Environmental Effects on the Formation of the Primary and Secondary Ozonides of Ethylene at Cryogenic Temperatures

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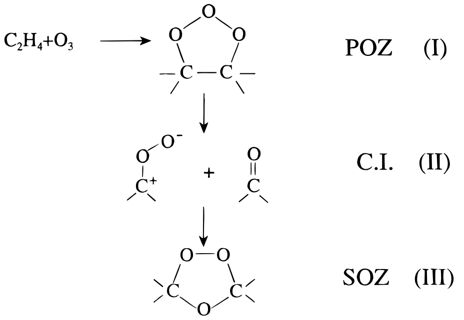
Abstract: Ethylene and ozone were co-deposited in a cryogenic matrix of argon at 15−26 K and of CO_2 at 12−20 K. In the argon matrix, no perceptible reaction took place at any temperature below the softening onset of the matrix, while formation of ethylene ozonides (both primary and secondary) was observed at temperatures as low as 25 K in the *amorphous* CO_2 matrix. The ozonides were identified by their infrared spectra, whose assignments were confirmed with the help of an ab initio calculation. The same reaction is imperceptible in a crystalline CO_2 matrix deposited at 65 K, becoming observable only at 77 K and higher temperatures. Molecular dynamics simulations carried out for the solid argon host indicate that a highly organized crystalline structure does not allow the motions required for the reactions. These restrictions are apparently less stringent in the amorphous solid CO_2, suggesting it as a suitable solvent for the study of reactions having a low activation barrier.

Introduction

The Criegee mechanism[1,2] of the ozonolysis of olefins is generally accepted as the best way to account for the characteristics of the reaction, which leads to the cleavage of the double bond and the formation of aldehydes (or ketones) and acids. The three-step mechanism involves three intermediates, the primary ozonide, **I** (POZ), the secondary ozonide, **III** (SOZ), and a carbonyl oxide, **II**, sometimes referred to as the Criegee intermediate (Scheme 1). Criegee was able to isolate and study some SOZ's,[3] which were later fully characterized by microwave,[4,5] and infrared[6] spectroscopies. The more reactive POZ's were first directly observed by NMR[7] and by infrared spectroscopies in low-temperature matrices,[8−10] and more recently the microwave spectrum of the ethylene POZ was obtained in a seminal paper by Gillies et al.[11] The Criegee intermediate turned out to be much more elusive, and has not yet been directly observed in an ozonolysis reaction, though the carbonyl oxide was spectroscopically identified in other systems.[12] Recently, the structure of the van der Waals complex between ethylene and ozone, which is presumably the precursor of the POZ, was determined by microwave spectroscopy.[13] Dioxirane was identified by microwave spectroscopy in the gas-phase reaction of ozone and ethylene at low temperatures,[14] but not in solution.[12] It has also never been reported as a product of the reaction in low-temperature matrices.[8−10]

Scheme 1. Criegee Mechanism of Ethylene Ozonolysis



Experimental attempts to verify Criegee's mechanism and identify the intermediates were accompanied by a considerable theoretical effort. Semiempirical[15] and ab initio[16] methods were used to study this mechanism and the properties of the intermediates involved in it: the relative energies of these species, the structures of the transition states, and the barriers of the different stages of the reaction. It was generally agreed that the formation of the POZ is the rate determining step, since it usually involves the higher barrier. The failure to observe the Criegee intermediate was explained by showing that the energy barrier for its transformation to the secondary ozonide (or directly to the final products) is smaller than the one required for its formation from the POZ. Equilibrium structures of the ozone−ethylene van der Waals complex and of the primary and

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secondary ozonides calculated by ab initio methods[13,17] were found to agree satisfactorily with experimental data.

In this paper we report that the primary and secondary ozonides of ethylene can be formed at much lower temperatures than previously observed, and that at a given temperature the reaction's progress depends on the matrix surrounding the reacting pair. Thus, no reaction was found to take place in an argon matrix at temperatures up to 35 K, while in a CO_2 matrix reaction products were identified at temperatures as low as 25 K. Molecular dynamics (MD) simulations of the trapping sites in an argon matrix are reported, and it is shown that their structure is unsuitable for ozonide formation. The apparently more open structure of amorphous CO_2 appears to allow the reaction to proceed at temperatures as low as 25 K.

In all experiments *both* the primary and secondary ozonides of ethylene were observed by their infrared spectrum, whenever reaction took place. The assignment of the spectra was aided by an ab initio calculation of the vibrational frequencies and infrared intensities of these two compounds. The implication of the simultaneous appearance of the ozonides (and the failure to observe directly the Criegee intermediate) on the applicability of the Criegee mechanism to this system is briefly discussed.

