The Reactions of Sulfur Atoms. 15. Absolute Rate Parameters for the $S(^3P_{2,1,0})$ + Alkyne Reactions

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Abstract: Using flash photolysis with vacuum UV kinetic absorption spectroscopy, absolute rate constants and Arrhenius parameters have been measured for the addition of ground state $S(^3P_{2,1,0})$ atoms to alkynes. The decay of sulfur atoms in COS, alkyne, and CO_2-diluent mixtures is first order in sulfur atom concentration and the first-order decay rate constants are proportional to the alkyne concentration. The following rate constants were determined at room temperature: $k(C_2H_2) = k(C_2D_2) = (2.3 \pm 0.4) \times 10^8$; $k(CHCCH_3) = (4.8 \pm 0.2) \times 10^9$; $k(CHCC_2H_5) = (3.3 \pm 0.2) \times 10^9$; $k(CH_3CCCH_3) = 1.6 \pm 0.2) \times 10^{10}$; $k(CH_3CCC_2C_5) = 1.8 \pm 0.3) \times 10^{10}$; and $k(CF_3CCCF_3) = (2.1 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}. The Arrhenius parameters determined are $k(C_2H_2) = (3.4 \pm 1.9) \times 10^{10} \exp[(-3000 \pm 400)/RT]$ L mol^{-1} s^{-1} and $k(CHCCH_3) = (2.0 \pm 1.2) \times 10^{10} \exp[(-900 \pm 200)/RT]$ L mol^{-1} s^{-1} where error limits represent standard deviations. The rate parameters are compared to those obtained for the addition of other electrophilic reagents to alkynes and the results discussed in terms of structural and kinetic factors. Theoretical treatment of the secondary H/D isotope effect in the acetylene reaction satisfactorily reproduces the experimental value.

The chemistry of sulfur atoms has been investigated for the past decade and a half, and a considerable amount of knowledge has accumulated on the subject during this period.

It has been shown that sulfur atoms are highly reactive and that the reactivity, as with other group 6 atoms, is markedly dependent on the electronic state.[1,2] Ground, triplet state sulfur atoms react readily with nonaromatic unsaturates but at room temperature are unreactive with saturated molecules. The reaction with olefins consists of a single step, stereospecific cycloaddition[3] to yield the lowest excited triplet state thiirane molecule[4] as primary product which, through collision-induced relaxation, gives ground state thiirane in high yields as the only retrievable end product. Relative[5] and absolute[6-10] rate parameters indicate a distinct electrophilic trend in the variation of the activation energy with molecular structure and the reaction with tetramethylethylene features a negative activation energy—an interesting facet also found in the cases of $Te(^3P_2)$[7] and $O(^3P_{2,1,0})$[11,12] atoms.

In contrast, the primary adducts formed in the addition of sulfur atoms to acetylenes are inherently unstable[13] rendering mechanistic interpretation more difficult. Excited $S(^1D_2)$ atoms have been postulated to form thiirenes[14,15] which could be trapped with varying degrees of success depending on the nature of the alkyne, by the excess alkyne in the form of thiophene. Ground-state atoms also add readily to acetylene and the primary product is probably the vibrationally excited ground-state triplet thioketocarbene[16] which could arrange to the lowest excited triplet state of thioketene, or by collision-induced intersystem crossing to ground-state thioketene, ethynylthiol, or thiirene, or initiate the polymerization of acetylene. By analogy, ground-state $O(^3P_{2,1,0})$ atoms have been postulated to react with acetylenes to give triplet ketocarbenes[17-19] as primary products.

The quantitative kinetic investigations of sulfur atom reactions which have been carried out during the past 8–9 years in several laboratories have led to the accumulation of a significant body of kinetic data, rate constants, and rate parameters.[5-10,20] Most of them refer to reactions with alkenes and the alkynes are poorly represented. Thus, relative rate parameters[5] have been reported for the reactions with acetylene, propyne, and 2-butyne and the only absolute rate constant reported to date is that for the room temperature reaction with acetylene.[20] In the former study a competitive chemical system was employed in which the rate of the alkyne reaction was

determined from the observed decrease in the thiirane yield from an alkene–alkyne mixture. These results, when combined with the more recent absolute measurements of the activation energy and preexponential factor for the ethylene[9,10] addition reaction, lead to activation energies in the range of 0.2–3.5 kcal/mol and preexponential factors in the range of (3–7) × 10^{10} L mol^{-1} s^{-1} for the above alkyne series. The apparent trend in the variation of the activation energy with molecular structure parallels that which would be expected for an electrophilic reagent and the values of the preexponential factors seem to reflect the gain in the entropy of activation which accompanies the geometrical changes during transition from the reactant state to the activated complex.

