previously described.[11b,d] Briefly, UV−vis spectra were obtained by diffuse reflectance measurements using a

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Shimadzu Model 2100 instrument with an integrating sphere set-up Model ISR-260. Zeolite NaY (LZ-Y52, Aldrich Chemical Co. Lot No. 03319TX) was pressed into self-supporting wafers of 12-mm diameter and a typical weight of 8 mg. The zeolite pellets were mounted inside a home-built miniature stainless steel cell described previously.[11b,d] Prior to loading of cyclohexane and O_2 from the gas phase, the zeolite pellet was dehydrated at 200 °C in the high-vacuum cell for 10−12 h. A turbomolecular pump Model Varian V-60 was used for evacuation during heating. All UV−vis measurements were conducted at ambient temperature (21 °C).

In one series of experiments the zeolite pellet was pretreated with a small amount of HCl. The gas was prepared on a vacuum line by the reaction of concentrated H_2SO_4 with dry NaCl powder. The dehydrated zeolite was heated to 200 °C and exposed to 0.6 Torr of the distilled HCl for 10 min. Thereafter, the pellet was evacuated at that temperature for 6 h.

For monitoring of photochemical reactions, cyclohexane and O_2 gas were loaded into a dehydrated zeolite pellet inside a miniature vacuum cell equipped with KBr windows. The chemistry was followed in situ by FT-infrared spectroscopy using a Bruker Model IFS 113 or an IBM-Bruker Model IR 44 spectrometer. Zeolite NaY is transparent in the infrared except for the region between 1200 and 920 cm^{-1}, and below 800 cm^{-1}. Photolysis was conducted with the emission of a prism-tuned continuous-wave Ar-ion laser (Coherent Model Innova 90-5 or 90-6). The laser beam was expanded to the full size of the pellet. For experiments above or below room temperature, the infrared cell was mounted inside a variable-temperature Oxford cryostat Model DN1714 (77K to 200 °C).[11b]

For determination of the product ratio of cyclohexanone to cyclohexyl hydroperoxide, the extinction coefficient ratio of the two molecules was estimated by recording infrared spectra upon thermal conversion of the hydroperoxide to the ketone. Following photoaccumulation of cyclohexyl hydroperoxide, the excess cyclohexane and O_2 were pumped off and the zeolite temperature was raised to 100 °C for several hours. The difference spectrum of the conversion, accelerated by the high temperature, allowed us to determine the relative integrated intensities of the 1367-cm^{-1} cyclohexyl hydroperoxide band and the 1705/1674-cm^{-1} doublet of cyclohexanone with an accuracy of 10%. Infrared spectra were calibrated for cyclohexanone yields by manometric measurement of the uptake of the molecule from the gas phase.

Cyclohexane (99%), cyclohexanone (99%), and cyclohexanol (99%, all from Aldrich) were distilled in vacuum before use. O_2 (99.99%) and N_2 gas (99.997%) were obtained from Air Products and used as received. Cyclohexyl hydroperoxide was synthesized from cyclohexyl chloride using a literature method.[12]

III. Results

1. Electronic Absorption. Zeolite NaY has no visible absorption (the material is completely colorless).[13] Figure 1 shows the optical absorption of zeolite NaY loaded with cyclohexane and oxygen as measured by diffuse reflectance spectroscopy. It was obtained by first loading the zeolite pellet at room temperature with the alkane by exposing it to 5 Torr of the gas. According to the room temperature adsorption isotherm of cyclohexane in Na^+ exchanged faujasite, this corresponds to 3−4 C_6H_{12} molecules per supercage on average.[14] No optical absorption (λ > 250 nm) resulted from the alkane loading. As in the case of olefins and toluene,[11] the only effect was an increase of the reflectance across the entire visible range due to the accompanying change in the refractive index of the pellet. In a second step, 500 Torr of O_2 gas was admitted to the UV−vis cell, corresponding to one O_2 molecule per five supercages.[10] It is this difference of the spectra taken after and before adding O_2 to the NaY pellet that is shown in Figure 1. Three consecutive spectra showed no change of the signal. This indicates that possible photochemical reaction induced upon recording by the spectrometer light source has no effect on the absorption profile. The intensity of the absorption was found to be linear in the partial pressure of O_2. From these observations we conclude that the small but significant absorption band of Figure 1 originates from a cyclohexane•O_2 complex in the zeolite.

