Photolysis of Hexafluoro-2-butyne/Ozone Mixtures in Cryogenic Matrices

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Abstract: Matrix studies on the photolytic reaction between ozone and hexafluoro-2-butyne have been performed at 11 K in argon and nitrogen matrices. The matrices were photolyzed with 640 and 642 nm light from a laser source, and with 254 nm light from a Hg arc lamp. The final products of the reaction are perfluorobutanedione and bis(trifluoromethyl)ketene. An intermediate species was also observed. It has been identified as perfluoroacetylmethylmethylene, a ketocarbene. The ketocarbene was also trapped as trifluoromethyl trifluoroacetylketene, a ketoketene, when the matrix was doped with CO. Photolysis of the ketocarbene with 427 nm light results in the direct formation of the ketene. The ketocarbene and ketene form as a result of O atom addition to the butyne, whereas the butanedione appears to be predominantly produced by a reaction between the ketocarbene and O_2. Product distribution was found to depend greatly on both matrix material and ozone concentration. This is the first direct evidence of a ketocarbene as an intermediate in the O atom addition to an alkyne.

Introduction

Ozone serves as an excellent source of oxygen atoms in cryogenic matrices,[1] allowing for mechanistic studies into O atom chemistry, studies that are of importance to atmospheric and combustion chemistry.[2] By careful selection of the photolysis wavelength one can investigate both ground-state and excited-state O atom chemistry.[1,3] Of particular interest to us is the addition of O atom to simple alkynes. A general mechanism for O atom addition to unsaturated hydrocarbons was suggested by Cvetanovic in 1963.[4] For an alkyne, the atom is expected to add across the triple bond, forming a 1, 3-diradical. Rearrangement of the diradical can result in the formation of oxirene and ketocarbene. The expected final product of the reaction is a ketene. The activation energy for O atom addition to an alkyne is below 1 kcal/mol.[5]

Because of its direct relevance to combustion and flame chemistry the mechanism for the addition of O atom to the simplest alkyne, acetylene, has received the greatest amount of attention. The bulk of the experimental investigations have been performed in gas phase or in solution. These investigations span a period of over 30 years and are well reviewed in combustion chemistry texts and in relatively recent publications.[2,6−8] Gas-phase $O(^3P)$ atom addition to acetylene has been shown to produce many stable final products such as carbon monoxide, propyne, and allene.[9] When Haller and Pimentel performed the reaction in a cryogenic matrix, only one product was observed, ketene.[10] Although low-temperature cryogenic matrices serve as an excellent environment for trapping and detecting intermediates, the suggested intermediates in the acetylene/O atom reaction (oxirene and formylmethylene) could not be detected by Haller and Pimentel. Theoretical work by Schaefer and co-workers indicates that both oxirene and formylmethylene are true minima in the potential energy surface that includes oxirene, the ketocarbene, and ketene.[11] However, the calculated barrier for the conversion of the two intermediates to ketene is in the range of 21−23 kJ/mol, a very small value when compared to the exothermicity of the addition of O atom to acetylene. The intermediacy of a diradical has been supported by molecular beam studies by Schmoltner, Chu, and Lee.[6]

O atom addition to simple alkynes such as dimethylacetylene could provide a greater opportunity for detection of unstable reaction intermediates such as oxirenes and ketocarbenes, if these species are truly involved in this addition. Fenwick and co-workers showed that oxirene involvement in various Wolff rearrangements was strongly dependent on the substituent groups.[12] Dimethyl substitution was shown to be the most conducive to oxirene involvement, suggesting that dimethyloxirene is a more stable species than its unsubstituted counter-

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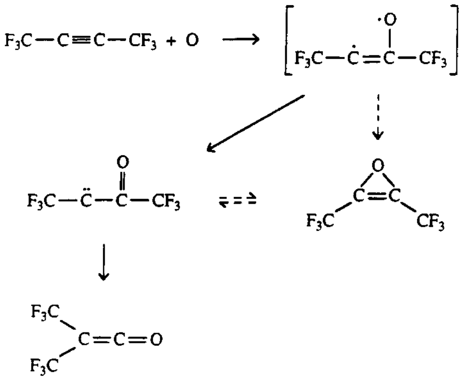
part, and thus has a higher probability of being trapped in a cryogenic matrix, a statement supported by Fowler, et al. theoretical work.[13] In 1986 Debu and co-workers reported that they had trapped dimethyloxirene as an intermediate in the photochemically induced Wolff rearrangement of 3-diazo-2-butanone in a cryogenic matrix.[14] Unfortunately similar success was not obtained when Nakata and Frei attempted to trap intermediates in the addition of O atom to dimethylacetylene in a cryogenic matrix environment.[8] Nakata and Frei were unable to obtain evidence to support an oxirene intermediate in this reaction, however strong indirect evidence was obtained to establish the formation of a ketocarbene intermediate, acetylmethylmethylene. Nakata and Frei's work provides the first evidence that a ketocarbene intermediate is involved in the O atom addition to substituted alkynes. These authors also questioned whether Debu and collaborators assignment of observed infrared bands to dimethyloxirene was correct. The dimethyloxirene is reported to possess its strongest infrared absorption at 2137 cm^{-1}. Nakata and Frei pointed out that it seems unlikely that the strongest band of this symmetric oxirene would be due to the carbon═carbon double bond. They speculated that the observed absorption could also be due to dimethylketene, the final product of the Wolff rearrangement. The infrared absorption of the ketene moiety is known to shift, depending on the mode in which it is prepared in the matrix.

Only one other simply substituted oxirene has been trapped in a cryogenic matrix, bis(trifluoromethyl)oxirene. Strausz' group produced this oxirene by photolysis of perfluoro-3-diazo-2-butanone in a cryogenic matrix.[15] Although the detection of this oxirene has also been clouded by some controversy, Strausz and co-workers have stood by their assignment.[16,17] The infrared bands assigned to this compound were shown to disappear upon photolysis with 360 nm light and upon heating to 15 K, generating the spectrum of bis(trifluoromethyl)ketene, the final product of the Wolff rearrangement. Additional work by this group with more complex perfluorinated diazoketones also supports this assignment.[15] The infrared bands belonging to the ketocarbene could not be detected in the matrix work; however, the ketocarbene was detected by ESR when solid perfluoro-2-diazo-3-butanone was photolyzed with wavelengths greater than 300 nm at 30 K.[18] Strausz and co-workers also performed gas-phase studies on the O atom addition to hexafluoro-2-butyne.[19] The products of the reaction also support the conclusion that a ketocarbene intermediate is involved in the gas-phase addition of O atom to the butyne.

The simplest ketocarbene detected by its infrared spectrum is the ketocarbene produced by the photolysis of 2-diazo-1(2H)-acenaphthalenone.[20] Several other large ketocarbenes were also detected as intermediates in the photolysis of diazoketones by McMahon, et al. The identification of these compounds was facilitated by chemical trapping with molecular oxygen and CO.

Scheme 1



Strausz' body of work suggested to us an alkyne with which to initiate our studies on the photolytic reaction between ozone and alkynes, hexafluoro-2-butyne. Unlike Nakata and Frei, we elected to have ozone rather than NO_2 as our O atom source. Although NO_2 will produce the less energetic O atom, it possesses a significant amount of additional nitrogen oxide chemistry, which could obscure important regions of the infrared region.[8] Ozone also affords us the possibility of easily investigating both the chemistry of ground-state oxygen atoms, produced by excitation into the Chappuis band of ozone, and the chemistry of an excited state of the atom, produced by excitation into the Hartley band of ozone.[3] In this work we report our initial investigations in the photolytic reaction between ozone and hexafluoro-2-butyne in a cryogenic matrix environment. O(^{3}P) was produced by photolysis of ozone with red light, while O(^{1}D) was produced by photolysis with UV light. We have made extensive use of Strausz, et al. and McMahon, et al. works to assist us in the difficult task of product identification. Scheme 1 presents a possible reaction mechanism for the O atom addition to an alkyne, as applied to hexafluoro-2-butyne. Most published work indicates formation of the ketene is through a ketocarbene intermediate.[8,11,12,14,21−23] Debu and co-workers indicated that an oxirene intermediate can also be present when a ketocarbene is formed, and thus we have included this species in the scheme even though there currently is no published evidence suggesting that an oxirene is produced in the O atom addition to an alkyne.