Experimental and Computational Details

Ozone was prepared from a purified oxygen (98.5%, main impurity N_2) by electric discharge. Ethylene (99.5%) from Aldrich was used as received; each gas was mixed separately with a carrier gas (argon or CO_2) to the desired concentration using standard manometric techniques. An all-glass vacuum line was used for ozone, and a stainless steel one for ethylene. The gases were codeposited (at a rate of 2−10 mmol/h) on a KBr window attached to the cold tip of a closed cycle helium cryostat (Air Products Model CS202). The infrared spectrum of the resulting matrix was recorded by a Fourier transform spectrometer (Nicolet Model 520, 0.5-cm^{-1} resolution) at any desired temperature higher than 12 K. The temperature was controlled by a Lake Shore Cryogenics Temperature Controller (Model 330 Autotuning) to within ±0.5 K. Three characteristic temperatures were used in the experiments: T_{dep}, the deposition temperature; T_{reac}, the reaction temperature; and T_{spec}, the temperature at which the spectra were recorded. The reaction temperature was defined as the highest temperature at which a reaction could be observed in a sample by monitoring its infrared spectrum. The time intervals, t_{reac}, at which the matrix was exposed to T_{reac} varied between a few minutes and several hours. In a typical experiment, ozone in CO_2 (1:265) and ethylene in CO_2 (1:310) were codeposited at 15 K. The matrix was warmed to 26.5 K in 128 min; during the heating period, spectra were recorded in the temperature intervals 16−17.4, 19−20.4, 22−23.4, and 25−26 K. The temperature was held at 26.5 K for 18 h; most of the spectral changes occurred in the first 2 h, and after 10 h further changes were minimal. The matrix was then warmed to 27 K in 10 min, and held at that temperature for 12 h, without showing any further changes. Warming gradually to higher temperatures at a very slow rate did not cause further reaction until the CO_2 began to evaporate.

Molecular dynamics simulations were performed as previously described,[18] except that the molecules were treated as rigid bodies using the RATTLE algorithm.[19] Lennard-Jones pairwise atom−atom interaction potentials were used, with the potential parameters listed in Table 1. Full technical details of the simulations can be found in a separate paper;[20] briefly, the geometry of the molecules was taken from microwave experimental data. The simulation was begun by constructing a small crystal lattice, consisting of a few hundred atoms, that serves as a template for further growth. Argon atoms were allowed to approach the surface of the template, which is kept at a low constant temperature. The molecules to be deposited were also allowed to approach the surface under the action of the interaction potentials. Periodic boundary conditions were imposed on the crystal surfaces perpendicular to the growing surface, thus simulating an infinite crystal. After the molecules were deposited, more argon atoms were deposited, at least as many as used for the template. The total number of argon atoms used in a typical simulation was 600. Many repetitions of the simulations were performed, in which the initial locations of the deposited atoms and molecules were varied at random, but always chosen from a 300 K Boltzmann distribution. Different trapping sites could be generated in different runs, and the most frequently encountered ones were considered the most stable ones, as discussed in more detail elsewhere.[18]

Table 1. Parameters of the Atom−Atom Pairwise Lennard-Jones 6−12 Potentials Used in the Molecular Dynamics Simulation[a]

atom pair	σ (Å)	ϵ (cm^{-1})
Ar−Ar	3.40	83
C−Ar	3.357	42 (for ethylene)
C−Ar	3.375	54 (for POZ)
H−Ar	3.207	18 (for ethylene)
H−Ar	3.105	22 (for POZ)
O−Ar	3.175	59
H−O	2.88	16
C−O	3.15	39
Xe−Xe	4.03	154
C−Xe	3.69	74
H−Xe	3.42	30
O−Xe	3.49	81

[a] Sources: Reference 19. Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; Wiley: London, 1973; p 45. The potential parameters for unlike atoms, were derived from the literature atom−atom parameters using the usual combination rules.[19]

Ab initio calculations were carried out using the Gaussian 92 program package[21] at the HF or HF-MP2 levels. Several basis sets were used: preliminary calculations were performed with a 6-31G, and more sophisticated ones with a 6-311G* basis set.[22] Complete structural optimization was performed for each species, and vibrational frequencies were calculated from the Hessian matrix using the harmonic approximation at the optimized geometries. No imaginary frequencies were found in the calculation, showing that the optimized structure was indeed a minimum. The resulting frequencies were uniformly scaled by 0.9427[23] for the smaller basis set and by 0.954 for the larger.

Results

Figure 1 shows a portion of spectra obtained in an argon matrix between 920 and 980 cm^{-1}. Ozone has no absorption bands in this range, and ethylene was found to exhibit two absorption features at 946.9 and 959.7 cm^{-1}, which are apparently due to two different trapping sites of monomeric ethylene in an argon matrix.[24] These two bands were observed for highly diluted ethylene in argon matrices (argon/ethylene ratio ~ 6000). A new band, which appeared only when both ozone and ethylene were codeposited, is clearly seen at 951.1 cm^{-1}; this band was not due to an oligomer of either ethylene or ozone, as verified by depositing the pure compounds at

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(24) Surprisingly little information is available on the spectra of ethylene in an argon matrix. To our knowledge, the most dilute spectra (argon/ethylene ratio = 999) were reported by: Rytter, E.; Gruen, D. M. *Spectrochim. Acta* **1979**, *35A*, 199. They found an incompletely resolved doublet at 948 and 959.5 cm^{-1}. As Figure 1 shows, we find a well-resolved pair at 946.9 and 959.7 cm^{-1} (these values vary somewhat with deposition conditions).