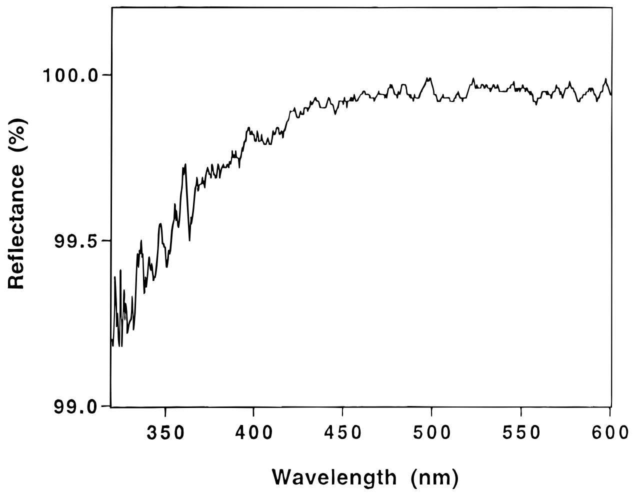

Figure 1. Diffuse reflectance spectrum of cyclohexane and O_2-loaded zeolite NaY at room temperature. The curve shows the ratio of the reflectance of cyclohexane-loaded zeolite after and before exposure to 500 Torr of O_2 gas.

2. Photooxidation with Visible Light. Upon loading of cyclohexane into NaY, infrared bands were observed at 2932, 2851, 1452, 905, and 861 cm^{-1}. Subsequent addition of 500 Torr of O_2 did not result in any notable spectral changes. Chemical reaction was observed when irradiating the room temperature zeolite matrix with green or blue light (514, 488, or 458 nm emission of an Ar ion laser), but no spectral changes were noticed when shining light on a zeolite pellet that contained either only cyclohexane or oxygen. An infrared difference spectrum following 120 min of photolysis at 458 nm (200 mW cm^{-2}) is displayed in Figure 2a. The negative features show the consumption of cyclohexane, while the positive bands originate from photoproducts. Recording of infrared spectra of authentic samples of cyclohexyl hydroperoxide, cyclohexanone, and H_2O in zeolite NaY confirmed that photolysis product absorptions originate from these three species. No unassigned product band remained. Specifically, no infrared band of cyclohexanol was observed. Considering the extinction coefficient of the alcohol absorptions in NaY in regions free of cyclohexyl hydroperoxide and cyclohexanone and taking into account the noise level in those regions, we calculate a lower limit of 50 for the cyclohexanone to cyclohexanol branching ratio. Infrared frequencies of photoproducts and of authentic samples are presented in Table 1. Since authentic spectra of cyclohexyl hydroperoxide loaded into NaY showed traces of cyclohexanone, the hydroperoxide spectrum was also recorded in CD_3CN solution. There was excellent agreement between the spectra in the two media. An exception is the ν(OH) mode which is red shifted in the zeolite by 200 cm^{-1} due to strong H bonding. We conclude that cyclohexyl hydroperoxide, cyclo-

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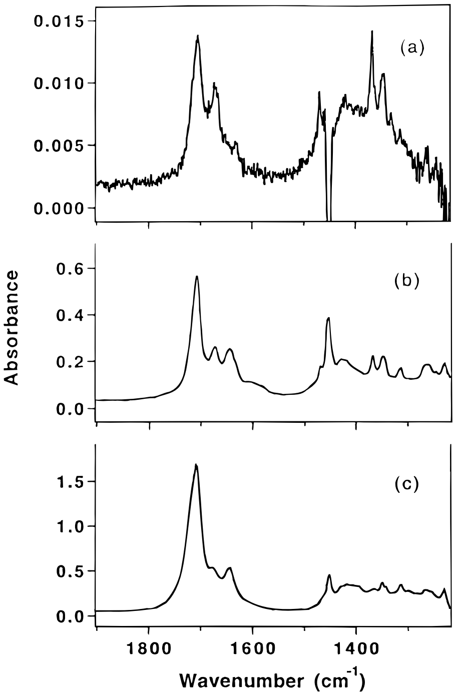

