J. Phys. Chem. **1987**, *91*, 1347–1354

Absorption Spectra of Contact-Charge-Transfer Bands and Photochemical Reactions of Simple Alkenes in the Cryogenic Oxygen Matrix

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(Received: August 18, 1986)

The UV–vis absorption spectra and photochemistry of alkene–oxygen pairs in solid oxygen at 10 K have been studied. The contact-charge-transfer (CCT) bands well separated from the intrinsic absorption bands of isolated alkenes were recorded with the maxima at 218, 243, 234, 235, 263, and 287 nm for propene, 2-methylpropene (MP), *cis*-2-butene (CB), *trans*-2-butene (TB), 2-methyl-2-butene (MB), and 2,3-dimethyl-2-butene (DMB), respectively. The vertical transition energy correlated linearly with the ionization potential of the alkenes. Photochemical reaction products in the excitation within the CCT bands were studied by using FTIR. The reaction in the ion pair state can be classified into the following four pathways: (i) photooxygenation to give an oxygen adduct, which is observed only for DMB; (ii) cis–trans isomerization, which is the major reaction path for CB and TB, suggesting the crossing to the alkene triplet state; (iii) double-bond scission to give two corresponding carbonyl compounds, which is observed for all alkenes studied with energy threshold higher than the photooxygenation and cis–trans isomerization; (iv) formation of CO_2, CO, and O_3, which occurs at still shorter wavelength than the double-bond scission. In the case of ethene and propene, HO_2 was also produced. Relevance of the present results to those in the CCT photochemistry in the oxygen-saturated organic liquid and on the semiconductor surfaces has been discussed.

Introduction

Recent investigation[1] from this laboratory has described the photooxidation reaction of 2,3-dimethyl-2-butene in the cryogenic oxygen matrix. The reaction has been characterized by the process via excitation of a contact-charge-transfer (CCT) complex with oxygen ($D^+\cdots O_2^-$). This observation prompted us to study the photochemistry of a series of hydrocarbons in solid oxygen since it is hoped to give insight into the photocatalytic oxidation process on metal oxide surfaces which has been thought[2,3] to contribute to the atmospheric degradation of organic compounds under certain conditions and has been proposed[4] to proceed via a similar ion pair ($D^+ + O_2^-$) as a reaction intermediate. Photooxidation of organic compounds via excitation of CCT pairs has also been studied[5] in liquid solution with a mechanistic interest. Photochemistry in these phases, however, suffers the obscurity due to the complex nature of surfaces and incorporation of solvent into reaction. Photochemistry in the cryogenic oxygen matrix could hopefully provide a model reaction via an excited charge-transfer state or an ion pair state without suffering complications due to surfaces and solvents. Absorption spectra and photolysis of C_2H_4–O_2 mixtures in liquid Ar at 87 K have been reported by Buschmann.[6] Formation of ozone by photolysis at 206.2 nm was studied, but no other reaction product was reported. The CCT bands of aromatic molecules in the oxygen matrices have been reported by Rest et al.[7]

Photochemistry in the oxygen matrix is also of interest from the view that new reaction channels and new intermediates might be observed, and has been investigated by Lee and co-workers for formaldehyde,[8a] glyoxal,[8b] and sulfur-containing compounds,[8c–e] and by Bandow and Akimoto[9] for ketene. A photochemical reaction induced by direct excitation of singlet oxygen bands has been studied by Frei and Pimentel[10] on dimethylfuran.

In the present study, photochemistry of a series of alkenes, ethene, propene, 2-methylpropene (MP), *cis*-2-butene (CB), *trans*-2-butene (TB), 2-methyl-2-butene (MB), and 2,3-dimethyl-2-butene (DMB), has been studied in the cryogenic oxygen matrix at 10 K. Prominent CCT bands of simple alkenes well separated from the intrinsic absorption bands of isolated molecules have been recorded. The product distribution for each alkene will be presented as a function of excitation energy. The characteristics of the CCT photochemistry of simple alkenes in solid oxygen will be discussed.

Experimental Section

Cryostat. The details of the cryostat system used have been described previously.[9] A sample plate made of sapphire for UV–vis or CsI for IR measurement was set in the cold head and positioned at the angles of 45° toward two pairs of optical windows. One pair of windows was fitted with quartz plates for UV–vis measurement and irradiation, and the other with KBr crystals for IR measurement. The cryostat chamber was maintained at $\sim 10^{-6}$ Torr before each cooling cycle. An evacuation port of the cryostat chamber was closed below 100 K, and the deposition and irradiation of the sample were made at 10 K without evacuation in order to avoid back diffusion of contaminants.

UV–vis Spectral Measurement. Optical transparency of a matrix is important to obtain a good UV–vis spectrum. An ordinal slow deposition method produces a matrix with low transmittance especially in a UV region due to optical scattering. To minimize the optical scattering, a pulsed deposition method similar to those used by Perutz and Turner[11] and Rest et al.[7] was employed. Ten portions of an alkene–oxygen gas mixture (1:250) with volumes of a few cubic centimeters loaded from a 4-L glass bulb at a pressure of 80 Torr were deposited successively on the sapphire plate at 10 K. The total amount of the mixture deposited was ca. 0.25 mmol. Each deposition took 30 s with a 90-s interval. No temperature increase was observed during the deposition. The spectrum was measured through the quartz window with a UV–vis spectrophotometer (Hitachi, 220A) communicating with a data processing system (NEC, PC-9800 system). The spectral range measured was 200–900 nm with a resolution of 2 nm. A spectrum of pure solid oxygen prepared under the same condition was also measured as a reference. Net absorption spectra were obtained by subtracting the pure oxygen reference from spectra of the mixture matrices.

Photochemical Experiments. For the photochemical experiments, a 500-W high-pressure mercury arc lamp was used as a light source. A water cell (15 cm in length) with a pair of Suprasil quartz windows and an interference band-pass filter combined with a suitable cut filter were used to remove the infrared radiation

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(1) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 529.
(2) Sancier, K. M.; Wise, H. *Atmos. Environ.* **1981**, *15*, 639.
(3) Takeuchi, K.; Yazawa, T.; Ibusuki, T. *Atmos. Environ.* **1983**, *17*, 2253.
(4) Sancier, K. M.; Morrison, S. R. *Surf. Sci.* **1979**, *83*, 29.
(5) Onodera, K.; Furusawa, G.; Kojima, M.; Tsuchiya, M.; Aihara, S.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron* **1985**, 2215.
(6) Buschmann, H. W. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 1344.
(7) Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 265.
(8) (a) Diem, M.; Lee, E. K. C. *J. Phys. Chem.* **1982**, *86*, 4507. (b) Tso, T.-L.; Lee, E. K. C. *Ibid.* **1984**, *88*, 5465. (c) Sodeau, J. R.; Lee, E. K. C. *Ibid.* **1984**, *84*, 3758. (d) Tso, T.-L.; Lee, E. K. C. *Ibid.* **1984**, *88*, 2776. (e) Tso, T.-L.; Lee, E. K. C. *Ibid.* **1984**, *88*, 2781.
(9) Bandow, H.; Akimoto, H. *J. Phys. Chem.* **1985**, *89*, 845.
(10) Frei, H.; Pimentel, G. C. *J. Chem. Phys.* **1983**, *79*, 3307.
(11) Perutz, R. N.; Turner, J. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 452.

