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Very Strong Stabilization of Alkene·O_2 Charge-Transfer State in Zeolite NaY: Red-Light-Induced Photooxidation of 2,3-Dimethyl-2-butene

Fritz Blatter and Heinz Frei*

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

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It is well-established that organic molecule·O_2 pairs give rise to contact charge-transfer absorptions and photochemistry. Such spectroscopic and chemical observations have been made in oxygen-saturated organic solution,[1] high-pressure O_2 gas,[2] and solid O_2.[3,4] Red shifts of hydrocarbon·O_2 charge-transfer (CT) absorptions from gas phase to solution are small (at most a few nanometers)[5] and are attributed principally to compression of the complex in the condensed phase.[6] Similarly, changing from a nonpolar to a polar organic solvent has little effect on the hydrocarbon·O_2 CT absorption.[1,7] Transition from O_2 saturated solution to a solid O_2 matrix involves typically red shifts on the order of 10 nm.[3,4] We wish to communicate an unprecedented stabilization of the excited charge-transfer state of 2,3-dimethyl-2-butene·O_2 complexes by more than 10 000 cm^{-1} (300 nm) upon enclosure of the reactants in the cages of an inert polar matrix, namely zeolite NaY.[8-11] In addition, chemistry that ensues from irradiation of the long wavelength absorption band is reported.

Upon loading of 2,3-dimethyl-2-butene (DMB) and O_2 into a dehydrated NaY matrix at -50 °C, alkene bands are observed at 1385, 1400, 1464, 2740, 2860, and 2920 cm^{-1}. The self-supporting zeolite wafer of 10 mg cm^{-2} was held inside a miniature infrared vacuum cell.[12] The latter was mounted in an infrared/optical cryostat that allowed us to vary the zeolite matrix temperature from 77 K to 200 °C. Reactants were loaded from the gas phase. The alkene concentration was approximately 0.2 molecule per supercage, and the loading level of O_2 was adjusted by the O_2 gas pressure inside the IR cell (typically 500 Torr). Photochemistry was explored by irradiating the matrix with visible CW dye laser light. Figure 1 shows the infrared difference spectrum before and after photolysis at 633 nm (300 mW cm^{-2}) for 2 h. Absorbance growth was detected at 3200, 3080, 2990, 2960, 2850, 1708, 1641, 1628 (shoulder), 1460, 1440 (both overlapped by decreasing DMB absorption), 1407, 1384 (overlapped by decreasing DMB), 1365, 1302, 920, 905, 875, and 830 cm^{-1}. Concurrently, all DMB bands decreased. No spectral changes were noticed during dark periods of similar duration.

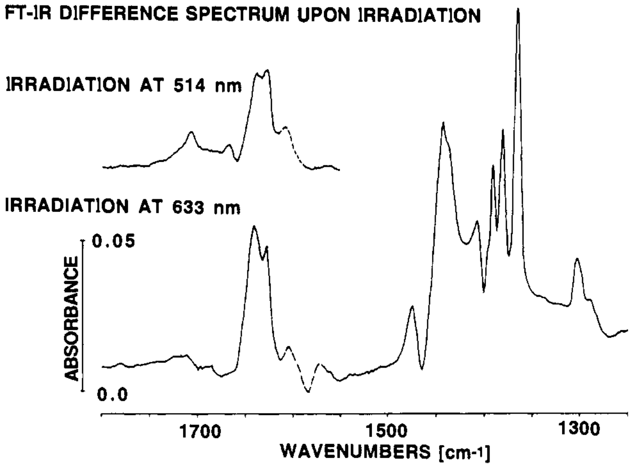

Figure 1. Infrared difference spectrum before and after CW dye laser photolysis at 633 nm (2 h, 300 mW cm^{-2}). Insert depicts product growth in the 1500-1800-cm^{-1} region upon irradiation at 514 nm (30 min, 400 mW cm^{-2}). The dashed lines indicate absorptions that were not reproducible and may originate from impurities (1610 and 1580 cm^{-1}).