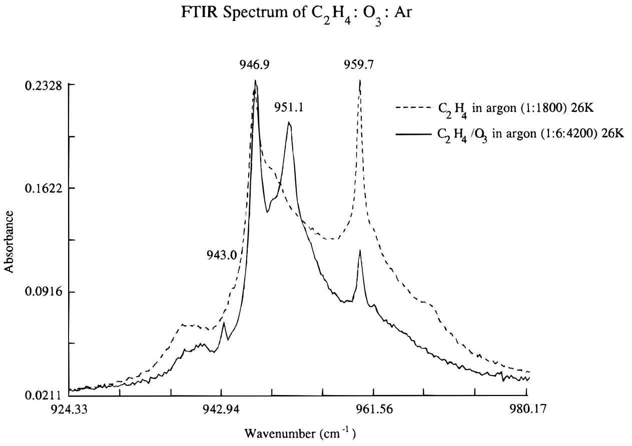

Figure 1. A portion of the absorption spectrum of an argon matrix taken at 26 K in which ozone and ethylene were codeposited at the same temperature (solid line). The dashed line shows the spectrum obtained when ethylene only was deposited under the same conditions.

different dilutions. It cannot be due to a cluster of ethylene with either water or CO_2, the most common impurities, as checked in separate experiments. It is also not likely to arise from a reaction product between ethylene and ozone: it was formed under conditons where no other new bands were observed, and the IR bands due to the first reaction product, the primary ozonide, were clearly seen upon subsequent heating of the matrix. Therefore, this band is tentatively assigned to the ethylene–ozone van der Waals adduct. (This conclusion is supported by the observation of weaker bands assignable to the adduct at 1440.2 cm^{-1}, very close to the 1440.7 cm^{-1} ethylene band, and at 2992.2 cm^{-1}; the latter is weak and broader than the other two—fwhm = 1.4 cm^{-1}. The fact that all three bands are found to be close to a strong ethylene absorption band is consistent with their assignment to an ethylene adduct.)

Warming the matrix to 35 K did not result in the appearance of new bands, nor in the decrease of the intensity of any of the old bands. Attempts were made to begin the reaction by irradiating the matrix by an infrared laser tuned to the absorption peak (the P(12) line of a pulsed CO_2 laser at 951.2 cm^{-1}), but no change in the IR spectrum could be discerned after a prolonged irradiation at 100 mJ/pulse (few hours at 1 Hz).

New bands appeared only when the temperature was raised beyond 44 K (a temperature at which the vapor pressure of the argon matrix becomes high and rapid evaporation is observed), and the previously observed absorption bands showed a marked decline. At that temperature argon was quickly pumped away, and the infrared spectra of the remaining species was found to contain a mixture of the primary (POZ) and secondary (SOZ) ozonides of ethylene, as determined by comparison with previously published spectra.[6,8−10] Warming the sample to 130 K and pumping away the remaining ozone and ethylene led to the spectrum shown in Figure 2, in which almost all absorption bands can be assigned to one of the two ozonides.

This experiment was repeated in a CO_2 matrix, deposited at temperatures between 12 and 20 K. Two ethylene bands were observed in the 950-cm^{-1} region, as in the case of an argon matrix, but they were less well resolved due to their smaller separation (~5 cm^{-1}) and rather large widths. In this matrix an absorption feature assignable to a van der Waals cluster band was also observed upon the codeposition of ozone and ethylene, although only as a small shoulder on one of the strong ethylene bands; its intensity varied between different runs, and often it could not be clearly discerned from the stronger pure ethylene bands. No IR bands due to either POZ or SOZ were observed after the deposition, as long as the matrix was kept at temperatures below 25 K, even for elongated periods of time (several days).