0022-3654/87/2091-1347$01.50/0

TABLE I: Relative Reaction Rates and Products Observed in the Irradiation of Alkenes in Cryogenic Oxygen Matrices

alkene	reaction threshold[a]/nm	rel reaction rates[b] 254 nm	rel reaction rates[b] 297 nm	products
ethene	237 ~ 220[c]			CO_2, CO, HO_2, O_3
propene	254 ± 17	0.032		CH_3CHO, HCHO, CO_2, CO, HO_2, O_3
2-methylpropene	297 ± 17.5		0.003	$(CH_3)_2CO$, HCHO, CO_2, CO, O_3
cis-2-butene	322 ± 12	0.43	0.045	*t*-2-C_4H_8, CH_3CHO, CO_2, CO, O_3
trans-2-butene	333 ± 19.5	0.41	0.005	*c*-2-C_4H_8,[d] CH_3CHO, CO_2, CO, O_3
2-methyl-2-butene	364 ± 20		0.088	$(CH_3)_2CO$, CH_3CHO, CO_2, CO, O_3
2,3-dimethyl-2-butene	500 ~ 532	0.27	0.27	TMT,[e] $(CH_3)_2CO$, CO_2, CO, O_3

[a] Specified by the center wavelength and bandwidth of the interference filter and by the wavelength of 10% transmittance of the long-pass filter. [b] Defined as a first-order decrease rate of the integrated absorbance of a reactant IR band being normalized to the photon flux at each wavelength. Apparent decrease of integrated absorption coefficient due to photochemical annealing has not been corrected. See text. [c] The slow reaction due to the oxygen atom or $O_2(^3\Sigma_u^+)$ was observed at 254 nm. See text. [d] *cis*-2-C_4H_8 was a sole product at 297 and 334 nm. [e] TMT (tetramethyl-1,2,3,4-tetraoxane) was a sole product at 406 and >500 nm.

and to isolate an appropriate wavelength region for excitation. The maximum transmission wavelength and the band width at half-maximum of the filter and the irradiance at the center of the sample plate are as follows: >620 nm (an interference long-pass filter combined with Corning 0-52, irradiance not measured), 579 ± 11.5 nm (14.7 mW/cm^2); >500 nm (an interference long-pass filter combined with Corning 0-52, irradiance not measured), 434 ± 16 nm (14.5 mW/cm^2), 406 ± 18 nm (9.1 mW/cm^2), 364 ± 20 nm (6.4 mW/cm^2), 333 ± 19.5 nm (0.90 mW/cm^2), 322 ± 12 nm (1.3 mW/cm^2), 310 ± 15.5 nm (5.2 mW/cm^2), 297 ± 17.5 nm (3.8 mW/cm^2), 254 ± 17 nm (0.54 mW/cm^2), >220 nm (Corning 9-54, irradiance not measured). About 0.8 mmol of an alkene–oxygen mixture (1:250) was deposited on the CsI plate at 10 K with a flow rate of 1 mmol/h for each photochemical run. IR absorption spectra were measured before and after each irradiation by FT-IR (Nicolet, 7199 system) under the condition of 0.5 cm^{-1} of resolution with a liquid N_2 cooled HgCdTe detector; the spectrum range studed was 4000–700 cm^{-1}.

An IR absorption spectrum of tetramethyl-1,2-dioxetane in an oxygen matrix was obtained as a reference. An all-glass deposition line leading to a PTFE nozzle in the cryostat was used in order to minimize the decomposition of the dioxetane. Authentic dioxetane was vaporized at 255–260 K from a sample tube connected about 40 cm before the PTFE nozzle. The vapor was swept into the cryostat with oxygen. Relative integrated absorption coefficients of CB, TB, CH_3CHO, CO, CO_2, and O_3 were determined by the spectra of standard mixtures, CB–CH_3CHO–CO–CO_2 (5:5:5:1), O_3–CO–CO_2 (5:5:2), and CB–TB (1:1) in solid oxygen (M/R ratio of 250) for the purpose of determining the yields of products in the CB–O_2 system. Frequency ranges of the bands used for the quantitative analysis were 1387.4–1382.8 (CB), 1382.8–1376.0 (TB), 1780–1715 (CH_3CHO), 2350–2335 (CO_2), 2150–2130 (CO), and 1046–1030 cm^{-1} (O_3).

Materials. Ethene, propene, MP, CB, TB, CO, and CO_2 (all from Takachiho, research grade) were used after degassing. Two liquid alkenes, MB (Wako) and DMB (Aldrich), were degassed and purified by trap-to-trap distillation. Oxygen (Nippon Sanso, research grade) was passed thorough a spiral glass tube at liquid nitrogen temperature. Authentic sample of tetramethyl-1,2-dioxetane was synthesized by the method of Kopecky.[12] Degassed acetaldehyde (Wako, 80% aqueous solution) in a sample tube cooled at about 270 K was distilled trap to trap repeatedly to obtain water-free acetaldehyde.

Results

UV–vis Spectra of Alkenes in Oxygen Matrices. Figure 1 depicts "net" absorption spectra of the simple alkenes in the oxygen matrix (1/250) when 0.25 ± 0.01 mmol of each sample was deposited. The spectra were obtained by subtracting the reference spectrum of pure oxygen whose apparent optical densities were 1.71 at 200 nm, 1.06 at 220 nm, 0.60 at 250 nm, and 0.27 at 300 nm. In addition to the Herzberg band ($A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$) absorption of O_2 (<270 nm),[6] surface scattering contributes to the optical density in the shorter wavelength region. Figure 1 demonstrates the CCT bands of the alkene–oxygen pairs in solid oxygen as will be discussed later. The absorption maxima are clearly seen at 218 nm (optical density, 0.16) for propene, 243 nm (0.14) for MP, 234 nm (0.20) for CB, 235 nm (0.24) for TB, 263 nm (0.17) for MB, and 287 nm (0.36) for DMB. In the case of DMB, a long tail extending into the visible region to about 550 nm was observed as reported in our previous letter.[1]

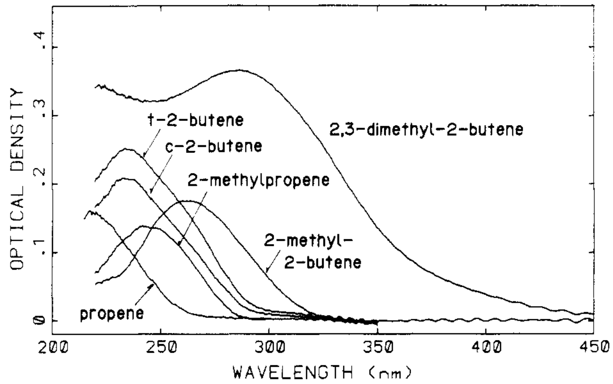

Figure 1. UV–vis absorption spectra of alkene–O_2 systems (M/R = 1/250) at 10 K, obtained by subtracting a pure oxygen reference from original spectra.

