calization occurs, thereby exerting a stabilizing effect.

Acknowledgment. We gratefully acknowledge the generous grant of computer time on a VAX 11/780 provided by the computer center of the Philadelphia College of Textiles and Science. We also thank the Advanced Scientific Computing Laboratory, NCI-FCRF, for providing time on the Cray XMP supercomputer. This work was also supported in part by grants CA-10925 and CA-06927 from the National Institutes of Health and BC-242 from the American Cancer Society and by an appropriation from the Commonwealth of Pennsylvania.

Supplementary Material Available: Tables IS–IVS, vibrational frequencies calculated using AM1 and the 6-31G basis set for O-protonated benzene oxide, and the trans, gauche, and cis rotamers of the *p*-quinonoid-type carbonium ion; Table VS, calculated values for internuclear distances between H_1, H_7, and O_7 and the adjacent carbons in the ring, C_2 and C_6, in the trans, TS, gauche, and cis rotamers of the *p*-quinonoid-type carbonium ion; Table VIS, the loss of electronic charge on the ring carbons and ring hydrogens, and the gain as the epoxide oxygen bonds the proton in the formation of O-protonated benzene oxide and the gauche rotamer of the *p*-quinonoid-type carbonium ion; Table VIIS, total atomic charges on H_2C_2 through H_6C_6 and H_7O_7, and the atomic charges on C_1 through C_6 and O_7, in the trans, gauche, and cis rotamers of the *p*-quinonoid-type carbonium ion (8 pages). Ordering information is given on any current masthead page.

Vibronic Excitation of Oxygen-Atom Transfer from NO_2 to Ethylene by Long-Wavelength Visible Light in a Cryogenic Matrix

Munetaka Nakata,[†] **Kazuhiko Shibuya,**[‡] **and Heinz Frei***

Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720 *(Received: February 14, 1990)*

Chemical reaction has been observed upon irradiation of ethylene·NO_2 pairs in solid Ar with continuous-wave dye laser light at visible wavelengths as long as 574 nm, well below the 398-nm dissociation limit of isolated NO_2. Reaction products were acetaldehyde, ethylene oxide, NO, and ethyl nitrite radical, as established by FT infrared spectroscopy. Kinetic analysis of product absorbance growth showed that acetaldehyde is the prevalent final oxidation product of direct, single-photon photolysis of ethylene·NO_2 pairs, while ethylene oxide is exclusively produced by yellow and shorter wavelength induced photodissociation of trapped ethyl nitrite radical. Experiments with *trans*- and *cis*-CHD=CHD yielded nitrite radical $\dot{C}$HD–CHD–ONO under retention of stereochemistry but with scrambling in the epoxide product. On the basis of these results and those of our earlier work on NO_2 photooxidation of *cis*- and *trans*-2-butene, a reaction path is proposed that involves O-atom transfer from NO_2 to the C=C bond to give a short-lived singlet oxirane biradical. The photolysis wavelength dependence of the reaction quantum efficiency indicates that NO_2 reactant vibrational excitation plays an essential role and opens a reaction path that is unique to visible light induced alkene + NO_2 chemistry in a matrix.

I. Introduction

We have recently reported oxidation of *trans*- and *cis*-2-butene by NO_2 excited at red or yellow wavelengths in an Ar matrix.[1,2] These long-wavelength photons excite NO_2 to vibronic levels tens of kilocalories per mole below the dissociation limit of the isolated reactant. Absorption of a single photon by reactant pairs led to exclusive production of 2,3-epoxybutane (plus NO) with a high degree of stereochemical retention. Concurrently a butyl nitrite radical was trapped, and its conformation established by FT infrared spectroscopy. Although optical absorption of NO_2 at long visible wavelengths is mainly due to the $^2B_2$ excited state, the molecule prepared by excitation in this spectral region has predominantly the character of a highly vibrationally excited $^2A_1$ ground-state species because of very strong coupling of the $^2B_2$ and $^2A_1$ states.[3] Indeed, our results of a photolysis wavelength dependence study of the reaction quantum efficiency of 2-butene·NO_2 were consistent with reaction of vibrationally unrelaxed NO_2. An observed correlation between the stereochemistry of the trapped butyl nitrite radical and the epoxide indicated that these products have a common transient precursor, most probably an oxirane biradical.[2] This would imply that the initial reaction step is O-atom transfer from NO_2 to the CC double bond.

We report here photooxidation of ethylene by selective vibronic excitation of C_2H_4·NO_2, *cis*-CHD=CHD·NO_2, and *trans*-CHD=CHD·NO_2 pairs in solid Ar with a continuous-wave (cw) dye laser at wavelengths as long as 575 nm. A study of this prototype alkene + NO_2 photoreaction in a matrix is of special interest for several reasons. First, since long-wavelength visible photons prepare NO_2 essentially as a highly vibrationally excited ground-state species, this system offers an opportunity to explore the effect of reactant vibrational excitation on bimolecular reactivity. Second, while vibronic excitation of alkene·NO_2 "sustained collisional pairs"[4] in the matrix initiates O-atom transfer, thermal reaction of NO_2 with ethylene and higher alkenes in the gas phase[5-7] or solution[8,9] leads to initial formation of a C–N bond to give nitroalkyl radicals. This difference in the chemical reaction path is particularly intriguing since in both the case of the matrix and the thermal gas phase (or solution) experiment the reacting NO_2 has predominantly $^2A_1$ ground-state character. A third interesting point is the interpretation of the photolysis

---

[†] Present address: Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183.

[‡] Tokyo Institute of Technology, Ohokayama, Meguro, Tokyo 152.

* To whom correspondence should be addressed.

(1) Nakata, M.; Frei, H. *J. Am. Chem. Soc.* **1989**, *111*, 5240.

(2) Nakata, M.; Frei, H. *J. Phys. Chem.* **1989**, *93*, 7670.

(3) Hsu, D. K.; Monts, D. L.; Zare, R. N. *Spectral Atlas of Nitrogen Dioxide*; Academic Press: New York, 1978.

(4) Frei, H.; Pimentel, G. C. In *Chemistry and Physics of Matrix Isolated Species*; Andrews, L., Moskovits, M., Eds.; Elsevier: Amsterdam, 1989; p 139.

(5) Cottrell, T. L.; Graham, T. E. *J. Chem. Soc.* **1953**, 556; *J. Chem. Soc.* **1954**, 3644.

(6) Atkinson, R; Aschmann, S. M.; Winer, A. M.; Pitts, Jr., J. N. *Int. J. Chem. Kinet.* **1984**, *16*, 697. See also: Sprung, J. L.; Akimoto, H.; Pitts, Jr., J. N. *J. Am. Chem. Soc.* **1971**, *93*, 4358; *J. Am. Chem. Soc.* **1974**, *96*, 654.

(7) Ohta, T.; Nagura, H.; Suzuki, S. *Int. J. Chem. Kinet.* **1986**, *18*, 1.

(8) Shechter, H. *Rec. Chem. Prog.* **1964**, *25*, 55.

(9) Giamalva, D. H.; Kenion, G. B.; Church, D. F.; Pryor, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7059. In the case of the reaction in solution, an additional path involving abstraction of allylic hydrogen is observed.

0022-3654/90/2094-8168$02.50/0 © 1990 American Chemical Society

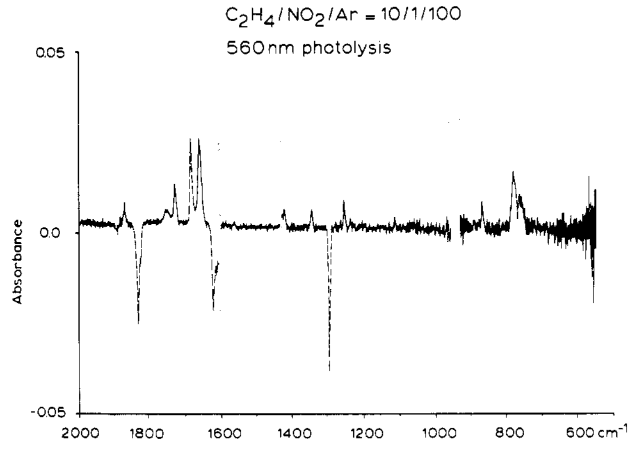


Figure 1. Infrared difference spectrum obtained upon 560-nm photolysis of a matrix $C_2H_4/NO_2/Ar = 10/1/100$ for 100 min at 375 mW cm^{-2}. Dotted bands are due to very intense C_2H_4 or NO_2 reactant absorptions, dashed ones to N_2O_3 impurity that isomerizes upon laser irradiation.

wavelength dependence of the reaction quantum efficiency and the product branching in terms of energetics and dynamics of the proposed transient oxirane biradical, which is aided by recently reported ab initio calculations on $\dot{C}H_2-CH_2-\dot{O}$.

