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INTERMEDIATES IN THE REACTION OF HEXAFLUORO-2-BUTYNE
WITH O ATOM IN AN ARGON MATRIX

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Supriya Jonnalagadda

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ABSTRACT

Intermediates in the Reaction Between Hexafluoro-2-butyne and O atom in an Argon Matrix

by Supriya Jonnalagadda

The reaction between alkynes and O atom is of relevance to both combustion and atmospheric chemistry. The mechanism for this reaction has been investigated in the gas phase; however gas phase conditions did not allow for the identification of reaction intermediates. The goal of our research is to provide experimental conditions that will favor formation and detection of the intermediates formed in the O atom addition to alkynes.

Our studies were performed using hexafluoro-2-butyne as the starting alkyne and ozone as the O atom source. The reaction was performed in cryogenic matrices at 11K. The extent of the reaction was followed by Fourier Transform Infrared Spectroscopy. The detected final product was bis(trifluoromethyl)ketene, consistent with gas phase studies. In addition we have isolated and identified one of the reactive intermediates, bis(trifluoromethyl) oxirene. A second intermediate, perfluoroacetylmethyl methylene, was indirectly observed by chemical trapping with CO. A mechanism which incorporates the two observed intermediates has been proposed.

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INTRODUCTION

The reaction of O atom with alkynes is of great importance to combustion as well as atmospheric chemistry.¹ Due to its relevance to combustion chemistry, the reaction has been studied in detail using various techniques. Some of the techniques used to investigate this reaction include fast flow methods with time resolved detection of labile species, crossed molecular beam, photo ionization followed by mass spectrometric detection, and low temperature matrix isolation, to name a few.

Gas Phase Studies

In a study involving crossed molecular beams of free jets, Blumenberg Hoyer mann and Sievert² (1976) studied the reaction of oxygen atoms with several unsaturated hydrocarbons, including acetylene, methylacetylene and substituted alkynes like hexafluoro-2-butyne, and phenylacetylene. O atoms, which were produced in discharge flow reactors from mixtures of O₂/Ar or O₂/He, are expanded into vacuum of 10⁻² to 10⁻⁴ torr. This beam of O atoms is crossed with a beam of the reactant (alkyne). Samples of gas from the crossed molecular beam are taken into an ion source where the beam is ionized and the resulting ions are detected by mass spectrometry. When hexafluoro-2-butyne was studied, the radicals observed were C₂ F₃, CF₃ CO, C₂ F₃ O and CF₃-C-CF₃.

The species observed with acetylene as the starting material were H , CH_2 , CO , HC_2O and $\text{H}_2\text{C}_2\text{O}$.

In a separate study, Avery and Heath³ (1970) studied the reaction of 2-butyne with ground state oxygen atoms (^3P), under static conditions at room temperature using N_2O as the O atom source. The reactants were placed in a cylindrical quartz vessel and irradiated with light of wavelength of 253.7 nm obtained from a low pressure mercury lamp. After irradiation, the mixture was cooled to 77 K and the condensed hydrocarbon and oxygenated products were analyzed by gas chromatography. The major products were CO, propylene, ethane, methyl vinyl ketone and a polymer. The results suggested to the authors that the initial step in the reaction between ground state O atoms and 2-butyne is the formation of a biradical intermediate (compound labeled as I in Scheme I). This intermediate then rearranges to a carbene like species(II). Further rearrangement of the biradical intermediate via an enol(III) gives the hot methyl vinyl ketone(IV) and a polymer. In a further step, it is suggested that the methyl vinyl ketone rearranges by internal migration of hydrogen atoms and methyl radicals to give rise to dimethyl ketene(V) which decomposes to propylene(VI) and CO.

In summary, gas phase studies provided much information on alkyne - O atom chemistry. A general scheme which summarizes most of the gas phase studies between O atoms and H or simple alkyl substituted alkynes up to 1980 is presented in Scheme II.¹ However, gas phase techniques are not useful in

Scheme I. Reaction of dimethylacetylene with O atom at room temperature (Avery and Heath³)

Scheme II. Summary of gas phase reaction between alkynes and O atom

isolating and characterizing intermediates. It is to be noted that all of the intermediates presented in Scheme I and II are “suggested.” In order to isolate and identify these intermediates, different techniques were required.

More recent gas phase studies have provided indirect evidence for the existence of ketocarbene as an intermediate in alkyne O atom studies. Gas phase reactions between hexafluoro-2-butyne and $O(^3P)$ atoms were studied by Strausz and his group in 1994.⁴ Ground state O atoms were generated by the mercury photosensitized decomposition of dinitrogen oxide at 298 K, with the photolysis being carried out in the presence of hexafluoro-2-butyne. The products observed were N_2 , tetrakis(trifluoromethyl)furan(I), CO and a white polymer. None of the intermediates were isolated but it was suggested that addition of $O(^3P)$ atom results in the formation of perfluoroacetyl methylmethylene(II) which then combines with an additional molecule of hexafluoro-2-butyne to form tetrakis(trifluoromethyl) furan (Scheme III). In 1981, Strausz and his colleagues also obtained an ESR (Electron Spin Resonance) spectrum of perfluoroacetylmethylmethylene(ketocarbene)⁵ which was generated in the $\lambda > 300\text{nm}$ photolysis of 3-diazo-hexafluoro-2-butanone polycrystal at 11 K.

Matrix Isolation Studies

Reactive intermediates like the ketocarbene have very short lifetimes in the gas phase. One reliable way to increase the life span of an intermediate, thereby facilitating their leisurely study, is by using a technique called "matrix isolation." In this technique, the reactants are isolated in an inert gas crystal typically held at temperatures below 60 K (for additional details refer to "materials and methods " section of this document). Using this technique some of the suggested intermediates of the gas phase studies mentioned earlier, have been detected or chemically trapped.

The earliest matrix isolation study of the reaction between an alkyne and O atoms was performed by Pimentel and Haller in 1962.⁶ The required O atom (^3P) was produced from nitrous oxide by photolysis using a xenon lamp emitting 1470 angstroms. This photolysis produces ground state O atoms. The photolysis was performed in the presence of acetylene or its deuterated forms at 20 K in a solid argon matrix. The reaction was followed by infrared spectroscopy. Infrared absorptions at 2143 cm^{-1} (when acetylene was used) and at 2142 cm^{-1} and 2117 cm^{-1} (with deuterated forms) were observed and attributed to ketene. The authors suggest that O atom addition to the triple bond results in the formation of a diradical which then quickly isomerizes to the ketene. An oxirene intermediate was ruled out because it does not conserve spin.

Ault used the technique of matrix isolation to study the photo-oxidation of simple alkynes.⁷ Photolysis was performed using an excimer laser

emitting a radiation of 193 nm. Several products were observed, including CO, CO₂, C₂H₂ O(ketene) and small amounts of C₂H₄. It was shown that the presence of only one atom of O lead to the ketene, whereas two atoms result in the formation of the secondary product CH₂ O(formaldehyde).

Frei and Nakata⁸ studied O atom transfer from NO₂ to dimethylacetylene in solid argon at 12 K using 610 nm radiation from a dye laser. Their detected products were acetyl methyl iminoxy radical(I), dimethyl ketene (II) and NO (Scheme IV). They suggested that the iminoxy radical was the result of NO reacting with acetylmethylmethylen, a ketocarbene(III). Thus a ketocarbene is suggested as an intermediate in the above reaction. An oxirene was not observed.

In summary we find that gas phase studies of O atom addition to alkynes, produces stable products like CO, CO₂ and alkenes. Ketenes are suggested intermediates. Under isolation matrix conditions, the ketenes can be trapped. Ketocarbenes and oxirenes are suggested intermediates in both gas phase as well as matrix studies but have yet to be isolated and detected in the O atom addition to alkynes. There are other systems for which ketocarbene and oxirene have either been implicated or have been isolated as intermediates. One reaction in particular is the photochemical Wolff rearrangement.

