J. Am. Chem. Soc. **1995,** *117,* 562−563

Detection of Ethylene−Ozone and Cyclohexene−Ozone Charge-Transfer Complexes in Cryogenic Matrices

S. Jonnalagadda, S. Chan, J. Garrido, J. Bond, and
K. A. Singmaster*

Department of Chemistry, San Jose State University
San Jose, California 95192-0101

Received August 22, 1994

In 1971 Bailey and co-workers reported the first observation of a charge-transfer complex of ozone with an aromatic π system.[1] At the time π complexes were suggested as possible precursors in the ozonolysis of alkenes and aromatics; detection of the charge-transfer band associated with these complexes provided additional mechanistic insight into these important and atmospherically relevant organic reactions.[2,3] Nearly 20 years later Singmaster and Pimentel reported that they had observed the visible−UV absorptions associated to the charge-transfer complexes of ozone with simple alkenes.[4] Singmaster and Pimentel noted that decreases in the absorption of the charge-transfer bands resulted in detection of ozonolysis products, suggesting that in an inert gas matrix environment the π complex serves as the precursor in the ozonolysis of alkenes. The alkenes they investigated were propene, isobutylene, *trans*- and *cis*-2-butene, trimethylethylene, and tetramethylethylene. As suggested by Nelander and Nord,[5] cryogenic matrices (T below 40 K) were needed to trap the complexes due to the low activation energy associated with the ozonolysis reaction of alkenes. Singmaster and Pimentel were unable to identify the simplest alkene−ozone charge-transfer complex, ethylene−ozone. They suggested that the ethylene−ozone complex exhibited a maximum below 300 nm, a region obscured by the strong absorption associated with ozone's Hartley band (200−300 nm).[6] In this communication we report the detection of the ethylene−ozone charge-transfer complex. We have also been able to detect an ozone complex for cyclohexene. The correlation between the charge-transfer-band maximum and the ionization potential of the alkene allows us to predict a possible maximum for the charge-transfer bands of these two alkenes. Using the data provided in ref 4 and the ionization potentials of ethylene and cyclohexene, we predict a maximum for the ethylene complex at 301 nm (IP = 10.51 eV);[7] for the cyclohexene complex the expected maximum is 397 nm (IP = 8.945 eV).[7]

Alkene/ozone/inert gas matrices were deposited onto a CsI window cooled by a Displex CS-202 (APD Cryogenics) closed-cycle helium refrigerator. Ozone was prepared by static electric discharge of oxygen and collected in a Pyrex tube at 77 K. Deposition rates ranged from 0.5 to 1.0 mmol/h. Ultraviolet−visible spectra were recorded with a Cary 3 spectrophotometer.

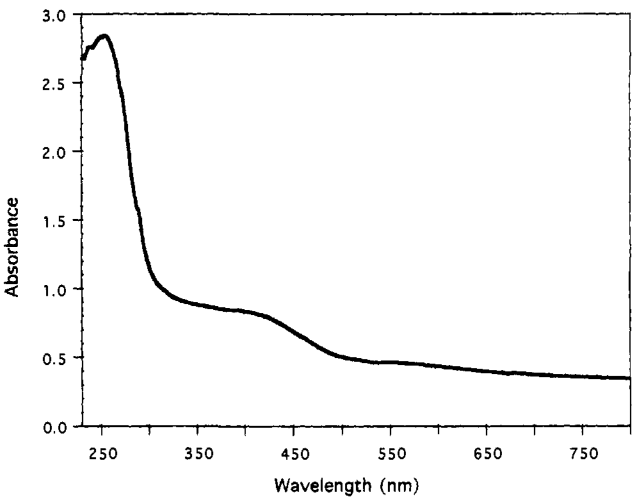

Figure 1. UV−vis spectrum of cyclohexene/ozone/Kr matrix at 30 K.

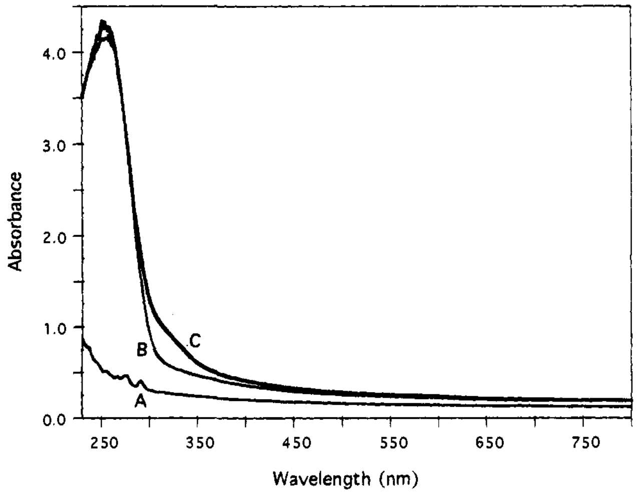

Figure 2. UV−vis spectra of (A) ethylene/Xe matrix at 50 K, (B) ozone/Xe matrix at 50 K, and (C) ethylene/ozone/Xe matrix at 50 K.