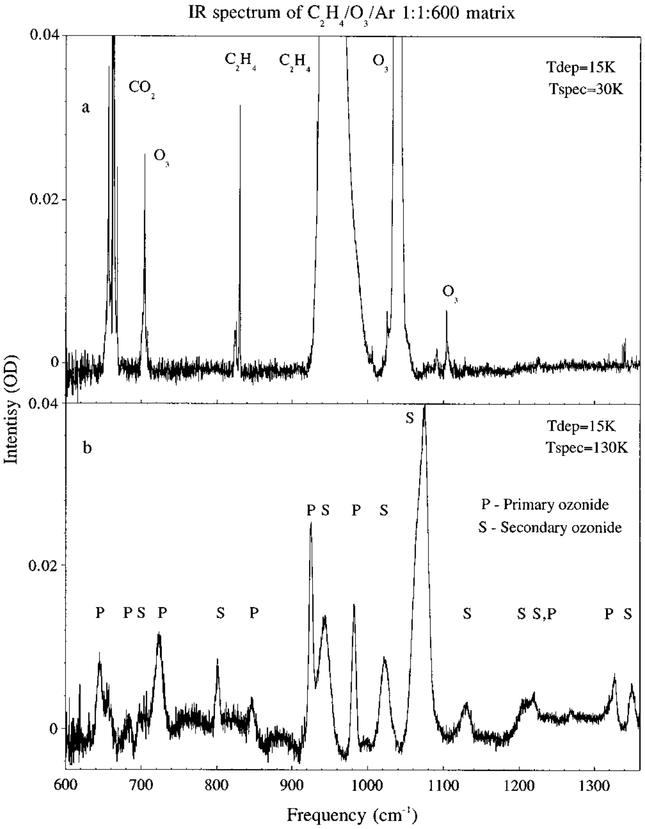

Figure 2. Infrared spectra of solid argon matrices obtained upon codeposition of ethylene and ozone (a baseline correction was applied to all spectra). (a) The spectrum of a matrix deposited at 15 K, recorded at 30 K. (b) The spectrum of the same sample after heating to 130 K and evaporating both argon and unreacted ozone and ethylene. Bands due to the POZ are marked by P and those due to the SOZ by S.

Warming the matrix to 25 K or to a higher temperature led to the appearance of SOZ and POZ bands; Figure 3 shows a spectrum recorded after the matrix was warmed to 30 K. Spectra similar to that shown in Figure 3 were recorded under different experimental conditions in which the concentrations of ethylene and ozone, the various characteristic temperatures of the experiment (T_{dep}, T_{reac}, and T_{spec}), as well as t_{reac}, were varied over a large range. Table 2 summarizes some of the results obtained under different experimental conditions; the data show that the SOZ bands were found to be more intense than the POZ ones for all experimental conditions used, with either argon or CO_2 as the matrix material. It is seen that the SOZ/POZ concentration ratio, as measured from the IR peaks' intensities, was remarkably constant for all of these experiments. This result was obtained under a large variety of different experimental conditions; in particular, the time between the deposition and the recording of the spectrum varied between 1 and 26 h. During the intervening period, the matrix was either kept at a constant temperature or subjected to programmed heating/cooling procedures.

The fact that a reaction was observed at a temperature as low as 25 K in CO_2 but not in argon might be due to the poorer heat conductivity of the amorphous solid CO_2. A possible scenario is that the actual temperature of some parts of the sample is higher than 25 K (the thermocouple was in thermal contact with the window, not with the deposited matrix). A reaction starts, and local heating (due to the exothermicity of the reaction) leads to the appearance of products. This

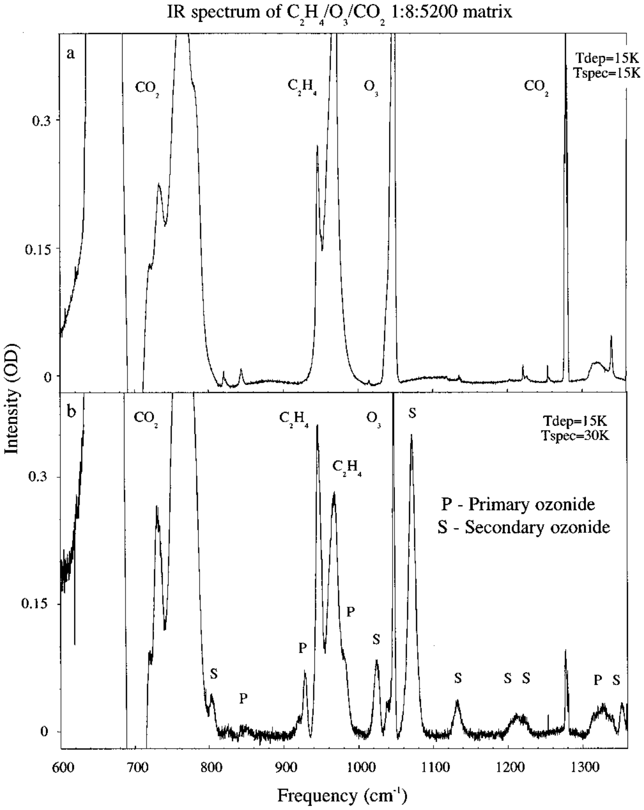

Figure 3. Infrared spectra of solid CO_2 matrices obtained upon codeposition of ethylene and ozone. (a) The spectrum of a CO_2 matrix deposited at 15 K, taken at 15 K. (b) The spectrum of the same matrix recorded at 30 K, after being kept at that temperature for 30 min.