Scheme III. Gas phase reaction between Hexafluoro-2-butyne and O atom (Strausz⁴)

Scheme IV. Reaction between dimethylacetylene and O atom under matrix isolation conditions

Photochemical Wolff Rearrangement

When diazoketones are photolyzed in the presence of water, alcohol or ammonia, Wolff rearrangement occurs to give ketene as the end product with the mechanism involving a ketocarbene as an intermediate. Another mechanism can also intervene when the Wolff rearrangement is carried out photochemically. Some of the ketocarbene originally formed can undergo a carbene-carbene rearrangement, through an oxirene intermediate. This was shown by ^{14}C labeling experiments, where diazoketones labeled in the carbonyl group gave rise to ketenes that bore the label at both carbons of the double bond.⁹ The scrambling process which implicates an "oxirene pathway" is least seen when "R" is small (Scheme V). The oxirene pathway is not implicated in the thermal Wolff rearrangement. Thus it is possible that an excited singlet state of the carbene is necessary for the oxirene pathway to intervene.

Evidence for the involvement of oxirenes and ketocarbenes as intermediates in the photochemical Wolff rearrangement was also obtained by Strausz and his group in 1989.¹⁰ They carried out photolysis of hexafluoro-3-diazo-2-butanone, octafluoro-3-diazo-2-pentanone and its isomeric octafluoro-2-diazo-3-pentanone under low temperature argon matrix conditions. Trifluoromethyl substituted diazoketones were used because it was considered that electron withdrawing groups would help stabilize the antiaromatic three membered heterocycle ring of oxirene. When hexafluoro-3-diazo-2-butanone

was photolyzed with light of wavelength greater than 335 nm two products were detected. One of the compounds was bis(trifluoromethyl)ketene (Scheme VI). The second compound was tentatively identified as perfluoroacetylmethyl methylene, the ketocarbene, and confirmed by isotopic labeling of the carbonyl oxygen by ^{18}O . When the diazobutanone was photolyzed with 270 nm light a third compound was detected. This compound was observed to both photodecompose and thermally decompose to produce the ketene suggesting that it was a precursor to the ketene.

Two compounds were considered as likely candidates for this new third species; they were the oxadiazole and the bis(trifluoromethyl) oxirene. In order to distinguish between these two possibilities, two isomeric diazoketones were used, octafluoro-2-diazo-3-pentanone(1) and octafluoro-3-diazo-2-pentanone(2). These two isomeric diazoketones will produce the same oxirene but two different oxadiazoles under similar photolysis conditions. Since only one spectrum was observed the compound was identified as the oxirene. (Scheme VII). In the same year that Strausz et al published their findings on the isolation of an oxirene, Laganis and Lemal¹¹ reported that they had performed experiments similar to Strausz but could not obtain the spectrum of bis(trifluoromethyl) oxirene. Laganis and coworkers used perfluoro-3-diazo-2-butanone in argon matrices at ~ 10 K and monitored the resultant reaction by infrared spectroscopy. They observed bis(trifluoromethyl)ketene as the end product at all wavelengths. They also observed an unknown species with

Scheme V. Photochemical Wolff Rearrangement using ^{14}C labeling studies

Scheme VI. Photolysis of perfluorodiazobutanone under matrix conditions (Strausz⁵)

absorption at 1761 cm^{-1} which was formed when a 320 nm cutoff filter was used but was not formed when a 280 nm cutoff filter was used. This unknown compound, on photolysis with wavelength $> 320\text{ nm}$, converted to the ketene as well the starting diazobutanone, hence it was concluded that this compound must contain nitrogen.

Several IR bands of this compound matched the ketocarbene spectrum obtained by Strausz. Since this compound contained nitrogen, it was suggested that it could be either a diazirine or an oxadiazole (Scheme VIII). To distinguish between the two, hydration reactions were carried out on the unknown compound which reacted immediately with water to form a hydrate - a reaction that is typical of fluorinated ketones. Hence they concluded that the compound was a diazirine. When perfluoro-3-diazo-2-butanone was photolyzed with light of wavelength $> 280\text{ nm}$, an oxirene spectrum was not observed.

In a more recent study, Bodot and colleagues carried out the photolysis of 3-diazo-2-butanone in rare gas matrices using light of $\lambda > 230\text{ nm}$.

Dimethylketene was observed along with dimethyloxirene. The reaction was monitored by infrared spectroscopy. A strong absorption at 2137 cm^{-1} was attributed to the oxirene.¹² This is surprising because oxirene being a symmetric molecule should not exhibit a C=C absorption. There are some questions regarding this assignment and it has been suggested by Frei⁷ that the infrared band could belong to a ketene.

Scheme VII. Photolysis of isomeric diazobutanones under matrix conditions (Strausz⁵)

Scheme VIII. Photolysis of perfluorodiazobutanone (Laganis and Lemal¹¹)

Theoretical Considerations

Oxirene, is an antiaromatic, $4n\pi$, three membered oxygen heterocycle. Because of its highly unstable nature, it has evoked strong interest among theoretical chemists. In 1983, Schaad et al employed 3-21G basis set and C_{2v} symmetry and calculated the vibrational frequencies of oxirene and other small antiaromatic systems, thiirene and azirene.¹³

In 1991 Schaefer and coworkers calculated the vibrational frequencies of oxirene at three levels of ab initio quantum mechanical theory namely the DZP SCF, DZP CISD and DZP CCSD levels of theory.¹⁴ It was concluded that oxirene is a genuine minimum on the respective potential hypersurfaces. However Tanaka and Yoshimine calculated the barrier to rearrangement of oxirene to the ketene is only 2 kcal/mole.¹⁵ In such a case, isolation by matrix isolation technique is not possible.

In 1994, the portion of the C_2H_2O potential energy hypersurface that includes oxirene, formylmethylene and ketene was studied by Schaefer and co-workers.¹⁶ They employed ab initio methods incorporating high levels of electron correlation and basis sets that included up to f and g functions. Their main conclusion was that there is little or no barrier separating ketocarbene from oxirene (rearrangement between the two), however there is a significant barrier from oxirene to formylmethylene to ketene (21-23 kJ/mol). This strongly

suggests that oxirene could be an intermediate in the photochemical Wolff rearrangement. Schaefer and his colleagues have investigated stability of variety of substituted oxirenes. Their results indicate that an substituted oxirene is expected to be a true potential energy minimum and not a transition state as suggested by Frei.⁷

Goal of Project

Gas phase as well as matrix studies of O atom addition to alkynes have indicated that a species whose stoichiometry is consistent with one O atom addition to the alkyne are initially formed. One such species is the ketene. Matrix isolation studies confirmed that ketenes are formed in the O atom addition to alkynes. Other species also possess this stoichiometry, in particular, oxirenes and ketocarbenes. Neither one of these species has been directly detected in the gas phase or the matrix environment, however, studies performed by Nakata and Frei strongly suggest the formation of a ketocarbene intermediate in the O atom addition to dimethylacetylene. With this body of literature in mind, we decided to approach O atom addition to alkynes from a different angle than Nakata & Frei. Our main goal is to obtain additional information on the mechanism of the reaction. In particular we are interested in creating experimental conditions which might allow us to detect oxirenes and ketocarbenes. Matrix isolation provides one of the best conditions for the detection of these species. In this technique the reactants are isolated in an argon

crystal at low temperatures. The cold environment allows for the investigation of reactions with low activation energies such as O atom addition to alkynes. In addition the matrix serves to remove excess energy from the reactive species increasing the probability of direct observation. The matrices will be investigated using Fourier Transformed Infrared Spectroscopy (FT-IR).

Selection of the reactants is also very important. Hexafluoro-2-butyne was selected as the starting alkyne for various reasons. As shown by Strausz and Lemal, CF_3 substitution helps stabilize strained rings such as oxirene. The alkyne is simple and symmetric, producing a simple infrared spectrum. In addition the molecule possesses C-F stretches which are known to be intense absorbers of infrared light. By stabilizing the oxirene and increasing the extinction coefficient of its vibrational bands, we increase the limit of detection of the species, if it is produced. In addition, the bulkiness of the CF_3 group could also hinder the formation of the ketene, the species formed when one CF_3 group migrates.