Figure 2. (a) Infrared difference spectrum of the NaY pellet loaded with cyclohexane and O_2 before and after Ar-ion laser photolysis at 458 nm (2 h, 200 mW cm^{-2}) at room temperature. (b) Prolonged irradiation of a cyclohexane and O_2 loaded pellet NaY at 488 nm. The product growth corresponds to reaction of 35% of the cyclohexane loaded into the zeolite. The trace shows the reaction products only (difference between spectra before loading of the pellet and after photolysis and pumping off of excess C_6H_{12}). (c) Irradiation of an HCl-pretreated NaY pellet loaded with cyclohexane and O_2 (750 Torr) for 5 h at 488 nm (500 mW cm^{-2}). Seventy-one percent of the cyclohexane has been converted. The trace shows the difference between spectra before loading of the pellet and after irradiation and pumping off of the excess reactants.

hexanone, and H_2O are the exclusive products of visible light-induced oxidation of cyclohexane by O_2 in zeolite NaY. This holds even upon conversion of as much as 35% of the cyclohexane loaded into the zeolite, as shown in Figure 2b.

Cyclohexyl hydroperoxide was found to rearrange thermally to cyclohexanone without side reaction. This process is readily observed by infrared difference spectroscopy when keeping a hydroperoxide-loaded NaY matrix in the dark at room temperature. It is strongly accelerated in acid (HCl) treated NaY. Figure 2c shows the infrared product spectrum upon blue light-induced oxidation of cyclohexane (488 nm, 500 mW cm^{-2}) in an HCl pretreated zeolite for 5 h. Comparison with Figure 2a, where the hydroperoxide to cyclohexanone ratio is about 4:1, shows that even the most intense cyclohexyl hydroperoxide band at 1367 cm^{-1} is barely visible in spectrum 2c. Thermal rearrangement of cyclohexyl hydroperoxide to cyclohexanone and water is an established intramolecular heterolytic reaction in acidic solution.[15]

Infrared spectra like the ones shown in Figure 2 constitute direct proof that the products are generated in the interior of the NaY particles rather than on their outer surface. If one exposes cyclohexanone at a fixed gas pressure to a pellet of zeolite NaY and a pellet of NaA particles, a strong infrared spectrum is observed in NaY while only extremely weak features appear in the case of NaA. Type Y and type A zeolites both have a three-dimensional network of α-cages of similar size, but the window openings of NaA are too small (4 Å) to permit diffusion of cyclohexanone into the zeolite.[10] Therefore, adsorption can occur only at the outer surface. By contrast, the window openings of zeolite Y α-cages have a diameter of 7 Å, hence cyclohexanone can readily diffuse into the zeolite particles.[10] We conclude that the infrared product absorptions shown in our spectra originate exclusively from molecules that reside inside the zeolite crystallites.

Table 1. Absorption Frequencies of $C_6H_{12} + O_2$ Reaction Products and Authentic Samples in NaY (in cm^{-1})

	authentic samples[a]		
reaction product	cyclohexyl hydroperoxide	cyclohexanone	water
3400[b]			3400
3200	3200		
2941	2941	2937	
2861	2859	2863	
1705		1705	
1670		1674	
1644			1643
1468	1469	1464	
1454[c]	1453	1451	
		1426	
		1420	
1413[d]	1411[d]		
1367	1367		
		1350	
1346	1346	1342	
1313		1313	
	1301		
1267		1268	
1259	1259		
1230		1229	
908[c]		907	
900	900		
892	893		
863[c]	865	862	
838	839		

[a] All product absorptions are assigned except for a weak band at 1330 cm^{-1} whose intensity was not reproducible from one experiment to another. [b] Very broad, fwhm ≈ 200 cm^{-1}. [c] Overlapped by decreasing cyclohexane band. [d] Broad.