Table 2. The Relative Concentrations of POZ and SOZ Formed in the Reaction

matrix composition			temp[a]			
C_2H_4	ozone	CO_2	T_{dep}	T_{spec}	T_{reac}	SOZ/POZ ratio[b]
			CO_2 Matrices			
1	9	7200	15	26	26	13.7
1	8.6	5200	15	29.5	29.5	11.1
1	8.6	5200	15	32.5	32.5	11.4
1	8.6	5200	65	65	77	11.8
1	8.6	5200	65	65	90	13.3
1	1	600	15	26.5	26.5	11.2
1	1	600	15	80	26.5	13.6
1	1	600	20	40	40	12.5
1	1	600	20	65	65	11.8
1	1	600	20	80	80	12.3
						12.3(1.0)[d]
			Neat Film[c]			
			15	43	43	7.1
			15	53	53	7.7
			15	60	60	7.5
			15	90	52	5.6
			15	100	52	7.3
			20	44	44	9.1
			20	60	60	9.9
			20	90	60	7.7
			20	130	60	7.7
						7.73(1.2)[d]

[a] T_{dep}, deposition temperature; T_{reac}, highest temperature at which reaction was observed before recording the spectrum; T_{spec}, the temperature at which the spectrum was recorded. [b] The ratio of the areas under the most intense lines of SOZ (1072 cm^{-1}) and POZ (926 cm^{-1}). [c] Prepared by co-depositing ethylene and ozone in an argon matrix and evaporating the argon. [d] Average (standard deviation).

Table 3. Observed and Calculated Vibrational Frequencies and Infrared Intensities of the Primary Ozonide of Ethylene (POZ)

freq (cm^{-1})		IR intensity[a]		
exp[c]	calc	exp	calc	approx description[b]
408	399	13	16	ring puckering
646	668	92	53	OOO out-of-plane skeletal deform.
686	682	7	6	OOO asymmetric stretch
725	717	57	94	CO in-ring deform.
	837		7	OOO symmetric str + CH bend
846		18		
	845		3	OOO symmetric str + bend
926	927	100	34	CO + CC stretch + CH wag
983	983	98	100	CO stretch
1214[d]	1214		6	CH in-plane bend
1328	1313	23	6	CH bend

[a] Normalized to the most intense band—926 cm^{-1} in the experiment, 983 cm^{-1} in the calculation. The experimental values are based on the integrated area under the absorption band. [b] Based on the ab initio calculation. [c] In a neat film. [d] Congested band region in our experiments, value taken from ref 8.

possibility was checked by repeating the experiment many times, under widely varying conditions: deposition rates and durations (leading to different sample thicknesses), different concentrations and different concentration ratios (that should lead to different local final temperatures). Under all these conditons, the reaction first became perceptible at the same temperature—25 K.

In order to further check the temperatures and environmental dependence of the reaction, CO_2 matrices were also prepared by depositing the same mixtures at 65 K, a temperature at which the compound is known to form a crystalline solid.[25,26] These conditions were used by Nelander and Nord[9] in their early experiments, and we repeated them in order to enable a proper comparison with the lower temperature results. In this case, a temperature of 77 K was required to observe a perceptible product absorption band as reported by ref 9. The second surge in POZ and SOZ formation reported by these authors at 90 K was also clearly observed. The SOZ/POZ signal intensity ratio under all these conditions was essentially the same as that observed for the low-temperature deposited matrix. Warming up the matrix to a temperature at which CO_2 evaporates (120−130 K) resulted in diminution of the SOZ signal, probably due to evaporation.

Some codepositions of ozone and ethylene at 15 K without any solvent were also made. Warming to 44−55 K resulted in the observation of POZ and SOZ absorption bands, in this case with a somewhat different ratio than in the CO_2 matrix case, as seen from Table 2. The experimental vibrational frequencies and relative IR intensities of the POZ are listed in Table 3 and compared with the values calculated by the ab initio quantum chemical method. Agreement with experiment is seen to be satisfactory, allowing proper assignment of the spectrum. A more detailed discussion of the calculation and assignment will be published separately.[27] The vibrational frequencies and relative IR intensities of the SOZ were also calculated by the same method, the results agreeing very well with the analysis of Günthard and co-workers.[6,28]

In order to convert the relative values to absolute ones, it is necessary to know the relative molar absorption coefficients of at least one band each for the POZ and the SOZ; this information is not available at the moment. A rough estimate may be made based on the *computed* results, according to which the absolute

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intensity of the strongest SOZ band at 1072 cm^{-1} is about 20 times larger than that of the strongest POZ band at 926 cm^{-1}. This result leads to a SOZ/POZ concentration ratio of about 1:2 in all the CO_2 matrix experiments reported above, and of 1:3 in the neat film experiments.

Attempts to identify absorption bands due to carbonyl oxide (the Criegee intermediate) and formaldehyde (which sould be formed together with it) were made throughout this work. In line with previous reports,[9,10] no such bands were observed. In some experiments, a strong and narrow absorption band appeared in the 1715−1722-cm^{-1} range; it is almost certainly due to a carbonyl compound. These bands were usually observed only after the matrix was subjected to relatively high temperatures, and the solvent was evaporated. Other known strong formaldehyde bands[29−31] at 1500 and 2797 cm^{-1} were sought, but were either not observed at all or observed at a much smaller relative intensity than observed for authentic formaldehyde samples. It is concluded that formaldehyde monomer are not formed under the experimental conditions used in this work, and the identity of the 1720-cm^{-1} band remains uncertain. One possibility is a polymeric form of a carbonyl compound.