The oscillatory structures in the long-wavelength part as shown in Figure 1 are artifacts of the optical fringe caused by interference. The thickness of the matrix can be estimate from the intervals of the fringe. The average thickness of matrices thus estimated is 5.61 ± 0.06 μm. Assuming that the sample plate of 2.0 cm diameter is covered evenly, the amount of sample actually deposited on the plate is estimated to be 0.078 mmol from the thickness and the density of solid oxygen (d = 1.426 at 21 K), which can be compared with the total amount of deposition of 0.25 mmol. Thus, the deposition efficiency is calculated to be 31%. The concentration of alkene in solid O_2 can be calculated to be 0.178 mol/L from the M/R ratio and the density. Then, the molar absorption coefficients (ϵ) of the CCT bands at their absorption maxima can be estimated from the thickness of the matrix and the concentration of alkene in solid oxygen by using the absorbance given in Figure 1: propene, 1.5 × 10^3; CB, 1.8 × 10^3; TB, 2.2 × 10^3; MB, 1.5 × 10^3; and DMB, 3.3 × 10^3 l mol^{-1} cm^{-1}.

Photochemical Reactions. Excitation of the alkene/oxygen matrices within the absorption bands shown in Figure 1 induced photochemical reaction in all the cases studied. The long-wavelength thresholds of the reactions as expressed by the central wavelengths of optical filters are shown in Table I and are found to coincide approximately with the absorption threshold within the range of the bandwidth of the interference filters. Table I also shows the relative photolysis rates of alkenes at 254 and 297 nm normalized to the photon flux.

Figures 2–5 show the IR spectra sets of reactants and products for ethene and propene, CB and TB, MP and MB, and DMB, respectively. The product spectra were obtained by partial sub-

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(12) Kopecky, K. R.; van de Sande, J. H.; Mumford, C. *Can. J. Chem.* **1968**, *46*, 25.

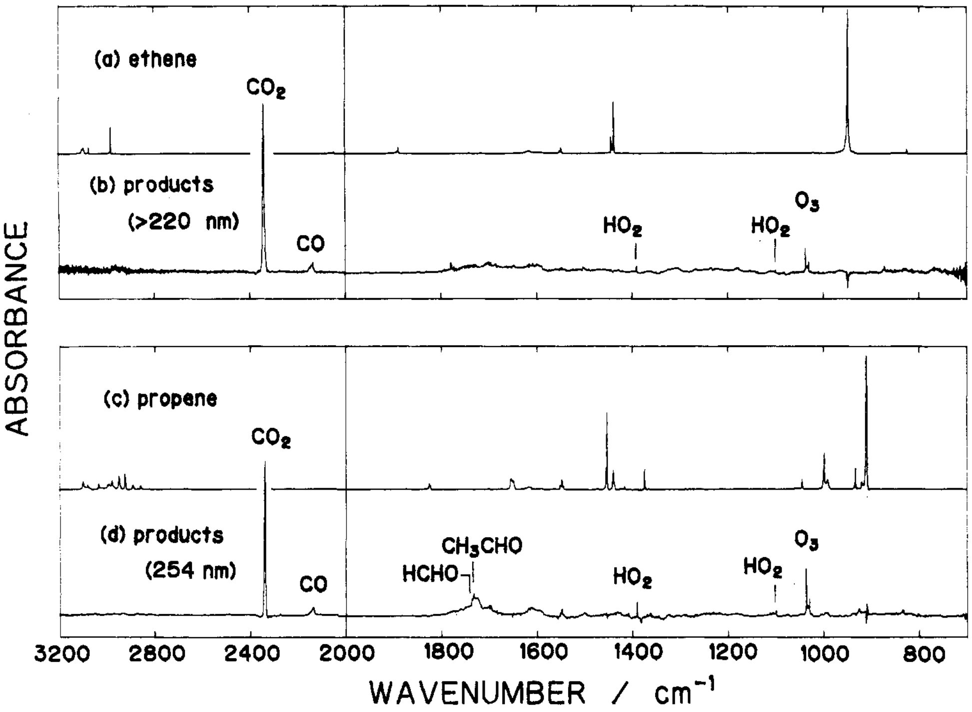

Figure 2. IR absorption spectra of (a) ethene in O_2 matrix (1/250); (b) the photochemical reaction products after the irradiation at >220 nm for 120 min; (c) propene in O_2 matrix (1/250); and (d) the photochemical reaction products after the irradiation at 254 nm for 190 min.

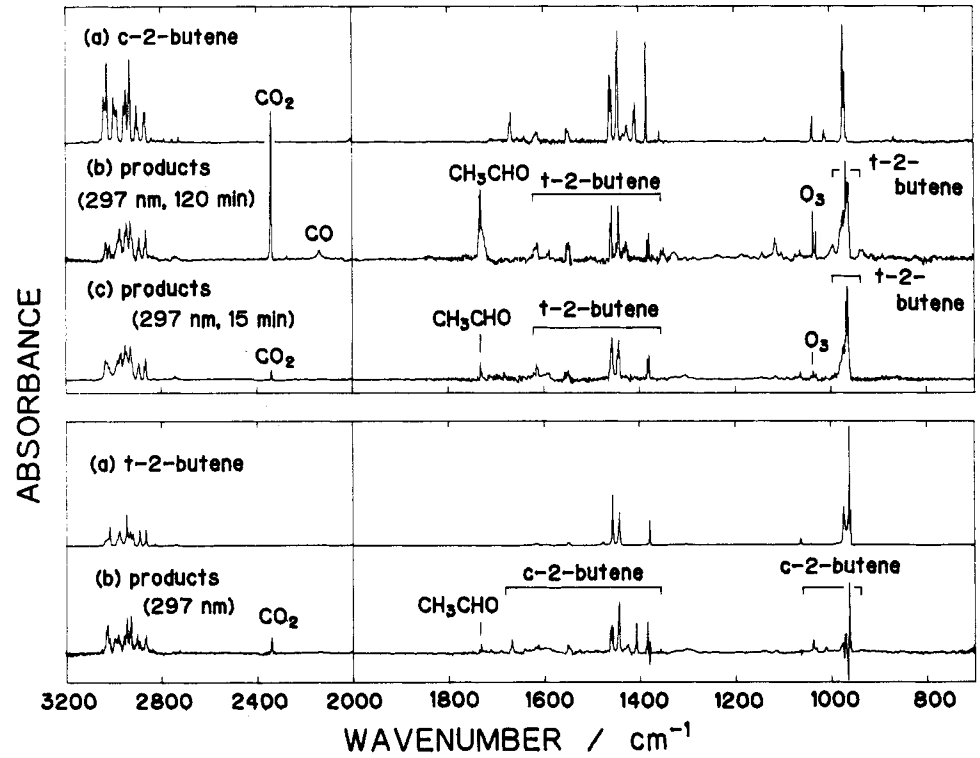

Figure 3. IR absorption spectra of (a) *cis*-2-butene in O_2 matrix (1/250); (b) the photochemical reaction products after the irradiation at 297 nm for 120 min; (c) at 297 nm for 15 min; (d) *trans*-2-butene in O_2 matrix (1/250); and (e) the photochemical reaction products after the irradiation at 297 nm for 140 min.

traction of the reactant spectra from those of reaction mixtures after irradiation at the specified excitation wavelengths. For these experiments irradiation time was controlled so as to cause typically 30% decrease of reactants. A standard spectrum of tetramethyl-1,2-dioxetane is also shown in Figure 5d as a reference.

Reaction products observed in the irradiation of simple alkenes in the oxygen matrix are summarized in Table I. Photolysis of ethene in solid oxygen occurred at >220 nm and formed CO_2, CO, HO_2, and O_3 as shown in Figure 2b. Trace peaks at 1740.1 and 1734.9 cm^{-1} may be due to formaldehyde (1740.0 cm^{-1})[13] and performic acid (1735.0 cm),[13] respectively. Other than these products, peaks at 1779.6, 1138.3, and 872.9 cm^{-1} are discernible but remain unidentified. Traces of these peaks and O_3 were observed after the long irradiation at 254 nm but none of CO_2, CO, and HO_2 was produced at this wavelength. In the case of propene (see Figure 2d), small amounts of formaldehyde and acetaldehyde were observed in addition to the same fragmentary products observed for ethene.