In the light of these results and particularly because of the indirect nature of the early relative rate measurements and the possible large experimental errors associated with them, it appeared highly desirable to extend our earlier absolute rate studies on sulfur atom reactions[6,7,21,22] to the family of alkynes. For this reason a study using flash photolysis with vacuum UV kinetic absorption spectroscopy was undertaken involving a series of structurally representative alkynes.

Experimental Section

The isothermal flash photolysis of COS in the presence of CO_2 was used as the source of $S(^3P)$ atoms.[2] The flash photolysis apparatus and technique have been described in earlier publications from this laboratory.[6,7,21,22] In most experiments the intense absorption of $S(^3P_2)$ atoms at 180.7 nm was used to monitor the kinetics of decay. In some cases the $S(^3P_1)$ atom concentration was also determined from the measurement of the 182.0-nm resonance line absorption intensity. The Beer–Lambert exponent for both resonance lines was 0.5 ± 0.1 and it was shown that the population of the triplet levels at room temperature corresponded to thermal equilibrium. The maximum decomposition of COS per flash was 3% and in order to prevent substrate depletion, the alkyne to initial sulfur atom concentration ratio was maintained at >20. Also, serious complications related to the possible photolysis of the alkyne can be discounted in light of the observation made in a recent photolysis study of the OH + C_2H_2 reaction[23] in which the extent of C_2H_2 photolysis was estimated to be less than 1% up to 500 J flash energies even when LiF windows were used. In the present study the falsh energies used were in the 400–1200-J range and windows were of quartz, which has a much lower transmittance below 180 nm where alkynes absorb than does LiF.[24]

Acetylene, propyne, 1-butyne (Matheson), acetylene-d_2 (Merck Sharp and Dohme), 2-butyne (Farchan Research Laboratories), 2-pentyne (C. P. L.), and 2-butyne-F_6 (Columbia Organic Chemicals) were research grade and purified by degassing at −196 °C and dis-

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Table I. Rate Constants for the Reactions of $S(^3P)$ Atoms with Alkynes[a]

| Substrate	$\dfrac{k,^b}{10^8 \text{ L mol}^{-1}\text{ s}^{-1}}$	No. of measurements
Acetylene	2.3 ± 0.4	40
Acetylene-d_2		
Propyne	48 ± 2	30
1-Butyne	33 ± 2	40
2-Butyne	160 ± 20	22
2-Pentyne	180 ± 20	30
Perfluoro-2-butyne	2.1 ± 0.4	30

[a] 25 °C. [b] Error in standard deviation.

Table II. Temperature Dependence of the Reaction of $S(^3P_2)$ Atoms with Acetylene

Temp, K	$\dfrac{k,}{10^8 \text{ L mol}^{-1}\text{ s}^{-1}}$	No. of measurements	Log k
298	2.3	40	8.36
389	6.0	10	8.78
450	10	10	9.00
484	19	10	9.28

tillation at a few Torr pressure. Carbonyl sulfide (Matheson) was purified by the procedure of Wiebe et al.[25] Carbon dioxide (Matheson) was dried over P_2O_5.

Results

The photolysis of COS at $\lambda > 200$ nm produces predominantly $S(^1D_2)$ atoms[26]

$$COS + h\nu \xrightarrow{\lambda > 200 \text{ nm}} CO + S(^1D_2)$$
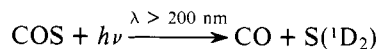
which are efficiently quenched to the ground-state triplet manifold by CO_2 or Ar $(S(^1D_2) + CO_2(Ar) \rightarrow S(^3P_{2,1,0}) + CO_2(Ar))$. The half-life of $S(^1D_2)$ atoms in the presence of 60 Torr CO_2 is approximately 0.01 μs and in the presence of 200 Torr Ar is 0.1 μs.[8,27] Therefore at the delay times and pressures employed in this study (>10 μs, 200 Torr CO_2) the $S(^1D_2)$ atom decay is complete and the distribution among the ground-state triplet components corresponds to thermal equilibrium. During decay in the presence of CO_2, Ar, CO_2 + olefin (C_2H_4, 1-butene, *trans*-2-butene, isobutene) the thermal equilibrium is not affected, indicating that thermalization with CO_2 or Ar is faster than reaction with the alkene.[10] Under appropriate experimental conditions the same should apply to all reaction systems including alkynes as well. Consequently, the rate parameters measured apply to equilibrated $S(^3P_{2,1,0})$ atoms, that is, to the experimentally observable rate constants $k(^3P_2) = k(^3P_1) = k(^3P_0)$. In most of the measurements the $S(^3P_2)$ atom decay was monitored, but in a few instances the decay of $S(^3P_1)$ atoms was also monitored and in each case the rate constant values obtained were identical with those from the decay of $S(^3P_2)$ atoms.

