Effect of Temperature on Sulfide Photooxidations. Evidence for a Reversibly Formed Exciplex?

Edward L. Clennan,* Kristine A. Oolman, Kang Yang, and Dao-Xin Wang

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

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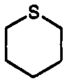
A kinetic study of the reactions of singlet oxygen with pentamethylenesulfide, 1,4-dithiane, and 3-hydroxy-3,4-dimethylpentyl *p*-methylphenyl sulfide has been conducted as a function of temperature. The total rates of singlet oxygen removal (k_T) and the chemical rates of sulfide disappearance (k_r) have been measured and the physical quenching rates determined from the relationship $k_T = k_r + k_q$. The activation barriers for the photooxidations are very different from those observed in photooxidations of other substrates and are explained by tighter binding in sulfide/oxygen exciplexes and bimolecular conversions of the exciplexes to products.

The aesthetically pleasing photooxidative transformation of a sulfide to a sulfoxide is a deceptively simple reaction.[1] An accurate description of the mechanism has proven difficult as a result of the inability of key reaction intermediates to be isolated and spectroscopically identified.[2] The ability of sulfides to both react (k_r) and physically quench (k_q) singlet oxygen has further complicated attempts to understand this important reaction.[3] We report here the activation enthalpies and entropies for the reactions (k_r) of pentamethylenesulfide (1), 1,4-dithiane (2), and 3-hydroxy-3,4-dimethylpentyl *p*-methylphenyl sulfide (3)[4] with singlet oxygen. These activation barriers are significantly different from those reported for the reactions of singlet oxygen with other organic substrates[5] and provide additional insight into the mechanism of sulfide photooxidation.[6]



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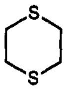

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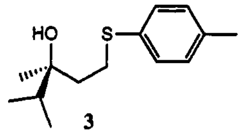

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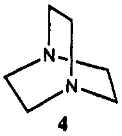
Results

The relative chemical rate constants of singlet oxygen removal $(k_r)_{rel} = k_r(X°C)/k_r(Y°C)$ were calculated by using equation 1. The concentrations of sulfoxide and sulfone products were measured after photolysis time t(s) by capillary GC at a variety of temperatures X °C under otherwise identical reaction conditions. These values at temperature X °C were converted to relative rate constants, $k_r(X°C)/k_r(Y°C)$, by dividing by the concentrations of products produced per unit time at Y °C.

$$\frac{k_r(X°\mathrm{C})}{k_r(Y°\mathrm{C})} = \left[\frac{([\text{sulfoxide}] + [\text{sulfone}])_{X°\mathrm{C}}}{([\text{sulfoxide}] + [\text{sulfone}])_{Y°\mathrm{C}}}\right]\left[\frac{t(\mathrm{s})_{Y°\mathrm{C}}}{t(\mathrm{s})_{X°\mathrm{C}}}\right] \quad (1)$$

These relative rate constants were converted to absolute rate constants (Table I) by multiplying by the chemical reaction rate constants, $k_r(Y°C)$, which were determined directly at Y °C by the competitive kinetic method of Higgins, Foote, and Cheng.[7] The chemical rate constant for 1 was measured at −78 °C (Y °C) in competition with tetramethylethylene [$k_r = (1.2 \pm 0.1) \times 10^7$ M^{-1} s^{-1} at −78 °C], for 2 at 25 °C (Y °C) in competition with 2,5-dimethyl-2,4-hexadiene ($k_r = 7.4 \times 10^5$ M^{-1} s^{-1}),[8] and for 3 at 25 °C (Y °C) in competition with limonene [$k_r = (1.74 \pm 0.13) \times 10^5$ M^{-1} s^{-1}] and at −50 °C (Y °C) in competition with cyclopentene [$k_r = (3.9 \pm 0.4) \times 10^4$ M^{-1} s^{-1}]. A plot of the data generated during the competitive photooxidation of 3 with cyclopentene at −50 °C is shown in Figure 1.