Experimental Section

Mixtures of hexafluoro-2-butyne/inert gas (1/100) and ozone/inert gas (1/150 to 4/100) were co-deposited through two separate jets at a combined flow rate of 1.0−1.5 mmol/h onto a cold CsI window. Two different matrix materials were used, Ar (Matheson, 99.9995%) and N_2 (Matheson, 99.998%). The window was cooled to 11 K by an Air Products two stage closed cycle helium refrigerator (model HC2 with DE-202 expander). All of the deposition and photolysis were carried out at 11 K. Infrared spectra were recorded at 11 K by a Mattson Nova Cygni II FT-IR spectrometer at a resolution of 0.50 cm^{-1} (200 scans) with a frequency accuracy of $\pm$ 0.1 cm^{-1}.

Photolysis sources were: a Bausch and Lomb medium-pressure mercury arc lamp (200 W Hg) and a Argon-ion pumped dye laser (Coherent Innova 70 and 599). Assorted Oriel and Corning filters were used to limit the lamp photolysis wavelengths. Laser powers at the cryostat ranged from 0.6 to 1.1 W and were measured using a Molectron

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power meter (model PM10). The beam, which was not focused, had an area of about 0.60 cm^2 at the cold window.

Ozone was prepared by static electric discharge (Tesla coil) of oxygen (Matheson 99.998%) and collected in a Pyrex tube at 77 K. Excess oxygen was removed by pumping. Diluted ozone samples were stored in a passivated stainless steel vacuum system and used within a few hours. Hexafluoro-2-butyne (Columbia Organics, 99%) samples were prepared by dilution of the middle of three fractions of condensed gas. $^{18}O_2$ was obtained from Cambridge Isotope Laboratories (98% ^{18}O and 60% ^{18}O). Carbon monoxide was obtained from Matheson (99.5%).

Results

Samples of hexafluoro-2-butyne and ozone were co-deposited for 2−3 h at 11 K. In the spectrum obtained after deposition all the infrared absorption bands could be attributed to the hexafluoro-2-butyne/ozone sample except for absorptions at 2344 and 667 cm^{-1} due to carbon dioxide, a common impurity in the ozone samples. The Supporting Information contains a sample spectrum for a 1/2/200 $C_4F_6/O_3/Ar$ matrix in which 2.57 mmol of the ozone mixture and 2.41 mmol of the C_4F_6 mixture were deposited. The deposition spectra show that several of the peaks are saturated due to the strong intensity associated with C−F stretches. Deposition of smaller amounts of materials would not have allowed us to detect some of the smaller absorption bands associated with the products.

Exposure of the C_4F_6/O_3/inert gas matrices to globar radiation (5000−500 cm^{-1}) for 24 h revealed no infrared induced reaction. After the deposition spectrum had been recorded, the matrices were photolyzed with the selected photolysis source, and spectra were collected intermittently throughout the photolysis to observe product growth. Since O_2 is a common impurity in ozone samples, hexafluoro-2-butyne/O_2/Ar (1:6:200) matrices were also photolyzed with the same photolysis source. A reaction was not observed. The UV−vis spectrum of a C_4F_6/ozone/Ar matrix was also collected. The spectra did not exhibit any absorptions in the visible. This is not surprising since the expected absorption of ozone in the visible (Chappuis band) is extremely weak.[1,3] Charge-transfer complexes between ozone and the alkyne or oxygen and the alkyne, if present, are not expected to exhibit absorptions in the visible.[24] Thus, the chemistry observed during the laser or lamp photolysis is directly due to ozone's photochemistry and dissociation to produce oxygen and oxygen atom. Thermal chemistry between the ozone and the alkyne was not observed when a 1:4:200 matrix was taken from 11 to 33 K. Again, an expected result since the thermal reaction between ozone and acetylene possess an activation energy of 10 kcal/mol.[25]

642 nm Laser Photolysis. Table 1 lists the photolysis product bands observed in the 642 nm photolysis of a 1:2:200 $C_4F_6/O_3/Ar$ matrix. The third column of the table lists the ^{18}O isotopic shifts observed. The second column provides the peak absorbances obtained after 128 min photolysis with 1.05 W for a 1/2/200 matrix. Figure 1 shows the difference spectrum corresponding to that data set. One band listed on the table, 1623.9 cm^{-1}, is not produced by the photochemical reaction between hexafluoro-2-butyne and ozone. This band appears in the photolysis of dilute concentrations of ozone in a argon matrix (2:200 and below) in the absence of the alkyne. It is not observed when a 4/200 O_3 to Ar mix is photolyzed. We are not certain at this moment in time of the identity of this peak, but we do know it is not the result of chemistry with the alkyne.

Table 1. Product Frequencies (in cm^{-1}) for a $C_4F_6/O_3/Ar$ Matrix (1:2:200) Photolyzed with 642 nm for 128 min with a Power of 1.0 W

$C_4F_6 + {}^{16}O_2$	peak absorbance	$C_4F_6 + {}^{18}O_2$	photo[a]	assignment
2193.3, 2195.5	0.116	2161.0		K
2183.7	0.026	2174.2		K
2138.3	0.009	2086.6		CO
1936.7	0.001	nd[e]		K
1908.6	0.002	nd		K
1862.7	*b*	nd		K
1771.9	0.022	1732.2		BD
1623.9	0.017	nd		O_3[c]
1591.9	0.003	nd		?[d]
1421.2	0.080	1410.8		K
1341.0	0.093	1341.0		K
1311.7	0.020	1308.2		K
1230.6, 1228.1	0.069	1229.2	X	X
1215.8	0.063	1215.2		BD
1160.8, 1158.5	0.093	1158.7	X	X
1131.2	*b*	1131.0		BD
1110.9	0.017	1110.8		K
999.6	0.002	*b*		K
992.5, 991.3	0.041	*b*		K
986.7	0.024	*b*		K
967.7	0.004	*b*		K
873.1	0.032	872.4	X	X
860.2	0.029	859.0		BD
764.5	0.002	761.7		K
733.2	0.009	731.4	X	X
726.9	0.011	725.0		K
707.4	*b*	704.3		BD
696.1	*b*	*b*		K
660.0	*b*	658.6	X	X
559.5	0.012	557.5	X	X
553.0	0.008	551.8		K
534.5	0.022	533.2		BD

[a] The bands marked with an X disappeared rapidly when the matrix was exposed to full arc of a 200 W Hg lamp (with no detected heating of the matrix by the lamp). [b] These bands are partially obsecured by reactant absorptions making it difficult to either give a correct peak absorbance or not being able to observe the band at all in the isotopically substituted matrix. [c] As mentioned in the text this band is observed when low ozone concentrations are photolyzed in an Ar matrix. Origin is unknown but it is not the result of C_4F_6 chemistry. [d] Band we were unable to identify in Ar matrix because of the weakness of the band. Identity is obtained in N_2 matrix work. See Table 4. [e] nd − not detected.