II. Experimental Section

Matrix isolation, spectroscopic, and photolysis laser equipment have been described in our previous reports.[1,2] Matrices ethylene/NO_2/Ar were prepared by slowly codepositing rare-gas mixtures ethylene/Ar and NO_2/Ar through separate deposition lines onto a 12 K cooled CsI window. Chemical reaction was monitored by FT infrared spectroscopy. For irradiation of the matrix with visible light from an Ar ion or a continuously tunable cw dye laser, the cold window was rotated by 90° to expose the matrix to the photolysis light entering the cryostat through a quartz window. Visible spectra were taken with a Shimazu Model UV 2100 UV–vis spectrometer.

Ethylene (Matheson, 99.98%), *cis*-1,2-dideuterioethylene (MSD, 98%), *trans*-1,2-dideuterioethylene (MSD, 98%), and Ar (Matheson, 99.998%) was used without further purification. Nitrogen dioxide (Matheson, 99.5%) was purified prior to use by the procedure described in a previous report.[1]

III. Results

Reactant and product infrared spectra of suspensions of ethylene (C_2H_4, *cis*-$C_2H_2D_2$, *trans*-$C_2H_2D_2$) and NO_2 in solid Ar will be presented in section 1. Then, the photolysis wavelength dependence of the product growth kinetics will be discussed, including kinetic isotope effects (section 2).

1. Infrared Spectra. A. C_2H_4 + NO_2. The spectral range 2000–400 cm^{-1} contains all the information necessary to characterize the observed chemistry, and hence we will confine the report of infrared data to this region. Prior to photolysis, spectra of matrices $C_2H_4/NO_2/Ar = 10/1/100$ show bands of C_2H_4 (1890, 1444, 949, and 829 cm^{-1})[10] and those of NO_2 (1609 and 749 cm^{-1}).[11] N_2O_4 isomers are also observed whose abundance depends on the reactant concentration used, as well as traces of NO and N_2O_3. Frequencies of these N_xO_y species and their behavior under visible light irradiation have been reported in Table I of ref 1.

The longest photolysis wavelength that induced spectral changes in matrices $C_2H_4/NO_2/Ar = 10/1/100$ that were not merely due to N_xO_y isomerizations was 574 nm. By far the two most intense of the product bands that appeared upon irradiation at this threshold wavelength were those at 1664 and 773 cm^{-1}. An infrared difference spectrum obtained upon 560-nm laser irradiation for 100 min at 375 mW cm^{-2} is shown in Figure 1. These two bands exhibit identical growth behavior upon yellow light irradiation and decrease at constant relative intensities when subsequently photolysing with shorter wavelength, 514- or 488-nm emission of the Ar ion laser. This indicates that the 1664- and 773-cm^{-1} product absorptions belong to a single species.

All additional, weaker product bands observed upon irradiation with yellow light (Figure 1) did not erode upon subsequent photolysis by blue-green Ar ion laser light. These absorptions could readily be assigned to ethylene oxide, acetaldehyde, and nitric oxide by comparison with infrared spectra available from the literature: 1872 cm^{-1} (NO); 1749, 1715, 1427, 1399, 1349, 1115, 923, 764 cm^{-1} (CH_3CHO);[13] 1466, 1462, 1264, 1165, 1160, 1150, 871, 857, 812 cm^{-1} ($\overline{CH_2-CH_2-O}$).[14] No other product bands due to C_2H_4 + NO_2 reaction were observed at any of the photolysis wavelengths used (574, 560, 555, 534, 514, and 488 nm).

Most informative regarding identification of the species absorbing at 1664 and 773 cm^{-1} was its secondary photolysis behavior. If after accumulation of this species by prolonged irradiation with yellow light the matrix was exposed for only a few minutes to shorter wavelength green or blue Ar ion laser emission, the decrease of the 1664- and 773-cm^{-1} bands was accompanied by growth of the absorptions of NO, ethylene oxide, and acetaldehyde. Since during such a brief photolysis period at this wavelength the yield of these final products from direct photolysis of $C_2H_4{\cdot}NO_2$ is negligible, we conclude that the species absorbing at 1664 and 773 cm^{-1} photodissociates to NO and C_2H_4O and therefore has the molecular formula $C_2H_4O_2N$. The fact that its two most intense bands are close to the very strong N═O and N–O stretching absorptions of previously identified butyl nitrite radical conformers (syn form, 1652 and 772 cm^{-1}; trans form, 1646 and 755 cm^{-1})[1,2] strongly suggests that $C_2H_4O_2N$ is an ethyl nitrite radical. The spectroscopic discussion presented earlier[1] specifically rules out a nitroethyl radical. Moreover, the $C_2H_4O_2N$ species observed here exhibits the long-wavelength-light-induced NO photoelimination that appears to be characteristic for alkyl nitrite radicals.[1,2]

B. $C_2H_2D_2$ + NO_2. Reactions of *cis*- and *trans*-CHD═CHD with NO_2 were studied to find out about the stereochemical course of the reaction. Infrared spectra of the reactants *cis*- and *trans*-1,2-dideuterioethylene agreed well with those reported in the literature.[12,15] Irradiation of a matrix *trans*-CHD═CHD/NO_2/Ar = 10/1/100 at 555 nm for several hours, followed by brief 458–514-nm ("blue-green") Ar ion laser photolysis revealed absorptions of partially deuterated ethyl nitrite radical at 1664 and 790 cm^{-1}. Interestingly, an analogous experiment with a matrix *cis*-CHD═CHD/NO_2/Ar = 10/1/100 revealed different absorptions of $C_2H_2D_2ONO$ in the fingerprint region, namely at 925 and 825 cm^{-1}, but none at 790 cm^{-1}. On the other hand, the same 1664-cm^{-1} band was observed for the N═O stretching mode. Infrared difference spectra in the region 1000–600 cm^{-1} that result from blue-green Ar ion irradiation of these matrices are shown in Figure 2, where ethyl nitrite radical absorptions are marked by arrows. The noise level of the two spectra in this region allows us to conclude that the intensity of the observed $C_2H_2D_2ONO$ bands of each isomer is at least 3 times higher than that of the $C_2H_2D_2ONO$ absorptions of the opposite isomer. Although we cannot assign the two isomers *cis*- and *trans*-$C_2H_2D_2ONO$ on the basis of the observed bands, the fact that different nitrite radical IR spectra are obtained upon photolysis of *cis*- and *trans*-$C_2H_2D_2{\cdot}NO_2$ strongly indicates that $C_2H_2D_2ONO$ is formed under stereochemical retention. On the other hand, no significant differences in band positions and intensities were observed in the final oxidation product spectra of *trans*- and *cis*-CHD═CHD + NO_2 reactions. The same relative yields of *cis*-$\overline{CHD-CHD-O}$ (3031, 2260, 2242, 2218 1394, 1345,

---

(10) Rytter, E.; Gruen, D. M. *Spectrochim. Acta* **1979**, *35A*, 199.

(11) Fateley, W. G.; Bent, H. A.; Crawford, Jr., B. *J. Chem. Phys.* **1959**, *31*, 204.

(12) Duncan, J. L.; McKean, D. C.; Mallinson, P.D. *J. Mol. Spectrosc.* **1973**, *45*, 221.

(13) Hollenstein, H.; Günthard, H. H. *Spectrochim. Acta* **1971**, *27A*, 2027.

(14) Cant, N. W.; Armstead, W. J. *Spectrochim. Acta* **1975**, *31A*, 839. LeBrumant, J.; Maillard, D. *C. R. Hebd. Seances Acad. Sci.* **1967**, *264*, 1107.

(15) Machida, K.; Tanaka, Y. *J. Chem. Phys.* **1974**, *61*, 5040.

