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Matrix Isolation Study of the Early Intermediates in the Ozonolysis of Cyclopentene and Cyclopentadiene: Observation of Two Criegee Intermediates

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Abstract: Matrix isolation studies, combined with infrared spectroscopy, of the twin jet codeposition of ozone into matrices containing either cyclopentadiene or cyclopentene have led to the first observation of several early intermediates in these ozonolysis reactions. Specifically, evidence is presented for the formation, identification, and characterization of the long sought-after Criegee intermediate for each system, as well as the primary and secondary ozonides. These were observed after initial twin jet deposition and grew ~300% upon annealing to 35 K. Extensive isotopic labeling (^{2}H, ^{18}O and mixtures) experiments provided important supporting data. Detailed theoretical calculations at the B3LYP/6-311++G(d,2p) and B3LYP/6-311++G(3df, 3pd) levels were carried out as well to augment the experimental work. Merged jet (flow reactor) experiments followed by cryogenic trapping in solid argon led to the formation of "late" stable oxidation products of cyclopentadiene and cyclopentene. In contrast, no thermal reaction between ozone and cyclopentane was observed. Photochemical reactions of ozone with all three organic substrates were studied as well.

Introduction

Detailed knowledge of the mechanism of the reactions of ozone with volatile organic compounds (VOCs) is of great importance for a complete understanding of the chemistry of the troposphere.[1,2] While O_3 does not react appreciably with alkanes in the troposphere, it plays a significant role in the oxidation of alkenes which arise from both biogenic and anthropogenic sources.[3−6] The importance of the reaction of O_3 with alkenes in the troposphere has led to many experimental and theoretical studies of the kinetics and mechanism of this reaction. Important early work was carried out by Criegee, leading to the first proposal of a mechanism for the reaction.[7,8] The Criegee mechanism is supported by extensive indirect experimental evidence, as well as high level theoretical calculations,[9−12] and is generally now accepted. The mechanism involves the initial formation of a primary ozonide by a 1,3 polar addition across the double bond of the olefin, forming a 1,2,3-trioxolane species. This reaction is quite exothermic, leading to further reaction and decomposition into an aldehyde and the proposed Criegee intermediate, a carbonyl oxide. The Criegee intermediate and the aldehyde may then recombine to form a secondary ozonide (1,2,4-trioxolane) or react further to form a range of products.

Many experimental studies have sought to isolate and characterize each of the intermediates in the proposed mechanism, with limited success. While primary ozonides have been observed for a few systems[13−15] and the more stable secondary ozonide have been observed for a number of systems, the Criegee intermediate has eluded observation and characterization. On the other hand, theoretical calculations have provided insight into the nature of the ozonolysis reaction, as well as to the reasons for the difficulties in observing the Criegee intermediate.[9−12] Of note is the activation barrier connecting the primary ozonide and the Criegee intermediate, about 19 kcal/mol. The primary ozonide is formed with nearly 50 kcal/mol excess energy, and it can easily continue over the barrier to form the Criegee intermediate and aldehyde. This pair will also be formed with excess energy and must either be quickly deactivated and stabilized, or they will react further to form

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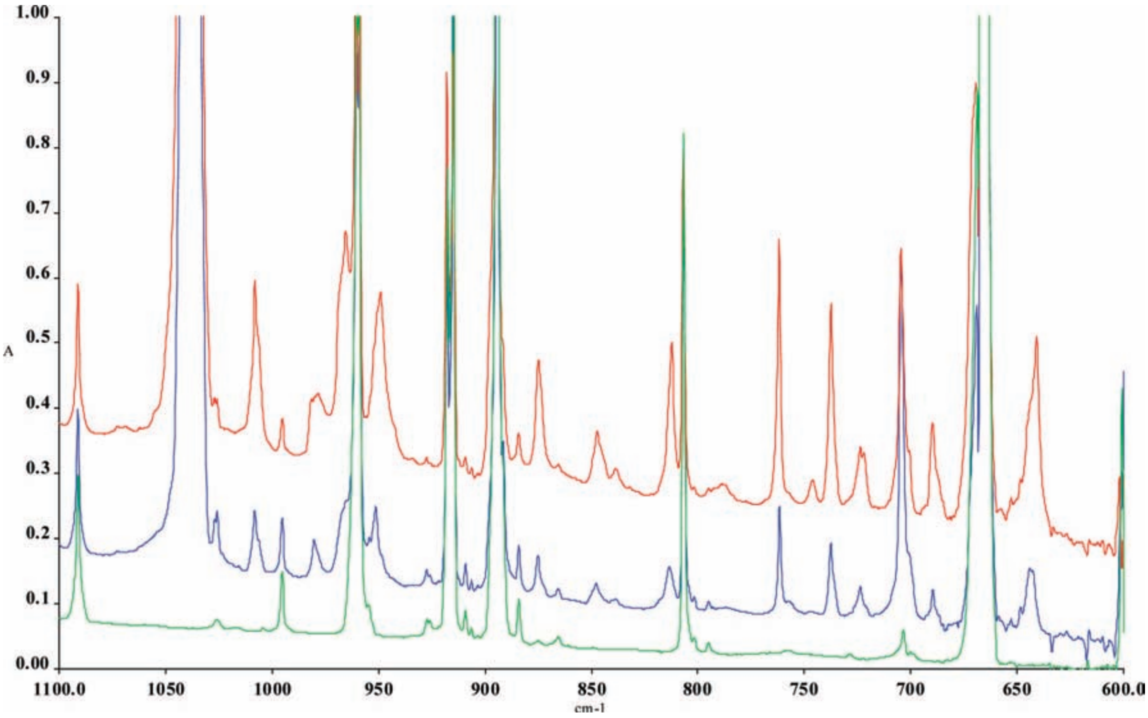

Figure 1. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/ozone = 500 with a sample of Ar/cyclopentadiene = 500, compared to a blank spectrum of Ar/cyclopentadiene = 500. The bottom trace is the cyclopentadiene blank, the middle trace is of the twin jet codeposited matrix before annealing, while the top trace is of the same matrix after annealing to 35 K and recooling to 14 K.

the numerous known products. One pathway to stabilization is ring formation, yielding the secondary ozonide 1,2,4-trioxolane.

Matrix isolation[16−18] was developed and has been employed for the isolation and characterization of a wide range of reactive intermediates, including radicals, ions, and molecular complexes. This approach has been used successfully by many laboratories to isolate many novel short-lived species and has the potential to be an effective tool for the stabilization of initial intermediates in the ozonolysis of alkenes. Numerous groups have tried this approach with limited success. These studies have demonstrated that the careful control of the time and energy available for reaction is crucial. The present study uses several different deposition techniques to vary the reaction time and energy dissipation rates to study the reaction of ozone with cyclopentene, cyclopentadiene, and for comparison, cyclopentane. Cyclopentene is known to have a relatively high rate constant for reaction with ozone which should provide access to the intermediates of interest, while very little is known about the reaction of ozone with cyclopentadiene. As described below, these experiments have led to the simultaneous observation of the primary ozonide, Criegee intermediate and secondary ozonide for both systems.

Experimental Section

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[19] Cyclopentadiene was prepared by cracking the dimer,[20] dicyclopentadiene (Aldrich, 95%). The resulting cyclopentadiene monomer, cyclopentene (Aldrich), cyclopentene-d_8 (CDN Isotopes, 98%), and cyclopentane (Aldrich) were each introduced into the vacuum system as the vapor above the room temperature liquid, after purification by freeze−pump−thaw cycles at 77 K. O_3 was produced by Tesla coil discharge of O_2 (Wright Brothers) and trapping at 77 K to remove residual O_2 and trace gases. $^{18}O_3$ was produced in the same manner from oxygen-^{18}O (94%, Cambridge Isotope Laboratories). Scrambled $^{16,18}O_3$ samples were produced in a similar manner from 50% ^{18}O-enriched O_2 (Cambridge Isotope Laboratories). Argon (Wright Brothers) was used as the matrix gas without further purification.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K window, allowing for only a very brief mixing time prior to matrix deposition. Several of these matrices were subsequently warmed or annealed to 25 and then to 35 K to permit limited diffusion and/or reaction. These matrices were then recooled to 14 K and additional spectra recorded. In addition, all of these matrices were irradiated for 0.5 h or more with the H_2O/quartz-filtered output of a 200 W medium-pressure Hg arc lamp, after which further spectra were recorded.