The activation barriers were calculated from the absolute chemical rate constants by using transition-state theory and are collected in Table I along with the rate constants for photooxidation of these compounds. The activation barriers for DABCO (4), tetramethylethylene (5), and 1,3-diphenylisobenzofuran (6) are also included in Table I for comparison.[5]



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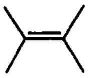

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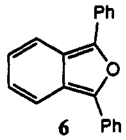

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Discussion

These data and those for compounds 1–3 are consistent with the exciplex mechanism and kinetic expressions depicted in Figure 2. Exciplexes have previously been invoked in order to explain sulfide quenching of aromatic hydrocarbon fluorescence.[9] Gorman and co-workers[5] demonstrated that the reaction of singlet oxygen with diphenylisobenzofuran exhibits two linear regions in its Arrhenius plot corresponding to the diffusion-controlled limit ($k_{-D} \ll k_p$) where $k_r = k_D$ and to the preequilibrium limit ($k_{-D} \gg k_p$) where $k_r = K(k_p)$. The negative activation enthalpies ($\Delta H^{\ddagger}_{obsd} = \Delta H^{\ddagger}_p + \Delta H°$) and entropies ($\Delta S^{\ddagger}_{obsd} = \Delta S^{\ddagger}_p + \Delta S°$) observed (obsd) in the preequilibrium limit represent composite values for product and exciplex formation.

Houk and co-workers have suggested that negative activation barriers are anticipated for very energetic species such as singlet oxygen and that no exciplex or complex is required to explain the experimental data.[10,11] This is a consequence of the absence of any substantial enthalpic barrier for these reactions and the necessity to overcome an entropic barrier. Houk and co-workers point out that

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[1] Ando, W.; Takata, T. In *Singlet O_2. Reaction Modes and Products. Part 2*; Frimer, A. A., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985; Vol. III, pp 1–117.

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[8] Separation of k_r and k_q and the k_r value for 2,5-dimethyl-2,4-hexadiene used in this study were taken from the following: Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.* 1983, *105*, 4710–4717.

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Table I. Rate Constants and Activation Parameters for the Reactions of Singlet Oxygen with Organic Substrates

compd	solvent	*T*, K	$k_r \times 10^{-5}$, $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, kcal/mol	r^c
1	acetone	293	4.7			
		273	8.6			
		253	15			
		233	35			
		213	54			
		198	94	−4.1 ± 0.3	−46 ± 1	0.993
	toluene[a]	293	3.8			
		273	10.8			
		253	35.4			
		233	75.8			
		213	116			
		198	200	−5.1 ± 0.8	−49 ± 4	0.970
2	acetone	293	2.4			
		273	6.7			
		253	22			
		233	84			
		213	113			
		202	166	−6.2 ± 0.6	−54 ± 2	0.970
3	acetone	293	0.65			
		263	1.9			
		243	3.9			
		223	9.7			
		208	26			
		195	34	−5.2 ± 0.3	−54 ± 1	0.995
4[b]	toluene	298	2100	−1.6 ± 0.3	−30 ± 1.2	
5[b]	toluene	298	360	−0.74 ± 0.11	−30.1 ± 0.5	
6[b]	toluene	298	8900	−1.3 ± 0.2	−25.9 ± 0.6[d]	
				1.0 ± 0.3[e]	−16.6 ± 1.2[e]	

[a] Assuming k_q = 0 at −78 °C. [b] Reference 5. [c] Correlation coefficient. [d] Preequilibrium limit. [e] Diffusion limit.