Analysis and Discussion

The structure of the ozone−ethylene van der Waals adduct was recently determined in the gas phase by microwave spectroscopy;[13] the two molecules are separated by about 3.24 Å and lie roughly parallel to each other. In the POZ, the oxygen atoms are much closer to the carbons, about 1.42 Å.[2,11] The molecular dynamics simulations performed on an fcc-based argon matrices show that several trapping sites are possible for ozone in argon, the most stable ones being mono- and disubstitutional sites (ozone replacing one or two adjacent argon atoms), in agreement with a recent analysis of the infrared spectrum of ozone in rare gas matrices.[32,33] The simulation shows that the most stable trapping site for ethylene is a disubstitutional one, a trisubstitutional one being also formed but with a smaller probability.

Over 20 simulation runs by POZ depositions were made, using the known gas-phase structure of the molecule.[11] The structure of the most frequently generated trapping site of POZ is shown in Figure 4. The molecule is seen to occupy a trisubstitutional site, the argon atoms being removed from a 111 plane. The MD simulation of the codeposition of ozone and ethylene leads to several trapping sites in which the two molecules lie close together; the calculated structures of two commonly encountered sites are shown in Figure 5. In both cases, the structure is found to be quite different from the most stable gas-phase one,[13] probably since it is determined predominantly by the argon lattice. It is immediately apparent from the trapping sites' structures shown that a considerable geometrical rearrangement is needed to attain a configuration that can evolve to the POZ structure. This rearrangement would require a major movement of the matrix argon atoms, which is extremely unlikely unless the matrix contains an appreciable number of vacancies. Thus, the absence of a reaction between ethylene and ozone in low-temperature argon matrices is accounted for by the MD simulations. Only when the matrix is severely softened, or eroded by evaporation of argon atoms, does the reaction to form the POZ become observable.

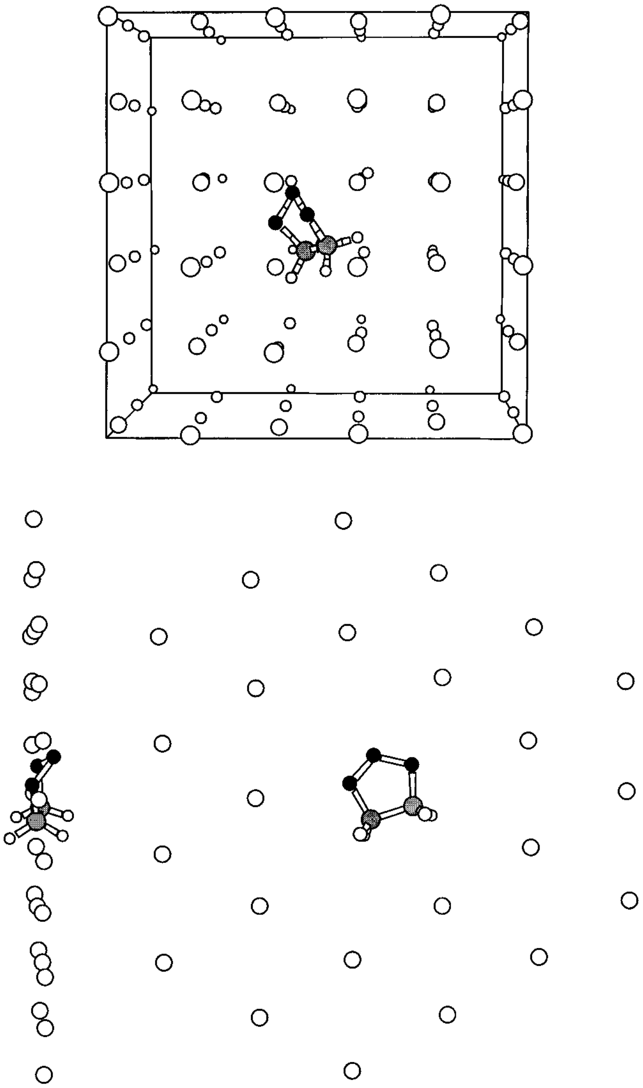

Figure 4. The structure of the most frequently obtained trapping site of POZ deposited in an argon fcc lattice at 25 K as calculated by the molecular dynamics simulation. Only a small portion of the actually calculated structure is shown, to facilitate the exposition of the geometry near the trapped molecule. The molecule is seen to displace three argon atoms from a 111 plane of the crystal lattice, the displaced atoms forming a triangle. The upper part shows a three-dimensional representation of the site. The bottom part shows cuts taken along the lattice planes in which argon atoms were replaced by the molecule. The key is as follows: argon atoms are shown as open large circles, hydrogen atoms as smaller open circles, oxygen atoms are black, and carbon atoms are gray.