Many experiments were conducted in the merged jet mode,[21] in which the two deposition lines were joined with an Ultra Torr tee at a predetermined distance from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region. The length of this region can be varied and was ~50 cm in length for this study. In both twin and merged jet, matrices were deposited at the rate of 2 mmol/h from each sample manifold onto the cold window. Final spectra were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using Gaussian 03 and 03W suite of programs.[22] Density functional calculations using the hybrid B3LYP and B3PW91 functionals were used to locate energy minima, determine structures, and calculate vibrational spectra. Final calculations with

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full geometry optimization employed the 6-311G ++(d,2p) and 6-311++G(3df,3pd) basis sets, after initial calculations with smaller basis sets were run to approximately locate energy minima. Thermodynamic functions for the reactants and potential intermediates were also calculated.

Results

Prior to any codeposition experiments, blank experiments were run on each of the reagents used in this study.[23−27] In each case, the blanks were in good agreement with literature spectra, and with blanks run previously in this laboratory. Each blank was then irradiated by the H_2O/quartz-filtered output of a 200 W Hg arc lamp for 1.0 h, and no changes were noted.

Ozone + Cyclopentadiene. In an initial twin jet experiment, a sample of Ar/ozone = 500 was codeposited with a sample of Ar/cyclopentadiene = 500. Numerous new bands were observed in the spectrum of this initially deposited matrix, as shown in Figure 1.

This indicates a very rapid reaction is occurring during the very brief time of matrix condensation. When this matrix was annealed to 25 K and then recooled, the initial product bands all grew slightly (10−20% increase). Then, this matrix was annealed to 35 K and recooled to 14 K. The initial product bands grew substantially, by factors between ~2 and 6 (200−600%), indicating that more than one product is present under these conditions. These new product bands are listed in Table 1. This matrix was then irradiated with a medium pressure Hg arc lap, using a quartz/H_2O filter for 30 min. All of the initial product bands were greatly reduced by irradiation, while many new bands grew in, as shown in Figure 2; key bands are listed in Table S1.

Numerous additional twin jet experiments were conducted, varying the concentration of the each reactants from M/R (matrix/reactant) = 500 to M/R = 900. These values were chosen to provide some variation in concentration, while maintaining relatively dilute conditions to reduce the likelihood of secondary reactions. The same product bands described above were observed throughout. The observed band intensities varied directly with the concentrations employed in these experiments, i.e., when the concentration of one reactant was reduced from M/R = 500 to M/R = 900 while the second reactant was held constant, the band intensities all decreased to ~5/9 of their intensities in the initial experiment.

A series of merged jet experiments was also conducted with samples of Ar/ozone = 600 and Ar/cyclopentadiene = 600, using a 50 cm merged or reaction region, held at room temperature. This configuration allows for increased gas phase reaction time for the reactions prior to matrix deposition. In each of the merged jet experiments, the parent bands of both reagents were reduced in intensity compared to twin jet experiments run at the same sample concentrations, indicating that reaction was occurring. In addition, many new product bands were observed throughout the spectrum, including several intense bands in the carbonyl stretching region. Figure 3 shows a portion of the spectrum from one of the merged jet experiments while key bands are listed in Table S2. These bands were reproduced in several experiments, all with the merged region held at room temperature.

Table 1. Band Positions and Assignments for the Initial Intermediates in the Thermal Reaction of Ozone with Cyclopentadiene

		^{18}O		
exptl bands[a]	calcd bands[b]	calcd shift	exptl shift	assignment
470	475	−6	−6	primary ozonide
520	500	−8	−15	secondary ozonide
643	604	−14	−33	primary ozonide
670	638	0	0	Criegee intermediate
689	689	−10	−31	Criegee intermediate
721	697	−10	−7	secondary ozonide
723				
737	738	−11	−15	primary ozonide
746	743	−8	−11	Criegee intermediate
761	790	−1	−1	Criegee intermediate
788	797	−10	−7	primary ozonide
813	818	−3	−4	primary ozonide
839	834	−37	−26	secondary ozonide
848	854	−7	−8	primary ozonide
875	900	−12	−6	secondary ozonide
948	954	−1	−6	primary ozonide
951	964	−9	−9	secondary ozonide
966	977	−30	−27	Criegee intermediate
977	977	0	−3	primary ozonide
980	981	−16	−13	primary ozonide
1007	1020	−4	−3	secondary ozonide
1030	1031	−3	0	Criegee intermediate
1045	1068	−14	0	secondary ozonide
1070	1083	−3	−5	primary ozonide
1152	1136	0	−3	primary ozonide
1178				
1191	1190	−2	−3	secondary ozonide
1210	1213	−2	−2	primary ozonide
1226	1220	0	−1	Criegee intermediate
1248	1249	−2	−2	Criegee intermediate
1251				
1312	1309	−1	−1	primary ozonide
1322	1322	−2	0	Criegee intermediate
1362	1359	−1	0	secondary ozonide
1395	1380	−2	−4	secondary ozonide
1434	1403	−2	−1	Criegee intermediate
1527	1507	−6	−1	Criegee intermediate
1637	1649	−1	−2	Criegee intermediate
1685				
1742	1805	−37	−32	Criegee intermediate
2848	2908	0	0	Criegee intermediate

[a] Frequencies in cm^{-1}. [b] Calculated at the B3LYP/6-311G++(d,2p) level of theory.

Ozone-^{18}O + Cyclopentadiene. Multiple twin jet experiments were conducted in which samples of Ar/ozone-^{18}O were codeposited with samples of Ar/cyclopentadiene. The results of these experiments paralleled closely those obtained for the normal isotope, with some shifting of bands to lower energy. Product bands in these experiments were observed upon initial deposition and grew substantially upon annealing to 35 K. These bands were greatly reduced by irradiation, while new bands grew in. Each ^{18}O product band could be identified as the counterpart of a ^{16}O band observed above; ^{18}O shifts are listed in Table 1 for each product band. Merged jet experiments were conducted with $^{18}O_3$ and cyclopentadiene as well, and the general outcomes were the same as for the normal isotope of ozone. A large number of product bands were observed, some of which were moderately intense. Many were shifted relative to the normal isotopic experiments, and ^{18}O counterparts were identified for each ^{16}O band. Again, the parent bands were reduced in intensity relative to comparable blank experiments.

