The Journal of **Physical Chemistry**

VOLUME 85, NUMBER 9 APRIL 30, 1981

LETTERS

Detection and Properties of Triplet State Thiiranes

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(Received: April 11, 1980; In Final Form: September 8, 1980)

The major primary step in the long wavelength ($\lambda > 240$ nm) photolysis of thiirane is intersystem crossing to the lowest excited triplet (T_1) state with a quantum yield of ~0.86. Triplet thiirane has a long radiative lifetime, is highly resistant to collisional deactivation, and is capable of undergoing reversible addition to alkenes and thereby inducing their geometrical isomerization. Inefficient irreversible addition also occurs. This provides a novel example of an excited triplet molecular sensitization not involving energy transfer. Thiirane T_1 has a cyclic structure which is retained in the alkene adduct and shows strong diradical character.

Triplet state thiiranes have been postulated to be the primary adducts in the addition reactions of ground (^3P) sulfur atoms to alkenes[3] on the basis of MO calculations[4] and by analogy with the $O(^3P)$ + alkene reactions.[5] The T_1 state of thiiranes has also been implicated in the low-temperature thermolysis of thiirane, methylthiirane, and dimethylthiirane.[6] We now report evidence for the involvement of the same T_1 state in the direct and triplet-sensitized photolysis of thiirane as well, and to describe the unusual chemistry of these excited thiirane molecules.

Photolysis in the first long wavelength absorption band of thiirane ($\lambda_{max} \sim 260$ nm)[7] leads to the formation of C_2H_4 (~90%) and small amounts of H_2S, C_2H_2, H_2, and CH_4. $\phi(C_2H_4) = 1.3$ at $\lambda > 240$ nm and is independent of pressure up to 200 torr, but decreases with increasing wavelength of photolysis. In order to test for the intermediacy of sulfur atoms in the decomposition, we flash photolyzed 0.6 torr of thiirane in 200 torr of CO_2. The atomic absorption line at 180.7 nm corresponding to the $S(^3P_2) \rightarrow S(^3S_1)$ resonance absorption was visible when unfiltered ($\lambda > 180$ nm) radiation was used, but was not detected when the photolyzing radiation was limited to $\lambda > 240$ nm. This result corroborated the negative results obtained in chemical-scavenging experiments using an alkane or an alkene to intercept atomic sulfur. It is therefore concluded that sulfur atoms are not involved in

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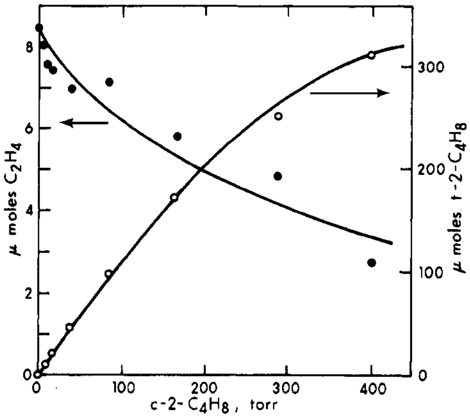


Figure 1. Yields of C_2H_4 and *trans*-2-C_4H_8 as a function of *cis*-2-butene pressure from the $\lambda > 240$-nm photolysis of 100 torr of thiirane.

the $\lambda > 240$-nm photolysis of thiirane.

Added alkanes, e.g., 300 torr of propane to 11 torr of thiirane, have no observable effect on the photolysis. Added alkenes, however, exert a suppressing effect on the yield of C_2H_4 and when *cis*-2-butene is used, geometrical isomerization takes place, and *trans*-butene forms in high yields (Figure 1).[8] At 400 torr of *cis*-butene pressure the C_2H_4 yield decreases by more than half and for each C_2H_4 produced more than a hundred molecules of *cis*-butene are isomerized, giving a quantum yield for *trans*-butene formation of ~50. Thus it is clear that isomerization does not take place as a result of energy transfer, but via reversible addition of an intermediate. For this there are only two candidates, excited triplet thiirane or the sulfur radicals S_2–S_7; however, when triplet thiirane is produced without sulfur radicals via the addition of $S(^3P)$ atoms from the photolysis of COS in the presence of CO_2 and *cis*-butene, isomerization of *cis*-butene still occurs with comparable yields. Triplet state thiirane, generated by the triplet benzene or biacetyl sensitization of thiirane, also induces isomerization of *cis*-butene although the yields of *trans*-butene are smaller in the latter system. Therefore, the agent responsible for isomerization in the direct photolysis must be triplet state thiirane.