Selection of the O atom source was also well thought out. Typical O atom sources are N_2O , NO_2 and O_3 . Frei and Nakata used NO_2 as their source of the O atom. Of the three species that can easily produce the O atom, NO_2 can photolytically produce the least energetic O atom. This is advantageous because the activation energy for the conversion of oxirene to ketene is only 2 kcal/mol, the less energetic the reactants, the more likely one can produce the species of interest. The main disadvantage of using NO_2 is that NO is also produced in the photolysis. The reactivity of NO did not allow Frei and Nakata

to observe either an oxirene or a ketocarbene. Instead they observed a methyl iminoxy radical, a possible trapping product of the ketocarbene.

N_2O is not a very useful photolytic source for O atom in our work. The photolysis region needed to produce the O atom is in the ultraviolet. The O atom is produced with a large amount of excess energy and it would be difficult to trap unstable species. We selected O_3 as our O atom source. Ozone, when isolated in a matrix, can be photolyzed with red light. The ozone is excited to its Chappius band. The energy associated with this absorption is greater than the dissociation limit of ozone thus photodissociation can occur leading to ground state O atom (or O^3P) and ground state O_2 ($^3\Sigma$).¹⁷ The atom is borne with some excess energy but not as much as when N_2O is used. The other product, ground state O_2 is not considered to be particularly reactive with alkynes. Some photooxidation studies between O_2 and alkenes have been reported in the literature,^{18,19} but they often require the existence of a charge transfer complex. We feel confident that O^3P atom produced by red laser photolysis, is the ideal choice for addition to hexafluoro-2-butyne to study desired intermediates like the oxirene and ketocarbene.

MATERIALS AND METHODS

Matrix Isolation

Matrix isolation using inert matrices was developed by Pimentel²⁰ and Porter²¹ in the mid fifties (1954). In this technique the chemicals of interest are diluted in an inert material and deposited onto a window which is held at temperatures ranging from 4 to 77K. These temperatures are routinely obtained by the use of closed cycle helium refrigerators. The inert gas is typically Ar or N₂ although many other gases such as CH₄, Kr, Xe, Ne, and SF₆ are being used. Dilution factors for the reactants in the inert gas can range from 1 in 25 to 1 in 5,000. Once produced, the matrix can be examined using many common spectroscopic techniques such as Fourier Transformed Infrared Spectroscopy (FT-IR), Ultraviolet-Visible Spectroscopy (UV-Vis), Electron Spin Resonance (ESR), and Raman Spectroscopy.

Matrix isolation technique is very useful in the study of reactive intermediates. The low temperatures greatly limit the extent of thermal reaction. Only reactions with activation energies well below 1 kcal/mol can still occur at these low temperatures. Thus reactions such as those between ozone and alkenes and fluorine and alkenes can be completely stopped even though the reactive species might be trapped together in the inert gas cage. The reaction between the reactive pair is initiated by heating the matrix or by photolysis with the appropriate wavelengths. By careful selection of the reaction conditions it is often possible to minimize the excess energy added to the reactive pair, allowing

for the trapping of reactive intermediates. Other possible methods for the trapping of intermediates involve generating the intermediate in a gas stream followed by trapping it in a matrix. Whether produced *in situ* or *ex situ*, the intermediate can then be investigated by a variety of methods. One of the most useful analysis techniques is infrared spectroscopy. Infrared spectra of molecules obtained through matrix isolation are highly resolved and appear as very sharp bands as compared to gas or liquid phase spectra. This is because, rotation of the molecule in the matrix is hindered and molecular interactions are non existent.²²

Equipment

In our study, a closed cycle helium refrigerator(APD Cryogenics Model HC-2) serves to cool a CsI window to temperatures as low as 11K. A digital temperature controller(Scientific Instruments, Model 9560) monitors the window's temperature. The cryostat is equipped with a heater which is regulated by the temperature controller. The cryostat is initially evacuated to a pressure of 10^{-5} torr by a liquid nitrogen trapped diffusion pump. The pressure in the cryostat is monitored by an ionization gauge(Granville Phillips Model 270). Once the cryostat is evacuated the compressor is turned on, a temperature of 11K is typically achieved within an hour.

The matrices were examined with Fourier Transform Infrared spectroscopy (FT-IR). The spectrophotometer was a Matson Instruments Nova

Cigny II model. Spectra were collected at a resolution of 0.5 cm^{-1} (200 scans). Operation of the spectrophotometer is fully described in the technical manual provided by the manufacturer.²³

Sample preparation

Dilute samples of the reactants are stored in glass bulbs. The bulbs are evacuated to the 10^{-6} torr range with a liquid nitrogen trapped diffusion pump. Gaseous reagents were purified by first condensing the species into a cold finger and utilizing the middle of three fractions. Liquid reagents were subjected to three freeze pump thaw cycles at 77K to degas the sample. The reagent was then allowed to expand into the evacuated manifold and bulb, and the sample is diluted with argon. The dilution factor is monitored manometrically.

Because of its reactivity, ozone is prepared in a separate metal manifold (Figure 1) which has been evacuated to the low 10^{-6} torr range with a liquid nitrogen trapped diffusion pump. Oxygen (30-45 torr) is admitted into the manifold and cold finger (77K). Ozone is produced by the static electric discharge from a Tesla coil and collected as a blue liquid in the cold finger. The excess oxygen left in the manifold is pumped off using a rough mechanical pump and the ozone is then allowed to expand into the manifold. This is followed by dilution in argon. Ozone samples are used within a few hours of synthesis due to the reactivity of the compound.

Figure 1 Schematic diagram of the ozone deposition line.

B - Bulbs, **D** - Diffusion Pump, **F** - Pyrex Finger, **TC** - Tesla Coil, **G** - Pressure Gauge, **T** - Thermocouple

Deposition and photolysis

The diluted samples were allowed to expand into evacuated manifolds that were connected to the cryostat. The mixtures are then allowed to diffuse onto the cold CsI window through needle valves (Nupro). If two different mixtures are to be deposited, then two different deposition lines are used. Thus the two reactants come into contact with each other only at the cold window. The amount of material deposited is determined by monitoring the pressure drop in the manometer that is attached to the deposition manifold. Typical deposition rates ranged from 1-2 mmol/hr. The total amount of material deposited ranged from 3-5 mmol. The final matrix compositions ranged from 1/8/200 to 1/0.7/200 (C_4F_6 / O_3 / Ar). Once the matrix is deposited a reference spectrum is collected. Photolysis is then initiated and spectra are collected periodically, thus allowing for kinetic studies of the reaction. After the deposition of alkyne and ozone mixtures, an infrared spectrum is obtained. This is the deposition spectrum and consists of all the absorptions of the reactants. During photolysis, spectra are collected periodically. Each spectrum is subtracted from the deposition spectrum and is called a difference spectrum. Thus in a difference spectrum, the products appear as positive peaks and the reactants appear as negative peaks.

Photolysis sources

Matrices were photolyzed with a Bausch and Lomb 200 W Hg arc lamp. The use of filters (Oriel) with this lamp minimized heating of the matrix. A Coherent dye laser (Model 599) was also used for photolysis. The laser was used with either DCM special or Kiton Red dyes. The dye laser was pumped by the multiline of a Coherent Ar ion laser (Model Innova 70). Operation of both laser and lamps are described in their respective manuals.^{24,25} Typical power at the laser was in the order of 0.5-1.2 watts as measured by a Molectron power meter (Mode 1 PM10). Spot size at the window was approximately 0.7 cm² (TEM₀₀). The photolysis wavelengths were 642 and 647 nm (+/- 2 nm).