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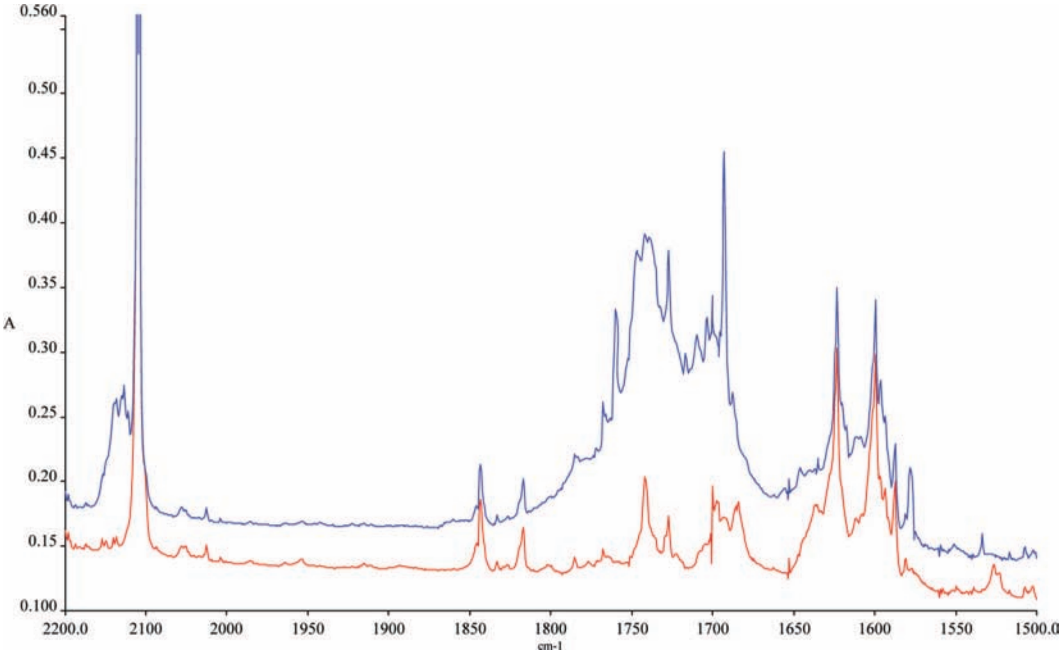

Figure 2. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/ozone = 500 with a sample of Ar/cyclopentadiene = 500. The lower trace is before irradiation, while the upper trace is after 0.5 h of irradiation with light of λ > 200 nm.

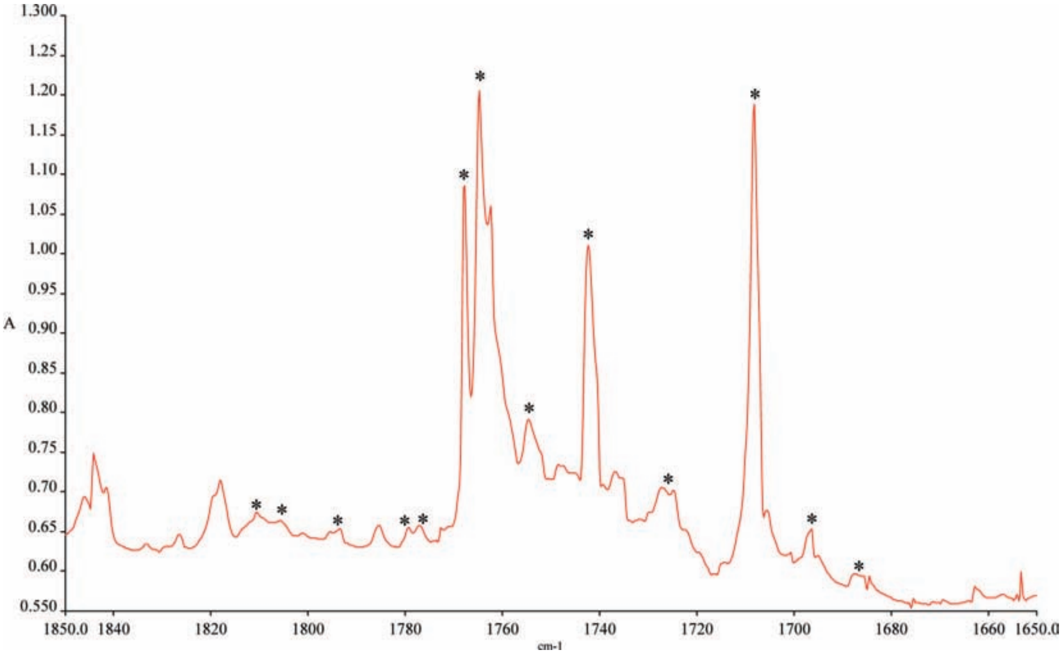

Figure 3. Infrared spectra of a matrix formed by the merged jet deposition of a sample of Ar/ozone = 600 with a sample of Ar/cyclopentadiene = 600. Product bands are marked with an asterisk.

Two additional experiments were carried out using 50% labeled ^{18}O, leading to a statistical mixture of the six isotopomers of O_3. In these experiments, the bands reported above for the $^{16}O_3$ and the $^{18}O_3$ experiments with cyclopentadiene were again observed, although with reduced intensity. In addition, new product bands were observed in the spectrum, in every case coming between the positions reported for the $^{16}O_3$ experiments and the $^{18}O_3$ experiments, as shown in Figures 4 and 5 (see also Discussion section). However, in some spectral regions, band overlap and the presence of parent bands restricted the observation of some potential product bands. All of these bands grew when the matrix was annealed to 35 K.

Ozone + Cyclopentene. In an initial twin jet experiment, a sample of Ar/ozone = 500 was codeposited with a sample of Ar/cyclopentene = 500. Weak new bands were observed in the spectrum of the initially deposited matrix, as shown in Figure 6. When the matrix was annealed, first to 25 K and then to 35 K and recooled to 14 K, the bands further grew substantially (approximately a 150−200% increase). These new product bands are listed in Table 2. This matrix was then irradiated with a medium pressure Hg arc lamp, using an H_2O/quartz filter for 1.0 h. All of the initial product bands were greatly reduced by irradiation, while many new bands grew in, as shown in Figure S1 and listed in Table S3.

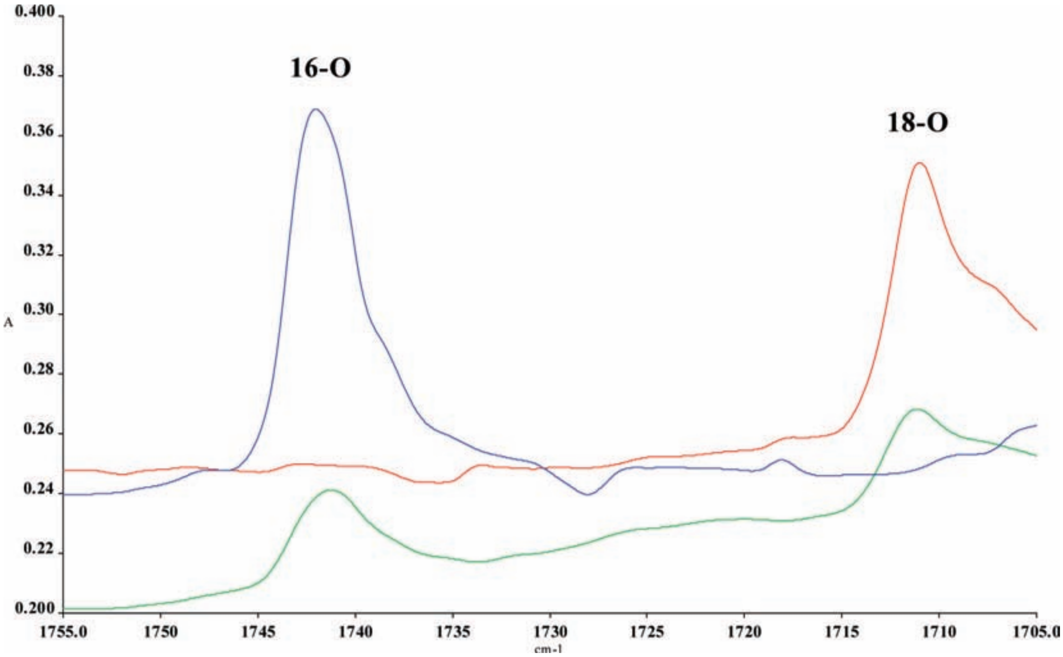

Figure 4. Expanded scale spectra, from 1705 to 1755 cm^{-1}, of the difference spectrum after−before annealing of a sample prepared by the deposition of a sample of Ar/CPD with $Ar/^{16,18}O_3$ with 50% ^{18}O (bottom trace, green), compared to spectra of Ar/CPD with $Ar/^{18}O_3$ (middle trace, red) and Ar/CPD with $Ar/^{16}O_3$ (top trace, blue).