Cis–trans isomerization was the major reaction pathway for *cis*- and *trans*-2-butene as seen in Figure 3. It should be noted

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(13) Tso, T.-L.; Diem, M.; Lee, E. K. C. *Chem. Phys. Lett.* **1982**, *91*, 339.

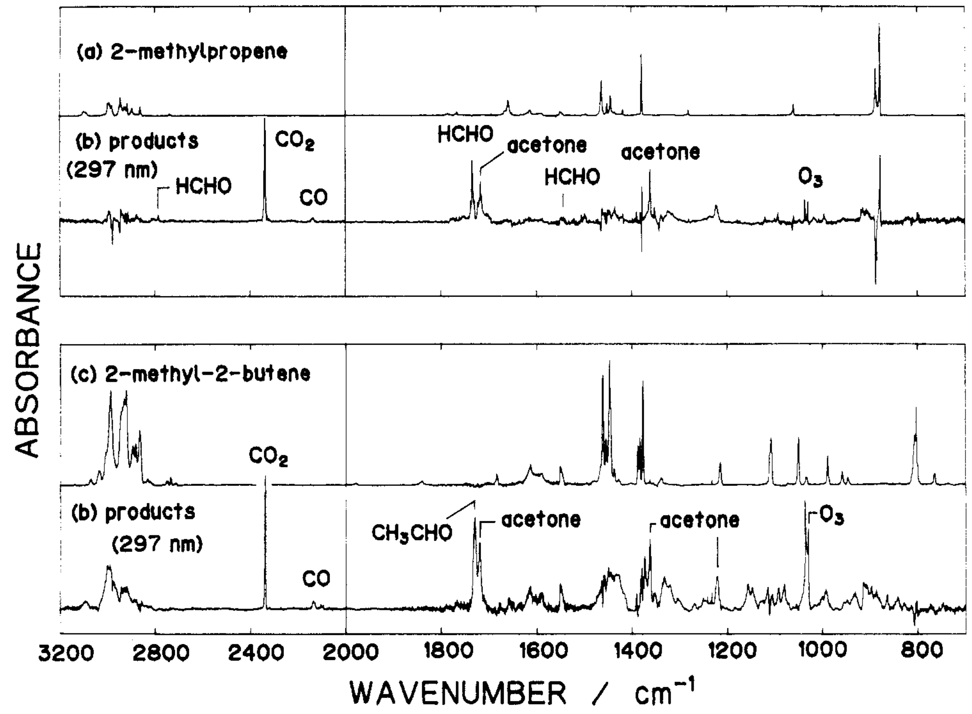

Figure 4. IR absorption spectra of (a) 2-methylpropene in O_2 matrix (1/250); (b) the photochemical reaction products after the irradiation at 297 nm for 180 min; (c) 2-methyl-2-butene in O_2 matrix (1/250); and (d) the photochemical reaction products after the irradiation at 297 nm for 15 min.

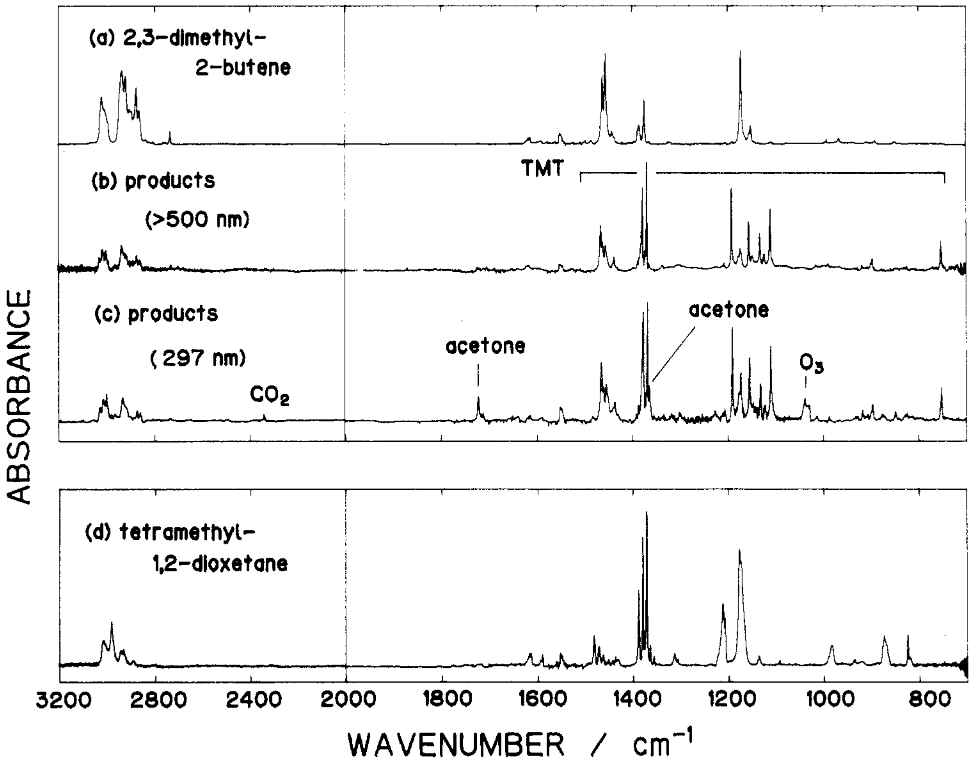

Figure 5. IR absorption spectra of (a) 2,3-dimethyl-2-butene in O_2 matrix (1/250); (b) the photochemical reaction product (TMT) after the irradiation at >500 nm for 30 min; (c) products after the irradiation at 297 nm for 2 min; (d) reference spectra of tetramethyl-1,2-dioxetane in O_2 matrix.

in Figure 1 that CB and TB gave substantially different spectra; the band for TB extends to longer wavelength than that for CB giving lower threshold energy to induce photochemistry (see Table I). The irradiation of TB in solid O_2 at 333 nm gives solely CB as a product while the irradiation of CB at 322 nm gives trace amounts of CH_3CHO, CO_2, and O_3 in addition to TB as a major product. All the fragmentary products, CH_3CHO, CO_2, CO, and O_3, were detected for the prolonged irradiation of both TB and CB at 297 and 254 nm, although their yields remain low as compared to the isomerization. Table II cites the material distributions of reaction mixtures in the CB–O_2 system after the irradiation. The percentage values are based on the relative integrated absorption coefficients of the reactant and products determined for standard mixtures. Although the product yield against the decrease of CB seems very low in Table II, it has been found that the thermal annealing of CB and TB at ~25 K for 3–5 min changes their band shape and decreases the integrated absorbance of their bands by 20–30%. Since the similar change of the band shapes was observed when they were irradiated within the CCT band, their integrated absorbance is also expected to decrease as in the case of thermal annealing. This causes the apparent low percentage value of the abundances of both CB and

TABLE II: Distributions (%) of Reactant and Products after the Irradiation of *cis*-2-Butene in Solid Oxygen Referenced to the Amount of the Reactant before Irradiation[a]

wavelength/ nm	time/ min	reactant and products					
		cis[a]	trans[a]	CH_3CHO	O_3	CO_2	CO
322	180	54	13	trace[b]	trace	trace	ND[c]
297	15	70	12	0.5	1.0	0.1	ND
254	10	77	6	0.2	0.2	trace	ND
254	30	48	11	1.1	1.6	0.2	trace

[a] Decrease of the integrated absorption coefficients of the bands of *cis*- and *trans*-2-butene due to photochemical annealing has not been corrected giving underestimated values for these compounds. [b] Lower than 0.1%. [c] Not detected.