We have identified the photoproducts by recording infrared spectra of candidate molecules loaded into NaY and by ^{18}O labeling experiments.[14] All bands except the 1708 cm^{-1} feature can be attributed to 2,3-dimethyl-3-hydroperoxo-1-butene according to an authentic IR spectrum of the hydroperoxide in NaY.[13] The 1708-cm^{-1} product absorption is attributed to ν(C=O) of acetone. The assignment is based on an authentic spectrum of CH_3COCH_3 in NaY and an ^{18}O isotope shift of 25 cm^{-1} when using $^{18}O_2$ as reactant. As can be seen from the insert of Figure 1, the acetone growth was more pronounced at higher photolysis photon energies (514 nm). Neither the absorbance of the hydroperoxide nor of acetone exhibited an induction period at any wavelength (700 nm > λ > 458 nm), consistent with our initial conclusion that both products emerge from single photon DMB + O_2 photochemistry.

We have recorded the infrared product growth upon laser irradiation of DMB and O_2-loaded zeolite at a number of wavelengths between 700 and 500 nm. The resulting laser reaction excitation spectrum is shown in Figure 2. Each point of the curve represents the growth of the hydroperoxide product band at 1365 cm^{-1} (peak absorbance) upon irradiation with 3.5×10^{21} photons. Visible absorption spectra of zeolite pellets showed that the scattering of the matrix increased by less than 10% between 700 and 500 nm. Hence, the laser reaction excitation profile constitutes a fairly undistorted representation of the red absorption profile of the DMB·O_2 system in zeolite NaY (more accurately, it represents the product of the absorption cross section and the reaction quantum efficiency). We attribute the observed structureless band to excitation of a DMB·O_2 charge-transfer state.[15-18]

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(1) (a) Evans, D. F. *J. Chem. Soc.* **1953**, 345-347. (b) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966-5974. (c) Onodera, K.; Furusawa, G.; Kojima, M.; Tsuchiya, M.; Aihara, S.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron* **1985**, *41*, 2215-2220. (d) Coomber, J. W.; Hebert, D. M.; Kummer, W. A.; Marsh, D. G.; Pitts, J. N. Jr., *Environ. Sci. Technol.* **1970**, *4*, 1141-1145.

(2) Itoh, M.; Mulliken, R. S. *J. Phys. Chem.* **1969**, *73*, 4332-4334.

(3) Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 265-273.

(4) (a) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 529-532. (b) *J. Phys. Chem.* **1987**, *91*, 1347-1354. (c) *J. Phys. Chem.* **1989**, *93*, 571-577.

(5) (a) Lim, E. C.; Kowalski, V. L. *J. Chem. Phys.* **1962**, *36*, 1729-1732. (b) Birks, J. B.; Pantos, E.; Hamilton, T. D. S. *Chem. Phys. Lett.* **1973**, *20*, 544-546.

(6) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969; p 66.

(7) Reference 6, p 64.

(8) "Inert" is meant to indicate that the zeolite matrix is free of Bronsted and Lewis acid sites.[9,10] The Lewis acid sites are electron acceptor sites that may give rise to guest molecule-zeolite framework charge-transfer complexes.[11]

(9) (a) Shih, S. *J. Catal.* **1983**, *79*, 390-395. (b) Rabo, J. A.; Poutsma, M. L. *Adv. Chem.* **1971**, *102*, 284-312. (c) Stamires, D. N.; Turkevich, J. *J. Am. Chem. Soc.* **1964**, *86*, 749-757.

(10) *Introduction to Zeolite Science and Practice, Studies in Surface Science and Catalysis Vol. 58*; van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds.; Elsevier: Amsterdam, 1991.

(11) Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1991**, *95*, 506-509.

(12) Blatter, F.; Frei, H., to be submitted for publication.

(13) The hydroperoxide was synthesized according to the method of Schenck: Schenck, G. O.; Schulte-Elte, K. H. *Ann.* **1958**, *618*, 185-193.

(14) The ^{18}O frequency shifts of the bands at 920, 875, and 830 cm^{-1} could not be determined.