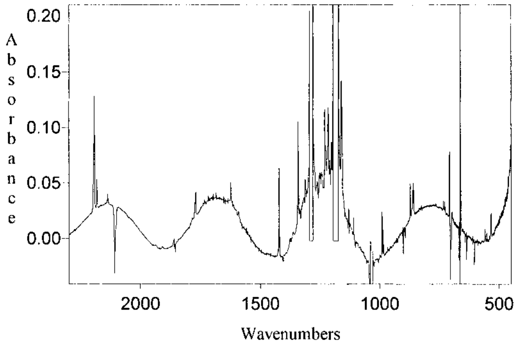

Figure 1. Difference spectrum for a 1/2/200 $C_4F_6/O_3/Ar$ matrix photolyzed for 128 min with 642 nm light (1.05 W). Positive peaks correspond to products while negative peaks correspond to reactants.

The infrared bands in Table 1 were assigned to different products (labeled K, CO, BD, and X) by several methods. Assignment was accomplished by comparing the peak intensity for runs with differing ozone concentrations and by following the photolytic behavior of each band as a function of time and wavelength. Table 1 partially documents some of these observa-

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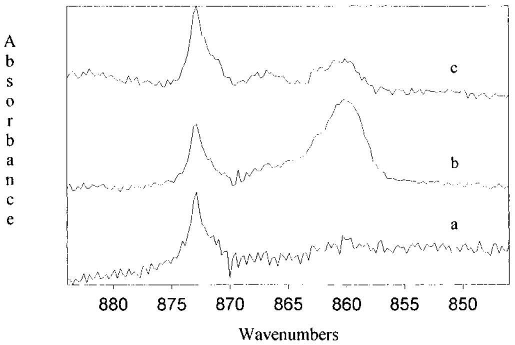

Figure 2. Product bands in the 642 nm photolysis of $C_4F_6/O_3/Ar$ matrices (a) 1/0.7/200, (b) 1/2/200 − uniform mixing during deposition (c) 1/2/200 − poor mixing during deposition.

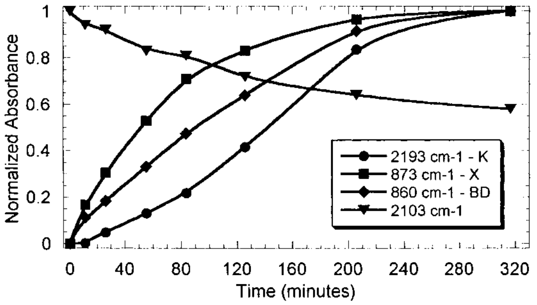

Figure 3. Product growth curves for 642 nm photolysis of $C_4F_6/O_3/$ Ar matrix (1/2/200). 2103 cm^{-1} band corresponds to ozone.

tions. The use of ozone concentration variations in assigning absorptions to a particular product is well illustrated with Figure 2. The 860 cm^{-1} and the 873 cm^{-1} bands are shown to belong to different products by just altering the alkyne-to-ozone ratio in the matrix. Figure 2 shows the 890−845 cm^{-1} spectral region for three different experiments. Spectrum a corresponds to a 1/0.7/200 alkyne/ozone/Ar matrix. Spectra b and c correspond to a 1/2/200 alkyne/ozone/Ar matrix. However, b is for a uniform deposition of the two gas mixtures (alkyne/Ar and ozone/Ar) and c corresponds to a poor deposition of the two gas mixtures, where more of one gas mixture was deposited than of the other at any given time, sort of a sandwiching effect. These three spectra show similar intensities in the 873 cm^{-1} band but differing intensities in the 860 cm^{-1} band. This does not necessarily imply that only the 860 cm^{-1} band is affected by ozone concentration but rather shows that varying the ozone concentration allows one to identify bands that belong to the same species. It is clear that the 873 cm^{-1} band corresponds to a different product than the 860 cm^{-1} band.

Not all of the bands in Table 1 could be categorized by comparison of peak absorptions between different runs either because some of the bands were not detected in one of the runs or because of overlaps with strong reactant absorptions. For most of these bands the assignment was made by following the bands photolytic behavior and comparing it to that of bands already categorized. Figure 3 shows the irradiation time dependence of several of the product bands and ozone (2103 cm^{-1}) for a 1/2/200 alkyne/ozone/Ar matrix. A similar plot was obtained for a 1/0.7/200 matrix. The data are plotted as a function of photolysis time versus normalized absorbance so as to allow for a comparison between bands of significantly different intensities. Bands due to K exhibit a clear time delay at both concentrations, indicating that they are secondary products of the photolytic reaction. Bands due to product X clearly are primary photoproducts of the reaction. Product BD bands also exhibit primary photoproduct behavior at all the concentrations investigated.

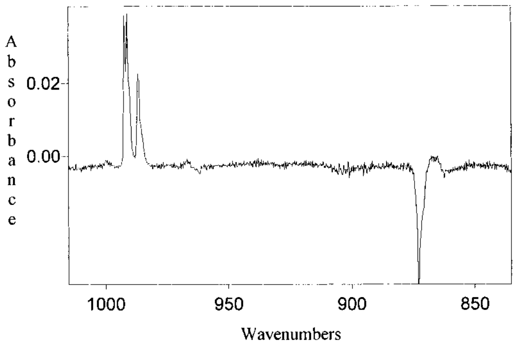

Figure 4. Effect of 427 nm photolysis (52 min) on product X band at 873 cm^{-1}.

Normalizing the absorbances makes for a convenient way of illustrating kinetic data, but it does not provide quantitative information regarding how much of a particular product was produced. It is difficult to obtain exact numbers for this since it is not trivial to obtain extinction coefficients for infrared bands in a condensed matrix environment. The only way we can quantify these differences is by comparing band intensities. It is clear from Figure 2 that the ratio of the 873 cm^{-1} band's integrated peak area to 860 cm^{-1} band's integrated peak area (A873/A860) is altered by changing the ozone concentration. Low ozone concentrations result in a larger A873/A860 ratio indicating that the reaction favors formation of product X under dilute conditions with reduced amount of product BD. At high ozone concentration product BD is favored and the A873/A860 ratio decreases. Both peaks are present in Ar matrices at all concentrations investigated.

Table 1 also indicates that bands assigned to product X exhibit photochemical activity. Exposure of a matrix that contains significant amount of product X to the full arc radiation from 200 W Hg lamp for 15 s causes product X bands to disappear. Bands due to product K and BD do not decrease in intensity when exposed to the Hg arc. Additional investigations into this photolytic reaction showed that product X bands could be converted to product K-bands by exposing a matrix to very dim 427 nm light (fwhm of 14 nm) produced by the combination of an Oriel 57510 filter with a Schot 3389 long pass filter. Figure 4 illustrates the effect 427 nm photolysis has on the infrared band of product X. The 873 cm^{-1} band shows up as a negative peak in the difference spectrum obtained after the photolysis with 427 nm light. The 992 cm^{-1} peak attributed to product K appears as a positive peak in this spectrum. No change was detected in either the ozone or alkyne bands if one was careful to use a matrix with low amounts of ozone. If significant amount of ozone were still present, the loss of product X and consequent production product K was still observed but in addition some of the other products are produced due to the fact that ozone photodecomposes with 427 nm light. Figure 5 illustrates the photolytic behavior of the 873 and 992 cm^{-1} bands during the course of the photoconversion of product X to product K with 427 nm light.

On the basis of all of the observations detailed above bands were categorized as belonging to products X, K, or BD. (A band due to carbon monoxide, CO in Table 1, was easily identified by comparison to literature and by its ^{18}O isotopic shift.) Typically, bands that behave in the same manner throughout several different experimental conditions are, as a first assumption, assigned to the same product. Product identification can be initiated by comparing our results with previous matrix studies on the O atom addition to simple alkynes. The expected final product in the O addition to an alkyne in a matrix

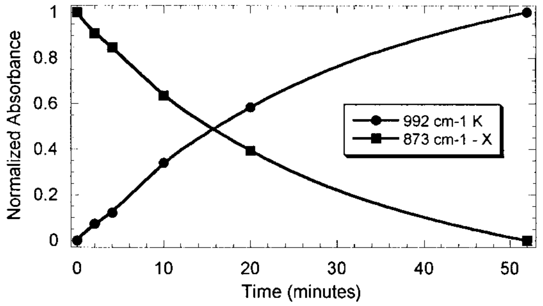

Figure 5. Kinetic curves for the photoconversion of product X to ketene by 427 nm light.