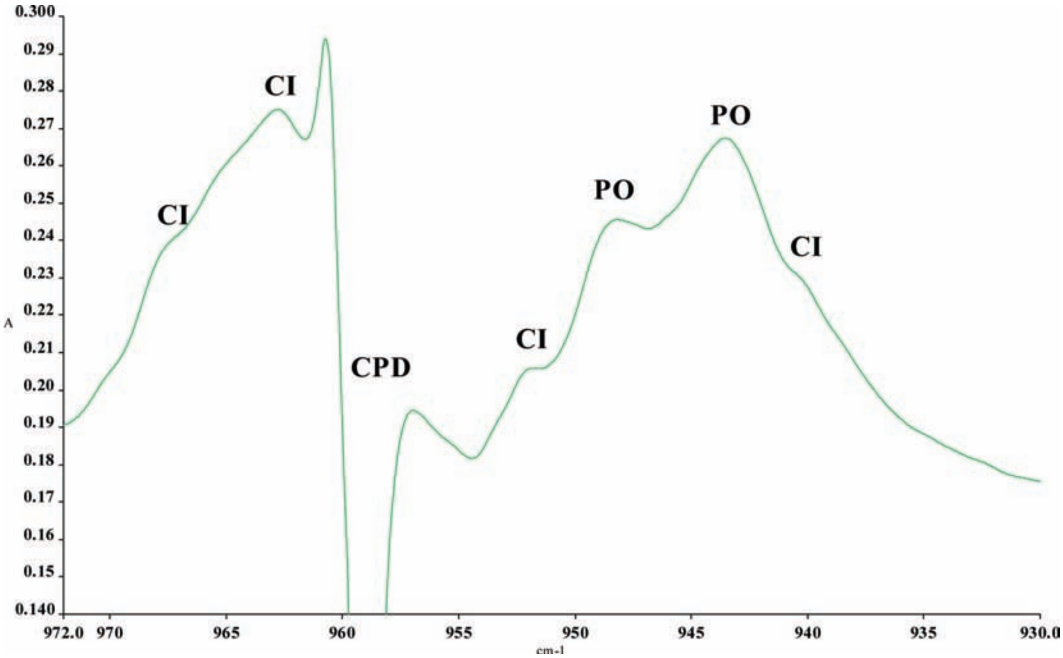

Figure 5. Expanded scale spectra, from 930 to 972 cm^{-1}, of the difference spectrum after−before annealing of a sample prepared by the deposition of a sample of Ar/CPD with $Ar/^{16,18}O_3$ with 50% ^{18}O.

Several additional twin jet experiments were conducted, varying the concentration of the each reactants from M/R = 500 to M/R = 700. The same initial product bands described above were observed throughout, with band intensities that varied directly with the concentrations employed in these experiments. In one experiment, the wavelength dependence of the photodestruction of these product bands was explored. A set of colored filters was used to determine the wavelength(s) at which the onset of photodestruction occurred. For a number of the initial product bands, a small amount of destruction could be detected at >530 nm, while more rapid destruction was noted at >410 nm. Several other product bands were not affected by irradiation at these wavelengths but were destroyed by light with $\lambda < 400$ nm.

Merged jet experiments were also conducted with samples of Ar/O_3 and $Ar/c\text{-}C_5H_8$, using a 50 cm merged or reaction region held at room temperature. M/R values ranged from 500 to 900. In all of the experiments, the parent bands of both reagents were reduced in intensity, indicating that reaction was occurring under these conditions. In addition, a large number

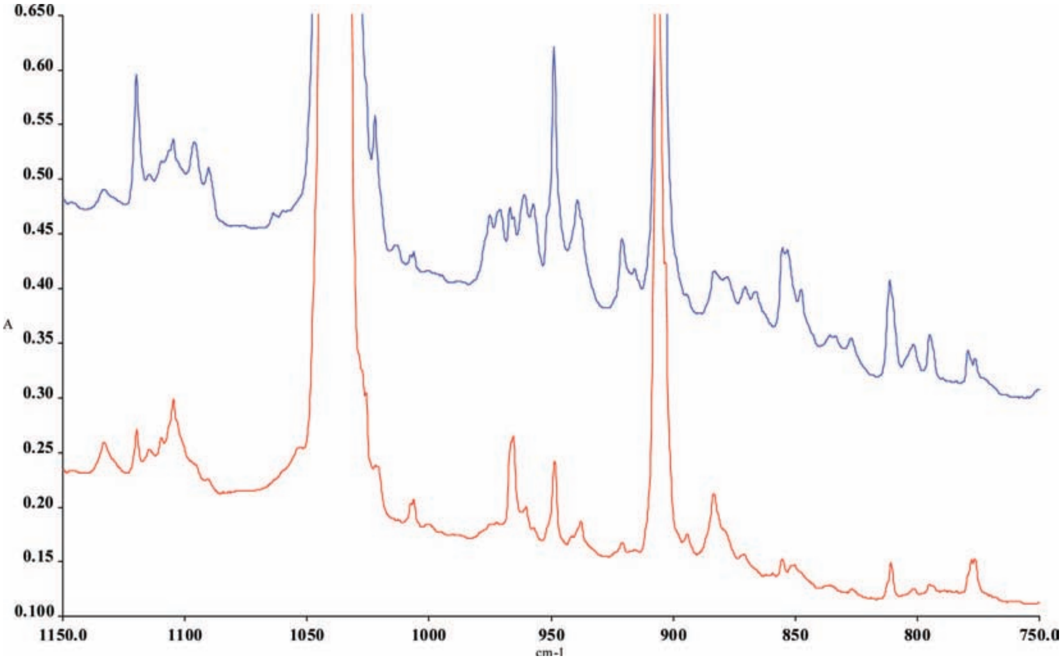

Figure 6. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/ozone = 500 with a sample of Ar/cyclopentene = 500. The lower trace is before annealing, while the upper trace is after annealing to 35 K and recooling to 14 K.

of product bands were observed, some of which were moderately intense. Figure 7 shows representative regions of this spectrum while key bands are listed in Table S4.

Ozone-^{18}O + Cyclopentene. Multiple twin jet experiments were conducted in which samples of Ar/$^{18}O_3$ were codeposited with samples of Ar/c-C_5H_8, with results paralleling these obtained for the normal isotopic species. Product bands were observed upon initial deposition and grew significantly on annealing to 35 K. These product bands were greatly reduced by irradiation, while new bands grew in. Merged jet experiments were also conducted with this pair of reagents, and the outcomes were the same as for the normal isotope of ozone. Many product bands were observed, some of which were moderately intense, while the parent bands were reduced in intensity.

Ozone + Cyclopentene-*d*$_8$. The reaction of these two reagents was explored in several twin jet experiments, using both $^{16}O_3$ and $^{18}O_3$ in separate experiments. The overall results were similar to those with normal isotopic cyclopentene, namely the observation of weak-to-medium product bands upon initial deposition followed by substantial growth upon annealing the matrix to 35 K. As anticipated, shifting of band positions due to change in isotope was observed. The product bands in these experiments are presented in Table S5.

Ozone + Cyclopentane. In an initial twin jet experiment, a sample of Ar/ozone = 600 was codeposited with a sample of Ar/cyclopentane = 500. In contrast to the above systems, after 22.0 h of deposition no product bands were observed. This matrix was then annealed to 35 K and recooled to 14 K. A spectrum was then recorded, and no changes were noted. This matrix was then irradiated for 1.0 h with the filtered ($\lambda > 200$ nm) output of a medium-pressure Hg arc lamp. This produced many new product bands, as listed in Table S6. Figure S2 shows representative regions of this spectrum. This experiment was repeated several times, using different sample concentrations. The results were consistent throughout, with product band intensities that varied directly with sample concentrations.