Synthesis of Perfluoro- 2, 3- butane dione

The procedure for the synthesis of perfluoro-2,3-butanedione was adapted from Ugi et al.²⁶ 2,3-dichlorohexafluoro-2-butene was used as the starting alkene. 50.0g (0.214 mol) of the alkene was bubbled into a stirred mixture of 50g of CrO₃ (0.5 mol) and 20% fuming sulfuric acid (200ml), contained in a three necked flask. The flask was fitted with an air condenser leading to three successive traps cooled by acetone dry ice mixtures. The flask was kept in an oil bath maintained at 65-70 C during the addition of the olefin. The reaction mixture was kept under a continuous stream of nitrogen gas. Perfluoro-2,3-butane dione was distilled from the contents of the first trap.

The yield of the product was not determined since only a small amount of the sample was needed for reference purposes.

Table 1

Reagents used

<i>Chemical</i>	<i>Manufacturer</i>	<i>%</i>
Hexafluoro-2-butyne	Columbia Organics	99.9
Oxygen	Matheson Gas Products	99.9
Argon	Matheson Gas Products	99.9
Perfluoro-2-butanone	Aldrich	99.9
Oxygen (O ¹⁸)	Cambridge Isotope	95.98
Hexafluoropropene	Aldrich	99+
2,3-dichlorohexafluoro-2-butene	Aldrich	99
CrO ₃	Aldrich	99+
Fuming H ₂ SO ₄	Aldrich	

RESULTS

Laser photolysis(642 nm) of C₄F₆/O₃/Ar matrices:

The matrix isolation infrared spectrum for each of the starting materials, hexafluoro-2-butyne and ozone, was obtained (Figures 2&3). Hexafluoro-2-butyne exhibits strong vibrational absorptions at 1593.2, 1312.3, 1167.2, 902.1, 895.6, 640.3, and 603.8 cm⁻¹. Ozone exhibits strong absorptions at 2279.9, 2150.5, 2110.0, 1593.2, 1042.6 and 1039.2 cm⁻¹, which is consistent with published matrix isolated infrared spectra of ozone.²⁷ Strong absorptions at 2350.2 and 664.2 cm⁻¹ observed in the ozone spectrum are due to carbon dioxide impurity which is present in the sample. This impurity cannot be eliminated from the sample. CO₂ is not expected to interfere with photolysis experiments as reported by Singmaster and Pimentel.²⁸ Hexafluoro-2-butyne matrix was photolyzed with the full arc of a medium pressure Hg lamp (wavelengths greater than 250 nm). Photochemistry was not observed; all bands of the butyne remained undisturbed. The matrix isolated ozone was not photolyzed independently since previous published work by Singmaster²⁹ had shown that ozone photodecomposes when exposed to red light. Exposure of matrix isolated ozone to 642 nm radiation should result in the production of an O atom and O₂ molecule, both infrared inactive species.

Several control experiments had to be performed prior to initiating studies on the photoinduced reaction between ozone and the alkyne. First, since oxygen

is a common impurity in the ozone samples, control experiments proving that the observed chemistry in the alkyne/ozone/argon matrix was not due to the oxygen impurity had to be designed. Hexafluoro-2-butyne/oxygen/argon (1:6:200) matrix was photolyzed with 251 nm light and the full arc of a medium pressure Hg lamp for extended periods of time. Infrared spectra collected intermittently throughout the photolysis did not indicate that a chemical reaction was occurring. Another possibility that needed to be investigated was whether the observed chemistry could be due to absorption by a charge transfer complex between ozone and the alkyne. Charge transfer complexes are characterized by strong charge transfer absorption bands typically absorbing near infrared, UV or visible region.³⁰ To discard this possibility, the UV-Vis spectrum of hexafluoro-2-butyne/ozone/argon matrix was collected using a Cary 3 spectrophotometer. The spectrum showed no absorptions in the visible clearly indicating the absence of a charge transfer complex. This is consistent with separate work performed by Singmaster and coworkers on charge transfer complexes between unsaturated hydrocarbons and ozone.^{30,31} The lack of a strong absorption in the red region of the spectrum is consistent with published data on the electronic spectrum of ozone.²⁷ The electronic absorption of ozone accessed by laser photolysis in the red is extremely weak.²⁹ Through these control experiments we established that the chemistry observed when the alkyne is photolyzed in the presence of ozone is exclusively a result of alkyne and ozone reacting with each other.

Figure 2 Matrix Isolated Infrared Spectrum of Hexafluoro-2-butyne/Ar (1: 100)

Figure 3 Matrix Isolated Infrared Spectrum of Ozone/Ar (4: 100)

Table 2 presents the photolysis product bands obtained when a matrix containing hexafluoro-2-butyne and ozone is photolyzed with laser radiation of 642 nm. Table 2 presents data from two separate experimental runs, which differ in the concentration of ozone used. In the first experimental run, 2.93 mmoles of hexafluoro-2-butyne in the ratio of 1: 100 in argon were codeposited at 11.5K with 2.84 mmoles of ozone in the ratio of 1: 50 in argon. In the second run, 2.81mmoles of alkyne in the ratio of 1: 100 in argon and 2.15 mmoles of ozone in the ratio of 1:150 in argon were deposited. Data from both runs is compared after 135 minutes photolysis time. Table 2 also presents intensities of all the absorption bands, along with O-18 shifts observed for some bands.

Table 2 (is also continued on page 29)

Photolysis product bands

<i>Bands ¹⁶O</i>	<i>Bands ¹⁸O</i>	<i>Run 1</i>	<i>Run 2</i>	<i>Absorption Ratio Run1/Run2</i>	<i>Band type</i>
2193.3,2195.5	2161	0.012	0.045	0.27	A
2183.7	2174.2	0.003	0.011	0.27	A
2138.3	2086.6	<0.002	<0.002		CO
1771.9	1732.3	0.010	0.007	1.40	C
1421.2	1410.8	0.008	0.039	0.21	A

Table 2 contd	Band ¹⁸ O	Run 1	Run 2	Absorption Ratio	Band type
Band ¹⁶ O				Run1/Run2	
1341.0	1341.0	0.009	0.040	0.23	A
1230.6,1228.1	1229.2	0.020	0.038	0.53	B
1215.8	1215.2	0.021	0.015	1.40	C
1158.7	1158.7	0.024	0.045	0.53	B
992.5,991.3	obs	0.004	0.020	0.20	A
986.7	obs	0.002	0.010	0.20	A
873.1	872.6	0.008	0.019	0.42	B
860.2	859.0	0.011	0.008	1.40	C

obs- observed

Table 3 presents the normalized absorbance data for run 1 and 2. These data were obtained by dividing the absorbances in one given run by the absorbance of the strongest peak in that particular run. Table 2 and 3 can be used to begin the difficult task of product assignment. From Table 2 one can observe three different ranges of product ratios. Four bands show ratios ranging from 1.4 to 1.7. This strongly suggest that the bands belong to the same product.

The 0.3 deviation is not unreasonable due to the low intensity of the bands and the fact that data is collected as peak intensity rather than peak area. The normalized intensity data on Table 3 also supports this conclusion. Note that the peak absorptions at 1771.9, 860.2 and 534.5 cm^{-1} retain their similar normalized intensity between the two runs, and the fourth peak at 1215.8 cm^{-1} is consistently twice as intense as the other three peaks in both runs. These bands were all labeled as C type bands. A fifth band at 707.4 cm^{-1} also qualitatively follows this behavior pattern, although it is not possible to quantify this in a table due to overlap with the disappearing ozone band.

Several bands possess a ratio between 0.27 and 0.20. Their normalized intensity is also consistent with these bands belonging to the same product, which has been identified as band type A. B type bands were also identified in a similar manner.

Figures 4 and 5 show difference spectra obtained for runs 1, 2 and isotopic oxygen run. Some of the bands listed in Table 2 are shown in these spectra.