Table 2. Infrared Bands (in cm^{-1}) of Bis(trifluoromethyl)Ketene

ref 32 gas phase[a]	ref 15 Ar matrix	our work Ar matrix	our work N_2 matrix
2194	2192	2193.3, 2195.5	2202.4, 2198.9
1417	1420	1421.2	1422.7
1343	1340	1341.0	1342.7
1313, 1308	1310, 1305	1311.7	1313
1282		*b*	*b*
1194	1188	*b*	*b*
1135		1110.8	1111.2
991	992	992.5, 986.7	991.1, 985.6
763		764.5	763.3
728		726.9	725.5
668		*b*	*b*
555, 550	550	553.0	551.8
540	535	534.5	534.5

[a] Medium to very strong bands only. [b] Obscured by infrared bands of the starting material(s).

environment is a ketene.[8,10] In the particular case of hexafluoro-2-butyne the ketene observed should be bis(trifluoromethyl)-ketene. The strong band in the 2100−2200 cm^{-1} region in band set K is consistent with a ketene moiety. Comparison of these product bands to both gas phase and matrix spectra for bis-(trifluoromethyl)ketene confirms the fact that we observe this ketene in our work (Table 2). The kinetic curves for the ketene indicate that it is not the initial species formed in the addition of the O atom to C_4F_6.

This leaves two distinct sets of bands to assign, of which one, or both, should be the precursor to the ketene. The infrared band set which includes the 860 cm^{-1} band, set BD, consists of only five strong bands, strongly suggesting a molecule with some level of symmetry. The observed infrared bands are: 1771.9, 1215.8, 860.2, 707.4, and 534.5 cm^{-1}. The isotopic shift on the 1771.9 cm^{-1} band indicates that the molecule possess a carbon oxygen double bond stretch. Although the existence of a C═O stretch is consistent with a ketocarbene structure, the high frequency for this absorption does not support this assignment.[20] This was confirmed in chemical trapping experiments to be mentioned later in this section. Comparison to gas-phase alkyne O atom chemistry did not provide us with any clues regarding the possible identity of product BD. Since the product's kinetic behavior indicated that it was easily and rapidly produced when ozone was photolyzed, we speculated that the stoichiometry of the product had to correspond to addition of O atom, O_2 molecule or O_3 molecule without requiring a major rearrangement of atoms within the molecule. A search of compounds of stoichiometry C_4F_6O, $C_4F_6O_2$, and $C_4F_6O_3$ provided us with the identity of the 860 cm^{-1} band set. The bands are due to perfluorobutanedione. This assignment was confirmed by synthesizing the butanedione and trapping it in a matrix. The synthesis was performed following Moore and Clark's method.[26] The bands observed for the synthesized butanedione in an Ar matrix, which match our product bands in both frequency and intensity, were 1768.5, 1216.4, 860.4, 708.5, and 534.7 cm^{-1}. Other bands observed for the butanedione could not be observed in our spectra because they were obscured by strong reactant bands.[27]

Table 3. Infrared Bands (in cm^{-1}) Due to Product X[a]

ref 15 Ar matrix	our work Ar matrix	our work N_2 matrix
nd	(1591.9)	1590.4
1325	nd	nd[c]
1275	*b*	1278.6
b	1230.6, 1228.1	1229.8, 1227.5
1160	1160.8, 1158.5	1157.1, 1155.7
875	872.4	872.1
730	733.2	733.7, 732.0
660	660.0	659.6
560	559.5	559.5

[a] Bands were attributed to bis(trifluoromethyl)oxirene by ref 15. [b] Obscured by infrared bands of the starting materials. [c] nd − not detected.

The remaining band set yet to be assigned consists of 1230.6, 1158.7, 873.1, 733.2, 660.0, and 559.5 cm^{-1}. This species must be the precursor to the ketene and has been shown to photolytically produce the ketene when irradiated with 427 nm light. On the basis of the suggested reaction mechanism, both bis-(trifluoromethyl)oxirene and its isomeric ketocarbene, perfluoroacetylmethylmethylene are possible candidates for product X. The lack of a C═O stretch would suggest that the species in not the ketocarbene. Thus, the species was tentatively identified as bis(trifluoromethyl)oxirene. Strausz and co-workers had previously trapped this oxirene in the photolysis of perfluroro-2-diazo-3-butanone. The bands observed by Strausz are in good agreement with the bands detected in our Ar matrix work (Table 3).

McMahon and co-workers have previously shown that doping of a matrix with CO allows for the trapping of ketocarbenes as ketoketenes (KK).[20] We were interested in determining whether the ketocarbene was produced in the reaction and whether the presence of CO would affect the infrared bands due to product X. On the basis of the suggested reaction mechanism the oxirene is produced via a ketocarbene.[8,14] We performed experiments with CO similar to those performed by McMahon and co-workers. When we repeated the laser photolysis experiments in a CO doped matrix (1/4/20/180 in $C_4F_6/O_3/CO/Ar$), we obtained the spectrum of a new molecule, which we believe is the ketoketene, trifluoromethyl trifluoroacetyl ketene. This assignment is based on comparison to the McMahon's work. Ketoketenes were shown to exhibit strong carbonyl and ketene moiety stretches. The new compound we observed exhibits strong absorptions at 2181 and 1726 cm^{-1}. Three other bands could also be assigned to this product: 1248, 877, and 715 cm^{-1}. Figure 6 shows the effect of CO doping on the 873 (X), 2193 (K), and 860 (BD) cm^{-1} bands. It is clear that the 860 cm^{-1} band is not significantly affected by the CO, whereas the intensity of the 873 cm^{-1} bands is greatly affected by the CO. Figure 7 shows kinetic curves for ozone(2103 cm^{-1}), products X, K, and BD and the new species, the ketoketene (KK). From Figure 6 it is clear that product X is still present but in greatly decreased amounts. This strongly suggests that product X is either the ketocarbene or a product produced via a ketocarbene.

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(26) Moore, L. O.; Clark, J. W. *J. Org. Chem.* **1965**, *30*, 2472−2474.

(27) We did not include the spectrum of the butanedione because it is not a clean spectrum. A side product of the reaction was also present in the sample. We were not able to completely remove this species from the butanedione sample without the butanedione decomposing.)

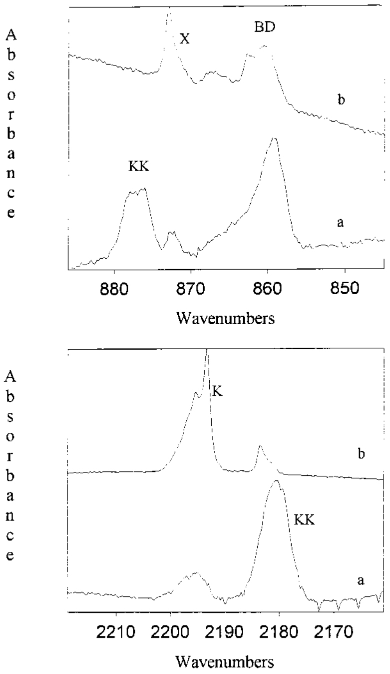

Figure 6. Selected spectral region of difference spectrum for 642 nm photolysis of a 1/4/20/180 $C_4F_6/O_3/CO/Ar$ matrix. (a) CO doped matrix, (b) undoped matrix.