Several merged jet experiments were conducted with samples of Ar/ozone = 500 and Ar/cyclopentane = 500. In the first experiment, the merged region was held at room temperature. The resulting spectrum was identical to blank experiments, with no product bands. In a subsequent experiment, the merged region was heated to 100 °C to increase the energy available to the reactants. Again, no product bands were observed.

Ozone-^{18}O + Cyclopentane. Two twin jet experiments were conducted in which samples of Ar/$^{18}O_3$ were codeposited with samples of Ar/c-C_5H_{10}. After deposition was completed, each matrix was irradiated for 1.5 h. Many new bands were observed after irradiation, including a distinctive band at 3630 cm^{-1}, as listed in Table S6.

Results of Calculations. The likely products in this study vary widely due to the several different experimental approaches that were employed. Many of the possible products in the merged jet experiments are known species for which experimental spectra are available for comparison. In the twin jet experiments with annealing, the intermediates proposed originally by Criegee, i.e., the primary ozonide, the Criegee intermediate, and the secondary ozonide must be considered. Since reference or literature spectra are not available for comparison, the structures, energetics, and vibrational spectra of a number of these products arising from the cyclopentadiene and cyclopentene systems were calculated using DFT methods, the B3LYP hybrid functional, and basis sets as high as 6-311G++(d,2p) and 6-311++G(3df, 3pd). In addition, there are potential stable products for which literature spectra are not available and calculations provide the only basis for comparison to experiments conducted here. The calculations were carried out to locate potential energy minima, compute infrared spectra, including ^{18}O isotopic shifts, and calculate thermochemical energies. Tables S7−S8 list the energies of the calculated likely products relative to ozone + cyclopentadiene, and ozone + cyclopentene. Figures 8 and S3 (intermediates **8a**−**c** and **S3a**−**c**) show a representation of the calculated products in argon matrices containing ozone and cyclopentadiene and cyclopentene, respectively. All of the species under consideration optimized to energy minima on their respective potential energy surfaces, with all positive vibrational frequencies.

Table 2. Band Positions and Assignments for Initial Intermediates in the Thermal Reaction of Ozone with Cyclopentene

		^{18}O		
exptl bands[a]	calcd bands[b]	calcd shift	exptl shift	assignment
422	419	−13	−13	primary ozonide
551	547	−9	−9	secondary ozonide
650	696	−27	−35	primary ozonide
660				
706	729	−37	−35	primary ozonide
725	703	−1	−4	Criegee intermediate
794	798	−2	−6	Criegee intermediate
801	808	−10	−11	primary ozonide
810	817	−6	−2	primary ozonide
826	829	−9	−5	primary ozonide
833	832	−42	−43	secondary ozonide
847	844	−20	−23	secondary ozonide
852	862	−16	−23	Criegee intermediate
865	860	−9	−19	primary ozonide
870	892	−17	−19	Criegee intermediate
914				
920	901	−21	−24	secondary ozonide
938	928	−13	−19	secondary ozonide
948	949	−10	−10	primary ozonide
956				
959	957	−7	−12	Criegee intermediate
972	983	−3	−10	Criegee intermediate
1012				
1021	1030	−2	0	primary ozonide
1030	1016	−5	−6	secondary ozonide
1090	1081	−2	−5	secondary ozonide
1095	1095	−7	−6	secondary ozonide
1119	1121	−2	−5	secondary ozonide
1194	1202	0	−2	primary ozonide
1197	1210	−2	−1	Criegee intermediate
1216	1236	−1	−1	primary ozonide
1252				
1257				
1308				
1315	1320	0	−5	primary ozonide
1328	1366	−3	0	secondary ozonide
1344	1343	0	−2	primary ozonide
1390	1392	−2	−6	Criegee intermediate
1411	1415	−6	0	Criegee intermediate
1435	1449	0	−1	Criegee intermediate
1442	1476	−1	0	Criegee intermediate
1464	1477	0	−2	primary ozonide
1733	1796	−35	−29	Criegee intermediate
2729				
2828	2905	0	0	Criegee intermediate

[a] Frequencies in cm^{-1}. [b] Calculated at the B3LYP/6-311G++(d,2p) level of theory.

In as much as computed vibrational frequencies at any level of theory have intrinsic limitations and since band positions and isotopic shifts are an important component of product identification, benchmark calculations were carried out for several known aldehydes (acetaldehyde and formaldehyde), as well as for carbon monoxide to calibrate the accuracy of the calculations for the types of vibrational modes under investigation. These species were chosen because their ^{16}O and ^{18}O band positions were well-known experimentally. Calculations were carried out with the B3LYP and B3PW91 functionals, using the 6-311++g(d,2p) and 6-311++G(3df, 3pd) basis sets. In summary, all calculations of the ^{18}O isotopic shift of a C=O stretching vibration for an aldehyde overestimated the vibrational frequency by ~4 cm^{-1}, for both gas phase and matrix band positions. Without invoking arbitrary scale factors based on these results, the interpretation of the results of this study need to keep in mind the systematic error demonstrated by these benchmark calculations. Complete results of these benchmark calculations are given in Table S9.

Discussion

Ozone + Cyclopentadiene. Twin jet codeposition of cyclopentadiene and ozone into argon matrices led to the formation of a substantial number of distinct, medium-to-weak product bands. Since reagent mixing during twin jet deposition occurs only on the surface of the condensing matrix, the species responsible for these absorptions must form very rapidly. Further, these product bands grow slightly upon annealing the matrix to 25 K and grow substantially (200−300% increase) upon annealing the matrix to 35 K. These observations indicate that the barrier to reaction must be very low ($3/2RT \approx 0.1$ kcal/mol at 35K). Also, the large number of product bands (~40) strongly suggests that more than a single product is formed under these conditions. Additionally, the product bands observed in the thermal twin jet experiments are entirely different than those observed in the merged jet experiments, where most of the products are known or anticipated stable oxidation products (see below). Likewise, the product bands observed in the thermal twin jet experiments were entirely different than those observed in the twin jet irradiation experiments, where single O atom transfer products are observed (see also below). Finally, all of the product bands formed on initial twin jet deposition and enhanced by annealing were subsequently greatly reduced or destroyed by irradiation, while new product bands grew in.

The arguments presented in the preceding paragraph strongly support assignment of the product bands formed in thermal twin jet reaction, including upon annealing, to early intermediates in the reaction of ozone with cyclopentadiene. A related solution phase study[28] of the reaction of cyclopentadiene derivatives (e.g., diphenylcyclopentadiene) has documented the formation of the secondary ozonides arising from the ozonolysis of *one* of the carbon−carbon double bonds, suggesting that the Criegee mechanism may be operative for this system. However, characterization of the secondary ozonide was by NMR only, so that direct comparison to the spectra observed here cannot be made. Nonetheless, this strongly suggests that the primary ozonide (PO) and Criegee intermediate (CI) are possible products in the present experiments, along with the secondary ozonide (SO). This is also consistent with the known, low activation barrier (~2 kcal/mol) for the reaction of ozone with cyclopentene[29] (the barrier to the reaction of ozone with cyclopentadiene has not been measured and is anticipated to be similar or somewhat lower than that of cyclopentene). This reaction is believed to lead initially to the PO, with an exothermicity on the order of 50 kcal/mol. If this energy is removed sufficiently rapidly by the surrounding matrix, the PO may be isolated. If this energy is not removed sufficiently rapidly, then the reaction proceeds over a second barrier leading to ring-opening reaction and the CI. This species contains an aldehyde functionality at one end of the chain and a carbonyl oxide at the other end. For small alkenes, the barrier separating the PO from the CI is ~18 kcal/mol, substantially less than the exothermicity of the initial reaction. The Criegee intermediate can either be stabilized in the matrix cage or can undergo a ring-closing reaction to form the SO. Further reaction leading to stable final products is not expected to occur within the matrix