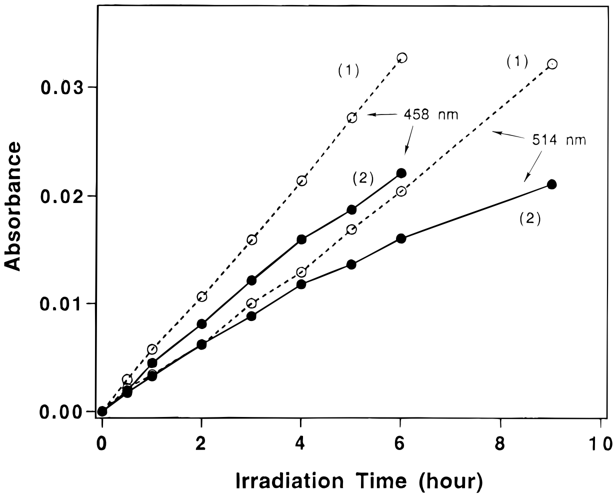

Figure 3. Absorbance growth kinetics of the 1705-cm^{-1} cyclohexanone band (curve 1) and the 1367-cm^{-1} cyclohexyl hydroperoxide absorption (curve 2) upon 458- and 514-nm photolysis at room temperature. The size of the circles indicates the peak-to-peak noise.

The growth kinetics of the products at two photolysis wavelengths, 514 and 458 nm, is displayed in Figure 3. The plot shows the infrared absorbance growth of the ν(C=O) mode of cyclohexanone at 1705 cm^{-1} (curve 1) and of the CH_2 bending mode of cyclohexyl hydroperoxide at 1367 cm^{-1} (curve 2). The extinction coefficient ratio of the cyclohexanone doublet

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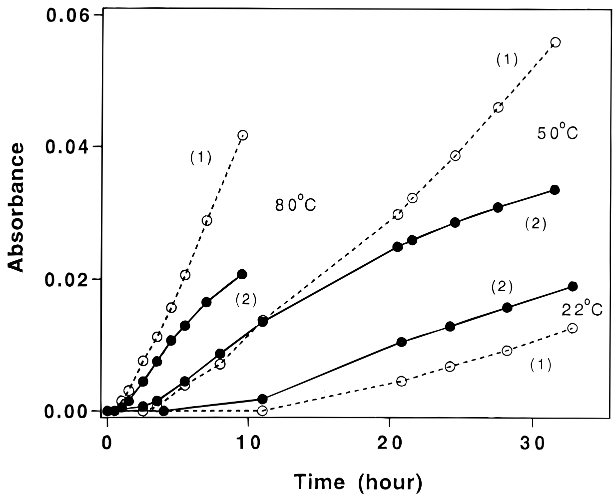

Figure 4. Absorbance growth kinetics of the 1705-cm^{-1} cyclohexanone band (curve 1) and the 1367-cm^{-1} cyclohexyl hydroperoxide absorption (curve 2) upon thermal reaction at 22, 50, and 80 °C. The size of the circles indicates the peak-to-peak noise.

at 1705/1670 cm^{-1} and the hydroperoxide absorption at 1367 cm^{-1} was determined to be 62. Hence, according to the two growth curves, the cyclohexanone to hydroperoxide branching ratio is around 0.1 at the start of photolysis. While the hydroperoxide curve is heading toward an asymptotic limit, the cyclohexanone growth clearly accelerates with increasing photolysis time. This behavior has its origin in the slow thermal rearrangement of cyclohexyl hydroperoxide to cyclohexanone under elimination of water mentioned above. It is important to note, however, that not all cyclohexanone seems to originate from slow thermal rearrangement of $C_6H_{11}OOH$ at room temperature because the cyclohexanone growth does not exhibit an induction period with zero growth at the start of photolysis. Comparison of the 514- and 458-nm photolysis curves shows that the cyclohexanone to cyclohexyl hydroperoxide ratio increases somewhat at higher photon energies.