TB in Table II since the values in the table are referenced to the relative integrated absorbance of the unannealed samples. If the corrections due to such effect are taken into account, both abundances of CB and TB after the irradiation should increase to give much higher yield of TB and thus to improve the material balance. The change of the spectral band shape and the apparent decrease of absorbance were not observed when irradiated outside the region of the CCT bands. As expected, the yield of CH_3CHO and other fragmentary products increased to a much higher value after the prolonged irradiation (see Figure 3b,c). It can be noticed in Figure 3b,c that the CO_2 yield relative to CH_3CHO also increases as the irradiation time increases, suggesting the formation of CO_2 via the secondary photolysis of CH_3CHO.

In the case of MP and MB, CH_3CHO and HCHO, and $(CH_3)_2CO$ and CH_3CHO were observed, respectively, as major products as well as other common fragmentary products (see Figure 4). It should also be noted that the substantial change in the spectral band shape of the reactant occurred after the irradiation as evidenced by the partially negative residue of most reactant bands in the product spectra. This feature is especially marked for MP as can be seen in Figure 4b. Although CO_2 is formed even at low conversion both for MP and MB, its yield relative to carbonyl compounds increases as the irradiation time increases, suggesting that secondary photooxidation of the carbonyl products contributes to the CO_2 formation as in the case of CB.

Parts b and c of Figure 5 show the product spectra of the DMB–O_2 system after the irradiation at >500 and 297 nm, respectively. The product spectra show characteristic IR bands at 3050–2800 (m), 1465.6 (m), 1377.1 (s), 1367.9 (vs), 1191.2 (s), 1173.1 (m), 1155.1 (s), 1132.0 (m), 1110.3 (s), 917.9 (w), 896.6 (w), 751.9 (m), and 630.1 (m) cm^{-1}, which has been tentatively identified as tetramethyl-1,2,3,4-tetraoxane (TMT), and adduct of DMB with two oxygen molecules, in our previous paper.[1] This product was found to be stable for the annealing at ~25 K for ~3 min. TMT was the sole product for the excitation at >500 and 406 nm. No reaction occurred for the excitation at 579 and >620 nm. Acetone, CO_2, CO, and O_3 start to appear at 364 nm but remain as minor products even at 297 nm as shown in Figure 5c. The product distribution changed drastically at 254 nm; the above fragment compounds become major products and TMT is seen only as a minor product. Apparently, secondary photolysis of TMT also contributed to the formation of $(CH_3)_2CO$.[1] As seen from the comparison of the product spectra with Figure 6d, tetramethyl-1,2-dioxetane was not formed at all as a product.

Figure 6 demonstrates the relative quantum yield of DMB photolysis as a function of exciting wavelength compared with the absorption spectrum. The relative quantum yield was obtained from the rate of decrease of DMB divided by the photon flux and the absorbance value at each wavelength. As shown in Figure 6, the relative quantum yield increases drastically at <400 nm and reaches an approximately constant value below 334 nm.

Discussion

Contact-Charge-Transfer Spectra. For the CCT absorption, the energy of vertical transition, E_{CT}, obtained from the energy of absorption maxima can be expressed as

$$E_{CT} = I_D - E_A - (\Delta E_E - \Delta E_N) \qquad (1)$$

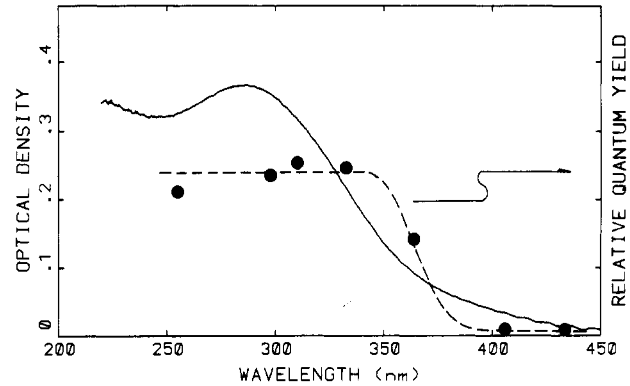

Figure 6. CCT absorption spectrum of 2,3-dimethyl-2-butene/O_2 system and relative quantum yield of the photochemical reaction at specified irradiation wavelengths calculated from apparent first-order decay rate of the reactant, optical density, and irradiance.

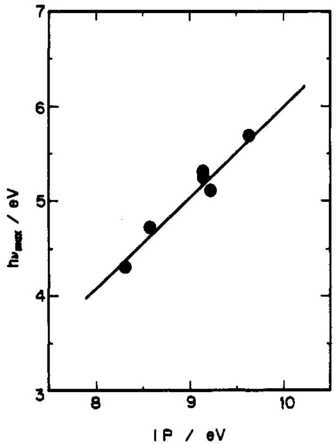

Figure 7. Correlation of the energy of absorption maxima of the CCT spectra of the alkene–O_2 systems against the ionization potential of alkenes. The slope is 0.96 ± 0.11.

TABLE III: Parameters for the CCT Pair of the Alkene–O_2 System

alkene	I_P/eV[a]	E_{CT}/eV[b]	ΔE_E/eV[c]	R_{DA}/Å[c]
ethene	10.51			
propene	9.73	5.69	3.61	3.99
2-methylpropene	9.23	5.11	3.68	3.92
cis-2-butene	9.13	5.30	3.39	4.25
trans-2-butene	9.13	5.28	3.41	4.23
2-methyl-2-butene	8.67	4.71	3.52	4.09
2,3-dimethyl-2-butene	8.30	4.32	3.54	4.07

[a] Data from: Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions"; National Bureau of Standards, June 1969; NSRDS-NBS26. Values determined by a photoionization technique are adopted. Associated errors are typically ±0.02 eV. [b] Determined from the absorption maxima of the CCT bands shown in Figure 1. Associated errors are typically ±0.07 eV. [c] Associated errors for ΔE_E and R_{DA} are estimated to be ±0.1 eV and ±0.12 Å.

according to the expression by Birks et al.[14] Here I_D is the ionization potential of the donor (alkene), E_A is the electron affinity of the acceptor (O_2), ΔE_E is the energy of formation of the excited complex $^3[D^+\cdots O_2^-]$ from D^+ and O_2^-, and ΔE_N is the energy of formation of the ground-state complex $^3[D\cdots O_2]$ from D and O_2. In the present case, the acceptor, O_2, is the same for all alkenes with $E_A(O_2) = 0.440 \pm 0.008$ eV,[15] and ΔE_N is thought to be negligibly small (<0.05 eV). Therefore, when we plot E_{CT} (in eV) against I_D (in eV) for the series of alkenes studied, the correlation is expected to be linear with a slope of unity if the upper

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(14) Birks, J. B.; Pantos, E.; Hamilton, T. D. S. *Chem. Phys. Lett.* **1973**, *20*, 544.