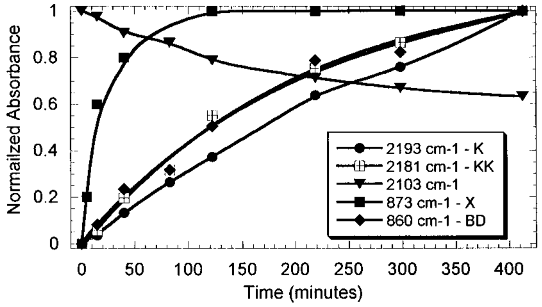

Figure 7. Product growth curves for 642 nm photolysis of a 1/4/20/180 $C_4F_6/O_3/CO/Ar$ matrix. The 2103 cm^{-1} band corresponds to ozone.

The ketene is still present, but the intensity of its bands is greatly decreased, again indicating that the ketene is produced via a ketocarbene species. Product BD is not affected by the presence of CO; thus, product BD is not connected in any way to a ketocarbene intermediate, and therefore possibly not the result of O atom attack on the alkyne.

Table 4. Product Frequencies (in cm^{-1}) for a $C_4F_6/O_3/N_2$ Matrix (1:2:200) Photolyzed with 642 nm for 150 min with a Power of 0.8 W

$C_4F_6 + {}^{16}O_2$	peak absorbance	$C_4F_6 + {}^{18}O_2$	assignment
2230.1	0.004	2228	N_2O
2202.4, 2198.9	0.105	2168.5, 2165.0	K
2182.6	0.006	2174.8	K
2139.4	0.018	2088.7	CO
1935.8	0.003	1902.9	K
1908.5	0.003	1875.0	K
1856.4	0.005	1856.4	K
1775.0	0.038	1736.5	BD
1590.4	0.044	1558.9	X
1422.7	*a*	*a*	K
1380.6, 1375.0	0.010	1378.3	K
1342.7	0.066	1342.7	K
1332.2	*a*	*a*	
1313.0	*a*	*a*	K
1297.0	*a*	*a*	
1278.6	0.610	1278.0	X
1229.8, 1227.5	0.210	1228.4, 1226.2	X
1216.7	0.110	1215.5	BD
1157.1, 1155.7	0.280	1157.0, 1155.6	X
1111.2	0.021	1110.8	K
1082.0	0.005	nd[b]	BD
991.1	0.064	*a*	K
985.6	0.020	*a*	K
967.8	0.011	966.5	K
872.1	0.300	871.5	X
860.6	0.070	859.0	BD
817.9	0.002	812.6	K
763.3	0.004	759.0	K
758.5	0.002	nd	K
733.7, 732.0	0.045	732.6, 730.3	X
725.5	0.018	724.6	K
716.6	0.005	nd	BD
708.1	*a*	704.6	BD
697.6	0.006	nd	BD
659.6	0.330	658.5	X
559.5	0.060	557.5	X
551.8	0.004	nd	K
534.5	0.037	533.5	BD
514.5	0.006	514.0	BD

[a] These bands are partially obscured by reactant absorptions making it difficult to either give a correct peak absorbance or not being able to observe the band at all in the isotopically substituted matrix. [b] nd − not detected.

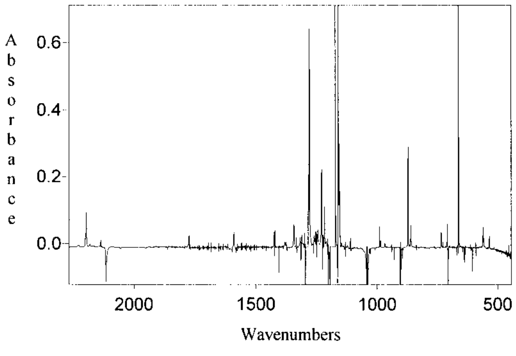

Figure 8. Difference spectrum for 642 nm photolysis of a 1/2/200 $C_4F_6/O_3/N_2$ matrix (120 min, 1.0 W).

The identity of product X has yet to be clearly established. If we base the assignment of product X on the spectrum reported in the literature by Strausz and co-workers, and on the fact that a C=O stretch could not be detected, then product X is clearly bis(trifluoromethyl)oxirene.[15] However, we would not be able to explain why we have strong evidence for a ketocarbene species but are yet unable to observe an infrared spectrum for this species. In addition, the oxirene should have at least one band, the carbon oxygen single bond, that should exhibit a significant ^{18}O isotopic affect (shift of 20 cm^{-1} or more). None of the bands assigned to product X show a significant isotopic effect. We decided that it might be worth the effort to change the matrix material. The chemical system being investigated, the photolytic reaction between ozone and an alkyne, is unlike most chemical reactions investigated using cryogenic matrices in that the product distribution is strongly dependent on small concentration changes of one of the reagents, in our case, the ozone. It is somewhat more common to observe changes in product distribution as a function of matrix material. For that reason we decided to also investigate what effect would a N_2 matrix have on the product distribution. Table 4 provides a listing of the vibrational bands observed in a nitrogen matrix. The peak absorbance data on the table are for a 1/2/200 $C_4F_6/O_3/N_2$ matrix photolyzed for 151 min with 0.80 W. Figure 8 shows the complete spectrum for the data listed on the table. It is immediately evident that product distributions were altered

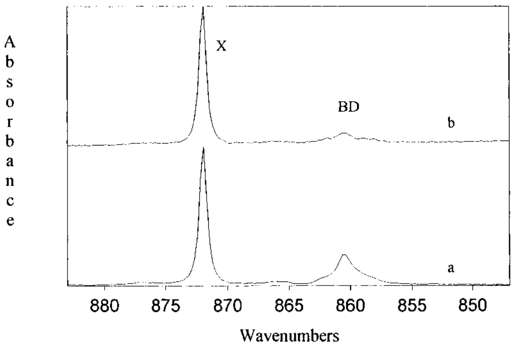

Figure 9. Effect of ozone concentration on 873 and 860 cm^{-1} bands in a nitrogen matrix. (a) 1/2/200 $C_4F_6/O_3/N_2$, (b) 1/0.5/200 $C_4F_6/O_3/N_2$.

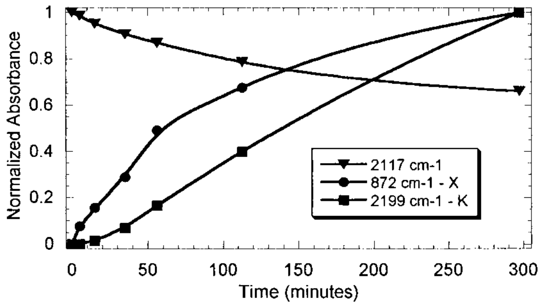

Figure 10. Product growth curves for 642 nm photolysis of a 1/0.5/200 $C_4F_6/O_3/N_2$ matrix. The 860 cm^{-1} peak could not be included because of its extremely small absorbance. The 2117 cm^{-1} band corresponds to ozone.

significantly by changing from Ar to N_2. Figure 9 shows the effect ozone concentration had on selected peaks in the nitrogen matrix work. Figure 10 illustrates the product growth curves for a matrix 1/0.5/200 $C_4F_6/O_3/N_2$ matrix. As was observed in the argon matrices, the intensity of the butanedione peaks is strongly dependent on the ozone concentration, greater ozone concentrations result in an increase in the butanedione peak intensity. The effect is so marked in the nitrogen matrices that at a low ozone concentration such as 1/0.5/200 alkyne/ozone/N_2 matrix the butanedione peaks are extremely weak in intensity and can only be easily observed at extended photolysis times. The differences between Ar and N_2 matrices product distributions are also very apparent (Figure 1 vs Figure 8 and Table 1 vs Table 4). Nitrogen matrices are much better suited for trapping product X and inhibiting its conversion to ketene, as well as strongly inhibiting the formation of the butanedione.