A UV−vis spectrum of a cyclohexene/ozone/Kr matrix (1:2:100) deposited at 30 K is illustrated in Figure 1. The spectrum exhibits a very strong absorption with maximum at 257 nm. This absorption is due to ozone (Hartley band). A weaker absorption with a maximum at 407 nm is observed. This band is not detected in ozone/Ar matrices or in cyclohexene/Ar matrices. We have assigned this absorption to the cyclohexene−ozone charge-transfer complex. Its observed maximum is only 10 nm higher than the value predicted above.

The observation of the cyclohexene−ozone charge-transfer complex is facilitated by the fact that the absorption is far removed from the ozone absorption. The ethylene complex absorption is expected to partially or fully overlap with the ozone absorption. The optical quality of the ethylene/ozone/inert gas matrix is crucial since scattering by the matrix could obscure the absorption. Figure 2 shows the spectra obtained for an ethylene/xenon matrix (1:100) (A), an ozone/Xe (3:100) matrix (B), and an ethylene/ozone/Xe (1:6:200) matrix (C), all at 50 K. Spectrum C shows an absorption around 300−350 nm that is not observed in either the ethylene/Xe or ozone/Xe matrix. This absorption is being attributed to the ethylene−ozone charge-transfer complex. Figure 3 shows the spectrum that results when the ozone/Xe spectrum is subtracted from the ethylene/ozone/Xe spectrum (C − B). The band observed exhibits a maximum at 310 nm, 9 nm higher than the predicted value for the ethylene−ozone charge-transfer complex. This

---

(1) Bailey, P. S.; Ward, J. W.; Hornish, R. E. *J. Am. Chem. Soc.* **1971,** *93,* 3552. Bailey, P. S; Carter, T. P.; Nick, E.; Fisher, C.; Khasbal, A. Y. *J. Am. Chem. Soc.* **1974,** *96,* 6136−6140.

(2) For an excellent review on ozonation in organic chemistry, see: Bailey, P. S. *Ozonation in Organic Chemistry: Volume I, Olefinic Compounds*; Academic Press: New York, 1978. Bailey, P. S. *Ozonation in Organic Chemistry: Volume II, Nonolefinic Compounds*; Academic Press: New York, 1982.

(3) For a discussion on the role ozonolysis of alkenes plays in atmospheric chemistry, see: Finlayson-Pitts, B. J.; Pitts, J. N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley-Interscience: New York, 1986 and references therein.

(4) Singmaster, K. A.; Pimentel, G. C. *J. Phys. Chem.* **1990,** *94,* 5226−5229. References in this article outline some of the history of ozone−olefin charge-transfer complexes.

(5) Nelander, B.; Nord, L. *J. Am. Chem. Soc.* **1979,** *101,* 3769−3770.

(6) Okabe, H. *Photochemistry of Small Molecules*; Wiley-Interscience: New York, 1978; pp 237−247.

(7) *CRC Handbook of Chemistry and Physics*; D. R. Lide, Ed.; CRC Press: Boca Raton, FL, 1992; pp 10-222, 10-227.

0002-7863/95/1517-0562$09.00/0

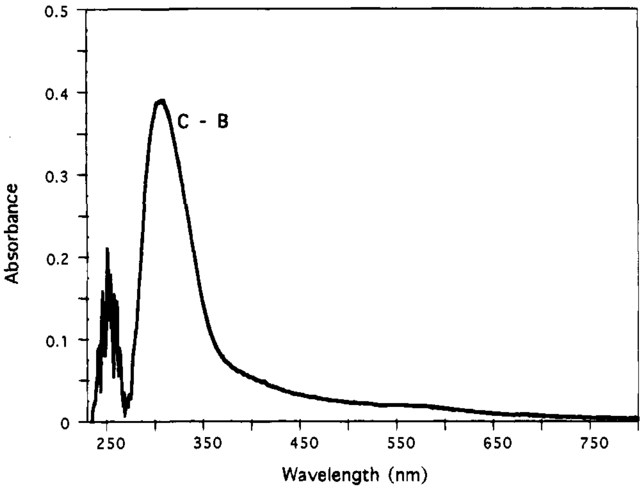

Figure 3. Difference spectrum illustrating the absorption attributed to the ethylene–ozone charge-transfer complex (C − B).

absorption is not due to ozonolysis products (such as trioxolanes). Temperature studies reveal that the ethylene ozonolysis reaction does not begin to occur in a matrix environment until 65 K.[8] Even at 65 K the reaction is very slow; thus the concentration of ozonolysis products would be too low to generate such a strong absorption. We feel confident that we have identified the ozone–ethylene charge-transfer complex. Further studies on the thermal chemistry and photochemistry of ozone charge-transfer complexes are in progress.

Acknowledgment. We thank the W. M. Keck Foundation, Research Corporation, NSF, and San Jose State University for providing the funds necessary to construct our matrix isolation laboratory. Acknowledgment also is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank the NSF and NIH-MBRS for continuing financial support of this research and for student stipends.

JA942794L

---

(8) Singmaster, K. Dissertation, University of California, Berkeley, 1987. Hawkins, M.; Kohlmiller, C. K.; Andrews, L. *J. Phys. Chem.* **1982**, *86*, 3154–3166. Andrews, L.; Kohlmiller, C. K. *J. Phys. Chem.* **1982**, *86*, 4548–4557.