It is reported that ethylene reacts with ozone in a xenon matrix at temperatures exceeding 50 K.[10] Xenon, as argon, forms a fcc crystal, and we ran simulations on this solid in a similar fashion. The main difference is the larger lattice constant of xenon (6.136 Å at 20 K as compared to 5.318 Å for argon),[34] which allows more space in substitutional sites. Molecular dynamics simulations were run for a fcc xenon lattice held at 50 K. It was found that in most runs, ethylene, as well as ozone, occupies a single substitutional site in solid xenon; the van der Waals pair occupies a disubstitutional site, and the POZ, a single (!) substitutional site, which tends to displace neighboring matrix atoms from their equilibrium positions somewhat, but occupies a volume *smaller* than that engaged by the van der Waals pair. It follows that according to the simulation, the transformation of the van der Waals adduct to the primary ozonide can take

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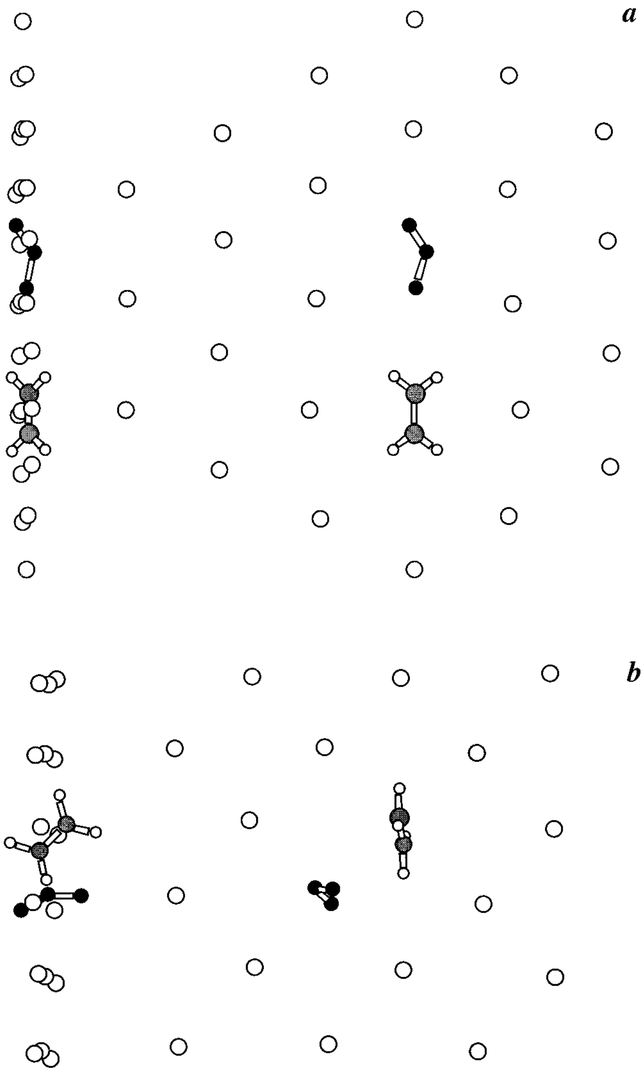
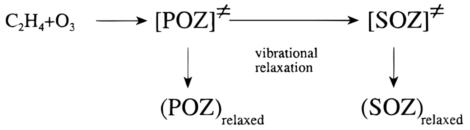


Figure 5. The structure of the two most commonly obtained trapping sites for the ozone−ethylene van der Waals adducts in a fcc argon lattice, as obtained by the molecular dynamics simulations (25 K deposition). See the caption of Figure 4 for an explanation of the symbols. One (a) is a three-substitutional site, in which the ethylene and ozone molecules substitute three argon atoms lying in a row in a 111 plane of the crystal lattice. The other (b) is a disubstitutional site in which the two molecules replace two adjacent argon atoms in a 100 plane of the lattice (compare with the triangular three-substitutional site of POZ shown in Figure 4).

place within a trapping site, without requiring a major motion of the surrounding solvent atoms. The agreement of the xenon matrix simulation with the experimental result enhances the significance of the negative result obtained by the simulation for the argon matrix.

Simulations of CO_2 matrices were not performed at this stage, but the observed data can be qualitatively accounted for from the known properties of solid CO_2.[25,26,35] Deposition in the temperature range of 15−30 K leads to the formation of an amorphous solid, while careful deposition at temperatures higher than 55 K results in a cubic T_h^6 crystalline structure. The amorphous form is considerably more “open” than the crystalline one, and presumably permits more translational and rotational motion than the latter, although the ambient temperature is lower. Several attempts to measure the temperature dependence of the POZ and SOZ formation were made; the reaction was found to be essentially complete in less than 30 min at 30 K, while at 26.5 K, about 30% conversion was found after 2 h. However, an exact value for the activation energy could not be established since rapid heating caused damage to the rather fragile matrix, and when slower heating was used, contribution from lower temperatures than 30 K to the reaction progress could not be neglected, nor quantified. In any case, a very low barrier (less than 2 kcal/mol, and probably as low as 0.2 kcal/mol) is indicated for the reaction in amorphous CO_2.