The quantum yield for reaction was calculated as the product growth per absorbed photon. In one typical photolysis experiment at 458 nm, the absorption of cyclohexane·O_2 at that wavelength was 0.04%. The incident photon flux corresponded to 8.3×10^{-3} mol photons (hence 3.3×10^{-6} mol photons absorbed by the C_6H_{12}·O_2 pairs) over an irradiation period in which the infrared absorbance growth was 0.016 at 1705 cm^{-1} (cyclohexanone) and 0.012 at 1367 cm^{-1} (cyclohexyl hydroperoxide). Taking into account the extinction coefficient of the absorptions, a total product growth of 1.0×10^{-7} mol was calculated for the 3.3×10^{-6} mol of 458-nm photons absorbed. Hence, the quantum yield to reaction is 0.03. This efficiency may be off by as much as a factor of 3 due to the large uncertainty in the absorption at 458 nm as estimated from the diffuse reflectance spectrum.

3. Thermal Oxidation. When keeping a cyclohexane and O_2-loaded NaY matrix in the dark at room temperature for 10 h, a very small growth of cyclohexyl hydroperoxide was noticed. After about 20 h, cyclohexanone growth was observed as well. An experiment with $^{18}O_2$ gave exclusively cyclohexanone-^{18}O, which confirms that no lattice oxygens are involved in the reaction. The kinetics of the reaction at room temperature is shown in Figure 4. While this thermal reaction is barely noticeable at 22 °C, rates increase steadily with temperature. Curves corresponding to thermal reaction at 50 and 80 °C are also displayed in Figure 4. At temperatures up to 80 °C, no products other than cyclohexyl hydroperoxide, cyclohexanone, and water are observed. The slightly increased rates of the ketone growth at long times signal, again, a slow hydroperoxide to cyclohexanone interconversion.

Comparison of the product growth curves upon thermal (Figure 4) and photochemical oxidation of cyclohexane (Figure 3) shows that these two reaction types can easily be distinguished on the basis of the kinetics. At all temperatures the thermal reaction has an induction period with zero slope at the start of reaction while the photochemical curves do not.

It is important to note that the heating effect which accompanies laser irradiation of the zeolite is far too small to account for the observed photochemical rates. We have recently reported several experimental observations which show that heating by the laser amounts to 10 deg at the most for the laser power levels used here (500 mW cm^{-2}). The most accurate estimates for laser heating stem from the desorption effect of small hydrocarbons monitored by FT-IR spectroscopy.[11c,e]

IV. Discussion

1. Electronic Absorption of Cyclohexane·O_2 in NaY. Optical absorption of a cyclohexane·O_2 contact complex can, in principle, originate from an O_2-enhanced triplet absorption of the hydrocarbon or from an alkane·O_2 charge-transfer absorption.[16] The former can readily be ruled out because the lowest triplet state of small alkanes lies at the threshold to the Vacuum UV.[17] Moreover, studies of phosphorescence spectra have shown that the lowest triplet state of organics loaded into zeolites do not exhibit large shifts relative to the solution phase.[18] On the other hand, our previous work on alkene + O_2 and toluene + O_2 systems in zeolite Y has revealed that the corresponding hydrocarbon·O_2 charge-transfer absorptions are shifted to the red relative to the conventional phase by 1.5 to 2.5 eV.[19] The onset of the cyclohexane·O_2 charge-transfer absorption in the O_2-saturated liquid is at 275 nm,[20] while that of the absorption in zeolite NaY is around 500 nm according to Figure 1. Note that no maximum of the absorption band is discernible in Figure 1, very similar to the case of cyclohexane·O_2 and most other hydrocarbon·O_2 charge-transfer absorptions in the gas phase or solution.[19-21] The red shift of 16 000 cm^{-1} (2.0 eV) by the zeolite environment is close to that observed previously in the case of olefin·O_2 and toluene·O_2 complexes. We attribute the shift to the stabilization of the excited state with its large dipole moment ($C_6H_{12}{}^+O_2{}^-$) by the high electrostatic field inside the zeolite cage.

The 13-Å supercage of zeolite Y carries a formal negative charge of seven which resides mainly on the framework oxygen atoms. It is counterbalanced by Na$^+$ ions, three to four of which are located in the supercage.[10] The poor electrical shielding of these cations by the cage oxygens gives rise to high electrostatic fields. Such fields have been predicted by model calcula-

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[19] Any alkane, alkene, or aromatic hydrocarbon has a contact charge-transfer band with oxygen, yet no stable complex is formed. The situation is similar to contact charge-transfer bands of alkanes and molecular iodine. These bands appear most often as structureless tails with no distinct absorption maximum, a direct consequence of the absence of a complex with defined geometry. For a general reference of contact charge-transfer absorptions, see: Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969; Chapters 1 and 14.