The major steps required for the interpretation of the long wavelength photolysis of thiirane are as follows:

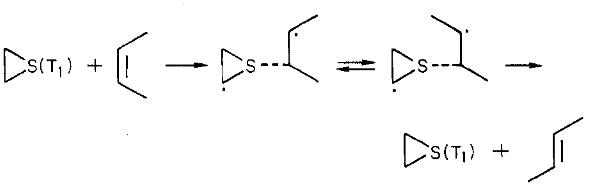
$$C_2H_4S(S_0) + h\nu \rightarrow C_2H_4S(S_1) \tag{1}$$

$$C_2H_4S(S_1) \rightarrow C_2H_2,\ H_2S,\ H_2,\ CH_4 \qquad \phi \sim 0.14 \tag{2}$$

$$C_2H_4S(S_1) \rightarrow C_2H_4S(T_1) \qquad \phi \sim 0.86 \tag{3}$$

$$C_2H_4S(T_1) + C_2H_4S(S_0) \rightarrow S_2 + 2C_2H_4 \qquad \phi \sim 0.65 \tag{4}$$

$$C_2H_4S(T_1) + C_2H_4S(S_0) \rightarrow 2C_2H_4S(S_0) \qquad \phi \sim 0.21 \tag{5}$$



(6)

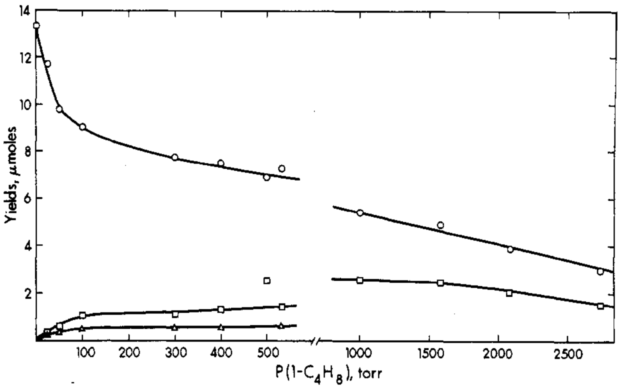
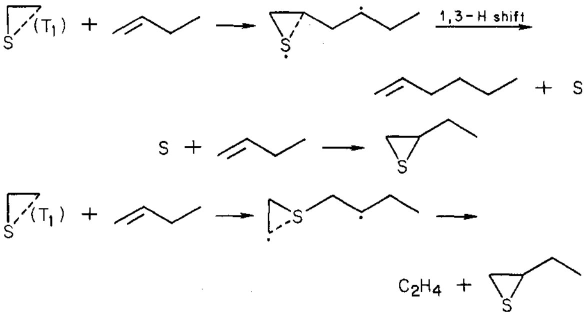


Figure 2. Yields of C_2H_4 (○), C_4H_8S (□), and 1-C_6H_{12} (△) as a function of 1-C_4H_8 pressure from the $\lambda > 240$-nm photolysis of 12 torr of thiirane.

The effects of added alkenes were examined in detail for the cases of C_3H_6, 1-C_4H_8, and 1-C_5H_{10}. In general, the C_2H_4 yields decline slowly with increasing alkene pressure and two additional products are formed in small yields: the thiirane analogue of the alkene, and a terminal alkene corresponding to a C_2H_4 + alkene adduct. The yields of these products are given in Figure 2 for the case of 1-butene. It thus appears that T_1 thiirane can also undergo a nonreversible addition, albeit inefficiently, with the alkene:



(7)
(8)
(9)

Further evidence in support of the occurrence of steps 7–9 comes from the isotopic distribution of products from the photolysis of C_2D_4S in the presence of 1-C_4H_8, giving C_4H_8 S and partially deuterated 1-hexene. The fact that the thiirane yield is about twice that of the alkene indicates that the carbon and sulfur radical sites in $C_2H_4S(T_1)$ are equally reactive.

It has been shown[1] that the addition of $S(^3P)$ atoms to olefins follows a stereoselective reaction path. Moreover, photolysis of *trans*- and *cis*-2,3-dimethylthiirane afforded ~95% *trans*- and *cis*-butene, respectively. Therefore the T_1 state must be cyclic. Indeed, MO calculations[4] predict a ring distorted equilibrium conformation for the T_1 state with a bond strength of ~24 kcal/mol for the stretched C–S bond and a value of ~40 kcal/mol for the excitation energy of the $^3(n,\sigma^*)T_1$ state. From this we conclude that the ring distorted equilibrium conformation of thiirane (T_1) is maintained in the alkene adduct, as indicated in eq 7 and 9. This is also in line with the reversible nature of the addition, since if an open triplet diradical structure $\cdot CH_2$–CH_2–$S\cdot$ were involved the addition would not be expected to be reversible at pressures of several hundred torr.