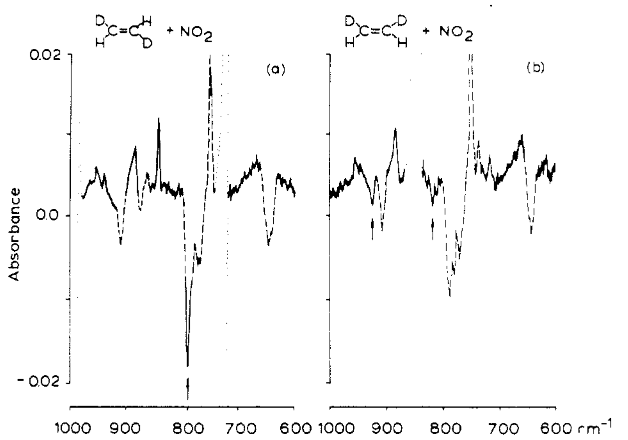
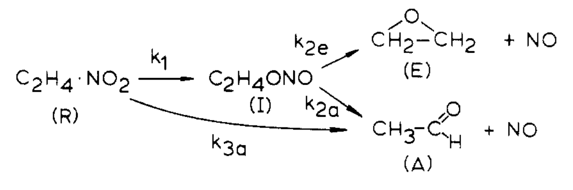


Figure 2. Absorption changes upon 10-min photolysis of matrices $C_2H_2D_2/NO_2/Ar$ = 10/1/100 by 458–514-nm Ar ion laser emission at 140 mW cm^{-2} following accumulation of intermediates by 7-h irradiation at 555 nm: (a) *trans*-CHD=CHD + NO_2, (b) *cis*-CHD=CHD + NO_2. Dashed bands belong to N_xO_y (ref 1, Table I), dotted bands are due to intense absorptions of *trans*-CHD=CHD (a) or *cis*-CHD=CHD (b). Arrows indicate absorptions of ethyl nitrite radical. Product bands at 955 and 884 cm^{-1} are due to *trans*-CHD–CHD–O, those at 943 and 843 cm^{-1} to *cis*-CHD–CHD–O.

SCHEME I



1326, 1236, 1109, 1069, 943, 843 cm^{-1}) and *trans*-CHD–CHD–O (3031, 2270, 2242, 1394, 1330, 1231, 1109, 955, 919, 884 cm^{-1}) were observed in both matrices. The spectra were assigned on the basis of a comparison with literature gas- and solid-phase spectra of these species.[14] Since acetaldehyde is the only other product found in the reaction of the parent isotope, we assigned the remaining product bands of the *cis*- and *trans*-CHD=CHD + NO_2 reactions at 2968, 2831, 2735, 2128, 2082, 1734, 1725, 1400, 1093, and 971 cm^{-1} to the (unknown) spectra of partially deuterated acetaldehyde. These absorptions may originate from as many as four species, namely C_1 and C_s conformers of CH_2D—CD=O and the C_1 and C_s forms of CH-D_2—CH=O. No intensity differences could be discerned among the bands of this set when comparing photoproduct spectra of matrices *cis*-CHD=CHD/NO_2/Ar and *trans*-CHD=CHD/NO_2/Ar. In particular, the intensity ratio of the 2735- and 2082-cm^{-1} absorptions, readily assigned to the CH and CD stretching mode of the aldehyde group[13] (both C_s and C_1 conformers), respectively, was the same for both $C_2H_2D_2$ diastereomers. This implies that the CHD_2-CHO/CH_2D-CDO branching ratio does not depend on the stereochemistry of the $C_2H_2D_2$ reactant.

2. Photolysis Wavelength Dependence of Kinetics. To discuss the mechanism of the photoreaction of ethylene with NO_2, the dependence of the growth kinetics of the nitrite radical and the final oxidation products on photolysis wavelength was investigated. Measured infrared bandwidths were found to be constant over the photolysis periods, and hence peak absorbances could be used in place of integrated absorbances.

The photolysis wavelength dependence of the growth of ethyl nitrite radical (I, 1664 cm^{-1}), acetaldehyde (A, 1349 cm^{-1}), and the ethylene oxide (E, 871 cm^{-1}) in matrices $C_2H_4/NO_2/Ar$ = 10/1/100 in the range 574–488 nm is displayed in Figure 3. The rate of nitrite radical formation increases steeply with decreasing photolysis wavelength, reaching rapidly a maximum at the shortest green and blue wavelengths. Acetaldehyde exhibits a partial induction period at low photolysis photon energies, and ethylene oxide a full induction period at all photon energies, consistent with secondary photolysis of accumulated ethyl nitrite radical to C_2H_4O and NO.

Kinetic analysis of the absorbance growth curves of ethyl nitrite radical, acetaldehyde, and ethylene oxide was initially performed on the assumption that both acetaldehyde and ethylene oxide are produced by direct, one-photon photolysis of ethylene·NO_2 pairs as well as by secondary photolysis of ethyl nitrite radical. Fitting of growth curves, described below, showed that the rate constant for direct formation of ethylene oxide from reactant pairs was zero within uncertainties, and hence we reduced the kinetic model to the one presented in Scheme I. The differential equations are

$$d[R]/dt = -(k_1 + k_{3a})[R] \quad (1)$$

$$d[I]/dt = k_1[R] - (k_{2e} + k_{2a})[I] \quad (2)$$

$$d[E]/dt = k_{2e}[I] \quad (3)$$

$$d[A]/dt = k_{3a}[R] + k_{2a}[I] \quad (4)$$

where R stands for the fixed reservoir of ethylene·NO_2 reactant pairs, and $k_1 = \epsilon_{vis}^{NO_2}\phi_1 I_{laser}$, $k_{2a} = \epsilon_{vis}^{I}\phi_{2a} I_{laser}$, $k_{2e} = \epsilon_{vis}^{I}\phi_{2e} I_{laser}$,

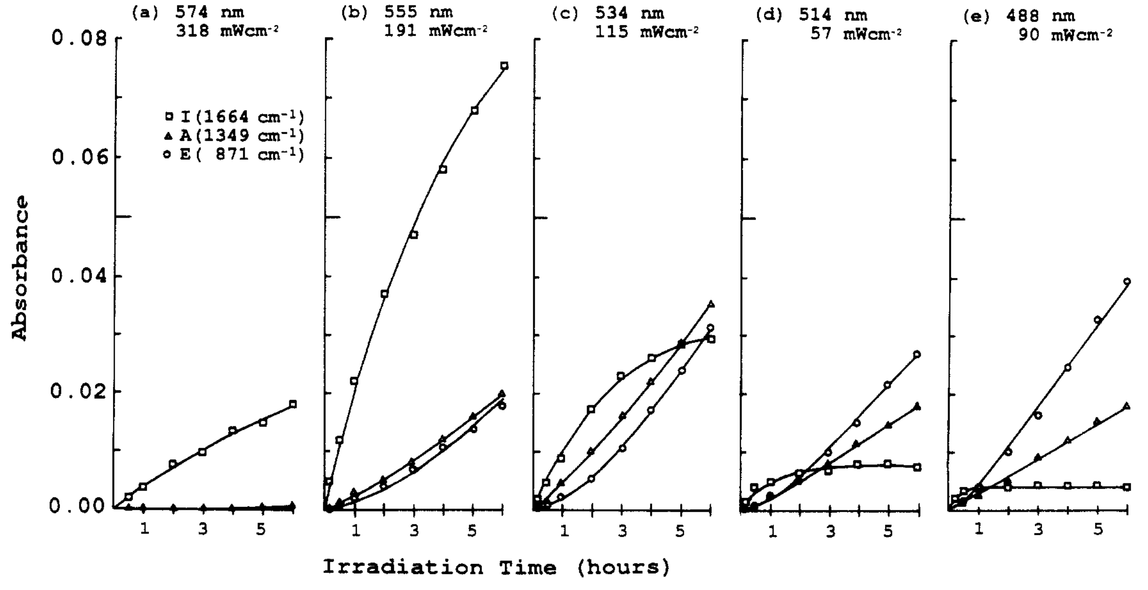


Figure 3. Absorbance growth behavior of ethyl nitrite radical at 1664 cm^{-1} (I), acetaldehyde at 1349 cm^{-1} (A), and ethylene oxide at 871 cm^{-1} upon irradiation of matrices $C_2H_4/NO_2/Ar$ = 10/1/100: (a) 574 nm, 318 mW cm^{-2}; (b) 555 nm, 191 mW cm^{-2}; (c) 534 nm, 115 mW cm^{-2}; (d) 514 nm, 57 mW cm^{-2}; (e) 488 nm, 90 mW cm^{-2}.