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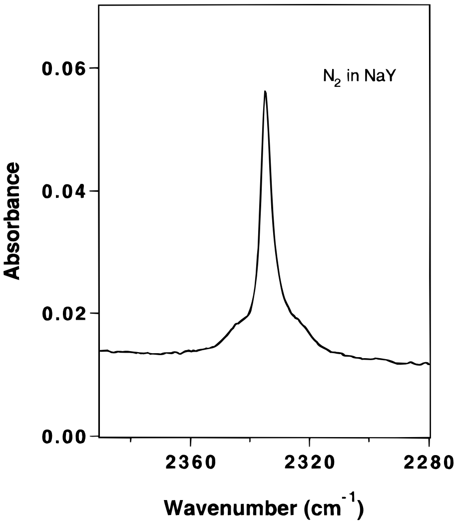
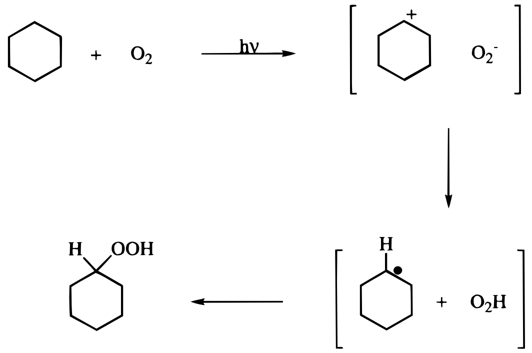


Figure 5. Induced infrared fundamental absorption of N_2 loaded into zeolite NaY at −78 °C. The loading level corresponds to 1.3 molecules per supercage.

tions[22,23] and established experimentally by several different methods. One method consists of the measurement of induced infrared bands of O_2 or N_2 stretch fundamentals. These infrared forbidden modes become active in the presence of the cage electrostatic field when the molecules are loaded into a cation-exchanged zeolite, and magnitudes of the fields can be determined from band intensities. This effect has been used by Cohen de Lara to measure electrostatic field strengths in zeolite A.[24] We have applied the method to cation-exchanged zeolite Y and found that the electrostatic fields experienced by N_2 or O_2 are around 0.4 V $Å^{-1}$. The induced absorption of N_2 loaded into a NaY matrix at −80 °C is shown in Figure 5. The band exhibits only a very small shift of 4 cm^{-1} relative to the gas-phase frequency. This shows that there is no chemical interaction between the molecule and the zeolite, which makes N_2 an ideal probe for the cage electrostatic fields. A full report on electrostatic field measurements in alkali and alkaline-earth zeolite Y will be presented in a forthcoming paper.[25] Another method is measurement of hyperfine coupling constants of guest radicals by ESR spectroscopy.[26] Electrostatic fields in the range 0.2−1.0 V $Å^{-1}$ were found in alkali-exchanged zeolite Y by this method. Fields of one to several volts per angstrom have been confirmed in NaA by analysis of electron densities from X-ray data,[27] in alkali and alkaline-earth zeolite X and Y by heats of adsorption of rare gases,[28] and by the measurement of frequency shifts of the infrared fundamental of CO.[29] The interaction of the very high electrostatic field inside a NaY cage with the large dipole generated upon excitation of the cyclohexane·O_2 pair to the charge-transfer state results in a strong stabilization of the excited state. Assuming a separation of 4 Å of the cycloalkane$^+$ and O_2^- charge centers (dipole moment $\mu = 14$ D), we calculate for a field of 0.4 V $Å^{-1}$ a dipole stabilization ($-\mu \cdot E$) of 1.6 eV if the dipole is oriented parallel to the field.