Small quantities of NO were found to quench efficiently the isomerization of *cis*-butene. Ethylene formation from the photolysis of pure thiirane is also suppressed to a limiting yield of $\phi \sim 0.86$ at a fourfold excess of NO, in agreement with the primary quantum yield of thiirane (T_1) and suggesting the following overall reaction:

$$C_2H_4S(T_1) + NO \xrightarrow{NO} C_2H_4 + SO_2 + N_2$$

Both SO_2 and N_2 are products of the reaction.

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[8] Isomerization of 2-butene upon photolysis of COS/2-butene mixtures at very low pressures has been observed previously: M. W. Schmidt and E. K. C. Lee, *J. Am. Chem. Soc.*, **90**, 5919 (1968); **91**, 2024 (1969).

The results presented here are of significance for two reasons. First, they shed light on the triplet state chemistry of thiirane for which information is sparse, as is the case with three-membered ring compounds in general. Second, they represent a unique example of geometrical isomerization of an olefin induced by an electronically excited molecule, but without energy transfer. For this type of sensitization the sensitizer should have the following properties: (a) a long radiative lifetime, (b) resistance against collisional deactivation, (c) an excitation energy lower than the nonvertical triplet energy of the olefin, and (d) the ability to form a partial but not a full covalent bond with unsaturated carbon centers. At present, few molecules may be imagined which would fulfill these conditions.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

Sequential Ion–Molecule Reactions in Acetylene

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In Final Form: March 10, 1981)*

Reactions of $C_2H_2^+$, $C_4H_2^+$, $C_4H_3^+$, $C_6H_4^+$, and $C_6H_5^+$ with acetylene have been studied by using pulsed ion cyclotron resonance mass spectrometry. In the pressure range from 2×10^{-6} to 3×10^{-5} torr of C_2H_2, overall disappearance rate constants for $C_4H_2^+$ and $C_4H_3^+$ of $(3.3 \pm 0.8) \times 10^{-10}$ and $(2.1 \pm 0.3) \times 10^{-10}$ cm^3/s, respectively, have been determined. Formation of long-lived ion–molecule reaction complexes, stabilized by collisions at pressures near 1×10^{-5} torr of C_2H_2 and favored over H· or H_2 elimination products, has been observed for $C_6H_n^+$ and $C_8H_n^+$ species. The possible relevance of these reactions to soot formation processes in flames is discussed.

Introduction

The existence of significant concentrations of ions in flames has been acknowledged for a number of years. Formation of the ions is generally accorded[1] to take place in a very thin reactive zone via the chemi-ionization reaction

$$\mathrm{CH(X^2\Pi) + O(^3P) \rightarrow CHO^+ + e^-} \qquad (1)$$

Extensive secondary ion–molecule reactions then lead ultimately to H_3O^+, NO^+, and electrons in the burnt gas region of the flame. Recent mass spectrometric sampling experiments[2–4] have confirmed the earlier identification of numerous flame ions, and have led to various reaction schemes[3,4] which explain the evolution of ion concentrations from an upstream region, through the reactive zone, and into the burnt gas region of certain laboratory flames. Whether these ions and ion–molecule reactions are relevant to any important combustion processes is, however, a subject of current controversy.

One area related to combustion in which ions may play a crucial role is soot formation. Studies by Prado and Howard[5] and by others have demonstrated the presence of large hydrocarbon ions (probably aromatic) in sooting flames. Experiments involving the effects of ionic additives[6] and of electric fields[7] on the amount of soot produced in such flames also indirectly point to participation of ions in these processes. However, almost equally compelling evidence has been given for the primary importance of radical–molecule as compared to ion–molecule reactions in the condensation reactions which lead to nucleation and ultimately to soot formation.[8]

At least one group[9] has postulated that rapid ionic polymerization of acetylenic species

$$\begin{aligned} \mathrm{C_{2n}H_{2n+1}^+ + C_2H_2} &\rightarrow \mathrm{C_{2n+2}H_{2n+3}^+} \\ &\rightarrow \mathrm{C_{2n+2}H_{2n+1}^+ + H_2} \end{aligned} \qquad (2a)$$

$$\mathrm{C_{2n}H_{2n-1}^+ + C_2H_2 \rightarrow C_{2n+2}H_{2n+1}^+} \qquad (2b)$$

is of crucial importance in sooting flames, since they observed large concentrations of polyacetylenic ions. Other workers[2,3] have detected similar ions in methane–oxygen and acetylene–oxygen flames, and large mole fractions of neutral acetylene have been found[10] in methane–oxygen flames.

The techniques of ion cyclotron resonance (ICR) mass spectrometry[11–14] have been shown in the past 10 years to

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† Camille and Henry Dreyfus Foundation Fellow, 1978–82.

(1) See, for example, W. J. Miller, *Symp. (Int.) Combust., [Proc.], 14th, 1972*, 307 (1973).

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