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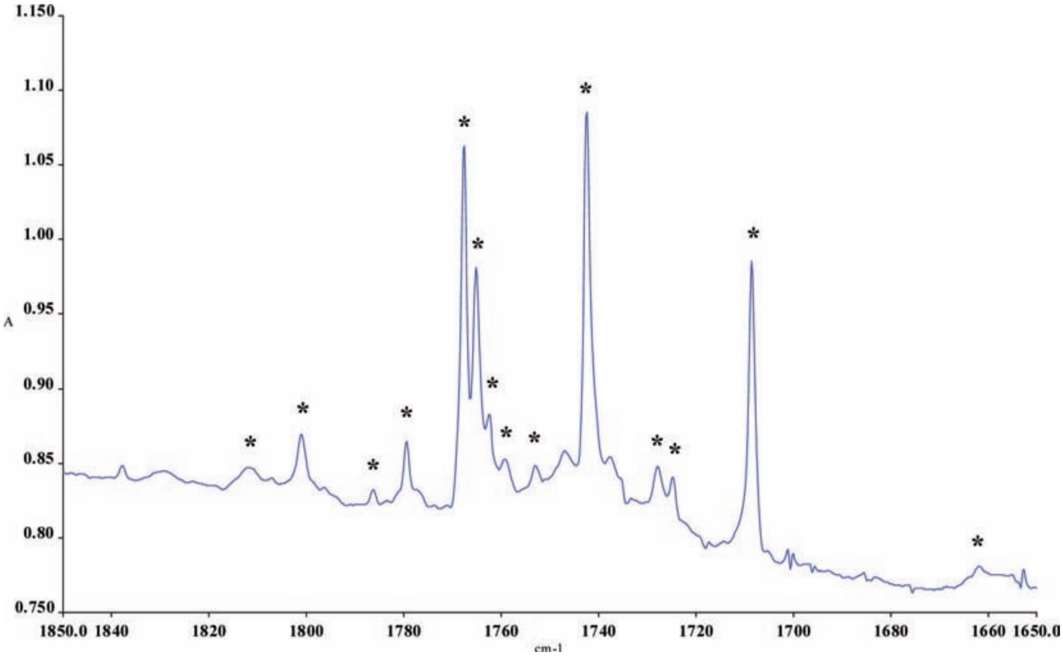

Figure 7. Infrared spectra of a matrix formed by the merged jet deposition of a sample of Ar/ozone = 600 with a sample of Ar/cyclopentene = 600. Product bands are marked with an asterisk.

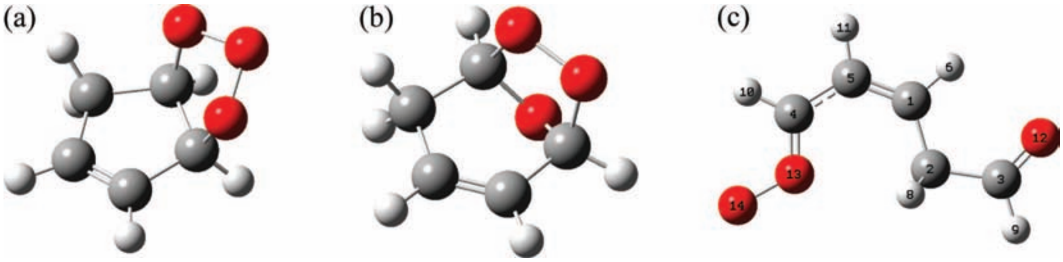

Figure 8. Calculated structures for the (a) primary ozonide, (b) secondary ozonide, and (c) Criegee intermediate arising from the reaction of ozone with cyclopentadiene.

cage due both to the nature of the physical environment (low temperature, argon cage) and to the known stability of secondary ozonides.

An additional possibility, leading to different products, is further reaction within the matrix cage, particularly given the likelihood that the Criegee intermediate is formed with substantial excess energy. The most likely step in a subsequent reaction would be decomposition, by CO_2 elimination from the carbonyl oxide moiety of the CI, or possibly O_2 elimination. In the former case, the product would be 3-butenal (or 2-butenal via a hydrogen shift) while in the latter case it would be 2,4-pentadienal. These two possibilities can be eliminated by comparison to theoretical calculations for 3-butenal and the literature spectrum[30a] for 2-butenal in the former case, and the literature spectrum[30b] in the latter case. Thus, the most probable alternative products for a 1:1 reaction within a single matrix cage are not observed, further supporting the possibility of formation of the PO, CI, and SO.

While the PO, CI, and SO are potential, reasonable products in this system, definitive identification and band assignment is challenging. Support comes from ^{18}O and mixed $^{16,18}O$ data and from theoretical calculations. ^{18}O isotopic shifts are identified for nearly all of the product bands, as shown in Table 1. As noted above, the calculations demonstrated that the PO, CI, and SO are all stable species (local minima on the $C_5H_6O_3$ potential energy surface), and the calculated exothermicity of the reaction to form the PO (−50.1 kcal/mol) is consistent with experimental values for similar systems. Vibrational spectra and ^{18}O isotopic shifts were calculated for all three species. A comparison of calculated bands and isotopic shifts with the experimental bands and shifts leads to the conclusion that a good fit between experiment and theory is best achieved by invoking the presence of all three species (PO, CI, and SO) in the argon matrix. Further, this is in agreement with the observation that some bands grew substantially more than did others, indicating the presence of multiple species. Since some bands were overlapped with parent bands or other product bands, good quantitative intensities could not be obtained for all product bands. Nonetheless, those bands that could be measured accurately could be reasonably assigned to three sets on the basis of growth rate with annealing. The conclusion that all three are present simultaneously in the matrix allows assignment of all of the observed bands, in good agreement with calculated bands positions and isotopic shifts, as shown in Table 1. Such a set of assignments accounts for nearly all of the calculated vibrational bands of these three species with calculated intensities greater than 10 km/mol. The only calculated bands with $I > 10$ km/mol that were not observed were predicted to fall very near experimentally observed, strong parent bands and are likely obscured.

Vibrational modes of the Criegee intermediate that are largely localized on bonds involving the oxygen atoms are particularly diagnostic in that they are calculated to show relatively large ^{18}O shifts. One such mode for the CI is the C=O stretch of the aldehyde functional group, observed at 1742 cm^{-1} with an ^{18}O shift of −32 cm^{-1}. This compares to a calculated position of 1751 cm^{-1} (scaled with a standard factor of 0.97 for the level of theory employed here) and an isotopic shift of −36 cm^{-1}. The only absorption of the PO and of the SO in this region is the weak C=C stretching mode, calculated between 1620 and 1650 cm^{-1} (scaled) with low intensity and zero ^{18}O shift. Thus, observation of the product band at 1742 cm^{-1} requires the presence of a carbonyl-containing species and the fit to the CI is excellent, keeping in mind the systematic 4 cm^{-1} overestimation in the calculations identified by the benchmark calculations. In addition, only two bands were observed in the mixed ^{16,18}O experiments, at the same positions observed in the reactions with $^{16}O_3$ and with $^{18}O_3$, as shown in Figure 4. This indicates formation of an aldehyde or carbonyl and rules out formation of an ester or carboxylic acid. A second distinctive mode is the O−O stretch of the carbonyl oxide moiety, observed at 966 cm^{-1} with an ^{18}O shift of −27 cm^{-1}. This compares to a calculated value of 977 cm^{-1} (unscaled, 949 cm^{-1} scaled) and a shift of −30 cm^{-1}. This mode should show a quartet in the mixed isotopic experiment due to the two inequivalent O atoms. This region is complex in the mixed isotope experiments, as shown in Figure 5. This figure shows the difference before and after annealing to 35 K. A parent band of cyclopentadiene is present between 958 and 961 cm^{-1}, with a differential shape due to loss of intensity and some broadening during annealing. In addition, the PO absorbs between 943 and 948 cm^{-1}, as indicated. Nonetheless, four peaks are identified near their calculated positions, labeled CI. The terminal bands, at 939 and 966 cm^{-1}, were also observed in the pure $^{18}O_3$ and $^{16}O_3$ experiments, respectively. The intermediate bands, at 951 and 962 cm^{-1}, are near the predicted positions for the two mixed ^{16}O−^{18}O species. While not completely definitive due to the overlapping bands, these observations are fully consistent with assignment to the O−O stretch of the CI of CPD. In addition, several groups have observed carbonyl oxides in cryogenic matrices (formed through different routes, not ozonolysis). For example, Sander et al. isolated propinal O-oxide in argon matrices.[31a] They report an intense O−O stretching mode at 933 cm^{-1}, with a −45 cm^{-1} ^{18}O shift. Sheridan et al. reported[31b] the formation of a bis-carbonyl oxide with an intense O−O stretch at 929 cm^{-1} and a −35 cm^{-1} ^{18}O shift. These data are in excellent agreement with the observations presented here, and, *thus, the results here strongly support identification for the first time of the Criegee intermediate arising from the ozonolysis of an alkene, a species predicted more than 50 years ago.*