TABLE I: Photolysis Wavelength Dependence of First-Order Rate Constants Obtained from Integrated Equations

λ, nm	power, mW cm^{-2}	k_1	k_{2e}	k_{2a}	k_{3a}
		Adjusted Parameters, h^{-1}			
574	318	0.0012 ± 0.0002	0.04 ± 0.01	0.04 ± 0.02	0.0
555	191	0.0070 ± 0.0004	0.13 ± 0.02	0.04 ± 0.02	0.0011 ± 0.0004
534	115	0.0054 ± 0.0004	0.39 ± 0.04	0.01 ± 0.04	0.0033 ± 0.0004
514	57	0.0052 ± 0.0004	1.08 ± 0.08	0.00 ± 0.08	0.0029 ± 0.0004
488	90	0.0114 ± 0.0008	2.64 ± 0.20	0.00 ± 0.20	0.0052 ± 0.0008
		Normalized Values[a]			
574		0.0007 ± 0.0002	0.03 ± 0.01	0.03 ± 0.01	0.0000
555		0.0070 ± 0.0004	0.13 ± 0.02	0.04 ± 0.02	0.0011 ± 0.0004
534		0.0093 ± 0.0007	0.67 ± 0.07	0.02 ± 0.07	0.0058 ± 0.0007
514		0.0189 ± 0.0015	3.91 ± 0.29	0.00 ± 0.29	0.0103 ± 0.0015
488		0.0275 ± 0.0020	6.37 ± 0.47	0.00 ± 0.47	0.0125 ± 0.0020

[a] Rate constants normalized to the laser photon intensity of 8.9 × 10^{-7} mol cm^{-2} s^{-1} used in the 555-nm irradiation experiment.

$k_{3a} = \epsilon_{vis}{}^{NO_2}\phi_{3a}I_{laser}$, ($\epsilon_{vis}{}^{NO_2}$, $\epsilon_{vis}{}^{I}$ are decadic extinction coefficients of NO_2 and ethyl nitrite radical, respectively, at visible photolysis wavelengths; ϕ is the reaction quantum efficiency; I_{laser} is the laser photon intensity). Application of the weak absorption limit approximation is justified by observation of weak absorption in the 450–600-nm range of matrices used in this work.

Integration of the different equations (1)–(4) using the integrating factor method in the case of eq 2[16] gives (expressed in absorbances)

$$A^{R} = A^{R}{}_{0}e^{-(k_1+k_{3a})t} \tag{5}$$

$$A^{I} = A^{R}{}_{0}\frac{\epsilon^{I}}{\epsilon^{R}}\,\frac{k_1}{k_{2e}+k_{2a}-(k_1+k_{3a})}\left(e^{-(k_1+k_{3a})t}-e^{-(k_{2e}+k_{2a})t}\right) \tag{6}$$

$$A^{E} = A^{R}{}_{0}\frac{\epsilon^{E}}{\epsilon^{R}}\left(\frac{k_1k_{2e}}{(k_1+k_{3a})(k_{2e}+k_{2a})} + \frac{1}{k_{2a}+k_{2e}-(k_1+k_{3a})}\left\{\frac{k_{2e}}{k_{2e}+k_{2a}}k_1e^{-(k_{2e}+k_{2a})t} - \frac{k_1k_{2e}}{k_1+k_{3a}}e^{-(k_1+k_{+a})t}\right\}\right) \tag{7}$$

$$A^{A} = A^{R}{}_{0}\frac{\epsilon^{A}}{\epsilon^{R}}\left(\frac{k_1k_{2a}/(k_{2a}+k_{2e})+k_{3a}}{k_1+k_{3a}} + \frac{1}{k_{2a}+k_{2e}-(k_1+k_{3a})}\left\{\frac{k_{2a}}{k_{2e}+k_{2a}}k_1e^{-(k_{2e}+k_{2a})t} - \left(\frac{k_1k_{2a}+(k_{2a}+k_{2e})k_{3a}}{k_1+k_{3a}} - k_{3a}\right)e^{-(k_1+k_{3a})t}\right\}\right) \tag{8}$$

Figure 3 shows fits of eqs 6–8 (solid curves) to nitrite radical, ethylene oxide, and acetaldehyde absorbance growth, respectively, using iterative approximation by the Gauss–Newton procedure.[17] To reduce the number of adjustable parameters, extinction coefficients of infrared product bands were estimated relative to that of the 1349-cm^{-1} acetaldehyde band. This was done by taking absorbance changes measured upon photolysis at the various wavelengths, plus the ratio of ethyl nitrite radical absorbance decrease to NO, aldehyde, and ethylene oxide absorbance growth under brief 514-nm irradiation. Assuming that in the latter experiment the final products result exclusively from ethyl nitrite radical photodissociation and exploiting the fact that the number of NO molecules equals the sum of acetaldehyde and ethylene oxide molecules at all photolysis wavelengths, the ratio $\epsilon^{I}/\epsilon^{A}/\epsilon^{E} = 5/1/3$ was obtained. Hence five adjustable parameters were needed to fit the equations, namely the four first-order rate constants of Scheme I, plus the parameter $A^{R}{}_{0}/\epsilon^{R}$, which is proportional to the initial reactant pair concentration. Values for the rate constants at various photolysis wavelengths are shown in Table I. Rows 6–10 of the table exhibit first-order rate constants normalized to the laser photon intensity of 8.9 × 10^{-7} mol cm^{-2} s^{-1} in the 555-nm irradiation experiment. Ratios of these normalized rate constants give relative values of the products of extinction coefficient and reaction quantum efficiency, $\epsilon\phi$.

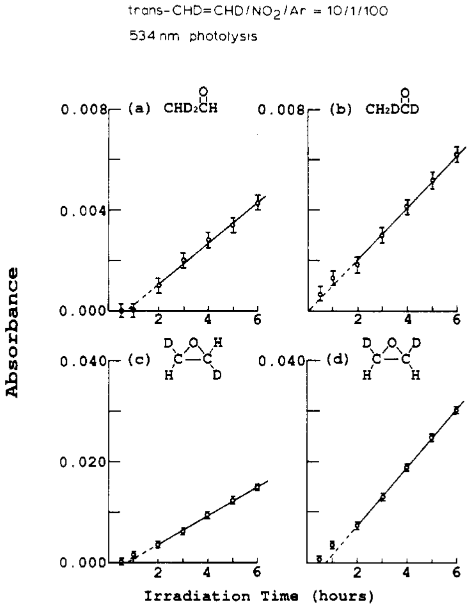


Figure 4. Initial part of the absorbance growth curves of CHD_2–CHO (2735 cm^{-1}), CH_2D–CDO (2082 cm^{-1}), *trans*-CHD–CHD–O (884 cm^{-1}), and *cis*-CHD–CHD–O (843 cm^{-1}) upon 534-nm (115 mW cm^{-2}) photolysis of a matrix *trans*-CHD=CHD/NO_2/Ar = 10/1/100. Straight lines are drawn through points in the range 2–6 h to visualize more clearly the presence (absence) of an induction period.

A marked kinetic isotope effect was observed on the induction period of the growth of partially deuterated acetaldehyde isomers CHD_2—CH=O and CH_2D—CD=O in matrices *trans*-CHD=CHD/NO_2/Ar as well as *cis*-CHD=CHD/NO_2/Ar. As shown in Figure 4a,b upon 534-nm irradiation the 2735-cm^{-1} aldehydic CH stretching absorption of CHD_2—CH=O exhibits a clear induction period, while the corresponding ν(CD) mode of CH_2D—CD=O at 2082 cm^{-1} does not. Apparently, CHD_2—CH=O is formed only along a two-photon path, in contrast to CH_2D—CD=O, which to a substantial degree must be produced along a one-photon path. Consistent with the finding of our kinetic analysis that no ethylene oxide is formed directly from ethylene·NO_2 pairs in a one photon process, both *cis*- and *trans*-CHD–CHD–O exhibit an induction period (Figure 4c,d).

IV. Discussion

1. Infrared Spectrum of Ethyl Nitrite Radical. Assignment of the conformation of the nitrite group of the observed ethyl nitrite radical is possible on the basis of comparison with literature infrared spectra of small, closed-shell alkyl nitrites. Methyl nitrite

---

[16] Smirnov, W. I. *Lehrgang der höheren Mathematik, Part II*; VEB Deutscher Verlag der Wissenschaften: Berlin, 1964; p 211.

[17] Walsh, G. R. *Methods of Optimization*; Wiley: New York, 1975.

isolated in solid Ar has intense N=O absorptions at 1665 and 1613 cm^{-1} attributed to trans and cis conformations, respectively, about the N–O bond.[18]

In the case of the ethyl nitrite molecule the corresponding gas-phase absorptions of the two conformers are at 1672 and 1624 cm^{-1}.[19] The closeness of the 1664-cm^{-1} absorption observed in our work to the ν(N=O) mode of the trans form of closed-shell methyl and ethyl nitrite strongly indicates that the conformation of the ethyl nitrite radical about the N–O bond is trans. The intense 773-cm^{-1} absorption of the radical, assigned to the ν(N–O) mode, is also close in frequency and relative intensity to the corresponding bands of *trans*-methyl and -ethyl nitrite (807 and 816 cm^{-1}, respectively).[18,19] This, in addition, indicates that in the ground electronic state the nitrite group is only weakly perturbed by the unpaired carbon electron of the radical.