The rates of decay of $S(^3P_{2,1})$ atoms in all the COS and CO_2 + alkyne systems examined were found to follow first-order kinetics as seen from the illustrative examples of decay plots given in Figure 1. The bimolecular rate constant for the reaction with substrate, in the present instance alkyne, can be obtained from the relation

$$k(\text{observed}) = k[\text{substrate}] + k' \qquad (1)$$

where k(observed) is the pseudo-first-order rate constant obtained from the slope of the decay plot and k' is the rate of decay of $S(^3P_{2,1})$ atoms in the absence of substrate. The value of k' was determined to be 1.1×10^3 s^{-1}. Equation 1 has been shown to be applicable for the reaction of sulfur atoms with
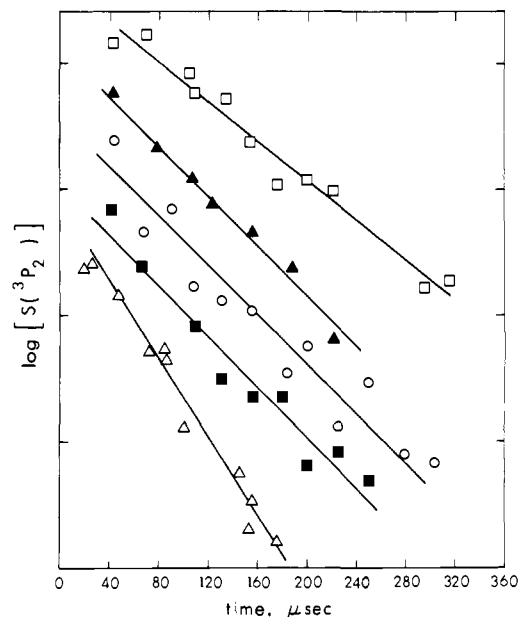
Figure 1. First-order decay plots of $S(^3P_2)$ atoms in the presence of alkynes: □, $CH_3C{\equiv}CCH_3$; ▲, C_2D_2; O, C_2H_2; ■, $CF_3C{\equiv}CCF_3$; △, $CH_3CH_2C{\equiv}CH$.

Table III. Temperature Dependence of the Reaction of $S(^3P_{2,1})$ Atoms with Propyne

Species	Temp, K	$\dfrac{k,}{10^9 \text{ L mol}^{-1}\text{ s}^{-1}}$	No. of measurements	Log k
$S(^3P_2)$	298	4.8	10	9.68
$S(^3P_2)$	358	4.8	10	9.68
$S(^3P_1)$	358	5.9	10	9.77
$S(^3P_2)$	368	7.3	10	9.86
$S(^3P_2)$	398	6.3	10	9.80
$S(^3P_1)$	414	7.1	10	9.85
$S(^3P_2)$	428	6.3	10	9.80
$S(^3P_1)$	449	7.3	10	9.86
$S(^3P_2)$	449	8.5	10	9.93

acetylene,[20] oxygen,[21] ethylene,[6,10] and tetramethylethylene[10] and was therefore assumed to hold for the higher alkynes examined in the present study.

Values of the bimolecular rate constants for the room temperature reaction with a series of seven representative alkynes are presented in Table I.

The bimolecular rate constants for the $S(^3P_2) + C_2H_2$ and $S(^3P_{2,1}) + C_3H_4$ systems were also determined as a function of temperature in the temperature range 300–480 K and the data are listed in Tables II and III. From the Arrhenius plot, Figure 2, the rate coefficients can be expressed as

$$k(C_2H_2) = (3.4 \pm 1.9) \times 10^{10}$$
$$\times \exp((-3000 \pm 400)/RT) \text{ L mol}^{-1}\text{ s}^{-1}$$

$$k(C_3H_4) = (2.0 \pm 1.2) \times 10^{10}$$
$$\times \exp((-900 \pm 200)/RT) \text{ L mol}^{-1}\text{ s}^{-1}$$

Discussion

The absolute rate constants, preexponential factors, and activation energies for the $S(^3P)$ + alkyne reactions obtained in the present study along with previously reported data are given in Table IV. For comparisons corresponding data for O, N, CBr, CCl, and CF_3 are also included.

For the acetylene reaction our room temperature rate constant, $(2.3 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}, is in good agreement with Little and Donovan's[20] value of $(3.0 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1} obtained by the same technique. The relative rate parameters

Table IV. Compilation of Rate Parameters for the Addition of Electrophilic Reagents to Alkynes