Table 3

Normalized Absorbance Data for Run 1 and Run 2

<i>Bands (cm⁻¹)</i>	<i>Absorbance</i>	<i>Normalized</i>	<i>Absorbance</i>	<i>Normalized</i>
	<i>Run 1</i>	<i>Absorbance</i>	<i>Run 2</i>	<i>Absorbance</i>
2193.3,2195.5	0.012	0.50	0.045	1.00
2183.7	0.003	0.13	0.011	0.24
2138.3	>0.002		>0.002	
1771.9	0.010	0.42	0.007	0.16
1421.2	0.008	0.33	0.039	0.87
1341.0	0.008	0.38	0.040	0.89
1230.6,1228.1	0.009	0.83	0.038	0.84
1215.8	0.020	0.88	0.015	0.33
1158.7	0.021	1.00	0.045	1.00
992.5,991.3	0.024	0.17	0.020	0.44
986.7	0.004	0.08	0.010	0.22
873.1	0.008	0.33	0.019	0.42
860.2	0.011	0.46	0.008	0.18
534.5	0.010	0.42	0.006	0.13

Figure 4 Difference spectra showing 2220-2150 cm^{-1} region using laser (642 nm) photolysis
 A - Difference spectrum for run 1 ($\text{C}_4\text{F}_6/\text{O}_3/\text{Ar}$, 1:2:200)
 B - Difference spectrum for run 2 ($\text{C}_4\text{F}_6/\text{O}_3/\text{Ar}$, 1:0.7:200)
 C - Difference spectrum for O^{18} shift ($\text{C}_4\text{F}_6/\text{O}_3^{18}/\text{Ar}$, 1:1:300)

Figure 5 Difference spectrum showing 890-840 cm^{-1} region using laser photolysis (642 nm)

A - Difference spectrum for run 1 ($\text{C}_4\text{F}_6/\text{O}_1/\text{Ar}$, 1:2:200)

B - Difference spectrum for run 2 ($\text{C}_4\text{F}_6/\text{O}_1/\text{Ar}$, 1:0.7:200)

C - Difference spectrum showing O^{18} shifts ($\text{C}_4\text{F}_6/\text{O}_1^{18}/\text{Ar}$, 1:1:300)

The kinetic behavior of these bands was also investigated. This behavior supports the assigning of each band type to one reaction product. For example, all the bands assigned to band type A exhibited the same kinetic behavior.

Figure 6 shows the change in absorbance (normalized) of three bands, one each of type A, B and C, as a function of photolysis time. In addition the loss of ozone is plotted to show that chemistry can be attributed to the photolysis of ozone.

Band type A behavior is illustrated with the 2193 cm^{-1} band. The bands belonging to this product are readily obtained at both concentrations of ozone as compared to the band set B which is more intense at lower concentrations of ozone (run 2) and band set C which is more prominent at higher concentrations of ozone (run 1). The other bands belonging to this band set are 2183.7 , 1421.2 , 1341.0 , 992.5 and 986.7 cm^{-1} . The 2193 cm^{-1} set exhibits a time delay in its growth (Figure 6). This strongly suggests that this product is not the initial product of the photolysis as opposed to band set B (illustrated in the graph by the 873 cm^{-1} band) whose kinetic behavior is consistent with that of a primary photoproduct at both ozone concentrations. Band type C (illustrated in the graph by the 860 cm^{-1} band) exhibited a time delay in its growth only when the ozone concentration is low.

Band type A set includes an absorption at 2193.3 cm^{-1} which shifts to 2161 cm^{-1} with isotopic oxygen. Absorptions in this region are typically associated with ketenes and alkynes. The strong isotopic effect suggests that the species is

Figure 6 Change in normalized absorbance as a function of photolysis time for run 1
 $\text{C}_4\text{F}_6/\text{O}_3/\text{Ar}$, 1:2:200 642 nm light, Power: .65 watts, 2193 cm^{-1} (band type A)
 873 cm^{-1} (band type B) 860 cm^{-1} (band type C) 2103 cm^{-1} (ozone)

a ketene, an expected end product in the O atom addition to an alkyne. The expected ketene in the O atom addition to hexafluoro-2-butyne is bis(trifluoromethyl)ketene. Table 4 compares the absorptions assigned A type behavior with literature data for bis(trifluoromethyl)ketene. The match with gas phase is excellent with deviations no greater than 4 cm^{-1} . Such deviations are not unexpected when comparisons are made between gas phase spectra and matrix trapped spectra. The match with previous matrix spectra might at first glance appear to be limited. The matrix spectrum of ketene obtained in the literature was not the result of isolation of the ketene in a matrix but was rather a partial spectrum obtained by photolytically producing the ketene in the matrix. The reactants for that synthesis partially obscure regions where the ketene absorbs, not allowing for a complete match. However, the deviation between bands observed in both matrix studies is 3 cm^{-1} or less, allowing for the confident identification of bis(trifluoromethyl)ketene as one of the reaction products in our study.

The compound whose spectrum consists of the 860 cm^{-1} band set(C) must possess some level of symmetry. This is due to the fact that the spectrum is simple, consisting of only six bands, which include 1771.9 , 1215.8 , 707.4 , and 534.5 cm^{-1} . When isotopic oxygen is used in the experiment, 1771 cm^{-1} band shows a shift of 39 cm^{-1} . This indicates the presence of a carbon oxygen double bond stretch. A ketocarbene intermediate is immediately suggested, however the high

Table 4

Comparison of band type A with bis(trifluoromethyl)ketene

<i>Bands</i>	<i>Gas Phase Studies</i>	<i>Strausz et al</i>
2193.3,2195.5	2194	2192
2183.7		
1421.2	1417	1420
1341.0	1343	1340
992.5 991.3	991	992
986.7	991	
726.9	728	
553	553	550

frequency for this absorption does not support the assignment. Chapman and coworkers have shown that C=O stretch ketocarbenes occur in the low 1700 cm^{-1} region. Chapman and coworkers have also shown that ketocarbenes can be trapped easily by CO to produce ketoketenes.³³ Therefore several trapping experiments were carried out in which the matrices were doped with CO ($\text{C}_4\text{F}_6/\text{O}_3/\text{CO}/\text{Ar}$ at 1:4:20:180). Table 5 lists all the absorptions that were obtained through this experiment. Band set C remains unperturbed by the presence of CO. A trace of the 873 cm^{-1} band can be observed but its intensity is greatly reduced by the presence of CO. Figures 7 and 8 compare selected regions of the runs where the matrix was doped with CO as opposed to the normal runs (run 2 is shown).

Table 5

List of bands observed under CO doping of $C_4F_6/O_2/Ar$ matrix

<i>Bands(cm^{-1})</i>	<i>Absorbance</i>	<i>Assignment</i>
2195.1	0.160	Ketene
2181.2	0.010	Ketoketene
1774.2	0.010	Band type C
1729.8	0.017	Ketoketene
1251.6	0.286	Ketoketene
877.9	0.010	Ketoketene
861.5	0.010	Band type C
714.0	0.020	Ketoketene
534.4	0.013	Band type C

Figure 7 Difference spectra showing effect of CO doping on C₄F₆/O₃/Ar matrix
 A - Matrix doped with C
 B - Undoped matrix

Figure 8 Difference spectra showing effect of CO doping on $\text{C}_4\text{F}_6/\text{O}_3/\text{Ar}$ matrix. The region shown is 890 - 840 cm^{-1} . A - Matrix doped with CO
B - Undoped matrix

Two conclusions can be drawn from the trapping experiment. First ketocarbene is produced in the O atom addition to hexafluoro-2-butyne albeit in low concentrations since the ketoketene trapping product is detected. Second, the 860 cm^{-1} band set does not belong to the ketocarbene. If it did belong its intensity would be strongly affected by the CO. A number of compounds with the stoichiometry of $\text{C}_4\text{F}_6\text{O}$, $\text{C}_4\text{F}_6\text{O}_2$ and $\text{C}_4\text{F}_6\text{O}_3$ were considered as possible candidates for the 860 cm^{-1} band set (C). One of the compounds considered was perfluoro-2,3- butane dione. This compound was first synthesized by Moore and Clark in 1965.³² Comparison of the infrared spectrum obtained by Moore and Clark shows that the band set C closely resembles the spectrum of perfluoro-2,3- butane dione(see discussion).