Scheme 1



It is important to keep in mind that cyclohexane·O_2 contact complexes, while existing at high steady-state concentrations in zeolites, are very short lived. The residence time of an O_2 molecule in a faujasite supercage at room temperature is estimated to be less than a nanosecond, that of cyclohexane tens of nanoseconds. These estimates are based on self-diffusion coefficients of O_2 and cyclohexane for the neat compounds reported in the literature.[30] In our experiments, there is at least one cyclohexane molecule per supercage and, hence, an O_2 hopping from one cage to the next will inevitably collide again with a hydrocarbon molecule. Therefore, the concentration of reactant collisional pairs is very high in this nanopore matrix. Some fraction of the collisional pairs will be oriented in such a way that the large dipole of the excited charge-transfer state is parallel to the cage electrostatic field; these are the states that will be stabilized and absorb in the visible. Other cyclohexane·O_2 contact pairs will be oriented close to perpendicular or antiparallel to the field. The excited states of these pairs will be unaffected by the field or even destabilized. Therefore, only a fraction of the hydrocarbon·O_2 collisional pairs (those parallel to the cage field) will contribute to the visible absorption tail. This is presumably the main reason why the absorption tail is weak (Figure 1).

2. Reaction Mechanism. The proposed mechanism for the photochemical $C_6H_{12}+O_2$ reaction is shown in Scheme 1. The initial step following excitation of the charge-transfer state is very likely proton transfer from the cyclohexane radical cation to O_2^-. Cyclohexane radical cation is a spectroscopically established transient[31] with a lifetime of just 300 ps with respect to deprotonation in the neat liquid at room temperature.[32] It is expected that the proton transfer is even faster in the presence of a base like O_2^-. Hydrocarbon radical cations are known to be highly acidic in general.[33] We consider efficient proton transfer quenching of the charge-transfer pair as the main reason for the rather high quantum yield to reaction. Cyclohexyl and hydroperoxy radicals so produced are expected to undergo cage recombination to yield the observed cyclohexyl hydroperoxide.

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While our observations clearly show that cyclohexyl hydroperoxide rearranges to cyclohexanone in a slow thermal process, the non-zero slope of the cyclohexanone growth curve indicates that some of the ketone emerges concurrently with cyclohexyl hydroperoxide as well (Figure 3). We attribute it to instantaneous elimination of H_2O from the photochemically produced $C_6H_{11}OOH$ before the excess energy is drained off by the cage environment.

A mechanism analogous to the one shown in Scheme 1 has previously been proposed for the initial events of the UV light-induced oxidation (λ < 260 nm) of cyclohexane by O_2 in the neat liquid.[34] However, secondary photolysis of the cyclohexyl hydroperoxide and random radical coupling reactions were found to destroy the selectivity already at very low conversion.

The observation of a slow thermal reaction of cyclohexane with O_2 in NaY is surprising in view of the fact that hydrocarbons with weaker C−H bonds and with lower ionization potentials than cyclohexane lack such a dark reaction. For example, the bond energy of the benzylic CH group of toluene is 85 kcal mol^{-1} versus 94 kcal mol^{-1} for cyclohexane.[35] The ionization potential of toluene is a mere 8.8 eV compared to 9.8 eV in the case of C_6H_{12}.[36] Yet, toluene does not even react thermally with O_2 in zeolite NaY and BaY at a temperature as high as 80 °C.[11c] Similarly, propylene and *cis*- or *trans*-2-butenes are not oxidized thermally by O_2 in NaY or BaY despite the fact that the energy of the allylic C−H bond is 7 kcal lower than that of cyclohexane[35] and the ionization potentials are smaller as well (9.7 (C_3H_6) and 9.13 eV (C_4H_8)).[36] This suggests to us that the thermal reaction of cyclohexane with O_2 occurs at sites, or for orientations, that are not accessible to the olefins or toluene.