Scheme 2. Proposed Reaction Sequence Leading To Formation of POZ and SOZ



In the highly ordered and more densely packed crystalline solid obtained upon deposition at 65 K, no reaction takes place. Heating to 77 K and higher temperatures appears to allow rotational motion in trapping sites containing the ethylene and ozone, generating a configuration that enables the transition state to be formed. The additional upsurge in reactivity observed at 90 K may be due to the onset of diffusion that allows molecules initially separated by lattice CO_2 molecules to approach each other and react, as suggested in ref 9. The solid state value is lower than the reported gas-phase activation energy—4.7−4.9 kcal/mol,[36,37] which was measured at much higher temperatures (down to 178 K). An artifact caused by local heating of the matrix due to the exothermicity of the reaction might conceivably be the reason for this discrepancy. This was carefully checked by varying the concentrations of the reactants over more than an order of magnitude. Since no differences in the temperature dependence of the reaction under these widely different conditions could be observed, this option appears extremely unlikely. The reason for the lower activation energy in the low-temperature deposited solid CO_2 (as compared to the gas phase) is not clear at this point. This phase is known to be characterized by a very large surface area.[38] Thus, this solid appears to contain large cavities, allowing ozone and ethylene to approach each other. Surface catalysis by this rather open structure is an option, but we cannot suggest a mechanism by which the energy barrier of the reaction is reduced. Further work is needed to clarify this issue.

A notable result of this study is the constant SOZ/POZ concentration ratio obtained in solid matrices whenever a reaction took place. This was found to be the case for very different concentrations, reactant ratios, heating rates, and reaction temperatures (Table 2). The constant ratio is seemingly at variance with the accepted Criegee mechanism, according to which the POZ is formed first, and subsequently transforms, via the Criegee intermediate, to the SOZ. In the low temperatures used in this study, POZ is indefinitely stable, and should not form SOZ at all. The latter must, therefore, be formed either before POZ has a chance to become vibrationally stabilized or in an independent route. Scheme 2 offers a model that can be used to qualitatively account for this apparent discrepancy. According to semiempirical calculations,[15] the overall barrier of the reaction is due to the formation of the POZ. In the cold environment of the matrix, the transition state formed by the encounter between ozone and ethylene is stabilized by collisions to form the POZ. Once in the bottom of its potential well (i.e.,

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vibrationally relaxed), the barrier to dissociation to the carbonyl oxide and formaldehyde (~20 kcal/mol) is much too large for a thermal reaction to take place at the temperatures used in this work. Indeed, the POZ is known to be thermally stable up to about 180 K.[11] Thus, any thermally relaxed POZ formed in the reaction is accumulated in the matrix. The SOZ, therefore, must be formed also upon the initial encounter between ozone and ethylene and not from a vibrationally relaxed intermediate. A possible SOZ precursor is the vibrationally excited POZ initially formed by the reaction. Assuming that the same barrier must be overcome to form both ozonides, their branching ratio is determined, in the Arrhenius description, by the pre-exponential factor, which according to the transition state theory relates to the entropy of activation of the reaction.

As mentioned above, all attempts to identify absorption bands due to carbonyl oxide (Criegee intermediate) and formaldehyde (which is expected to form alongside it) failed. Experimental evidence for carbonyl oxide existence in the ozonation reaction depends solely on trapping experiments.[2] However, the possibility that the trapping agents react with some reactive species (such as vibrationally excited POZ) cannot be excluded. Such reactions could lead to the same final products as those of the Criegee intermediate. The experimental observation of the POZ and SOZ at low temperatures allows, in principle, the direct assessment of the sequence of events assumed by the Criegee mechanism. Perusal of the available literature shows that whenever these two ozonides were observed, the SOZ was detected simultaneously with the POZ, rather than sequentially (see for instance ref 11 for gas-phase results). It is concluded that as far as existing kinetic and spectroscopic evidence goes, both ozonides may be formed from the same precursor state.

The fact that the reaction is observed in amorphous CO_2 at temperatures as low as 25 K indicates that considerable translational and rotational motions are possible in this environment. This suggests the use of this porous “solvent” for the quantitative study of the kinetics of reactions characterized by low activation barriers. In order to realize this option, it would be necessary to find ways to mechanically stabilize amorphous CO_2 solids, which tend to be rather fragile under the conventional preparation scheme used in this work.

Summary

The reaction between ozone and ethylene was studied at low temperatures in the solid state. No reaction was observed in an argon matrix, while in a solid CO_2 the reaction proceeded at temperatures as low as 25 K. The two major products identified by infrared spectroscopy were the primary and secondary ozonides of ethylene; they were produced at a constant ratio under a wide variety of experimental conditions. The identification of the primary ozonide was supported by an ab initio calculation of the IR spectrum. Molecular dynamics simulation of the deposition indicates the trapping sites formed in the rigid argon matrix are not suitable for the formation of the primary ozonide from the ozone−ethylene van der Waals adduct. In contrast, the trapping sites in a xenon matrix, which has a larger lattice constant than argon, are calculated to be able to allow a reaction without the need to disrupt the solid. The facile reaction in amorphous CO_2 at very low temperatures is apparently due to the open structure of this solid.

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