Key structural parameters calculated for the CI are given in Table 3. Of note is the O−O bond length of 1.37 Å, while the C=O distance for the carbonyl oxide is 1.27 Å, elongated relative to the C=O distance for the aldehyde group of 1.21 Å. Also, the C−C single bond immediately adjacent to the carbonyl oxide group was calculated to be 1.43 Å, shortened relative to a distance of 1.51 Å for the C−C bond immediately adjacent to the aldehyde group. This suggests some conjugation and delocalization near the carbonyl oxide. This delocalization is absent in the Criegee intermediate for cyclopentene (see discussion below) due to the lack of a carbon−carbon double bond. For this species, the C−C bond adjacent to the carbonyl oxide is lengthened to 1.486 Å, as shown in Table 3. Finally, it the should be noted that the ozone/cyclopentadiene system represents a somewhat special case in terms of the search for the Criegee intermediate, in that this intermediate contains both the carbonyl oxide and the aldehyde subunits. For acyclic alkenes, carbon−carbon bond breakage is proposed to occur, leading to two separate species, an aldehyde, and a carbonyl oxide.

Table 3. Key Structural Parameters Calculated[a] for the Criegee Intermediates of Cyclopentadiene (I) and Cyclopentene (II)

parameter[b]	type	calcd value (I)	calcd value (II)
R(1,2)	C−C	1.494 Å	1.532 Å
R(1,5)	C=C	1.352 Å	−
R(3,12)	C=O	1.205 Å	1.207 Å
R(4,5)	C−C	1.431 Å	1.486 Å
R(4,13)	C=O	1.274 Å	1.259 Å
R(13,14)	O−O	1.369 Å	1.374 Å
A(4,13,14)	C=O−O	118.23°	119.23°
A(1,5,4)	C−C=C	127.40°	−

[a] Calculated at the B3LYP/6-311++g(2,dp) level. [b] See Figure 8c for atom numbering.

UV irradiation of matrices following twin jet deposition of O_3, and cyclopentadiene led to the destruction of the bands formed on initial deposition and the growth of many new bands. The number and location of the product bands strongly supports the formation of multiple products in these experiments. O_3 photochemistry in cryogenic matrices has been shown to be dominated by ^{3}O atom formation and subsequent reaction.[32,33] Possible primary reactions include O atom addition to form a cyclic ketone or epoxide, O atom addition and ring opening to form ketenes or dienals, and O atom insertion to form an alcohol. Secondary reactions might involve the reaction of a second O atom after diffusion through the matrix. Thus, such products as carboxylic acids were considered as well. Table S7 lists all of the potential products that were considered for the photochemical reaction of O_3 with cyclopentadiene and their calculated energies relative to the parent species. Many of these compounds are well-known, and infrared spectra in either cryogenic matrices or solution are available for comparison.[34−39] In the latter case, solution-to-matrix shifts needs to be recognized. In addition, many of the products share structural similarities and consequently will have a number of quite similar product bands. Thus, a single, unique set of assignments of all of the product bands is not readily achieved. The data certainly indicate the formation of ketones and aldehydes, along with one or more ketenes. On the other hand, the O−H stretching region characteristic of alcohols contains no bands, so these species are not formed under these conditions. The most likely assignments are to 2,4-

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pentadienal, cyclopenta-2-enone, cyclopenta-3-enone, the ketenes penta-1,3-dien-1-one and penta-1,4-dien-1-one, cyclopentadiene oxide, and 3-butenal. The main conclusion is that the photochemical reaction is dominated by O atom formation and reaction to form relatively well-known, stable products.

Merged jet reactions were employed as well to study the thermal reaction of O_3 with cyclopentadiene for longer times than were accessible with twin jet deposition. In these experiments, many product bands were observed, some with moderate intensity. In addition, a significant decrease in the intensity of the parent bands was noted. These observations demonstrate that extensive reaction is occurring in the merged region. Several of the product bands were the same as seen in the twin jet experiments, while others were seen only in the merged jet experiments. Numerous products can be envisioned as a result of primary and secondary reactions in this system. Where literature spectra were available for comparison,[34−42] specific product identifications could be made. These include the two ketenes, penta-1,3-dien-1-one, and penta-1,4-dien-1-one, as well as the acylic (chain) ketone 1,4-pentadien-3-one. On the other hand, the spectral evidence did not support formation of open chain aldehyde formation. Additional products that could be identified include δ-valerolactone and γ-butyrolactone based on absorptions in the 1760−1820 cm^{-1} region, as well as the fragmentation products[43−46] formaldehyde, ethene, CO, and CO_2. The primary conclusions from the merged jet reactions are that reaction was extensive during transit time through the reaction zone and that the observed products are generally known, stable species. Only the twin jet experiments, with annealing, that are described above provide sufficient control of the course of the reaction to permit observation of the sought-after early intermediates in this system.

Ozone + Cyclopentene. The twin jet deposition experiments involving ozone and cyclopentene were similar in many ways to those involving ozone and cyclopentadiene described above. Numerous weak bands were observed on initial deposition. These grew moderately upon annealing to 35 K and were destroyed by irradiation. However, overall the yield of these initial products, as measured by band intensities, was less than for the cyclopentadiene system. Since annealing generally allows reaction of cage pairs or nearest neighbors only, this suggests that fewer such pairs are formed in the cyclopentene systems, perhaps due to weaker van der Waals interactions with ozone. Alternatively, these initial products may be weaker absorbers than those formed in the cyclopentadiene system. One additional piece of information for the ozone/cyclopentene system comes from the study of the wavelength dependence of the photochemical reaction. This study demonstrated that while all of the product bands were destroyed by the full light of the Hg arc, some were destroyed by light with $\lambda > 410$ nm and others by light with $\lambda < 400$ nm. This observation requires the presence of two or more species upon initial deposition and subsequent annealing.