Nitrogen matrices also proved to be better suited for detecting a chemical reaction at shorter times. On the average, product peaks in the N_2 matrix were observed at earlier photolysis times with extended photolysis producing markedly more intense features. This is why Table 4 possesses so many more vibrational bands. Not all of the bands in this table have been assigned; however, we are quite certain that the new small bands are due to vibrational bands associated with one of the three previously identified products. That is to say, no new products are observed in the nitrogen matrix work. The nitrogen matrices did provide us with additional infrared bands for product X. These two new bands were easy to detect because product X is photolabile. Their rates of disappearance match the rates of disappearance of other product X bands. These two new bands were detected at 1590 and 1278 cm^{-1}. The 1278 cm^{-1} peak is located very close to a saturated C_4F_6 band. In Ar the overlap between these two bands is greater, not allowing us to detect the band. The 1590 cm^{-1} band is detected in the N_2 work only because we have greatly enhanced the amount of product X formed. In Ar the band is so small and the overlap with gaseous water spectra is such that we could not produce the small band consistently, and thus it is not identified in Table 1 as belonging to product X.

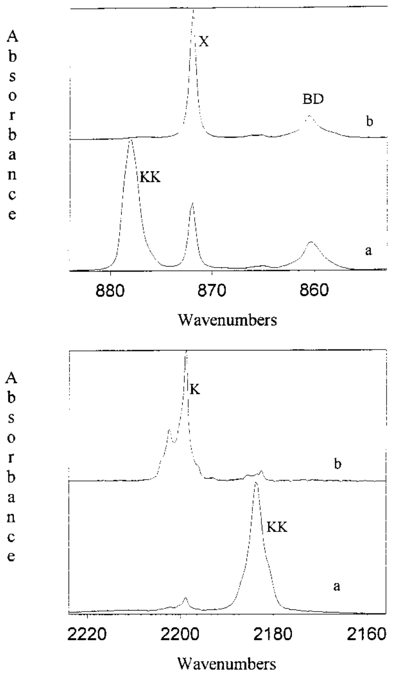

Figure 11. Selected spectral region of difference spectrum for 642 nm photolysis of a 1/4/20/180 $C_4F_6/O_3/CO/N_2$ matrix. (a) CO doped matrix, (b) undoped matrix.

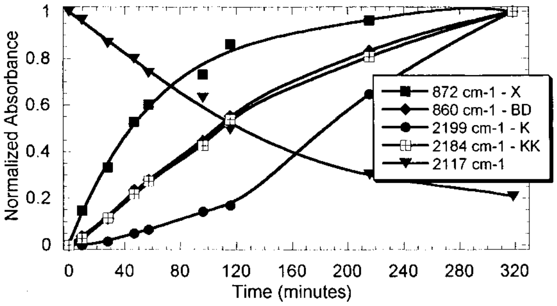

Figure 12. Product growth curves for 642 nm photolysis of a 1/1.3/20/180 $C_4F_6/O_3/CO/N_2$ matrix. The 2117 cm^{-1} band corresponds to ozone.

The results of CO doping on N_2 matrices although apparent are not as obvious as in Ar matrices because of the large amount of product X produced in N_2 matrices. New peaks attributed to the ketoketene were easily detected in the nitrogen matrices (See Supporting Information Figure 2). The strongest of the new bands due to the ketoketene are: 2183.7, 1758.1, 1730.7, 1725.2, 1387, 1361.8, 1257.3, 1254.3, 878.1, 758.7, 715.1, 546.2, and 496.4 cm^{-1}. The ketoketene bands are more intense and the spectrum richer in nitrogen matrices as compared to argon matrices because N_2 matrices favor product X formation. Figure 11 corresponds to two expanded regions of the spectrum for a 1/1.3/40/160 $C_4F_6/O_3/CO/N_2$ matrix photolyzed with 642 nm for 215 min with 1.0 W of power. It shows how the intensity of the ketene and product X decreases while the intensity of the butanedione does not. The new bands belong to the ketoketene. Figure 12 shows the product growth curves of products X, the ketene, the ketoketene, and butanedione. The ketene's behavior is definitely showing the strain of having CO present in the matrix. Product X still retains its primary

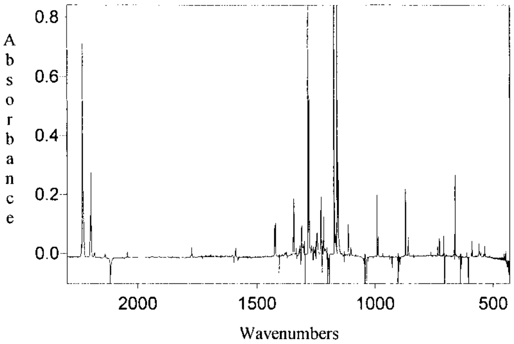

Figure 13. Difference spectrum for 251 nm photolysis of a 1/0.7/200 $C_4F_6/O_3/N_2$ matrix.

photoproduct behavior while the ketoketene does show a small delay in its appearance as one might expect.

254 nm Hg Arc Lamp Photolysis. Figure 13 shows the difference spectrum of a 1/0.7/200 $C_4F_6/O_3/N_2$ matrix photolyzed for 288 min with 254 nm light from a 200 W Hg lamp using Oriel filter no. 56400. Figure 14 shows the difference spectrum of the effect 15 s full Hg arc photolysis has on the products produced by the 254 nm photolysis. For this spectrum we have subtracted the spectrum in Figure 13 from the spectrum obtained after the 15 s photolysis. Note that the ketene bands grow in, indicating that they are a product of the 15 s full arc photolysis. The bands for product X appear as negative peaks, indicating that these bands are very sensitive to full arc exposure as was previously mentioned. (Although a spectrum was not provided, Ar matrices photolyzed with 254 nm light exhibit quite a few more bands than when photolyzed 642 nm light. No attempt has been made to identify all of the new bands in the Ar spectrum.)

A graph illustrating the product growth behavior of ketene, product X, and butanedione in a N_2 matrix is provided in the Supporting Information. Product X is sensitive to 254 nm photolysis, since at extended photolysis times the bands associated with this product disappear. Product X still behaves as a primary photoproduct when 254 nm light is used. In none of the laser or lamp experiments performed has product X ever exhibited anything other than primary photoproduct behavior. The ketene still exhibits secondary photoproduct behavior as does the butanedione to some extent.

Product X was also shown to be thermally unstable. Raising the temperature of an Ar matrix containing X from 12 to 20 K showed a marked loss in the absorbance of product X bands with an increase in ketene bands.

Discussion

Product Identification. The ketene, bis(trifluoromethyl)ketene, was identified by comparison to literature values (Table 2). Perfluorobutanedione was identified by comparison to a matrix spectrum of a synthesized sample of the butanedione. In both cases the match is excellent. The third species, product X, requires a more detailed discussion for a conclusive assignment. The discussion follows below.

In 1983 Strausz' group observed a set of bands very similar to our ketene precursor, product X, which they attributed to bis(trifluoromethyl)oxirene (Table 3).[15] Their species was shown to photochemically and thermally produce ketene, just like product X. Unfortunately a spectrum for this compound was not published in the literature, and thus we were unable to obtain information about the intensity of these bands (with the exception of some qualitative descriptions provided by the authors). Strauz produced his compound by the photolysis of perfluoro-3-diazo-2-butanone, which undergoes a photochemical Wolff rearrangement. For a long time it has been suggested that both oxirenes and ketocarbenes are intermediates in this rearrangement, and thus the suggested detection of an oxirene, although controversial, was logical. Many of the bands observed by Strausz match the bands we observed (to within 4 cm^{-1} or less). Some of the bands observed in our work were not observed by Strausz, most likely due to overlaps with his starting material, the diazobutanone. In a similar manner, some bands observed by his group are not observed in our work due to overlap with our starting materials, the butyne and ozone. However, the match between the bands observed by both our groups is so strong that we feel very confident in concluding that the compound observed by Strausz is that same as our product X. If we are to fully agree with Strausz' group, then the conclusion would be that the product we have both produced is bis(trifluoromethyl)oxirene. However, we prefer to continue this discussion with the possibility that this product could either be the oxirene or its isomeric ketocarbene, perfluoroacetylmethylmethylene, since both of these species are also suggested intermediates in the O atom addition to alkynes. The obvious reason for incorporating the second possibility is because an additional band of product X was detected at 1591 cm^{-1}, which is consistent with a carbonyl group.