We can only speculate on the nature of these sites and as to why they do not promote thermal reaction of unsaturated hydrocarbons. Sensitive tests[37] for Brönsted or Lewis acid sites such as the formation of NH_4^+ or pyridinium ions upon adsorption of ammonia or pyridine into our NaY pellets were negative.[11] A very specific test for acid sites, namely oligomerization of propylene and other small olefins,[38] also gave a negative result.[11] Moreover, Trifunac has demonstrated that NaY is an inert zeolite that can stabilize species as reactive as hydrocarbon radical cations.[39] While acid sites can be ruled out, a small concentration of radical defects such as unterminated Si or Al bonds might be present in these pellets, and efficient turnover at such sites could explain the slow thermal reaction of cyclohexane. The radical sites may abstract a H from cyclohexane, which would be followed by addition of O_2 to the cyclohexyl radical to form a cyclohexyl peroxy radical. The latter is expected, in turn, to abstract H from cyclohexane to yield the observed cyclohexyl hydroperoxide and another cyclohexyl radical. This is the familiar chain propagation of cyclohexane autoxidation in the liquid phase with an activation energy of 18 kcal mol^{-1}.[3,40] A plausible explanation for the lack of a similar thermal olefin or toluene oxidation in NaY would be the fact that these hydrocarbons reside preferentially at cation sites in the zeolite cage. This is well established by infrared and NMR spectroscopic studies of hydrocarbons in faujasites.[18,41] Restriction to hopping among cations may prevent occupation and turnover of unsaturated hydrocarbons at radical defect sites, in contrast to alkanes which show no preference for trajectories along cation sites.[42]

Since we lack any independent evidence for radical defect sites, we consider explanation in terms of supercage sites with exceptionally high electrostatic fields more likely. Fields calculated on the basis of point charge models were found to be extremely high in the vicinity of Na^+ ions located at site III inside the supercage.[10] For example, the field is estimated at 3 V $Å^{-1}$ at a distance of 1 Å from the Na^+ ion surface.[22,23] Cages with naked Na^+(III) sites are probably quite rare because any remaining water molecules will be attracted to these highest field cations and shield their charge. Cyclohexane·O_2 pairs exposed to the field at a Na^+(III) site (and oriented parallel to the field) may spontaneously convert to alkane radical cation and O_2^- because a 3 V $Å^{-1}$ field will cause the charge-transfer state to fall energetically below the ground state of the neutral contact pair. Cyclohexyl hydroperoxide and cyclohexanone would be formed according to a path similar to Scheme 1. This dark reaction may be blocked for unsaturated hydrocarbons such as olefins and aromatics because molecules with π systems are known to be strongly attracted to the Na^+ ions with very high fields. The result is an antiparallel orientation of the hydrocarbon·O_2 collision contact complex with respect to the electrostatic field, preventing stabilization of the charge-transfer state.

V. Conclusions

This is, to our knowledge, the first observation of completely selective oxidation of cyclohexane by O_2 to cyclohexanone and cyclohexyl hydroperoxide, its precursor. Several factors contribute to the tight control of the reaction. One is the very strong stabilization of the excited alkane·O_2 charge-transfer state by the electrostatic field of the zeolite cage. This allows the use of low-energy visible instead of UV photons to access the excited state which, in turn, results in minimal excess energy in the primary products (cyclohexyl, HOO radicals). It may prevent diffusion out of the cage and subsequent random coupling reactions, or homolytic fragmentation of the cyclohexyl hydroperoxide intermediate. Moreover, visible photons cannot induce secondary photolysis of the hydroperoxide. None of the liquid phase byproducts, like cyclohexanol, are observed. Loss of product selectivity in liquid cyclohexane autoxidation stems from coupling of two cyclohexyl peroxy radicals and from homolysis or secondary bimolecular chemistry of cyclohexyl hydroperoxide.[1a,c,3] These processes are suppressed by the positional constraints imposed by the zeolite matrix. The importance of the positional constraints in terms of product control is highlighted by the selectivity of the thermal cyclohexane oxidation as well. This very mild method of cyclohexane photooxidation by O_2 opens up selective activation of secondary C−H bonds of light alkanes.

Successful upscaling of our experiments with micromolar quantities reported here requires (i) a reduction of the scattering of photolysis light and (ii) operating conditions that allow continuous desorption of the products from the zeolite host. The preferred solution for the light-scattering problem would be

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translucent zeolite membranes. Such membranes have been reported very recently for pentasil-type zeolites (ZSM-5).[43] Although release of small oxygenated hydrocarbons from zeolite Y by polar organic solvents is routine,[44] a solvent-free method would be preferable. Use of a carrier gas and modestly elevated temperatures may be sufficient to effect desorption of the polar products at acceptable rates. A more detailed discussion of challenges for scale up is presented elsewhere.[45]

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