(15) Celotta, R. J.; Bennett, R. A.; Hall, J. L.; Siegel, M. W.; Levine, J. *Phys. Rev.* **1972**, *6*, 631.

state is a charge-transfer state with a potential characterized by a pure Coulombic attraction. Figure 7 demonstrates the linear correlation between the experimental values of E_{CT} and the literature values of I_D (given in Table III) with a slope of 0.96 ± 0.11. Thus, the CCT character of the observed bands in the present study has been established and the upper states are found to be purely Coulombic ion pair states.

The ultraviolet absorption spectra caused by the interaction of organic molecules with oxygen has been well-known since the study of Tsubomura and Mulliken.[16] As for simple alkenes, comparable data are available for MB and DMB in the oxygen-saturated liquid[17] and for propene, MP, TB, MB, and DMB in the vapor phase[18] at 70 atm of O_2. The main features of the CCT bands of DMB in the oxygen-saturated liquid[17] are similar to those obtained in the present study, but a long tail of absorption extending to >500 nm was observed[1] only in solid oxygen. In the vapor-phase spectra,[18] only a long-wavelength edge of the oxygen enhanced absorption has been observed. They were assigned to the T ← N transition for propene, MP, and TB, and to the CCT absorption for MB and DMB.

The CCT absorption spectra for aromatic hydrocarbons in oxygen matrices have been reported by Rest et al.[7] In their experiments, singlet–triplet absorption bands of benzene and toluene have been observed overlapping to the CCT bands. On the contrary, no oxygen-enhanced singlet–triplet absorption[18,19] accompanying a vibrational structure was clearly observed in the range of 280–350 nm for either alkene under our experimental conditions. This result agrees well with the previous data[16,20] that the oxygen-enhanced singlet–triplet absorption bands have much smaller transition moment than those of the CCT bands.

Table III gives the estimated values of ΔE_E calculated from eq 1 using the values of I_D and E_{CT} cited in the table. Further, the energy of formation of an electric dipole pair from two elementary charges is given by Birks et al.[14] as

$$\Delta E_E = 14.41/R_{DA} \text{ eV} \qquad (2)$$

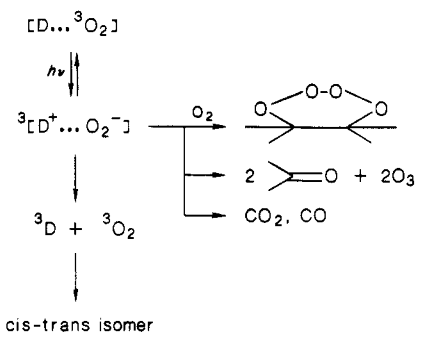
where R_{DA} is the charge separation in Å. R_{DA} values thus calculated from the ΔE_E values neglecting ΔE_N are also given in Table III. Using the van der Waals radii of oxygen atom (1.40 Å) and carbon–carbon double-bond plane (1.70 Å), the separation between the dipole pair may be estimated to be 3.1 or 4.5 Å when the oxygen molecule lies parallel or perpendicular to the plane, respectively. The observed value of 4.1 ± 0.2 Å, being nearly independent of the number of methyl substituents, lies between these values, suggesting that the oxygen molecule lies on the tilt to the double-bond plane in the ground state. The long-wavelength tail of the CCT band for DMB might be due to the DMB–O_2 pair in which O_2 lies parallel to the double-bond plane. For such a CCT pair with a different geometric configuration, the upper-state potential surface would also be different.

An analogous treatment has been made[7] for the CCT pair of aromatic molecules in the oxygen matrices. The values obtained for R_{DA} for benzene and toluene, 4.4 and 4.7 Å (corrected for E_A = 0.44 eV instead of 0.67 eV in the literature) are slightly longer than those for alkenes and closer to the value of perpendicular coordination of oxygen molecule to the aromatic plane.

Photochemistry. The type of reaction products in the photooxidation of simple alkenes in solid oxygen depends on the type of alkene molecule and also on the excitation wavelength. The reaction can be classified into the following four pathways.

(i) Photooxygenation to give an oxygen adduct. This type of reaction was observed only for the DMB–O_2 system. The product, the oxygen adduct, has been identified[1] tentatively as tetramethyl-1,2,3,4-tetraoxane. Absence of the reaction at >620 and 579 nm implies that the photochemistry induced by the direct excitation of the singlet oxygen bands is negligible under our experimental conditions since the excitation wavelength of 579 nm matches well with the (1 ← 0) band of the transition $2O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g^-)$ and the irradiation at >620 nm covers the fundamental band of that transition.

SCHEME I



(ii) Cis–trans isomerization. The cis-to-trans and trans-to-cis isomerization was observed for CB and TB at the excitation wavelength region of 250–300 nm as a major reaction channel. The observation suggests that the triplet alkene was formed after the CCT excitation. The cis–trans isomerization of simple alkenes via triplet state in which two methylene planes are twisted by 90° has long been known,[21] while the isomerization does not occur in the ionic state[22] since the planes are twisted only by ~25°.[23] Therefore, the cis–trans isomerization would be ascribed to the formation of the triplet state of alkene. For other alkenes, the change in the spectral band shape of reactants after the irradiation, particularly noticed for MP and MB, is suggestive of the internal rotation about the double bond, which in turn would indicate the formation of triplet alkenes. It is also interesting to note that the reaction rate of CB was much faster than that of TB at 297 nm, but they are very close at 254 nm as shown in Table I. This fact would be ascribed to the higher barrier of TB for the crossing from the CCT state to the alkene triplet state.

(iii) Double-bond scission to give carbonyl compounds. The C=C double bond scission to give corresponding two carbonyl compounds was observed for all alkenes studied. The wavelength of the reaction threshold for the double-bond scission was shorter than that for the photooxygenation and cis–trans isomerization in case of DMB and TB, respectively. In the reaction of CB, acetaldehyde formation was observed only in a trace amount at the threshold energy of the cis–trans isomerization as shown in Table II. For other alkenes the double-bond scission was observed at any excitation wavelengths within the CCT bands. For 2-butenes, the scission process is much slower than isomerization at all the wavelengths studied.

(iv) Formation of CO_2, CO, HO_2, and O_3. Fragmentation to give CO_2, CO, and HO_2 was observed at the shorter excitation wavelengths than the reaction threshold to form the carbonyl compounds, and its importance increases as the excitation energy increases. This mode was the most important reaction pathway observed for ethene. A part of CO_2 and CO are apparently secondary products via the photooxidation of carbonyl products as judged from the increased yield ratio of CO_2 and CO against the carbonyl compounds for increased irradiation time. However, CO_2 and CO has also been seen in a short reaction time for ethene, propene, MP, and MB. The possibility of initial formation of these products cannot be excluded in these cases. Ozone was always produced when this type of fragmentation was observed. The initial yield of ozone is in general much higher than that of CO_2. About twice as much of acetaldehyde was formed in the reaction of CB at 297 nm as shown in Table II. Formation of ozone has been reported in almost all photooxidation studies[8,9] of organic molecules in solid oxygen.

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(16) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966.

(17) Coomber, J. W.; Hebert, D. M.; Kummer, W. A.; Marsh, D. G.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1970**, *4*, 1141.

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

(19) Evans, D. F. *J. Chem. Soc.* **1960**, 1735.

(20) Chien, J. C. W. *J. Phys. Chem.* **1965**, *69*, 4317.