Type B bands clearly show primary photoproduct behavior at all ozone concentrations studied, which range from 1/8/200 to 1/0.7/200($\text{C}_4\text{F}_6/\text{O}_3/\text{Ar}$). This suggested the possibility that this band set would be due to the precursor for the ketene, possibly the oxirene or the ketocarbene. Many attempts using different photolysis wavelengths were made to determine whether these bands would photodecompose. This behavior was observed using 420 nm of light. Figure 9 shows the kinetic curves obtained for this photolysis, Figure 10 shows a difference spectrum in which the 873 cm^{-1} is a negative peak because it is disappearing with 420 nm photolysis. The ketene bands are positive peaks because they are produced by the 420 nm photolysis. Note that the 900 cm^{-1}

bands due to hexafluoro-2-butyne are not perturbed by this photolysis. This clearly shows that the 873 cm^{-1} band set is a precursor to the ketene band set. Figures 7 and 8 show that bands belonging to the ketene as well as to type B are affected by the presence of CO. Thus both these species are in some way related to the ketocarbene. The lack of a CO double bond stretch would suggest that the type B bands are not due to the ketocarbene although additional discussion might be needed to eliminate this possibility.

Figure 9 Effect of 420 nm photolysis on normalized absorbance of band type B (873 cm⁻¹) and concomitant increase in band type A (990 cm⁻¹)

Figure 10 Difference spectrum showing 990 cm^{-1} bands (type A) as product bands and 873 cm^{-1} (type B) as reactant bands

KE- Ketene bands

OX - Oxirene bands

DISCUSSION

The results obtained in this work clearly indicate that three different chemical species were produced by the red laser photolysis of a cryogenic matrix containing ozone and hexafluoro-2-butyne. The three products were identified by one of their absorptions: 2193 cm^{-1} (Type A), 873 cm^{-1} (Type B) and 860 cm^{-1} (Type C). Based on kinetic behavior and comparison to literature, we have positively identified the 2193 cm^{-1} band set as belonging to bis(trifluoromethyl) ketene.³⁴ According to the literature, ketenes are the expected products in $\text{O}(^3\text{P})$ atom addition to alkynes. In the gas phase, the ketene would undergo decomposition producing other species. The expected decomposition products for bis(trifluoromethyl)ketene are CO and hexafluoropropene. Traces of CO detected in our matrix work are most likely the result of decomposition of the ketene. Hexafluoropropene could not be detected. This is most likely since very little decomposition occurs. CO is an extremely strong IR absorber thus allowing us to detect very small amounts of the compound.

The compound belonging to the 860 cm^{-1} band set (type C) must be a simple one, possessing some level of symmetry. This is based on its simple spectrum, consisting of five bands, 1771.9, 1215.8, 707.4, 860.2, and 534.5 cm^{-1} . The kinetic behavior of this compound shows that it grows in almost as fast as band type B bands (873 cm^{-1}) and before the type A ketene bands. However

subsequent photolysis using broad band photolysis sources does not result in its destruction suggesting that type C bands is not a precursor to the ketene. The presence of a strong absorption at 1771 (a carbonyl absorption) lead us at first to tentatively assign these bands to the ketocarbene. If it indeed was the ketocarbene then trapping experiments with CO should have resulted in the complete disappearance of its spectrum and the appearance of ketoketene spectrum. Trapping experiments with CO left the spectrum of type C bands undisturbed suggesting that these bands do not belong to the ketocarbene. A spectrum of ketoketene was however obtained suggesting that ketocarbene was produced in the photolysis of hexafluoro-2-butyne in the presence of O atom, albeit in small quantities.

^{18}O shift of the 1771 cm^{-1} band suggests that this is a carbonyl stretching frequency. Various compounds of $\text{C}_4\text{F}_6\text{O}$, $\text{C}_4\text{F}_6\text{O}_2$, and $\text{C}_4\text{F}_6\text{O}_3$ stoichiometry were considered as possible candidates for band type C absorptions. One particularly interesting compound with $\text{C}_4\text{F}_6\text{O}$ stoichiometry was the trifluoromethyl trifluorovinyl ketone, a species that would result from a ketocarbene undergoing a fluorine atom migration. Very little information is available on this compound in the literature. The only published information shows that there are absorptions at 5.6 and 5.9μ (gas phase studies).³⁵ The carbonyl stretch at 1771 cm^{-1} is in reasonable agreement with one of the bands. However, we have not been able to detect a band that we could assign to the carbon-carbon double

bond stretch of the vinyl ketone. Trifluoromethyl vinylketone was not observed by Strausz or Lemal in their studies on the photolysis of diazobutanones.

Further searches in the literature yielded a possible candidate for our 860 cm^{-1} band set, perfluoro-2, 3-butanedione ("perfluoro biacetyl" of Moore and Clark).³² Our type C bands bear a close resemblance to the infrared absorptions of perfluoro-2, 3-butanedione synthesized first by Moore and Clark.³² A matrix spectrum obtained by us for perfluoro-2, 3-butanedione confirmed that we had produced the butanedione in the laser photolysis of ozone in the presence of hexafluoro-2-butyne.

Identification of the compound responsible for the group of bands which include the 873 cm^{-1} absorption is somewhat more difficult. In 1983, Strausz and coworkers observed a set of bands very similar to our 873 cm^{-1} band set which they attributed to the bis(trifluoromethyl) oxirene (Table 6). Their species was also shown to photochemically and thermally decompose to give bis(trifluoromethyl)ketene. The oxirene species was produced by photolysis of perfluoro-2,3-diazobutanone (photochemical Wolff rearrangement). It has long been suggested that both oxirenes and ketocarbenes are intermediates in the Wolff rearrangement so detection of an oxirene or ketocarbene was not unexpected. Many of the bands observed by Strausz match our bands (to within 4 cm^{-1} or less). The 1230 cm^{-1} band was not observed by Strausz most likely due to overlap with reactant bands, the diazobutanone. In a similar manner some of

Table 6

Comparison of type B bands to literature

<i>Experimental (cm⁻¹)</i>	¹⁸ O	<i>Strausz (cm⁻¹)</i>
nd ^a		1325
reactant overlap		1275
1230	1129	reactant overlap
1159	1159	1160
873	873	875
733	731	730
660		660
559	557	560

a - not detected

the bands observed in his work, for example the 1275 cm⁻¹ band, cannot be detected by us due to overlap with the butyne . We are unable to locate the absorption at 1325 cm⁻¹ in spite of the spectral region being clear. Barring the overlapping reactant regions it is apparent that the photolysis of perfluoro-2,3-diazobutanone produces a species the bands observed in his work, for example the 1275 cm⁻¹ band, cannot be detected by us due to overlap with the butyne . We are unable to locate the absorption at 1325 cm⁻¹ in spite of the spectral region being clear. Barring the overlapping reactant regions it is apparent that the

photolysis of perfluoro-2,3-diazobutanone produces a species which is in common with the chemistry observed when ozone is photolyzed in the presence of hexafluoro-2-butyne. In both cases the compound is produced as a primary photoproduct and it photodecomposes to produce bis (trifluoromethyl)ketene. This limits the identity of this species to two possible compounds; bis(trifluoromethyl)oxirene (Species I) and its isomeric ketocarbene, perfluoro acetylmethylmethylene (Species II).