(15) The following alternatives could be ruled out: (i) Excitation of an O_2 enhanced triplet absorption of DMB, since the lowest triplet state of the alkene lies in the UV region.[2,16] (ii) Excitation of $(O_2)_2$ cooperative absorptions in the visible spectral range, because these exhibit well-established discrete absorption bands.[17] Reversible formation of the complex was demonstrated by the fact that product growth ceased when O_2 was selectively removed by evacuation.

(16) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, New York, 1973.

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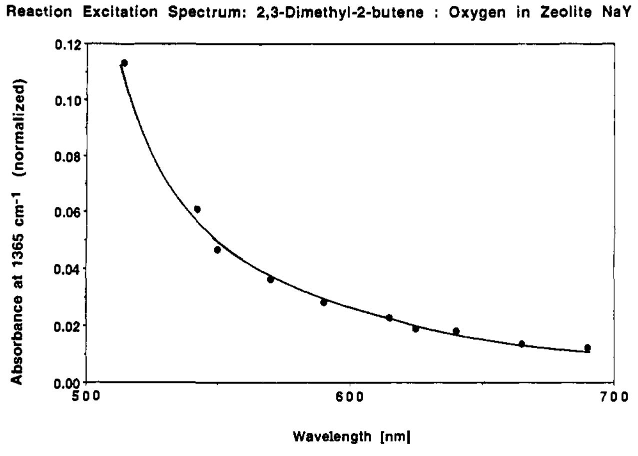
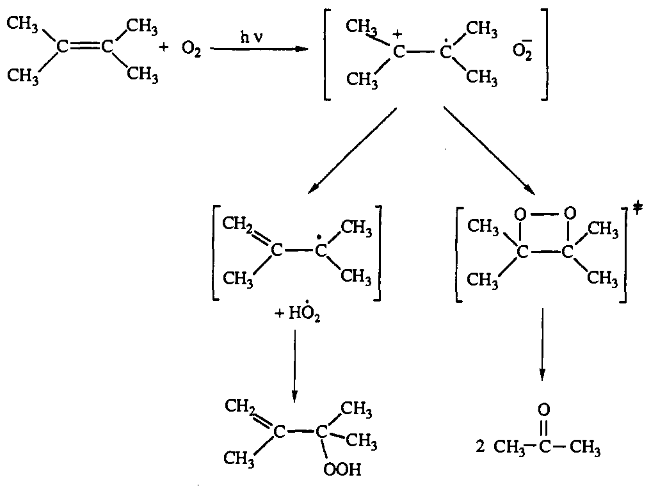


Figure 2. Laser reaction excitation spectrum of the DMB + O_2 system in zeolite NaY. Each point of the curve represents the absorbance growth of the hydroperoxide product absorption at 1365 cm^{-1} upon irradiation with 3.5×10^{21} photons.

This assignment is strongly supported by the observation that the onset of the long wavelength alkene·O_2 absorption in NaY depends, in the expected way, on the ionization potential of the hydrocarbon.[19] For example, no reaction of 3,3-dimethyl-1-butene·O_2 was observed in NaY upon irradiation at wavelengths longer than 458 nm, consistent with the 1.2 eV higher ionization potential of the 1-butene when compared with DMB.[20] Since the onset of the DMB·O_2 charge-transfer absorption in O_2 saturated solution[1d] and O_2 gas phase lies around 400 nm,[2,21] the excitation spectrum presented in Figure 2 implies that the zeolite cage stabilizes the excited charge-transfer state of this complex by approximately 11 000 cm^{-1} (300-nm shift). Typical red shifts of charge-transfer bands from solution to zeolite environments that have been reported for organic systems lie in the 10–30-nm range (aromatic (donor)–pyridinium (acceptor) complexes).[22] Since the observed shift of the CT absorption of the DMB·O_2 complex lies far beyond what would be predicted from the change in bulk dielectric properties,[7,22] we speculate that specific interactions of the excited charge-transfer state with the cage environment are responsible for the unexpected stabilization (for example, the positively charged hydrocarbon moiety may face the negative zeolite wall, and the negatively charged O_2 part may point toward a sodium cation).