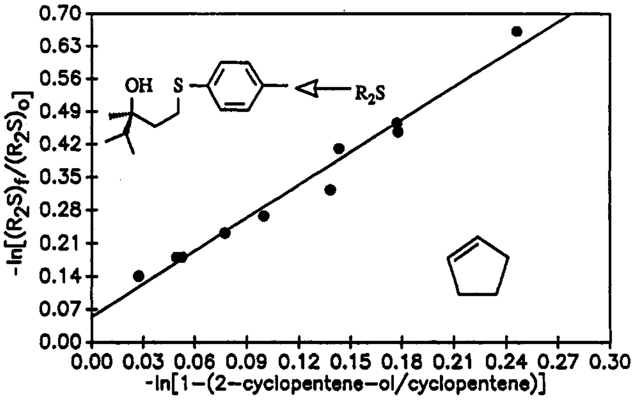

Figure 1. Competitive photooxidation of **3** and cyclopentene at −50 °C; [c-C_5H_8] = 5 × 10^{-2} M; [R_2S] = 2 × 10^{-2} M.

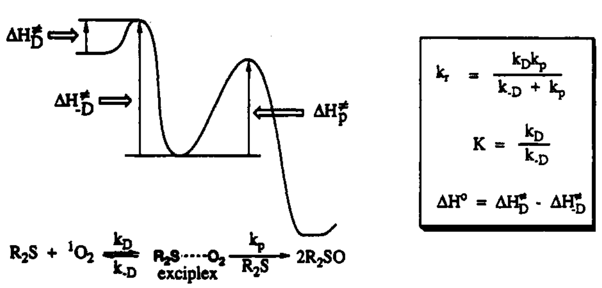

Figure 2.

this phenomenon will be observed for reactions that have $\Delta S^{\ddagger}$ more negative than approximately −6.7 eu.[12] Gorman,[5] on the other hand, has pointed out that the mechanistic diversity of singlet oxygen reactions that exhibit negative activation barriers, as well as a large body of photochemical precedent, argues against the Houk proposal and that the data is more consistent with a reversibly formed intermediate.

If an exciplex is an authentic intermediate, the substantially negative activation enthalpies observed for photooxidations of sulfides **1**–**3** in comparison to photooxidations of **4**–**6** most reasonably represent a tighter binding (more negative $\Delta H°$) in the sulfide/oxygen exciplex. The heat of reaction for the photooxidation of 1 mol of **1** to its sulfoxide (−37.17 kcal/mol)[13] is smaller than for the conversion of **5** to its hydroperoxide (−42.40 kcal/mol)[17] and larger than for physical quenching by **4** (−22.5 kcal/mol). This argues against but does not rigorously exclude the alternative possibility that a substantially smaller $\Delta H^{\ddagger}$ alone is responsible for the more negative activation enthalpies.

The tighter binding in the sulfide/oxygen than in the DABCO/oxygen exciplex is surprising, given the similarity in the ionization potentials of sulfides [Et_2S (8.42 eV); Me_2S (8.69 eV); MeSH (9.44 eV)][18] and amines [Et_2NH (8.4 eV); Me_2NH (8.9 eV); $MeNH_2$ (9.4 eV)].[19] The more diffuse lone-pair orbitals and reduced steric environment around sulfur, in comparison to amines, however, may promote exciplex formation. The importance of steric effects upon exciplex stability is well established.[20]

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(12) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555–1563.

(13) Calculated by using the Benson group[14] thermochemical data. C–$(H)_3$(C) = −10.08 kcal/mol; C_d–$(C)_2$ = 10.34 kcal/mol; C_d–$(H)_2$ = 6.26 kcal/mol; C–(O)$(C)_3$ = −6.60 kcal/mol; O–(O)(H)[15] = −16.3 kcal/mol; cis correction for **5** = 3.00 kcal/mol; excitation energy of singlet oxygen = 22.5 kcal/mol.[16]

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(17) Calculated by using the Benson group[14] thermochemical data and equal to one-half of the heat of the following reaction: $2(CH_2)_5S + {}^1O_2 \rightarrow 2(CH_2)_5SO$. C–$(H)_2(C)_2$ = −4.95 kcal/mol; S–$(C)_2$ = 11.51 kcal/mol; SO–$(C)_2$ = −14.41 kcal/mol; C–(C)$(H)_2$(S) = −5.65 kcal/mol.