Species I

Species II

The question now is which species is responsible for the spectrum that includes the 873 cm^{-1} band, the oxirene or the ketocarbene. All the evidence points towards the oxirene. Strausz's work with isomeric diazopentanones and the fact that a $\text{C}=\text{O}$ stretch could not be observed in either Strausz or our work supports the oxirene assignment. In addition, in 1981 Strausz investigated the photolysis of perfluoro-2,3-diazobutanone at 30 K using ESR.⁵ The ESR spectrum of the ketocarbene was obtained and assigned. The ketocarbene was produced by photolysis with wavelengths greater than 300 nm, conditions which have shown by both Laganis and our group to not allow for the observation of the 873

cm⁻¹ band set. It thus seems unlikely that the 873 cm⁻¹ band set would be due to the ketocarbene. Based on this discussion, we feel confident that the 873 cm⁻¹ band set belongs to the bis(trifluoromethyl) oxirene. Our work has provided additional evidence to support Strausz's initial claim of trapping an oxirene and also serves as *the first detection of an oxirene intermediate in the photolytic reaction between ozone and an alkyne.*

If the oxirene was detected then where is the ketocarbene? Unfortunately, we have yet to find conditions which favor the detection of the infrared spectrum of the ketocarbene. This species was shown to exist by Strausz using ESR when he photolyzed diazo-2,3-butanone, although he was unable to detect it using infrared spectroscopy.¹⁰ ESR is typically a much more sensitive technique than IR thus it is capable of detecting lower concentrations of species which can interact with magnetic fields. This is most likely the reason why we cannot directly observe the ketocarbene. However, the chemical trapping experiments strongly support the conclusion that the ketocarbene is an intermediate in the O atom addition to hexafluoro-2-butyne. The ketocarbene reacts with CO to produce the ketoketene (Species III). It has been well documented by Chapman that ketocarbenes will produce a ketoketene when they are produced in the presence of CO.³³ The lack of observation of the ketocarbene is also consistent with the initial goal of Strausz and our work. We both specifically chose to work with CF₃ substituted starting materials (hexafluoro-2-butyne in our case and perfluoro-2,3-diazobutanone for Strausz) because it was documented in the

literature that trifluoromethyl groups help stabilize strained ring, thus greatly increasing the chances of observing the oxirene as compared to the ketocarbene.

Species III

Reaction Mechanism

Excited States and Photodecomposition of Ozone

The reaction is initiated by the photolysis of ozone with red light (640-650 nm, 642 nm photolysis is equal to 44.5 kcal/mol). The ground state of ozone is a singlet (1A_1). Red laser light excites the ozone to an excited electronic state. This absorption is known as the Chappuis band of ozone.¹⁷ The identity of the excited state is not known. Because of the low extinction coefficient of the Chappuis band absorption it has been assumed that the excited state is a triplet. Several theoretical calculations suggest that both singlet and triplet states are well within the 44.5 kcal/mol energy of excitation. Thunemann et al³⁶ found five possible excited states below or near this energy : 3B_2 (27.7 kcal/mol); 3A_2 (33.2 kcal/mol); 3B_1 (36.7 kcal/mol); 1A_2 (39.7 kcal/mol); 1B_1 (45.0 kcal/mol). Other theoretical

studies also place these excited states within an energy range of 44.5 kcal/mol although there is some ambiguity about the energies and sequence of the states.²⁸ It is clear however that there could be as many as three triplet states and two singlet states that could be produced by 642 nm light.

In 1989, Singmaster and Pimentel showed that the spin multiplicity accessed with laser photolysis in the red could be manipulated by the choice of the inert gas.²⁸ Using UV-Vis spectra it was shown that xenon matrices favor spin forbidden processes such as the ground state singlet to excited triplet transition suggested as the Chappuis band. In an argon matrix, spin conservation is favored, thus the electronic transition associated with red light excitation is that of ground state singlet to excited state singlet. This is the process that most likely dominates in our study.

Excitation of ozone above 25 kcal/mol results in dissociation of ozone into ground state oxygen atoms ($O(^3P)$) and ground state oxygen molecule ($O_2(^3\Sigma)$).¹⁷ Dissociation of the excited singlet state to give these two species is spin allowed. The energy provided by the laser source (44.5 kcal/mol) is not sufficient to produce either the atom or the molecule in an excited state.¹⁷

O (3P) Atom Chemistry

The O atom produced by the decomposition of ozone will possess excess energy. This could be as much as 19.5 kcal/mol (the difference between the energy provided by the laser and the energy needed to dissociate the ozone).

The O atom can react with a neighboring alkyne, if present, or it can use some of that energy to diffuse out of the matrix cage and react with an isolated alkyne molecule. Which pathway it follows will most likely have some effect on the branching of the reaction. If two neighbors react, the oxygen atom brings a significant amount of excess energy into the reaction since O atom addition to alkynes exhibits activation energies in the range of 2 kcal/mol and below. This would mean that the products of the reaction would be formed with excess energy, allowing for additional reactions to occur. If the atom has to diffuse away from the site in which it is produced, it will have to use some of the excess energy in the diffusion process. Under such conditions, when reaction with an alkyne occurs, it is much less likely that a secondary reaction will occur.

Once the O atom reacts with the alkyne, the first species that is expected to be produced is the ketocarbene. This reaction is spin allowed under both reaction with neighboring alkyne and a "distant" alkyne, since the ketocarbene's ground state is a triplet. If the ketocarbene is produced with large amounts of excess energy, isomerization to the ketene will most likely be favored. If the ketocarbene is produced cold then rearrangement to the oxirene would be possible. These suggested reaction pathways can be tested with our experimental observations. Both the ketene and the oxirene are expected to be produced as the result of the ketocarbene's formation. As this would then suggest, anything that perturbs the formation of the ketocarbene would also hinder formation of the oxirene and ketene. This was observed experimentally in

the CO doping experiments. The presence of CO greatly reduced the amount of oxirene and ketene detected in the run, thus indicating that both species are produced via the ketocarbene. The effect of remote vs neighboring alkyne O atom chemistry is also experimentally observed as an effect on the branching ratio between ketene and oxirene. As the concentration of ozone in the matrix is reduced, the amount of O atom - remote alkyne chemistry is increased. Under these conditions the intensity of the oxirene bands increases. Scheme XI summarizes the proposed mechanisms for O(³P) atom addition to hexafluoro-2-butyne.

Formation of perfluoro-2,3-butanedione

As mentioned in the beginning of the discussion, the 860 cm^{-1} band set was originally thought to be due to the ketocarbene. The trapping experiments eliminated this option, as well as any possibility of this species being due to ketocarbene chemistry since the band set was not perturbed by the presence of CO. Since the ketocarbene/oxirene/ketene pathway is the only one expected for O atom addition to an alkyne this indicated that the chemistry producing the butanedione (or 860 cm^{-1} band set) was most likely not due to O atom chemistry. This leaves only the possibility that this product is the result of molecular oxygen reacting with the alkyne, an unexpected process since ground state molecular oxygen has not been shown to react with any simple unsaturated hydrocarbons. The chemistry between the alkyne and molecular oxygen is only observed as a result of the photochemistry of ozone. That is to say, when O_2 and the alkyne are isolated in an Ar matrix and photolyzed with red light chemistry is not detected. Thus the butanedione is not the result of excitation of a charge transfer complex between molecular oxygen and the alkyne. As mentioned previously, such a species, if it exists, would not be expected to exhibit a charge transfer band in the visible. Thus, for some reason, the ground state oxygen molecule produced by ozone photolysis is much more reactive towards the alkyne than one might expect. The condition in which this reactivity is enhanced is under high ozone concentrations. As the concentration of ozone is decreased

the intensity of the butanedione bands decreases. This strongly suggests that the butanedione is produced by reaction of oxygen molecule with a neighboring alkyne rather than by diffusion of O_2 through the matrix. Two factors might be greatly responsible for greatly increasing the reactivity of O_2 . First, when the O atom and molecule are produced they possess an excess of 19.5 kcal/mol which is distributed among the two species. Second, the O_2 is in the cage with a ground state singlet alkyne and a ground state triplet O atom. The symmetry of this three body system allows for a reaction between the oxygen molecule and the alkyne. Scheme X tries to illustrate this process. Decomposition of the ozone produces two triplet state molecules. If one considers only the triplet O_2 and the singlet alkyne, formation of the singlet butanedione is not spin allowed. If one considers that the triplet ground state oxygen atom is also present and is part of the "caged supermolecule" then formation of a singlet butanedione is possible.