(21) Cundall, R. B. *Prog. React. Kinet.* **1964**, *2*, 165.

(22) Fujisawa, J.; Sato, S.; Shimokoshi, K.; Shida, T. *J. Phys. Chem.* **1985**, *89*, 5481.

(23) Köppel, H.; Domcke, W.; Cederbaum, L. S.; Niessen, W. V. *J. Chem. Phys.* **1978**, *69*, 4252.

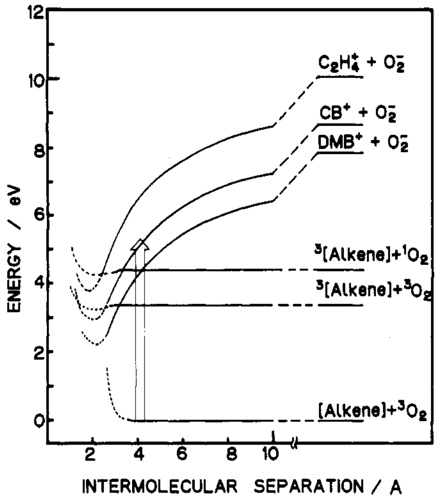


Figure 8. Energy diagram of the alkene–O_2 systems.

Excitation and Reaction Mechanism. Photochemistry of simple alkenes in solid oxygen via excitation of the CCT bands is proposed to be as follows according to the observation described so far (Scheme I). The energy diagram of the system can be visualized as shown in Figure 8.

As shown in Figure 8, the triplet state of simple alkenes lies at ~3.4 eV above the ground state.[18,19] The potential surface correlating to ^{3}[alkene] + $^3O_2$ would cross the ion pair state (excited charge-transfer state) at a certain level whose energy ranges between the above value and ~1 eV higher than this depending on the twisting angle of the methylene–methylene planes. For the alkenes with sufficiently low ionization potential, excitation to the ion pair state lower than the crossing point to the alkene triplet is possible. This is the case only for DMB, and the excitation at 406 and >500 nm gave TMT as a sole product. Although intersystem crossing from the triplet CT surface to the singlet surface correlating to DMB + $^1O_2$ should not be excluded, the relevance of the $^1O_2$ reaction has been excluded in our previous study. Therefore, it can be concluded that the formation of the adduct containing two O_2 molecules is a reaction pathway specific to DMB from the triplet CT state in solid oxygen. Other than the adduct formation, deactivation to the ground-state triplet pair is expected[5] since the ion pair state lies close to the ground state. Low quantum yield of photochemical reaction of DMB at >400 nm as demonstrated in Figure 7 verifies this is actually the case. As the excitation energy increases, the double-bond scission to form two carbonyl compounds starts to occur. This process is thought to proceed through the triplet CCT state rather than after crossing to the triplet state of alkene. The reasoning is as follows: in the case of DMB, a rather sharp increase of the quantum yield of the photochemical decay of reactant at ≤364 nm (see Figure 7) accompanies the increased yield of TMT and the appearance of acetone, but no evidence of triplet formation verified by the change in the band shape was observed. The increase in the reaction quantum yield can be interpreted as the decrease of deactivation process; in the case of *trans*-2-butene, the reaction thresholds of the cis–trans isomerization (333 nm) and the acetaldehyde formation (297 nm) do not coincide.

No adduct was observed except for DMB. TMT type compounds would not be stabilized for the smaller alkenes and further degradation via this type of intermediate would cause double-bond scission to give two carbonyl compounds. Here, it should be noted that ozone formation was observed in many cases in this study. Since the (0–0) transition of the Herzberg bands of O_2 ($A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$) lies at 280.0 nm and the convergence limit of this transition lies at 5.116 eV (242.3 nm),[24] ozone formation through the processes

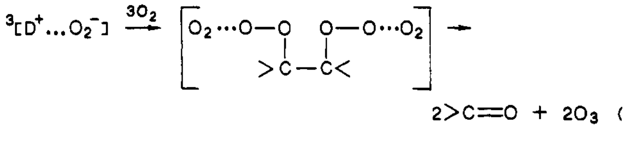
$$O_2(X^3\Sigma_g^-) + h\nu \xrightarrow{280\ \mathrm{nm}} O_2(A^3\Sigma_u^+) \tag{3}$$

$$\xrightarrow{242\ \mathrm{nm}} 2O(^3P) \tag{4}$$

$$O_2(A^3\Sigma_u^+) + O_2(X^3\Sigma_g^-) \rightarrow O_3 + O(^3P) \tag{5}$$

$$O(^3P) + O_2(^3\Sigma_g^-) \rightarrow O_3 \tag{6}$$

are possible only for excitation at wavelengths shorter than those discussed above. Therefore, ozone formation wavelengths longer than 297 nm as observed in CB, TB, MP, MB, and DMB cannot be explained by the excitation of matrix oxygen molecule. Even for the excitation at 254 nm, ozone yield in the presence of alkene is much higher than that for oxygen alone, so that the contribution of the process 5 is minimal at this wavelength. Since the ozone formation in the present study always accompanies the double-bond scission, one possible process could be conceived as



(7)

Only in the case of ethene, the CCT absorption at >220 nm would not be strong enough as compared to the Herzberg transition judged from the absorption spectra in liquid argon presented by Buschmann.[6] Formation of a trace amount of an unidentified product with bands at 1779.6, 1138.3, and 872.9 cm^{-1} at 254 nm suggests that this compound may be a product of the oxygen atom or $O_2(A^3\Sigma_u^+)$ reaction.

For alkenes with the CCT bands starting at 3.9 ± 0.2 eV, i.e., MP, CB, and TB, excitation at 334–254 nm (3.7–4.9 eV) leads to the ^{3}[alkene] + $^3O_2$ state followed by cis–trans isomerization as a major reaction pathway. Direct reaction from the CCT state to form carbonyl compounds, CO_2, CO, and O_3 occurs in parallel with the isomerization as a minor reaction pathway. The photochemistry of MP would be an intermediate case between 2-butenes and DMB.

Comparison with Other Charge-Transfer-State Photochemistry. It would be interesting here to compare the results of our study with those of the photochemistry of the CCT pairs between alkene–O_2 pairs in other media. Although the CCT photochemistry of the ethene–O_2 pair in liquid argon studied by Buschmann[6] is apparently most closely related to ours, unfortunately, only ozone production was studied and no further comparison is possible. Onodera et al.[5] summarized their results of the CCT photochemistry of a series of organic molecule–oxygen pairs in conventional oxygen-saturated organic solution and classified the possible processes into three types: (1) formation of a pair of the substrate cation radical and the superoxide ion; (2) conversion to the triplet substrate and singlet oxygen; and (3) deactivation to the starting materials. The first process, formation of a completely separated ion pair ($D^+ + O_2^-$), is possible only in the polar solvents and is impossible in solid oxygen from energetics in the near-UV region. Thus, while the formation of a certain type of product was interpreted as a result of a radical cation–solvent reaction in their study, our study demonstrated the alkene–O_2 reactions can be directly ascribed to the excited CCT pair in solid oxygen. The second process of the triplet alkene formation was assessed by its cis–trans isomerization in the present study while the singlet oxygen formation due to the $^3(D^+\cdots O_2^-) \rightarrow {}^3D + {}^1O_2$ or $^3(D^+\cdots O_2^-) \rightarrow {}^3D + {}^3O_2 \rightarrow D + {}^1O_2$ processes was assessed by its specific reaction products in their study. The third process of deactivation to the ground state has been observed both in the present cryogenic system and in the room temperature organic solvent. Although the 2,3-dimethylbutene is the species studied commonly in both media, direct comparison of the results is difficult since the excitation of the CCT pair at 313 nm (3.96 eV) in methanol produced $(CH_3)_2C(OCH_3)C(CH_3)_2OH$ and $CH_2=C(CH_3)—C(CH_3)_2OOH$, which were ascribed[5] to the reaction of the radical cation. In solid oxygen, TMT formation was the major process in this energy range.