2. Reaction Mechanism and Dynamics. A first insight into the mechanism and dynamics of alkene + NO$_2$ reaction induced by excitation of reactant pairs at long visible wavelengths in a matrix was obtained in our previous study to the photooxidation of *cis*- and *trans*-2-butene.[1,2] Direct photolysis of 2-butene·NO$_2$ pairs in solid Ar gave epoxide (plus NO) and butyl nitrite radical as sole products. Crucial information regarding elucidation of the mechanism of the reaction came from the epoxide and nitrite radical product stereochemistry. In the case of the *trans*-2-butene + NO$_2$ reaction, stereochemical retention was complete in both products under any matrix conditions, i.e., the only products obtained were *trans*-2,3-epoxybutane and butyl nitrite radical with anti (trans) conformation about the central CC bond with respect to the methyl groups. Photooxidation of *cis*-2-butene by NO$_2$ gave high degree of stereochemical retention (i.e., *cis*-2,3-epoxybutane and *syn*- (*cis*)-butyl nitrite radical) at low reactant concentrations, while photolysis at increased *cis*-2-butene and NO$_2$ concentrations produced partially inverted products. The key finding was that the cis/trans stereochemical branching of epoxide and butyl nitrite radical changed by the same factor when the reactant concentration was altered. This indicated that the two products have a common transient precursor whose conformation dictates the stereochemical branching of both products. For reasons discussed previously,[2] of the two conceivable transient precursors, oxirane biradical and vibrationally hot butyl nitrite radical, we consider the former as the far more probable candidate. We postulate that NO$_2$ excited at long visible wavelengths transfers an O atom to the alkene double bond to form oxirane biradical. Product branching between epoxide (plus NO) and alkyl nitrite radical is determined by competition between ring closure and trapping of the transient biradical by combination with the NO cage partner.

2.1. Potential Energy Diagram. A potential energy diagram for the oxirane biradical path is presented in Figure 5. Exothermicities for ethylene + NO$_2$ → ethylene oxide + NO of 11.4 kcal mol^{-1} and ethylene + NO$_2$ → acetaldehyde + NO of 38.5 kcal mol^{-1} were determined from known standard enthalpies of formation.[20] The $\Delta H°$ of ethyl nitrite radical formed from ethylene and NO$_2$ was estimated to be close to thermoneutral, −1.7 kcal mol^{-1}. This is based on an estimated standard enthalpy of formation of 18.7 kcal mol^{-1} for ethyl nitrite radical, which was derived as described in the Appendix of ref 1. The energy of the oxirane biradical $\dot{C}H_2-CH_2-\dot{O}$ in the diagram is that of its ^{1}D($\sigma\sigma$) ground electronic state (see below) taken from an ab initio calculation reported by Fueno et al.,[21] which gives $\Delta H° = 41$ kcal mol^{-1} for $C_2H_4 + NO_2(^2A_1) \rightarrow \dot{C}H_2-CH_2-\dot{O}(^1D(\sigma\sigma)) + NO(^2\pi)$.

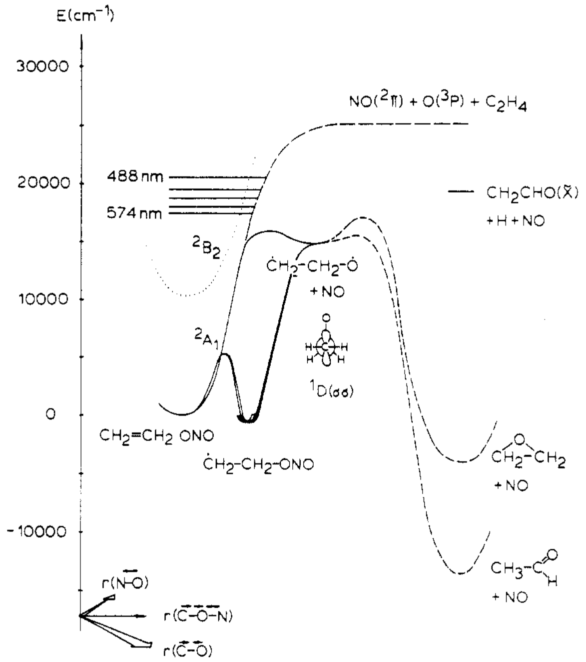


Figure 5. Potential energy diagram for the proposed reaction path.

$\dot{C}H_2-CH_2-\dot{O}$ has two low-lying biradical singlet states, denoted as ^{1}D($\sigma\sigma$) and ^{1}D($\sigma\pi$), and a corresponding pair of biradical triplet states.[21-24] The first orbital symbol indicates in-plane (σ) or perpendicular (π) orientation of the lone electron p-orbital on carbon with respect to the CCO plane, the second character the corresponding orientation of the singly occupied p-orbital on the oxygen. D($\pi\sigma$) and D($\pi\pi$) are perpendicular conformations of $\dot{C}H_2-CH_2-\dot{O}$ with respect to rotation about the C–C bond in the covalent biradical states. According to ab initio work, their energies lie less than 1 kcal mol^{-1} above that of the ($\sigma\sigma$) or ($\sigma\pi$) form, respectively, indicating a very small barrier to internal rotation of the oxirane biradical.[24] The two zwitterionic states of the species lie tens of kilocalories per mole above the covalent biradical states.[22,25]

The high degree of stereochemical retention in both epoxide and trapped nitrite radical upon O-atom transfer from NO$_2$ to *cis*- and *trans*-2-butene observed in our previous work[1,2] implies that the corresponding transient oxirane biradical is very short lived. More precisely, it is short lived on the time scale of the flow of internal kinetic energy into the torsional coordinate since photolysis wavelength dependence studies of the reaction quantum efficiency indicates that the oxirane biradical reacts while carrying excess vibrational energy.[1,2] This could readily be rationalized if the biradical were born in its ^{1}D($\sigma\sigma$) ground electronic state (in which C and O unpaired p-electron orbitals are in the CCO plane) since it lies on the same potential surface as the ground state of the epoxide, i.e., ring closure would be adiabatic on the zeroth-order surface and hence would be very fast. Oxirane biradical formed initially in the ^{1}D($\sigma\pi$) or one of the triplet excited states would require internal conversion or intersystem crossing, respectively, prior to ring closure, processes that would prolong the lifetime of the biradical and hence could adversely affect the stereochemical integrity of the reaction. We conclude that the observed products and the stereochemical course of the reaction are most readily explained if we assume that the oxirane biradical is directly formed in the ^{1}D($\sigma\sigma$) ground state. If the excited ^{1}D($\sigma\pi$) or one of the triplet biradical states were also populated initially, relaxation to the ^{1}D($\sigma\sigma$) ground state would have to be extremely fast (picoseconds) in order to account for the observed product specificity.[26]

---

(18) Gosh, P. N.; Günthard, H. H. *Spectrochim. Acta* **1981**, *37A*, 1055.

(19) Klaboe, P.; Jones, D.; Lippincott, E. R. *Spectrochim. Acta* **1967**, *23A*, 2957.

(20) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

(21) Fueno, T.; Takahara, Y.; Yamaguchi, K. Proceedings of the Symposium on Molecular Structure, Tokyo, 1986; *Chem. Phys. Lett.*, submitted. We thank Prof. Fueno for a preprint of this work.

(22) Bigot, B.; Levin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1095.

(23) Yamaguchi, Y.; Yabushita, S.; Fueno, T.; Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *70*, 27.

(24) Dupuis, M.; Wendoloski, J. J.; Takada, T.; Lester, Jr., W. A. *J. Chem. Phys.* **1982**, *76*, 481.

(25) Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley: New York, 1982; p 60.

2.2. Quantum Efficiencies and Dynamics. According to Table I the sum of the normalized rate constants for one-photon photolysis of ethylene·NO_2 pairs, $k_t = k_1 + k_{3a}$, increases very sharply from the longest (574 nm) to the shortest photolysis wavelength used (488 nm). Increases relative to k_t at 574 nm are factors of 11.6 at 555 nm, 21.6 at 534 nm, 41.7 at 514 nm, and 57.1 at 488 nm. Relative absorption cross sections of NO_2 as determined by visible absorption measurements of NO_2/alkene/Ar matrices increase much more slowly in this spectral range: $\epsilon_{555}{}^{NO_2}/\epsilon_{574}{}^{NO_2} = 1.5$, $\epsilon_{534}{}^{NO_2}/\epsilon_{574}{}^{NO_2} = 2.4$, $\epsilon_{514}{}^{NO_2}/\epsilon_{574}{}^{NO_2} = 3.1$, $\epsilon_{488}{}^{NO_2}/\epsilon_{574}{}^{NO_2} = 4.5$. Since the total rate constant is proportional to the quantum efficiency $\phi_t = \phi_1 + \phi_{3a}$, $k_t = \phi_t(\lambda)\epsilon_\lambda{}^{NO_2}I$, the ratios $(k_t(\lambda)/k_t(574))/(\epsilon_\lambda{}^{NO_2}/\epsilon_{574}{}^{NO_2})$ give the photon energy dependence of the $C_2H_4 + NO_2$ reaction quantum yield. These $\phi_t(\lambda)/\phi_t(574)$ ratios are 7.7 at 555 nm, 9.0 at 534 nm, 13.4 at 514 nm, and 12.7 at 488 nm. Clearly, the data indicate a fast increase of the reaction quantum yield with photolysis photon energy in the yellow-green spectral region.