On the basis of the proposed Criegee mechanism and the results for the ozone/cyclopentadiene system, likely candidates for these initial products are the primary ozonide (PO), Criegee intermediate (CI), and secondary ozonide (SO) of cyclopentene. There are no reports in the literature related to any of these three species, so assignment must come through ^{18}O isotopic shifts, comparison to calculations and by analogy to the ozone/cyclopentadiene system. A particularly diagnostic band was observed at 1733 cm^{-1} and an ^{18}O shift of −29 cm^{-1}. This indicates the formation of a C=O group, is in excellent agreement with the C=O stretch aldehyde group of the Criegee intermediate calculated (scaled) at 1742 cm^{-1} with a −34 cm^{-1} ^{18}O shift, again keeping in mind the systematic 4 cm^{-1} overestimation in the calculations identified by the benchmark calculations. The O−O stretch of the CI for cyclopentene is somewhat mixed with other vibrational modes and less distinctive. Product bands at 852 and 870 cm^{-1} with ^{18}O shifts of −23 and −19 cm^{-1}, respectively are the best candidates; calculations show that the 852 cm^{-1} vibration is a mixture of the O−O stretch and a C−H wag, while the 870 cm^{-1} vibration is a mix of the O−O stretch and a C−C stretch. These were calculated to come at 862 and 892 cm^{-1} (unscaled) with ^{18}O shifts of −16 and −17 cm^{-1}. Likewise, the agreement between calculated and observed band positions in experiments reacting cyclopentene-d_8 with $^{16}O_3$ and $^{18}O_3$ was very good as well, for those bands not overlapped by parent absorptions. The overall agreement for these diagnostic modes is excellent and strongly supports the formation and stabilization of the Criegee intermediate of cyclopentene.

Alternative explanations involve products from fragmentation, including butanal formed through CO_2 elimination from the CI, or 4-pentenal formed through O_2 elimination. These two possibilities can be rigorously excluded by comparison of the spectra obtained here to authentic argon matrix spectra of these two compounds run in this laboratory for comparison.

For the primary ozonide, particularly characteristic and intense bands were observed at 706 and 948 cm^{-1}, with shift of −35 and −10 cm^{-1}, respectively. The two most intense bands of the PO were calculated to be the antisymmetric O−O−O stretching mode at 708 cm^{-1} (scaled) with a −36 cm^{-1} shift, and the ring stretching mode at 948 cm^{-1} with a −10 cm^{-1} shift. This agreement for the two most distinct modes is strong support for the identification of the PO. In a similar manner, two intense bands assigned to the SO were observed at 938 and 920 cm^{-1}, with ^{18}O shifts of −19 and −24 cm^{-1}, respectively. Two of the most intense bands of the SO were calculated at 928 and 901 cm^{-1}, with shifts of −13 and −21 cm^{-1}, respectively. This is also very good agreement, and supports identification of the secondary ozonide of cyclopentene. Beyond this, the overall lower band intensities make complete assignment challenging. Nonetheless, nearly complete assignments have been made and are presented in Table 2. The presence of all three species, PO, CI, and SO, are required to make these assignments. It is noteworthy that the all of the bands assigned to the CI showed a different wavelength dependence of photochemical destruction than did the bands assigned to the two ozonide species. Thus, the spectroscopic evidence presented here supports the first observation and characterization of the three initial intermediates (PO, CI, and SO) in the reaction ozone with cyclopentene, providing direct support for the mechanism proposed by Criegee.

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Irradiation of these matrices led to the destruction the bands due to the PO, CI, and SO and formation of many new bands. Many products are possible, primarily arising from O atom reaction with cyclopentene via addition or insertion, with or without ring-opening. Assignment of these bands is very difficult, given the wide range of possible products, the lack of literature spectra and the close structural similarities of many (hence, bands in close proximity to one another). The product band at 3627 cm^{-1} clearly indicates the formation of an alcohol, but there is very little basis to distinguish between the three cyclopentenol isomers that might form. Their similarities are such that calculations will not readily distinguish them. Open chain pentadienyl alcohols can be ruled out by the absence of the moderately intense C═C modes predicted for these species. Ketene formation is likely based on the growth of a strong band at 2137 cm^{-1} upon irradiation, with a -32 cm^{-1} ^{18}O shift. 1-Penten-1-one (ketene) has a very strong absorption band calculated at 2136 cm^{-1} with an ^{18}O shift of -27 cm^{-1}. This provides support for the formation of 1-penten-1-one. However, no literature spectra are available for 4-penten-2-one and 3-penten-2-one, and they cannot be excluded. On the other hand, 3-penten-2-one and 4-penten-3-one can be eliminated from consideration on the basis of comparison to authentic spectra of these compounds obtained as a part of this study. Additional compounds that could be excluded on the basis of comparison to authentic spectra include 2-pentenal and cyclopentanone. Finally, comparison to the published spectrum[47] of cyclopentene oxide fit very well and this is a likely product in these experiments. While a complete fit of all of the product bands cannot be achieved on the basis of the available data and literature spectra, the key conclusion reached in the cyclopentadiene studies, that the photochemical reaction is dominated by O atom formation and reaction to form relatively well-known, stable products, is valid here as well.

The merged jet results for the ozone/cyclopentene system paralleled those for the ozone/cyclopentadiene system described above. Through comparison to authentic spectra, formaldehyde, 3-buten-2-one, CO, and cyclopentene oxide appear to be produced in these reactions, while evidence did not support the formation of any alcohols, ketenes, or aldehydes. Between 1760 and 1815 cm^{-1}, the spectra are essentially identical to those obtained for the ozone/cyclopentadiene system and are likely due to the lactones, δ-valerolactone, and γ-butyrolactone. Overall, in these merged jet experiments reaction was extensive during transit time through the reaction zone, and the observed products are generally known, stable species.

Ozone + Cyclopentane. In contrast to the above systems, no product bands were seen on initial twin jet deposition of this pair of reactants. Further, annealing these matrices to 35 K did not lead to the formation of any product bands. This is consistent with the small rate constant for the reaction of ozone with cyclopentane, with alkanes in general.[29] These observations also reinforce the conclusion that the site of reactivity of ozone with cyclopentadiene and cyclopentene is at a carbon−carbon double bond. In addition, no product bands were observed during merged jet deposition of these reactants at temperatures as high as 100 °C, again consistent with the small rate constant.

The photochemical reaction of ozone with cyclopentane did, however, occur readily, leading to the series of product bands listed in Table S6. This result is characteristic of the photodetachment of an O atom from ozone and subsequent O atom chemistry. Of particular note is a product band at 3641 cm^{-1} with an ^{18}O shift of -11 cm^{-1}, strongly suggesting the formation of an alcohol. The O−H stretch of cyclopentanol in the gas phase has been reported[48] at 3653 cm^{-1}. Gas phase-to-argon matrix shifts are typically on the order of 1% or less, so assignment to cyclopentanol is very reasonable. Further, the O−H stretch of this species is calculated at 3721 cm^{-1}, with a shift of -13 cm^{-1}. This mode is expected to be relatively anharmonic and should occur at somewhat lower energy that the purely harmonic calculation indicates. Finally, nearly all of the remaining product bands agree well with the calculated bands for cyclopentanol, including ^{18}O shifts. Thus, the product bands formed in the photochemical reaction of ozone with cyclopentane are assigned to cyclopentanol through O atom insertion into a C−H bond. (There are actually several isomers of cyclopentanol due to its nonplanar structure. These are calculated to have nearly identical infrared spectra and cannot be distinguished in this study).

Conclusions

The variation of conditions for the deposition of ozone and cyclopentadiene and cyclopentene into argon matrices has led to the observation of both initial reaction intermediates and stable reaction products. Twin jet deposition followed by annealing led to moderately intense product bands which have been assigned to the primary ozonide, Criegee intermediate, and secondary ozonide of these two cycloalkenes. These results provide strong evidence that these ozonolysis reactions follow the mechanism proposed by Criegee in the 1950s. These intermediates were destroyed by irradiation, leading to the formation of more stable products. Merged jet deposition, which allows for a longer gas phase reaction time, led to stable, known species as well. In contrast, the ozonolysis of cyclopentane did not occur thermally under the conditions employed here, indicating that a carbon−carbon double bond is required for rapid reaction. The photochemical reaction of ozone with cyclopentane led to O atom insertion into a C−H bond and the formation of cyclopentanol.

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Supporting Information Available: Additional tables of observed vibrational frequencies, calculated frequencies, and the calculated energies of possible reaction products, additional experimental spectra and structures, and complete ref 22. This material is available free of charge via the Internet at http://pubs.acs.org.

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