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[24] Huber, V. P.; Herzberg, G. *Molecular Spectra and Molecular Spectroscopy, IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

Formation of the radical ion pair ($D^+\cdots O_2^-$) has been postulated[4,25] during the course of photooxidation of organic molecules on n-type semiconductor surfaces, e.g., TiO_2, ZnO, CdS, etc., in the presence of oxygen. Although the reaction mechanism on the surfaces could be more complex due to the incorporation of metal ions and oxygen atoms of metal oxides, it is very interesting to note that in these reactions double-bond scission of alkenes to form carbonyl molecules followed by rapid secondary photooxidation to yield CO_2 is often observed.[3,25,26] The marked similarity of the products from photooxidation on semiconductor surfaces and those from CCT pair photochemistry in solid oxygen suggests the importance of the reaction of the radical ion pair state or excited charge-transfer state as a common process. Thus, the photochemistry in cryogenic oxygen matrices could provide information on the prototype of the photooxidation via the excited CCT pair, which might be important in the heterogeneous oxidation of environmental organic compounds.[2,3]

Note Added in Proof. An alternative interpretation for the cis–trans isomerization was proposed by Martinez.[27] The experimental evidence in this study alone does not allow us to distinguish between the mechanism of relaxation via a triplet alkene as suggested in the present study vs. O_2 release from an internally rotated O_2-added biradical as suggested in ref 27.

Registry No. O_2, 7782-44-7; propene, 115-07-1; MP, 115-11-7; CB, 590-18-1; TB, 624-64-6; MB, 513-35-9; DMB, 563-79-1; propene·O_2, 106376-81-2; MP·O_2, 106376-82-3; CB·O_2, 106376-83-4; TB·O_2, 106376-84-5; MB·O_2, 106376-85-6; DMB·O_2, 106376-86-7.

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(25) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, *21*, 467.

(26) Pichat, P.; Herrmann, J.-M.; Disdier, J.; Mozzanega, M.-N. *J. Phys. Chem.* **1979**, *83*, 3122.

(27) Martinez, R. I. *J. Phys. Chem.*, this issue.

The Electronic Spectrum of Thioketene and the Excited-State Structure of Ketene

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(Received: September 2, 1986)

The electronic absorption spectra of thioketene-h_2 and -d_2 in the gas phase have been observed for the first time. Although rotationally diffuse, the spectra are vibronically discrete and analysis suggests an in-plane bent excited-state structure. The results are correlated with previous experimental and theoretical work on ketene.

Introduction

The UV–visible absorption spectrum and the nature of the low-lying electronic states of ketene continue to present a challenge to experimental ingenuity. Below 50 000 cm^{-1}, the electronic spectrum of ketene vapor consists of broad, diffuse bands superimposed on a continuum.[1-3] High-resolution studies under a variety of conditions have not revealed any evidence of structure in these bands.[2] Dixon and Kirby[2] have analyzed the low-frequency vibrational progressions observed among the diffuse bands in terms of two transitions: $^1A'' \leftarrow {}^1A_1$ in the 260–385-nm region and $^3A'' \leftarrow {}^1A_1$ in the 385–475-nm region. Application of Walsh diagrams suggests an in-plane bent excited-state structure. Subsequently, Laufer and Keller[3] reexamined the spectrum and concluded that only the $^1A'' \leftarrow {}^1A_1$ band system was involved. They argue that the excited triplet and singlet electronic term values are less than 19 200 and 21 300 cm^{-1}, respectively. Despite considerable effort,[4] ketene has not been reported to fluoresce or phosphoresce. Therefore, it has not been possible to directly determine the lowest excited-state geometry, vibrational energy levels, or the nature of the electronic transition of ketene by experimental methods.

There have been a large number of ab initio and semiempirical calculations on ketene. These have culminated in a recent, very detailed study of the low-lying electronic states by Allen and Schaefer.[5] Since these authors have reviewed the state of ketene calculations in detail, only a brief outline will be given here. The C_{2v} ground-state occupied orbitals are[6]

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2$$

There are π bonds both in the molecular plane and perpendicular to it and the nonbonding oxygen orbital found in ketones can now conjugate with the C=C system. This fact was recognized in the early ab initio work by Del Bene,[7] in which it was emphasized that the first singlet absorption in ketene should be very different in character from the lowest n → π^* transition in formaldehyde. The $2b_1 \rightarrow 3b_2$ electron promotion involves removal of an electron from a π-type orbital to an unoccupied π^* orbital which lies in the molecular plane. Detailed calculations[5] suggest that the lowest excited states are therefore $^3A''$ and $^1A''$ with an in-plane bent geometry. The oxygen is predicted to be displaced about 50° from the linear CCO configuration and the C=C bond elongated by ~0.15 Å relative to the $\tilde{X}^1A_1$ state. The calculated T_0 values for the $^3A''$ and $^1A''$ states are 16 700 and 19 000 cm^{-1}, supportive of the conclusions of Laufer and Keller.

Confirmation of the theoretical predictions concerning the excited states of ketene is unlikely to come directly from further studies of the diffuse electronic absorption spectrum. However, past experience with thiocarbonyl compounds, in which the oxygen is replaced by a sulfur atom, suggests that the study of the electronic spectrum of thioketene may be a way to advance our understanding of ketene. For example, spectroscopic work on thioformaldehyde has led to the identification of the $\pi \rightarrow \pi^*$ transition, which has never been found in the UV spectrum of formaldehyde.[8] Thioformaldehyde has also been shown to be photochemically inactive in the lowest excited singlet and triplet states,[9] due to the low excitation energies involved ($T_0(^1A_2)$ = 16 394.595 cm^{-1} and $T_0(^3A_2)$ = 14 507.385 cm^{-1} for H_2CS). If the thioketene spectrum is similarly shifted into the visible, it might also be expected to be rovibrationally discrete. Detailed rotational analysis could then establish the nature of the transition and a

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(1) Norrish, R. G. W.; Crone, H. G.; Saltmarsh, O. *J. Chem. Soc.* **1933**, 1533.

(2) Dixon, R. N.; Kirby, G. H. *Trans. Faraday Soc.* **1966**, *62*, 1406.

(3) Laufer, A. H.; Keller, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 61.

(4) Noyes, W. A.; Unger, I. *Pure Appl. Chem.* **1964**, *9*, 461.

(5) Allen, W. D.; Schaefer III, H. F. *J. Chem. Phys.* **1986**, *84*, 2212.

(6) Dykstra, C. E.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 2689.

(7) Del Bene, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 3713.

(8) For a detailed review see Clouthier, D. J.; Ramsay, D. A. *Annu. Rev. Phys. Chem.* **1983**, *34*, 31.

(9) Goddard, J. D. *Can. J. Chem.* **1985**, *63*, 1910.

0022-3654/87/2091-1354$01.50/0