Such a steep increase of the reaction quantum efficiency with photolysis photon energy has already been observed in the case of the 2-butene + NO_2 reactions. As discussed previously,[1,2] the implication is that NO_2 reacts from vibrationally excited levels well below its 398-nm dissociation threshold. Although the NO_2 absorption cross section in the 500–600-nm range is due to $^2B_2 \leftarrow \tilde{X}^2A_1$, mixing of isoenergetic $^2B_2$ and $^2A_1$ levels is so strong that the prepared NO_2 reactant state is best described as having predominantly $^2A_1$ electronic ground-state character.[1] Hence the steep rise of the quantum efficiency with increasing photolysis photon energy may reflect RRK behavior for O-atom transfer to the CC double bond from highly vibrationally excited ground-state NO_2. Since RRK theory predicts the steepest increase of the reaction rate in the vicinity of the barrier, the observed sharp rise in the range 575–550 nm would imply a barrier to $C_2H_4 + NO_2$ reaction around 45 kcal mol^{-1}, in good agreement with the energy of ground-state oxirane biradical determined by ab initio calculation[21,27] (Figure 5).

According to our proposed mechanism, the branching between trapped ethyl nitrite radical, ethylene oxide, and acetaldehyde is determined by subsequent reaction of transient oxirane biradical. Insight into the dynamics of the transient is obtained from the wavelength dependence of the ratio $k_{3a}/(k_1 + k_{3a})$, which is equal to the quantum yield to acetaldehyde formation from $\dot{C}H_2-CH_2-\dot{O}$. Table I shows that this ratio increases rapidly with photolysis photon energy, from the 574-nm threshold (0.0) to 555 nm (0.14), leveling off around 0.35 at green and blue wavelengths. This may be explained by different activation energies for combination of $\dot{C}H_2-CH_2-\dot{O}$ with NO, and H migration to give acetaldehyde, if we assume that the biradical reacts while still carrying excess kinetic energy. While we expect no barrier for radical combination with a NO cage neighbor to form ethyl nitrite radical, that for intramolecular H migration will depend on the electronic state of the biradical. Fueno et al. predicted a barrier to H migration of 6 kcal mol^{-1} for $^1D(\sigma\sigma)$ ground-state biradical on the basis of ab initio calculation,[21] which is consistent with earlier ab initio work by Lester.[28] Indeed, the threshold to acetaldehyde formation observed here, combined with the ab initio calculated energy[21] of $\dot{C}H_2-CH_2-\dot{O}$ (Figure 5) yields a small barrier to H migration of about 2 kcal mol^{-1}, in reasonable agreement with the ab initio estimate of the barrier. Formation of acetaldehyde from a triplet biradical is very unlikely since ab initio calculations predict an inaccessibly high barrier of about 50 kcal mol^{-1} for H migration on the triplet biradical surface.[21,28] Hence the rise of the oxidation product yield with increasing photolysis photon energy is consistent RRK behavior of the transient oxirane biradical,[29] and $^1D(\sigma\sigma)$ is the most probable state in which $\dot{C}H_2-CH_2-\dot{O}$ is born. The lifetime of the biradical has indeed to be extremely short (at most a few picoseconds) as the observed stereochemical retention in the $\dot{C}HD-CHD-ONO$ product of the *cis-* and *trans-*CHD=CHD + NO_2 reactions requires that the oxirane biradical reacts prior to flow of its excess kinetic energy into the CC torsional coordinate.[30] Note that the intramolecular kinetic H/D isotope effect to acetaldehyde formation observed upon direct photolysis of CHD=CHD·NO_2 pairs is consistent with formation of aldehyde by internal H migration in the oxirane biradical (only the H-atom transfer product CH_2D-CDO is observed upon one-photon photolysis of *cis-* or *trans-*CHD=CHD·NO_2 but no CHD_2-CHO, which would require D-atom migration).

An alternative path to acetaldehyde formation would be H expulsion from transient $\dot{C}H_2-CH_2-\dot{O}$ to form "vinoxy" radical $CH_2=CH-\dot{O}$, followed by cage recombination to give CH_3-CHO. Several observations argue against this possibility. First, as pointed out by Hunziker and co-workers in their discussion of the corresponding reaction of triplet $\dot{C}H_2-CH_2-\dot{O}$ formed by $O(^3P) + C_2H_4$ in the gas phase,[31] formation of "vinoxy" radical in its ground electronic state requires $D(\pi\pi)$ as the initial state of the oxirane biradical. In particular, the carbon lone-electron p-orbital would have to be oriented perpendicular to the CCO plane. The implication would be scrambling of cis and trans conformers in the case of CHD=CHD + NO_2, inconsistent with our observation of stereochemical retention in the $\dot{C}HD-CHD-ONO$ radical product. Second, concurrently with acetaldehyde we would expect the alternative radical recombination product, vinyl alcohol, to be formed along the "vinoxy" radical path as well. The matrix infrared spectrum of $CH_2=CH-OH$ has been reported by Andrews et al.[32] with absorptions at 3625, 3242, 1631, 1084, 819, and 413 cm^{-1}. None of these are observed in the product spectrum of the $C_2H_4 + NO_2$ reaction, which further supports our conclusion that acetaldehyde is formed by intramolecular H migration from $\dot{C}H_2-CH_2-\dot{O}$. Moreover, the ab initio work by Fueno et al.[21] puts electronic ground-state $CH_2=CH-\dot{O}$ + H 15 kcal mol^{-1} above $\dot{C}H_2-CH_2-\dot{O}(^1D(\sigma\sigma))$ (Figure 5). Hence the "vinoxy" radical path would be inconsistent with our observation of acetaldehyde at photolysis wavelengths as long as 555 nm. It is interesting to note that another transient oxirane biradical with a methylene group, $(CH_3)_2\dot{C}-CH_2-\dot{O}$, formed upon O-atom transfer from red-light-excited NO_2 to isobutylene also undergoes H migration to form aldehyde,[33] while none is observed in the case of the 2-butenes.[1,2]

---

(26) A Salem correlation diagram of the NO_2 + alkene reaction (see section 2.3) indicates that the nascent singlet biradical state ($^1D(\sigma\sigma)$ or $^1D(\sigma\pi)$) would depend on the orientation of the reactants. If NO_2 and alkene are aligned in such a way that the reactant N–O bond to be broken lies in the plane defined by O···C=C, the biradical would be formed directly in the $^1D(\sigma\sigma)$ ground state. On the other hand, if NO_2 is oriented such that the reacting N–O bond points out of the O···C=C plane, oxirane biradical would also be formed in the $^1D(\sigma\pi)$ excited state. This reactant orientation dependence of the electronic state in which the oxirane biradical is born may explain the reactant concentration dependence of cis/trans stereochemical branching observed previously in the case of the *cis*-2-butene + NO_2 reaction.[2]

(27) Given the strong electron affinity of NO_2 of 2.3 eV, one may also consider involvement of an excited alkene$^+NO_2^-$ charge-transfer state along the reaction path. However, visible spectra of C_2H_4/NO_2/Ar matrices did not reveal any absorption in the green-red spectral range other than that of nitrogen dioxide. Moreover, estimates of charge-transfer absorptions based on known ionization potentials of ethylene and 2-butenes predict absorption maxima in the UV rather than the long-wavelength visible spectral range. The clearest evidence that charge-transfer states are not involved along the energy path comes from our observation that reaction thresholds do not vary according to the ionization potentials of individual olefins.

(28) Lester, Jr., W. A.; Dupuis, M.; O'Donnell, T. J.; Olsen, A. J. *Frontiers in Chemistry*; Laidler, K. J., Ed.; Pergamon Press: New York, 1982; p 159.