Scheme X. Formation of Perfluoro-2,3-butanedione

Resolution of Strausz - Laganis dispute

Our work also resolves an experimental inconsistency reported in the literature. As mentioned in the introduction Strausz and coworkers were the first to isolate an oxirene. However their work was disputed by Laganis. Strausz photolyzed perfluoro-2, 3-diazobutanone with 270 nm light and observed the oxirene whereas Laganis photolyzed the same starting material with wavelengths of 280 and higher, and with 320 nm and higher. In both cases, Laganis and coworkers were not able to detect the oxirene, thus casting some doubts over the oxirene assignment in Strausz's work. As shown in our work wavelengths of 420 nm result in rapid loss of oxirene with the production of ketene. This loss is greatly accelerated if a broader band source such as cut off filters used by Laganis are used. The oxirene bands we produced were shown to completely disappear within less than 10 seconds when we used a filter similar to Laganis is used. The reason Laganis did not observe the oxirene was that he was photolyzing and decomposing the oxirene even as he produced it.

This also brings up another dispute present in the literature. In 1985 Bodot and coworkers reported that they were able to trap the dimethyloxirene in the photolysis of perfluoro -2,3 -diazobutanone. The oxirene was produced by 470 nm photolysis of the diazobutanone. The oxirene exhibited a strong carbon-carbon double bond stretch above 2100 cm^{-1} . This was so surprising that Frei commented on the possibility that the observed stretching frequency was due to

ketene and not oxirene. Our work also suggests that Bodot and coworkers did not correctly assign their products. Dimethyloxirene is expected to be significantly more reactive than bis(trifluoromethyl)oxirene, particularly since methyl group migration is much more likely than trifluoromethyl group migration in a matrix environment. We have already shown in agreement with Laganis that oxirene is sensitive to wavelengths above 320 nm. It seems unlikely that the wavelengths used by Bodot would not result in photolysis of the oxirene produced. In addition, the oxirene we produced, bis(trifluoromethyl)oxirene, is of the same symmetry as dimethyloxirene, yet we are unable to detect a strong band that we could associate with the carbon-carbon double bond stretch as observed by Bodot. Actually we are pleased that such a band was not detected in our work since the double bond stretch in the molecule is symmetric, greatly lowering the possibility of it being detected using infrared spectroscopy.

Conclusions

Based on the interpretation of our data, we conclude that reaction of hexafluoro-2-butyne with O (3P) atom in an argon matrix results initially in the formation of perfluoroacetylmethylmethylene (ketocarbene). Indirect evidence for the existence of ketocarbene was obtained by trapping the ketocarbene with CO to produce 1-trifluoroacetyl-1-trifluoromethyl ketene (ketoketene). Bis(trifluoromethyl)oxirene and bis(trifluoromethyl)ketene were both directly observed. This is the first time that an oxirene intermediate has been detected in

the O atom addition to an alkyne. An additional product, perfluoro-2,3-butanedione was also detected. It is produced by the reaction of the photochemically produced O_2 with the alkyne. The matrix environment allows for this spin forbidden process to occur.

REFERENCES

- 1) Hucknall, D.J *Chemistry of Hydrocarbon Combustion*. Chapman & Hall: New York, 1985.
- 2) Blumenberg, B.; Hoyerman, K.; Sievert, R. 16th Symposium (Int) on Combustion, Combustion Institute, Pittsburgh, 1977,841.
- 3) Avery, H.E.; Heath, S.J. *J.Chem.Soc.,Faraday Trans.I* **1972**, 68 ,512
- 4) Mahaffy, G.P.; Van der Woude, A.; Strausz, O.P.*J.Org.Chem.* **1991**, 58, 4289
- 5) Murai, H; Ribo, J.; Torres, M.; Strausz, O.P. *J.Am.Chem.Soc* **1981**, 103, 6422
- 6) Haller, I.; Pimentel G.C. *J.Am.Chem.Soc.* **1962**, 84, 2855
- 7) Ault, B.S. *J. Phys.Chem.* **1989**, 93, 2456
- 8) Frei, H.; Nakata, M. *J.Am.Chem.Soc* (1992) 114, 1363-1372
- 9) Czismadia,I.G.; Font, J.; Strausz,O.P.*J.Am.Chem.Soc..* 90, **1968**, 90 , 7360
- 10)Torres, M.; Bourlande, J. L .; Clement A.; Strausz, O. P. *J.Am.Chem.Soc.* **1983**, 105, 1698
- 11) Laganis, D. E,; Janik D.S.; Curphey T. J.; Lemal D.M *J.Am.Chem.Soc.* **1983**, 105, 7457
- 12) Debu, F.; Monnier, M.; Verlaque, P.; Davidovics, G.; Pourcin, J.; Bodot H.; Aycard, J.P. *C. R. Acad. Sci. Paris* . **1986**, 303.
- 13) Carsky, P.; Andes Hess Jr B.; Schaad, L. *J. Am. Chem. Soc..* **1983**, 105, 396
- 14) Vacek G.; Colegrove B. T.; Schaefer III, H. *Chem. Phys. Letts.* **1991**, 177
- 15) Tanaka K.; Yoshimine M. *J. Am.. Chem. Soc..* **1980**, 102, 7655

- 16) Scott A.P.; Nobes, R.H.; Schaefer, III H.F.; Radom, L. *J. Am. Chem. Soc.* **1994**, 116, 10159
- 17) Okabe, H. *Photochemistry of Small Molecules* ; Wiley- Interscience: 1985;
Chapter-3
- 18) Hashimoto, S.; Akimoto, H. *J.Phys. Chem.*. **1986**, 90, 529
- 19) Sander, W.; Patyk, A. *Angew. Chem.* .**1987**, 99, 495
- 20) Becker, E.D.; Pimentel, G.C. *J.Chem.Phys*, **1956**, 25, 224
- 21) Norman, I.; Porter, G. *Nature*. **1954**, 174, 508
- 22) Hallam, H.E In *Vibrational Spectroscopy of Trapped Species*; Hallam, H.E., Ed.;
John Wiley and Sons : 1973
- 23) “ Mattson Instruments for the Scientific Laboratory” Technical Manual for
Operation of FT-IR
- 24) “ Innova 70 Series Ion Laser” Technical Manual for users
- 25) Technical Manual for operation of lamps
- 26) Ramirez, F.; Chaw, Y.F.; Marecek, J.F.; Ugi, I. *J.Am. Chem. Soc*, **1974**, 96, 8
- 27) Andrews, L.; Spiker, R,C. *J. Phys. Chem*, **1972**, 76, 22
- 28) a) Singmaster, K.A.; Pimentel, G.C. *Journal of Molecular Structure*, **1989**, 194
b) Singmaster, K.A.; Pimentel, G.C. *Journal of Molecular Structure (Theochem)*
1989, 200
- 29) Karen Singmaster, Ph.D Thesis, University of California, Berkeley, California.
1987.

- 30) Singmaster, K.A.; Pimentel, G.C. *J. Phys. Chem.* **1990**, 94
- 31) Jonnalagadda, S.; Garrido, J.; Chan, S.; Bond, J.; Singmaster, K.A. *J. Am. Chem. Soc.* **1995**, 117, 562-563
- 32) Moore, L.O.; Clark, J.W. *J. Org. Chem.*, **1965**, 30
- 33) McMahon.; Chapman, O.L.; Hayes, R.A.; Hess, T.C.; Krimmer, Hans-Peter. *J. Am. Chem. Soc.* **1985** 107
- 34) Miller, F.A.; Kiviat, F.E. *Spectrochimica Acta*, **1969**, 25A
- 35) Anderson, B.C. *J. Org. Chem.*, **1968** 33
- 36) Thunemann, K.H.; Peyerimhoff, S.D.; Buenker, R.J. *J. Mol. Spectrosc.* **1978**, 70