Scheme I



The proposed mechanism of the observed DMB·O_2 photochemistry in NaY is shown in Scheme I. The path leading to acetone has a precedent in the electron-transfer sensitized photooxidation of olefins by dyes[23] or at semiconductor surfaces.[24] It has also been proposed in the case of photooxidative cleavage, by UV light, of phenylethenes in solution and adsorbed on silica gel and alumina.[25] Deprotonation of the transient DMB radical cation followed by combination with the HO_2 to yield 2,3-dimethyl-3-hydroperoxo-1-butene (Scheme I) has been proposed by Onodera *et al.* in the case of UV light-induced reaction of DMB with O_2 in solution.[1c] An alternative mechanism would involve $O_2(^1\Delta)$ formed directly from the $DMB^+O_2^-$ charge-transfer state.[26] Singlet O_2 is known to react with DMB to yield mostly 2,3-dimethyl-3-hydroperoxo-1-butene.[13,27] However, it is unlikely that this reaction path plays a substantial role. The principle reason is our observation of a dramatic change of the acetone to hydroperoxide product branching ratio in favor of the ketone when replacing zeolite NaY by the much less polar high-silica faujasite (Si/Al > 100).[12] There is no precedent for a reversal of the acetone/hydroperoxide branching ratio in favor of acetone in the DMB + $O_2(^1\Delta)$ reaction in any medium, and we do not see how this could come about. By contrast, the change in the branching ratio can readily be explained by the mechanism proposed in Scheme I. In the much less polar high-silica matrix, deprotonation of DMB^+ is expected to be inhibited and, hence, formation of hydroperoxide to be quenched. While we have not observed any thermal reaction of DMB with O_2 when keeping the zeolite temperature at –50 °C, dark DMB + O_2 chemistry occurred upon warm up of the matrix above –20 °C. New bands appeared at 1282, 1325, 1360, 1370, 1420, 1484, and 1699 cm^{-1}, which agreed with the spectrum of pinacolone loaded into NaY. Clearly, the thermal reaction path is distinct from the photochemical one, and experiments are in progress to further elucidate the mechanism of the dark reaction.

In conclusion, this study shows that enclosure of alkene and O_2 in the cages of inert zeolites allows us to tune the charge-transfer absorption to very long wavelengths. Such low-energy charge-transfer states of reactant pairs in inert solid matrices offer an opportunity to achieve product controlled photochemistry by furnishing optical access to very low-lying reaction surfaces,[28,29] an aspect of photochemistry in zeolite matrices[30] that is yet to be explored.

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(17) Landau, A.; Allin, E. J.; Welsh, H. L. *Spectrochim. Acta* **1962**, *18*, 1–19.

(18) We can rule out that this absorption is due to a low-energy butene·zeolite lattice electronic transition as diffuse reflectance spectra of olefins loaded into zeolite Y do not exhibit such long wavelength absorptions (e.g., Garbowski, E. D.; Praliand, H. *J. Chim. Phys.* **1979**, *76*, 687–692).

(19) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; p 406.

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

(21) Results of DMB + O_2 photochemistry in solid O_2 by Akimoto and co-workers[4] will be discussed in our full report.[12]

(22) (a) Sankararaman, S.; Yoon, K. B.; Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 1419–1421. (b) Yoon, K. B.; Kochi, J. K. *J. Phys. Chem.* **1991**, *95*, 3780–3790. (c) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321–339.

(23) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221–2227.

(24) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314–321.

(25) *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991; p 506. (b) Aronovitch, C.; Mazur, Y. *J. Org. Chem.* **1985**, *50*, 149–150.

(26) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1989**, *93*, 5493–5500.

(27) Bogan, D. J.; Lee, D. H. *J. Phys. Chem.* **1992**, *96*, 9304–9310.

(28) Blatter, F.; Frei, H. *J. Phys. Chem.* **1993**, *97*, 1178–1183.

(29) Frei, H. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1992; Vol. 20, pp 1–66.

(30) (a) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219–1229. (b) Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991; pp 429–493.