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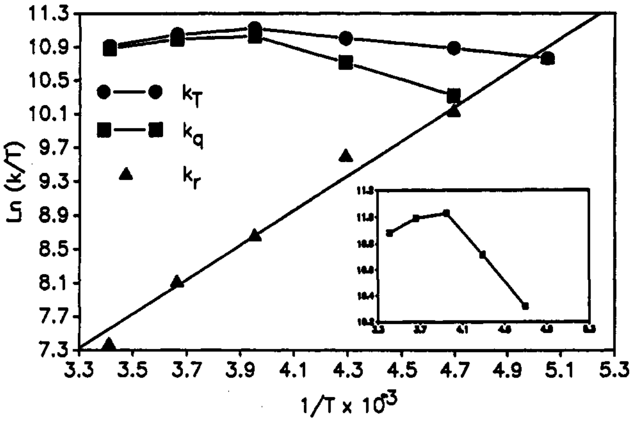

Figure 3. Arrhenius plot for the photooxidation of 1.

The activation entropies for sulfide photooxidations in comparison to the photooxidations of **4**–**6** are also substantially more negative. The entropies of exciplex formation, $\Delta S°$, have been measured in several cases and exhibit values as negative as −25 cal mol^{-1} K^{-1} (e.g., α-cyanonaphthalene/1,2-dimethylcyclopentene exciplex; $\Delta S°$ = −23.3 cal mol^{-1} K^{-1} at 273 K).[21] It is unreasonable, however, to assume that $\Delta S°$ for sulfide/oxygen exciplexes would be substantially more negative than these measured values or different from $\Delta S°$ for the DABCO/oxygen exciplex. We suggest that the very negative activation entropies for the sulfide photooxidations are due to a very negative ΔS^{*}_{p} and provide evidence that the exciplex is converted to the product in a bimolecular reaction.

The total rate of disappearance of singlet oxygen, k_T, was also measured for the reaction of **1** in acetone as a function of temperature, using the previously described time-resolved infrared emission apparatus.[22,23] These data are displayed graphically in Figure 3 along with the values for k_r and k_q (measured by difference $k_q = k_T - k_r$). The response of k_q to temperature is blown up in the insert in Figure 3. It appears that both the diffusion and preequilibrium regions are observed for k_q, but unfortunately not enough points are available to accurately define the activation barriers in either region.

The tighter binding in the sulfide/oxygen exciplex in conjunction with an unfavorable entropy for its collapse to products suggests that the exciplex may be directly observable and could provide evidence to distinguish between the Houk and exciplex proposals. Studies designed to verify this suggestion are currently in progress.

Experimental Section

Proton and carbon NMR spectra were obtained on a JEOL GX270 instrument at 270 and 67.83 MHz and on a JEOL GX400 instrument at 400 and 100.47 MHz, respectively, and the chemical shifts were referenced to TMS. Analytical gas chromatographic measurements were carried out on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector and a HP 10 m × 0.53 mm cross-linked FFAP or HP-1 capillary column. Chromatographic separations were carried out on a Harrison Research Model 7624T chromatotron using plates coated with EM Science 7749 silica gel 60PF254.

Rose Bengal, tetraphenylporphyrin, triphenylphosphine, potassium permanganate, *m*-chloroperbenzoic acid, methyl vinyl ketone, *p*-methylthiophenol, cyclopentene, and magnesium sulfate were all obtained from Aldrich and used without further purification. Limonene was obtained from Eastman Kodak, 2-bromopropane from Aldrich, and 2,2,4,4-tetramethyl-3-pentanone from Chemical Samples Co., and all were distilled prior to use. 1,4-Dithiane (**2**), was obtained from Aldrich and recrystallized from ethanol prior to use. Pentamethylenesulfide (**1**), 2,5-dimethyl-2,4-hexadiene, diphenylmethane, and triethylene glycol dimethyl ether were all obtained from Aldrich and purified by literature procedures.[24] Spectral grade acetone for kinetic studies was obtained from Baker and used without purification. Bulk solvents such as hexane, ethyl acetate, ethanol, methanol, and chloroform were purified by simple distillation. Carbon tetrachloride was purified by distillation from P_2O_5. Sodium *p*-toluenethiolate was prepared according to a literature procedure.[25]