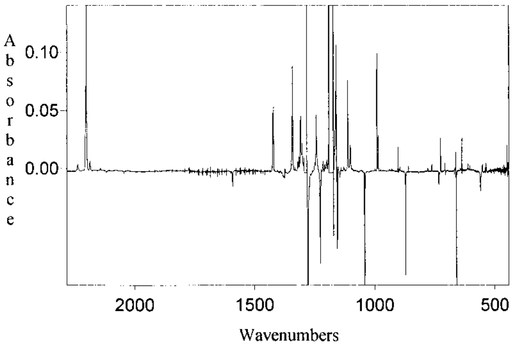

Figure 14. Effect 15 s full mercury arc photolysis has on the products of spectrum in Figure 16. Positive peaks correspond to products of the 15 s full arc exposure. The negative peaks correspond to products photolyzed by the 15 s full arc exposure.

The first question to answer is why limit the possibilities to just the oxirene and the ketocarbene. It is clear that product X is a precursor to the ketene (Figures 4 and 5) and the suggested intermediates to both the Wolff rearrangement and the O atom addition to alkynes. No other intermediates have been suggested, and we do not feel the need to invoke a new intermediate to solve the puzzle. The primary photoproducct behavior under every experimental condition investigated in our work and the conversion of product X to ketene clearly point to the fact that this is an intermediate product in the formation of ketene. The carbonyl stretch clearly suggests that species X is the ketocarbene. It shifts from 1590.4 to 1558.9 cm^{-1} when ^{18}O is used (N_2 matrix). This peak was barely detected in our Ar matrix work and not detected at all by Strausz; however, in our N_2 matrices, where product X is favored, the peak was easily observed. The lack of a carbonyl stretch in Strausz work would, of course, skew the choice toward the oxirene. Additional support for the ketocarbene assignment also comes from other experimental observations listed below.

(1) Every attempt was made to locate a carbon−oxygen single bond, to suggest the possibility of an oxirene. Although many of the bands for product X do shift a little with ^{18}O substitution, indicating that compound X contains oxygen, none of them shift sufficiently to allow for the conclusion that it corresponds to a

carbon−oxygen single bond. This also strongly corroborates the fact that the 1591 cm^{-1} band is a carbonyl and not a combination or overtone of some other bands that shifted significantly with ^{18}O substitution.

(2) The 1591 cm^{-1} band is only the sixth strongest band in the product X spectrum (see Table 4). Typically one expects a carbonyl absorption to be one of the most intense bands in the spectrum of a typical organic compound. On the basis of our band intensities all of the bands detected by Strausz were found to be more intense than the carbonyl stretch, and therefore it is possible that this group did not produce sufficient concentration of the compound so as to detect the carbonyl stretch, or maybe that portion of the spectrum was obscured by their starting material. This relative lack of intensity of the carbonyl is consistent with the spectrum obtained for the most similar stoichiometry, commercially available chemical's spectrum, the spectrum of perfluoro-2-butanone. In perfluoro-2-butanone, the carbonyl stretch, which is observed as a triplet in the 1801.7 cm^{-1} region in an Ar matrix, is the eighth strongest band set in the spectrum.[28]

(3) The frequency of the 1591 cm^{-1} band is very low for a typical carbonyl. This is consistent with McMahon and coworkers observations on more complex ketocarbenes. They indicated that in all of their studies the ketocarbene's carbonyl stretch was at a lower frequency than that of the carbonyl stretch for its counterpart diazoketone due to the fact that the electron-deficient carbon center weakens the adjacent carbon oxygen double bond. This is consistent with the observed carbonyl stretch of our ketocarbene; the frequency for its corresponding diazoketone is observed at 1745 and 1712 cm^{-1}.[29] (Two frequencies are provided for this molecule that are attributed to the carbonyl stretch.)

(4) Trapping of ketocarbenes with CO results in the formation of ketoketenes.[30] When we doped our matrices with CO, a new set of bands was observed. These bands are in general agreement with a carbonyl and ketene moiety (in 1726 and 2181 cm^{-1} in Ar matrix). The bands attributed to the ketocarbene diminished in intensity but still retained primary photoproduct behavior as seen in Figures 7 and 12.

It is important to note that there are two expected conformers of the ketocarbene, perfluoroacetylmethylmethylene. These were detected by ESR in 1981 by Murai, Ribo, Torres, and Strausz.[31] The ketocarbenes were produced by photolysis of perfluoro-3-diazo-2-butanone in a glass and in polycrystal phase at temperatures below 30 K. The Z conformer, which has a cis arrangement between the lone electron pair of the carbene and the carbonyl, was found to be 9 times more favored than the E conformer. It seems likely then that all the ketocarbene infrared bands produced in our work are due to the Z conformer. The E conformer, being significantly less favored at the low matrix temperatures might not be produced in significant amounts for us to detect its infrared bands. However, we have no way of ascertaining whether we have bands due to one conformer only or one conformer predominantly. The photochemistry of both conformers is expected to yield ketene, and therefore, we cannot separate one conformer from the other by its chemistry. Murai and co-workers were able to distinguish one isomer from another by observing different thermal kinetics. The Z isomer was found to be stable up to temperatures of 100 K, while the E isomer decayed at temperatures between 50 and 70 K. Unfortunately we cannot use this information to distinguish between these two in our work because Ar and N_2 matrices cannot be taken to these temperatures without destroying the matrix.

The ketocarbene was produced by both 642 and 254 nm photolysis. The molecule was photoconverted to the ketene with 254 and 427 nm photolysis. This photochemical behavior provides a possible explanation to an old controversy. Several months after Strausz published his letter on his identification of bis(trifluoromethyl)oxirene,[15] Laganis and co-workers reported that they had been unable to reproduce the spectrum attributed to the oxirene starting from the same reactant as the Strausz group, perfluoro-3-diazo-2-butanone.[16] Laganis, et al., attempted to produce the spectrum attributed to the oxirene by photolysis with wavelengths greater than 320 nm, greater than 280 nm, and with full mercury arc. Their inability to detect the spectrum of this compound is consistent with the fact that the ketocarbene is photolabile in the visible. We, too, were unable to produce the bands of ketocarbene by using long pass filters or full arc.

Unfortunately, we have been unable to identify conditions that allow for the trapping of the bis(trifluoromethyl)oxirene.

Reaction Mechanisms and Matrix Effects. The first step of the reaction is the photodecomposition of ozone; 642 nm light is absorbed by the ozone. The band associated with this absorption is the Chappuis band.[3] Because of the low extinction coefficient of this absorption it has been assumed that the transition is from a ground-state singlet to an excited triplet. However, theoretical work suggests that there could be some singlet excited states of ozone also accessible with 642 nm light. A full discussion with references on the possible excited states of ozone accessed with this wavelength can be found in ref 1.