(29) An alternative explanation of the increased final oxidation product yield with rising photolysis photon energy in terms of increased expulsion of NO from the reactant matrix cage is unlikely because of the observed increase of the quantum efficiency of alkyl nitrite radical formation with increasing photon energy. A decrease would be expected if a NO diffusion barrier would appear at shorter photolysis wavelengths.

(30) Observation of H migration on one hand and stereochemical retention with respect to the C–C bond of the trapped $\dot{C}HD-CHD-ONO$ radical on the other hand are consistent with the proposed intermediacy of an oxirane biradical. Even complete alignment of the singly occupied carbon p-orbital with a vicinal C–H bond in the biradical would not involve passage through an H–C–C–O coplanar configuration that would result in stereochemical scrambling.

(31) Hunziker, H. E.; Kneppe, H.; Wendt, H. R. *J. Photochem.* **1981**, *17*, 377.

(32) Hawkins, M.; Andrews, L. *J. Am. Chem. Soc.* **1983**, *105*, 2523.

(33) Nakata, M.; Frei, H. *J. Chem. Soc. Jpn.* **1989**, 1412.

Within experimental uncertainty, no ring closure of the oxirane biradical to epoxide is observed along the one-photon reaction path (i.e., direct photolysis of ethylene·NO_2 pairs). Apparently, the barrier to ring closure of the biradical exceeds that for H migration sufficiently to render the former reaction channel inaccessible. This may be due to the considerable distortion of the oxirane biradical that is required before a nuclear configuration is reached in which the stabilizing effect of the C–O bond begins to manifest itself (narrowing of the CCO bond angle, rehybridization at the $\dot{C}H_2$ center). On the other hand, ethylene oxide is the main product of ethyl nitrite radical secondary photolysis, especially at green and blue irradiation wavelengths. The lack of stereospecificity of $\overline{CHD-CHD-O}$ products contrasts with the stereochemical integrity observed in the case of the one-photon photolysis product $\dot{C}HD-CHD-ONO$. Possible explanations for these differences are different electronic state and/or larger excess internal kinetic energy of oxirane biradical photofragment produced by nitrite radical dissociation compared with $\dot{C}H_2-CH_2-\dot{O}$ obtained along the one-photon path. A trend toward higher ring closure over aldehyde yield at shorter photolysis wavelengths was also observed in the case of $(CH_3)_2\dot{C}-CH_2-ONO$ secondary photolysis.[33]

2.3. Differences between Chemistry in Matrix and Gas (Solution) Phase. Thermal chemistry of ethylene with NO_2 in the gas phase differs strongly from the long-wavelength visible light induced chemistry of matrix-isolated $C_2H_4\cdot NO_2$ reported here. Cottrell and Graham reported CO_2, CO, and NO as main final products of the $C_2H_4 + NO_2$ gas-phase reaction in the temperature range 160–280 °C.[5] The kinetics of the reaction was found to be consistent with addition of NO_2 to the double bond as the first reaction step. Two activation energies were reported for the reaction, namely 12.5 (160–220 °C) and 18 kcal mol^{-1} (220–280 °C). The authors speculated that these may originate from initial formation of a C–N bond (nitroethyl radical) and a C–O bond (ethyl nitrite radical). Formation of C–N bonds has since been proposed for thermal gas-phase reaction of NO_2 with a number of other small alkenes by several groups,[6,7] and Atkinson et al. reported direct evidence for formation of nitroalkyl radicals by FT infrared spectroscopy.[6] Similarly, thermal reactions of NO_2 with alkenes in solution have been found to involve initial formation of a C–N bond as well.[8,9] Thus, thermal alkene + NO_2 chemistry in gas and solution phase involves addition of NO_2 to the double bond to form a nitroalkyl radical as the first reaction step, in contrast to vibronically induced chemistry of NO_2·ethylene and NO_2·butene pairs,[1,2] which is initiated by O-atom transfer according to our results. This difference between matrix- and fluid-phase chemistry is particularly intriguing in view of the fact that NO_2 excited by low-energy visible photons has predominantly the character of a highly vibrationally excited electronic ground-state species. Hence one would expect its chemistry to be similar to that of thermally excited $NO_2(^2A_1)$.

Before interpretation of this interesting situation, it is useful to explore the question as to why, in the case of the photoinduced reaction in the matrix, the system prefers O-atom transfer with its ≈45 kcal mol^{-1} barrier over electrophilic addition of NO_2 to the CC double bond with a much lower, approximately 15 kcal mol^{-1} barrier that would directly yield alkyl nitrite radical (Figure 5). An answer may be furnished by the correlation of the reactant and product electronic states. Restricting to σ- and π-orbitals of electrons on C, O, and N atoms that are involved in bond making and breaking and assuming $N{-}O{\cdots}C{=}C$ as the reaction plane (Salem correlation diagram),[34-36] we find that conservation of symmetry with respect to that plane results in correlation of $NO_2(^2A_1)\cdot C_2H_4(S_0)$ with zwitterionic biradical (Z_2) and excited $NO(^2\Delta)$.[37] On the other hand, excited $NO_2(^2B_2)\cdot C_2H_4(S_0)$ correlates with ground-state $\dot{C}H_2-CH_2-\dot{O}$ ($^1D(\sigma\sigma)$)·$NO(^2\pi)$. Similarly, $NO_2(^2A_1)\cdot C_2H_4(S_0)$ correlates with a highly excited, zwitterionic state of $\dot{C}H_2-CH_2-ONO$, while $NO_2(^2B_2)\cdot C_2H_4(S_0)$ correlates with electronic ground-state ethyl nitrite radical. Hence reaction of ground-state $NO_2(^2A_1)\cdot C_2H_4(S_0)$ pairs either to ground-state $\dot{C}H_2-CH_2-\dot{O}(^1D(\sigma\sigma))$ + $NO(^2\pi)$ or to ground-state ethyl nitrite radical involves the same type of avoided crossing.[38] We conclude that electronic-state correlations alone do not yield an explanation as to why O-atom transfer in the sustained collisional pair prevails over electrophilic addition.

The most likely explanation for the preference of O-atom transfer in the case of the $C_2H_4 + NO_2$ matrix reaction is furnished by consideration of the types of reactant nuclear motions involved in the two possible reaction paths. As discussed above, NO_2 prepared at long visible wavelengths is a highly vibrationally excited species. With a spatially fixed CC double bond nearby, NO_2 in a highly excited stretch overtone level performs a motion that would have a strong component along the reaction coordinate to O-atom transfer (extension of N–O bond, shortening of C–O bond). In contrast, the reaction coordinate for addition of NO_2 to the C=C bond to form a nitrite radical would be reactant translational motion, which in the matrix would correspond to a van der Waals motion of the cage partners. The energy of the photoexcited NO_2 is indeed expected to dissipate to the bulk phonon bath via localized phonon modes, van der Waals modes being among them. The finding that no direct addition of NO_2 to the alkene bond takes place may be due to the fact that accumulation of the very large number of quanta in the van der Waals mode that are needed to reach an excitation exceeding 15 kcal mol^{-1} is very improbable. The coupling among localized phonon modes and between these and bulk photon modes may be sufficiently strong to prevent buildup of high levels of excitation in a single mode. Therefore we believe that in the case of the C_2H_4 + NO_2 matrix reaction O-atom transfer prevails over electrophilic addition because of the type of nuclear motion that is initiated by reactant photoexcitation. On the other hand, under conditions where translational degrees of freedom are accessible, such as in gas or solution phase, the lower barrier, addition mechanism does prevail. The fact that nitroalkyl and not alkyl nitrite radicals are formed upon thermal NO_2 + alkene reaction in the fluid phase is a consequence of the fact that $NO_2(^1A_1)$·alkene (S_0) correlates with ground-state nitroalkyl radical but not with ground-state alkyl nitrite radical, as discussed above.

2.4. Comparison with $O(^3P)$ + Ethylene Reaction. In light of the proposed intermediacy of an oxirane biradical, it is interesting to compare the $C_2H_4 + NO_2$ matrix photochemistry with the well-studied $O(^3P) + C_2H_4$ system. Since extensive CC and CH fragmentation occurs in molecular beam[40-43] and bulk gas,[31,39,44-46] the initial short-lived adduct can only be inferred and is assumed to be triplet $\dot{C}H_2-CH_2-\dot{O}$, as it is for reaction in cryogenic condensed phase.[47,48] Triplet oxirane biradical undergoes two competing proceses, namely H elimination to give "vinoxy" radical and intersystem crossing to yield singlet $\dot{C}H_2-CH_2-\dot{O}$. The latter undergoes internal H shift to give acetaldehyde or ring closure to form ethylene oxide. Under conditions where

---

[34] Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486.