Competitive Kinetics. Competitive kinetics runs were conducted as described by Higgins, Foote, and Cheng.[7] Calibration curves were constructed for all compounds by using either diphenylmethane, 2,2,4,4-tetramethyl-3-pentanone, or triethylene glycol dimethyl ether as an internal standard. The competitive kinetics runs were carried out in acetone with the following concentrations: [**1**]/[tetramethylethylene] = $(2.2 \times 10^{-2}$ M)/(1.1 $\times 10^{-2}$ M); [**2**]/[2,5-dimethyl-2,4-hexadiene] = $(4.98 \times 10^{-2}$ M)/(2.92 $\times 10^{-2}$ M); [**3**]/[cyclopentene] = $(2 \times 10^{-2}$ M)/(5 $\times 10^{-2}$ M); [**3**]/[limonene] = $(2 \times 10^{-2}$ M)/(1.5 $\times 10^{-2}$ M). The appearance of sulfide oxidation products was monitored during the reactions of **1** and **2** and the disappearance of starting sulfide in the reaction of **3**. The disappearance of 2,5-dimethyl-2,4-hexadiene and limonene and the appearance of the oxidation products of cyclopentene and tetramethylethylene were also monitored by capillary GC.

Data Treatment. The activation parameters were determined by plotting ln (k/T) vs $1/T$, and the confidence limits were calculated by the method of Bevington[26] and propagated into the activation parameters at the 95% confidence level.

Photolysis Conditions. The singlet oxygen reactions were conducted in either acetone or toluene, and the temperature was maintained by submersion in a methanol bath held at −78 °C by the use of a refrigerator probe (FTS Systems Inc. Flexicool). Prior to photolysis, the samples were saturated with oxygen for 20 min. The concentrations of the starting materials and dye were approximately 2–15 $\times 10^{-2}$ M and 1–3 $\times 10^{-5}$ M, respectively. The irradiation was conducted under continuous oxygen bubbling by using a 750-W, 120-V tungsten halogen lamp and by filtering out the high-energy light with a 1-cm 0.5% $K_2Cr_2O_7$ filter solution. The hydroperoxides from tetramethylethylene and cyclopentene were reduced with triphenylphosphine prior to GC analysis.

***p*-Methylphenyl 3-Oxobutyl Sulfide.** A solution of 1.5 g (12.1 mmol) of *p*-thiocresol and 0.67 g (12.4 mmol) of sodium methoxide in 35 mL of ethanol was refluxed for 4 h. To this solution was added 0.85 g (12.1 mmol) of methyl vinyl ketone, and the mixture was refluxed for an additional 4 h. Ethanol was removed, and the residue was extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$. The product was obtained in 62.7% yield after purification on a chromatotron using hexane/ethyl acetate: ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3 H), 2.33 (s, 3 H), 2.73 (t, J = 7.7 Hz, 2 H), 3.09 (t, J = 7.7 Hz, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-Methylphenyl Sulfide (3). Mg turnings (1.2 g, 48 mmol) and a small I_2 crystal were placed in 10 mL of dry ether, and 6.1 g of isopropyl bromide was added at a rate that maintained a vigorous reflux. After complete addition of the bromide, 0.58 g (30 mmol) of *p*-methylphenyl 3-oxobutyl sulfide in 2 mL of ether was added dropwise. After 20 min of stirring, water was added and the products were extracted with ether. The combined extracts were washed with water and dried over $MgSO_4$. The alcohol was obtained in 21% yield after purification by chromatotron with hexane/ethyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 7.0 Hz, 3 H), 0.93 (d, J = 7.0 Hz, 3 H), 1.10 (s, 3 H), 1.36 (s, 1 H), 1.70 (heptet, J = 6.8 Hz, 1 H),