The excited state of ozone dissociates to produce ground-state O (^3P) atom and ground-state $O_2(^3\Sigma)$. The threshold energy required for ozone to dissociate is 24.2 kcal/mol.[3] This means that the O atom and O_2 molecule are produced with a combined excess energy of approximately 20.3 kcal/mol when ozone is photolyzed with 642 nm light. If a hexafluoro-2-butyne molecule is in close proximity or in the same cage as where the oxygen atom is born, the excess energy of the oxygen atom would be incorporated into the reaction most likely favoring the formation of ketene, the final product of the matrix reaction between the alkyne and the O atom. That is to say, the excess energy is less likely to allow for the trapping of intermediates. On the other hand, if the oxygen atom has to travel through the matrix before reacting with the alkyne, it will lose some of its excess energy. These conditions would favor trapping of the reaction intermediates, the ketocarbene and the oxirene. These observations are consistent with the presented data. Low concentrations of ozone in either Ar or N_2 matrices resulted in an increase in the amount of ketocarbene produced. Figure 2 also indicates that poor mixing of the two gas mixtures being co-deposited artificially creates conditions in which the local concentration of ozone is lower than what is expected and thus skews product distributions

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(28) Perfluoro-2-butanone was purchased from Aldrich. A matrix spectrum of the butanone was obtained (1:200 Ar matrix) for the comparison.

(29) Laganis, E. D. Ph.D. Thesis, Dartmouth College, 1979 Hanover, NH.

(30) The ketocarbene can also be trapped as perfluoroacetic anhydride by doping a matrix with O_2.[20] Although we did not perform O_2 doping experiments, traces of perfluoroacetic anhydride could be detected in our work after extended photolysis times. This assignment was confirmed by obtaining the matrix IR spectrum of perfluoroacetic anhydride purchased from Aldrich. As one might expected, extended photolysis the concentration of oxygen molecule produced by the photolysis of ozone increases, and the trapping abilities of the oxygen become apparent.

(31) Murai, H.; Ribo, J.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1981**, *103*, 6422−6426.

(32) Miller, F. A.; Kiviat, F. E. *Spec. Acta* **1969**, *25A*, 1577−1588.

(33) We have initiated studies on the O atom addition to dimethylacetylene that suggest we have trapped the ketocarbene in this system as well as another intermediate that is very IR-sensitive. Wade, E. A.; Clemes, T.; Clohessy, C.; Singmaster, K. A. unpublished work.

toward the ketocarbene. The product distribution changes observed as a function of matrix material (N_2 vs Ar) suggest that the nitrogen matrix is more suited for removing excess energy from the O atom, thus allowing for more ketocarbene to be detected.

The fact that dilution of ozone allows for better detection of the ketocarbene is consistent with the suggested “in cage” reaction versus diffusion of the O atom through the matrix. In addition, it is also consistent with the spin effects on the reaction. Under dilute conditions the O atom will most likely need to travel through the matrix to find the alkyne. Once the triplet state O atom finds an alkyne the reaction would need to occur on a triplet surface, again favoring the formation of triplet ground state ketocarbene. On the other hand, if the atom remains in the cage in which it is produced with the triplet ground state oxygen molecule and the singlet alkyne, the formation of singlet ground state ketene in the presence of the oxygen molecule is spin allowed. This would suggest that under high ozone concentrations (maybe 6/200 or greater) the ketocarbene would not be detected. Although we did not fully extend our study in this direction we did do one run 1/8/200 alkyne/ozone/argon in which we could not detect the ketocarbene.

It is possible to construct an energy diagram similar to those found in refs 8 and 14. However, the number of assumptions made would be significant since these authors are using calculations done for unsubstituted and dimethyl substituted ketene, oxirene, and ketocarbene. Their assumptions are most likely valid for their system; however, it is clear that trifluoromethyl substitution would alter the location of some or all of the ground and excited states of these molecules. No calculations have been published using trifluoromethyl substitution for any of these molecules. In addition, heats of formation for the products are not available. The reaction forming bis(trifluoromethyl)ketene and oxygen molecule starting from ozone and perfluoro-2-butyne is expected to be exothermic. However, the relative location for the formation of the oxirene and ketocarbene in an energy diagram as compared to the ozone and butyne is difficult to ascertain since heats of formation are not available. Attempts to use average bond energies are inadequate since values for heats of reaction obtained by using the average bond energies are not very exothermic. It is well established that the use of average bond energies to approximate heats of reaction is most reliable when the reaction is highly exothermic or endothermic. In addition, the average bond energies are unable to account for ring strain in the oxirene.

O atom addition to the alkyne explains the formation of the ketocarbene and ketene but it does not explain how the butanedione is produced. Two possible mechanisms, based on the stoichiometry of the butanedione, are suggested ; the sequential addition of two O atoms to an alkyne, or the reaction of the ketocarbene with O_2. The 642 nm growth behavior of the butanedione appears to be consistent with that of a primary photoproduct. The amount of butanedione produced is dependent on the concentration of ozone; lower ozone concentrations result in significantly less butanedione. It seems logical to suggest that the butanedione is produced by the addition of an oxygen atom to the ketocarbene. Two reactive species such as the ketocarbene and the O atom are expected to react very readily. This would explain why the kinetics for the butanedione peak for the most part, exhibits first order kinetics; the second step of the reaction is fast because of the extremely low activation energy one associates with the reaction between two very reactive species, that for all practical purposes the reaction is completely controlled by the first step. However, there is one set of experimental data that cannot be explained by this mechanism. That is the fact that the butanedione peaks are not significantly affected by the presence of CO (Figures 6 and 11). If the two-step addition of O atoms was the sole mechanism by which the butanedione is formed, then, as the amount of ketocarbene decreases, the expectation would be that the amount of butanedione would also decrease. That is not what is observed in Figures 6 and 11.

The second possible mechanism for the formation of butanedione is the reaction between the ketocarbene and oxygen molecule. The triplet ketocarbene can react with $O_2(^3\Sigma)$ producing the butanedione and $O(^3P)$. The reaction is spin allowed. This mechanism can explain the observation that as the ozone decreases the relative amount of butanedione produced also decreases. The lower concentration of ozone results in the ketocarbene being produced by diffusing O atom reacting with alkyne. Access to O_2 would be greatly decreased. The presence of butanedione in the CO-doped matrices can be explained by the fact that given the choice the ketocarbene prefers to react with O_2 in the cage than CO. The reaction between the triplet ketocarbene and CO, producing the ketoketene, is not spin allowed.

Previous matrix studies on O atom addition to alkynes. Our goal was to obtain additional insight into the mechanism of O atom addition to alkynes with the hopes of trapping reaction intermediates. Previous matrix work by Haller and Pimentel on O atom addition to acetylene had only produced unsubstituted ketene. Haller and Pimentel produced the O atom by UV photolysis of N_2O.[10] On the basis of our observations it seems unlikely that any ketocarbene (and possibly, oxirene) produced under these conditions would have survived the photolysis. A more recent study by Nakata and Frei had determined that a ketocarbene intermediate was involved in the O atom addition to dimethylacetylene.[8] Like us they were unable to obtain any experimental data that would support the oxirene intermediate, even though Schaefer and co-workers have calculated that dimethyloxirene is a true minimum in the potential energy diagram.[13] Nakata and Frei were unable to directly observe the ketocarbene, but rather they trapped it with NO in the form of acetyl methyl iminoxyl radical. In their system, the oxygen atom is transferred from NO_2 to the alkene in the matrix via visible photolysis (610 nm and other visible wavelengths well above the dissociation wavelength of 398 nm for NO_2). The resulting ketocarbene is produced in the same cage as the NO, thus trapping by the NO is facilitated. In our work the observation of the ketocarbene is greatly the result of allowing the oxygen atom to diffuse out of the matrix site where it was produced. This decreases the excess energy of the O atom as well as allows for the O atom to react with an isolated alkyne molecule.

Conclusions

It is clear from the data that O atom addition to hexafluoro-2-butyne goes through a ketocarbene intermediate. We have direct observation of this intermediate. It is also clear that the ketocarbene then rearranges to form a ketene. This is the first time that the stepwise formation of a ketocarbene followed by formation of a ketene has been directly observed in the O atom addition to an alkyne.[33] To the best of our knowledge, this is the simplest ketocarbene for which an infrared spectrum has been obtained.

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Supporting Information Available: Deposition spectrum, difference spectrum, and product growth curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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