[35] Dauben, W.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

[36] Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982; p 136.

[37] Okabe, H. *Photochemistry of Small Molecules*; Wiley: New York, 1978; p 175.

[38] For NO_2 excited at long visible wavelengths the crossing along both paths is strongly avoided, however, because of some $^2B_2$ admixture of the photoexcited levels.

[39] Cvetanovic, R. J.; Singleton, D. L. *Rev. Chem. Intermed.* **1984**, *5*, 183.

[40] Kleinermanns, K.; Luntz, A. C. *J. Phys. Chem.* **1981**, *85*, 1966.

[41] Buss, R. J.; Baseman, R. J.; He, G.; Lee, Y. T. *J. Photochem.* **1981**, *17*, 389. Schmoltner, A. M.; Chu, P. M.; Brudzynski, R. J.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 6926.

[42] Clemo, A. R.; Davidson, F. E.; Duncan, G. L.; Grice, R. *Chem. Phys. Lett.* **1981**, *84*, 509.

[43] Clemo, A. R.; Duncan, G. L.; Grice, R. *J. Chem. Soc., Faraday Trans 2* **1982**, *78*, 1231; **1983**, *79*, 637.

[44] Endo, Y.; Tsuchiya, S.; Yamada, C.; Hirota, E.; Koda, S. *J. Chem. Phys.* **1986**, *85*, 4446.

[45] Smalley, J. F.; Nesbitt, F. L.; Klemm, R. B. *J. Phys. Chem.* **1986**, *90*, 491.

[46] Sridharan, U. C.; Kaufman, F. *Chem. Phys. Lett.* **1983**, *102*, 45.

[47] Hirokami, S.; Cvetanovic, R. J. *Can. J. Chem.* **1973**, *51*, 373.

[48] Ponomarev, A. N. *Kinet. Katal.* **1966**, *7*, 237.

collisional deactivation is insufficient, these hot oxidation products fragment and lead to further secondary chemistry. When the C_2H_4 + $O(^3P)$ reaction was conducted at 77 K in liquid nitrogen[47] or at 65 K in solid ethylene,[48] only acetaldehyde and ethylene oxide were observed. Interestingly, the ethylene oxide/acetaldehyde branching ratio in both condensed phase experiments was found to be around 1, hence much higher than in the case of direct photolysis of $C_2H_4{\cdot}NO_2$ in solid Ar reported here. This could be due to the fact that in the case of the $O(^3P)$ reaction the triplet biradical that precedes singlet $\dot{C}H_2{-}CH_2{-}\dot{O}$ is born with up to 22 kcal mol^{-1} more excess internal energy than the biradical form upon photolysis of $C_2H_4{\cdot}NO_2$ pairs. Moreover, for $O(^3P)$ + C_2H_4 all singlet $\dot{C}H_2{-}CH_2{-}\dot{O}$ precursor of acetaldehyde and ethylene oxide is formed by intersystem crossing from triplet oxirane biradical but not in the case of the C_2H_4 + NO_2 reaction.

V. Conclusions

The main results of this study of the $C_2H_4{\cdot}NO_2$ reaction in a matrix are (a) chemical trapping by combination with NO, of the prototype transient oxirane biradical $\dot{C}H_2{-}CH_2{-}\dot{O}$, and (b) the finding that reactant vibrational energy plays an essential role in the long-wavelength visible light induced reaction of $C_2H_4{\cdot}NO_2$ sustained collisional pairs. The latter conclusion is based on the photolysis wavelength dependence of the reaction quantum efficiency. Moreover, our results indicate that high vibrational excitation of NO_2·ethylene pairs opens up a new reaction path, namely O-atom transfer, while lower energy, addition paths that are operative in thermal gas- and solution-phase reaction remain suppressed. This has interesting implications for controlled chemical synthesis of photoexcitation of reactants below their dissociation threshold while they are held together in a sustained collision in a matrix.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76 SF00098. K.S. was supported by a grant from the Japan–U.S. Cooperative Photoconversion and Photosynthesis Research Program. We thank the late Professor George C. Pimentel for invaluable support.

Xenon Matrix Photochemistry of 1,1-Dichloroethene: Matrix-Dependent Surface Crossing and Hydrogen-Bonding Geometries

Sandra L. Laursen*,† **and George C. Pimentel**‡

Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 *(Received: March 20, 1990)*

The photoproducts of 1,1-dichloroethene (DCE) in Xe matrix at 12 K differ from those observed in Kr. With 239-nm photolysis, chlorine is eliminated from 1,1-DCE in solid Xe, but not in Kr, although HCl elimination and DCE isomerization occur in both matrices. Just as in the 1,2-dichloroethenes, Cl_2 elimination proceeds in the heavy Xe matrix via spin–orbit-enhanced intersystem crossing to a triplet reaction surface. At higher photolysis energies, a novel product appears in Xe and is identified with the aid of isotopic substitution as a second $HCl{\cdot}C_2HCl$ isomer, σ-hydrogen-bonded through the acetylenic proton. The product dependence on wavelength, parent, and matrix indicates that it is formed through a triplet-surface process under geometric constraints specific to the 1,1 isomer. Loss of Cl from a dissociative triplet state to form an excited chlorovinyl radical, with further cage reaction of the energetic fragments, is postulated.

Introduction

Photoelimination of HCl is the major reaction pathway for chloroethenes under both direct and $Hg(^3P)$-sensitized photolysis, in matrices[1-4] as well as in the gas phase.[5-7] These prior studies, along with the availability of IR spectra and excited-state energies for many of the possible reactants and products, contribute to the overall suitability of these molecules for investigation of photochemical dynamics in a matrix. For matrix-isolated dichloroethenes (DCEs) in particular, Cartland and Pimentel showed that all three isomers exhibit different photochemistry depending on the multiplicity of the reaction surface excited, the singlet via direct excitation or the triplet surface via $Hg(^3P)$ sensitization.[3] To further probe this surface dependence without the complicating factor of metal atom photoreaction, the xenon matrix studies were initiated.[8] The 1,2-dichloroethenes were examined first, as their chemistry was found to be simpler, apparently due to the minimal involvement of free-radical processes,[3] and these were found to demonstrate dramatically the effect of a heavy-atom matrix on the photoproduct distribution.[8]

Our interpretation of the xenon matrix effect as matrix-induced intersystem crossing is most easily confirmed through study of the third member of the family, 1,1-dichloroethene. The *cis*- and *trans*-DCE isomers are expected to, and do, exhibit similar photochemistry because they lie in proximity along a simple reaction coordinate, rotation about the C═C bond. The geometry of 1,1-dichloroethene places it on a quite distinct portion of the ground-state surface, yet it shares with the 1,2 isomers many of the same, well-characterized, possible photoproducts, intermediates, and excited states. This provides an opportunity to generalize and further characterize the matrix heavy-atom effect without a simultaneous drastic change of absorption curves, reaction rates, and other factors—to survey familiar territory from a different benchmark. Furthermore, the 1,1-DCE isomer is of interest because both the observed elimination processes are geometrically limited: HCl to the α,β route and Cl_2 to the α,α route. This contrasts with the 1,2 isomers, for which only chlorine elimination geometry is defined by the precursor structure.

We present here the photochemistry of 1,1-dichloroethene in Xe matrix, with comparison to the results in solid Kr. As expected, we observe xenon-induced photoproduct changes similar to those

---

(1) Warren, J. A.; Smith, G. R.; Guillory, W. A. *J. Photochem.* **1977**, *7*, 263.
(2) McDonald, S. A.; Johnson, G. L.; Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1980**, *102*, 2892.
(3) Cartland, H. E.; Pimentel, G. C. *J. Phys. Chem.* **1986**, *90*, 5485.
(4) Cartland, H. E.; Pimentel, G. C. *J. Phys. Chem.* **1990**, *94*, 536.
(5) Berry, M. J. *J. Chem. Phys.* **1974**, *61*, 3114.
(6) Ausubel, R.; Wijnen, M. H. J. *Int. J. Chem. Kinet.* **1975**, *7*, 739; *J. Photochem.* **1975**, *4*, 241; *J. Photochem.* **1976**, *5*, 233.
(7) Bellas, M. G.; Wan, J. K. S.; Allen, W. F.; Strausz, O. P.; Gunning, H. E. *J. Phys. Chem.* **1964**, *68*, 2170.
(8) Laursen, S. L.; Pimentel, G. C. *J. Phys. Chem.* **1989**, *93*, 2328 ("1").

---

† Present address: James Franck Institute, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637.

‡ Deceased.

0022-3654/90/2094-8175$02.50/0 © 1990 American Chemical Society