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1.71–1.84 (m, 2 H), 2.32 (s, 3 H), 3.01–3.09 (m, 2 H), 7.09 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 16.84 (q, J = 125 Hz), 17.52 (q, J = 125 Hz), 20.98 (q, J = 111 Hz), 22.79 (q, J = 125 Hz), 28.97 (t, J = 134 Hz), 37.17 (d, J = 125 Hz), 38.89 (t, J = 127 Hz), 129.65 (d, J = 159 Hz), 129.82 (d, J = 160 Hz), 132.7 (s), 136.0 (s).

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Supplementary Material Available: The competition data for the reactions of 1 with tetramethylethylene, 2 with 2,5-dimethyl-2,4-hexadiene, and 3 with limonene and the derivation of the equations for the observed enthalpy and entropy of activation (4 pages). Ordering information is given on any current masthead page.

Gas-Phase Reaction between Oxygen (^{3}P) Atoms and Hexafluoro-2-butyne

Peter G. Mahaffy and Alex VanderWoude

Department of Chemistry, The King's College, Edmonton, Alberta, Canada T5H 2M1

Otto P. Strausz*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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The gas-phase addition of oxygen (^{3}P) atoms from the mercury-sensitized photodecomposition of nitrous oxide to hexafluoro-2-butyne has been studied at 298 K. Tetrakis(trifluoromethyl)furan (4) is the major final product that arises from the reaction of the initial triplet ketocarbene adduct with a second molecule of hexafluoro-2-butyne.

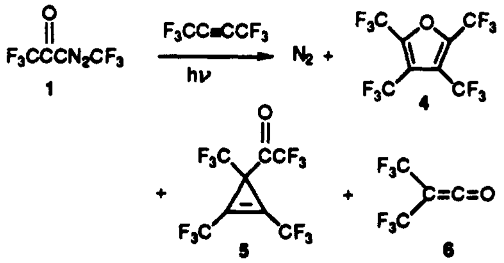
Introduction

A great deal of effort has been devoted in recent years to elucidating the mechanism of the photochemical Wolff rearrangement. Of fundamental theoretical interest has been the involvement of transient ketocarbene and antiaromatic 4π-electron oxirene species. One aspect of recent experimental investigations has been to carry out the photolysis of precursor diazo ketones with substituents potentially capable of stabilizing the elusive oxirene intermediates.[1,2] Since perfluoroalkyl substituents have been shown[3-5] to have the capability of providing remarkable stabilization of certain highly strained compounds, we have investigated and reported the photolysis of several perfluorinated α-diazo ketones in the gas phase[6] and inert matrices.[7,8]

Concurrently, theoretical studies of the various species on the unsubstituted formylmethylene–oxirene surface have provided insight into the nature and relative energies of various structures that might be involved in the Wolff rearrangement of the parent system.[9,10]

The addition of ground-state oxygen atoms to substituted acetylenes provides another entry point to one of the possible intermediates in the diazo ketone photolysis. There are many reports of the addition of ground state O(^{3}P) atoms to alkenes[11-15] and a few reports of the addition to alkynes.[16-20] Most of these reactions appear to proceed via initial formation of a triplet diradical. Thus, the investigation of the reaction between O(^{3}P) atoms and selected alkynes may facilitate the interpretation of results from mechanistic studies of the Wolff rearrangement.[21]

Scheme I



This paper presents the first report of the gas-phase reaction of O(^{3}P) atoms with a perfluorinated alkyne, hexafluoro-2-butyne. This study was undertaken to supplement our previously reported investigation of the gas-phase photolysis of hexafluoro-3-diazo-2-butanone (1), octafluoro-2-diazo-3-pentanone (2), and octafluoro-3-dia-

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