Substrate	S(^{3}P)			O(^{3}P)			N			CBr($\bar{X}^2\pi$)	CCl($\bar{X}^2\pi$)	CF$_3$($\bar{X}^2\pi$)		
	E	Log A	Log k	E	Log A	Log k	E	Log A	Log k	Log k	Log k	E	Log A	Log k
Acetylene	3.0	10.53	8.34[a]	3.0	10.15	7.96[e]	2.7	7.34	6.0 (440 K)[m]	7.91[q]	8.04[r]	2.8	8.74	7.20 (395 K)[t]
	3.5	10.84	8.29[b]			7.90[f]	2.0	8.82	7.83 (440 K)[n]		7.54[s]			
			8.48[d]			7.86[g]								
Acetylene-d_2			8.34[a]			7.90[f]				7.86[q]	7.62[s]			
Propyne	0.9	10.30	9.64[a]	1.95	10.15	8.73[h]	1.48	7.84	7.10 (435 K)[o]	9.68[q]	9.38[r]	2.2	8.72	7.51 (395 K)[t]
	2.4	10.84	9.09[b]			8.60[i]	1.63	8,80	7.87 (384 K)[p]		9.34[s]			
1-Butyne			9.52[a]	1.6	10.23	9.06[j]	2.24	8.54	7.41 (435 K)[o]	9.79[q]	9.57[s]			
	0.6	9.96	9.52[c]											
2-Butyne			10.20[a]	1.8	10.78	9.47[k]	1.84	8.27	7.35 (435 K)[o]	10.38[q]	10.26[s]	2.1	8.29	7.13 (395 K)[t]
	0.20	10.49	10.34[b]											
	−0.6	9.76	10.20[c]											
2-Pentyne			10.26[a]							10.30[q]	10.40[s]			
	−0.85	9.64	10.26[c]											
2-Butyne-F_6			8.32[a]							7.30[q]				
Dicyanoacetylene				5.5	9.90	5.89[l]								
1-Pentyne							2.08	8.47	7.43 (435 K)[o]	9.56[q]	9.63[s]			
1-Hexyne							2.45	8.66	7.43 (435 K)[o]					
3-Hexyne							2.19	8.53	7.43 (435 K)[o]					
2,2,5,5-Tetramethyl-3-hexyne										9.99[q]	9.90[s]			
Phenylacetylene											9.58[s]	1.1	8.47	7.86 (395 K)[t]

[a] Present work. [b] Reference 5, relative values. [c] Present work, estimated from Figure 4 and measured rate constants. [d] Reference 20. [e] Reference 28. [f] Reference 29. [g] Reference 30. [h] Reference 31. [i] Reference 32. [j] Reference 33. [k] Reference 34. [l] Reference 35. [m] Reference 36. [n] Reference 37. [o] Reference 38. [p] Reference 39. [q] Reference 40. [r] Reference 41. [s] Reference 42. [t] Reference 43.
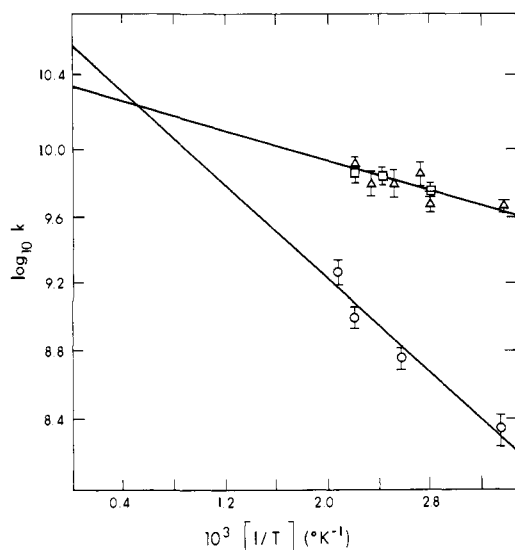

Figure 2. Arrhenius plot showing temperature dependence of the reaction of S(^{3}P) with acetylene and propyne: O, acetylene + S(^{3}P$_2$); △, propyne + S(^{3}P$_2$); □, propyne + S(^{3}P$_1$).

Figure 3. Plots of log k vs. the ionization potentials of the alkynes: O, S(^{3}P); ●, S(^{3}P) (relative measurements); ▲, CCl($\bar{X}^2\pi$); ◊, CBr($\bar{X}^2\pi$).

reported earlier from this laboratory[5] using a competitive chemical technique with conventional product analysis, when normalized to the absolute value of the ethylene reaction,[10] E_a = 1.5 kcal/mol, $A = 1.15 \times 10^{10}$ L mol^{-1} s^{-1}, although somewhat scattered, are still close to the absolute values measured directly, which of course are considered to be more reliable.

It is also seen from Table IV that the species S(^{3}P), O(^{3}P), and N atoms, CBr($\bar{X}^2\pi$), CCl($\bar{X}^2\pi$), and the CF$_3$($\bar{X}^2\pi$) radicals provide the most extensive array of rate data for addition reactions involving alkynes. As in their addition reactions to alkenes the above reagents (with the exception of N atoms) exhibit a distinct electrophilic character in the sense that their reactivity increases with the number of alkyl substituents and decreases with fluoroalkyl substituents attached to the acetylenic carbons. This variation in reactivity appears to be due
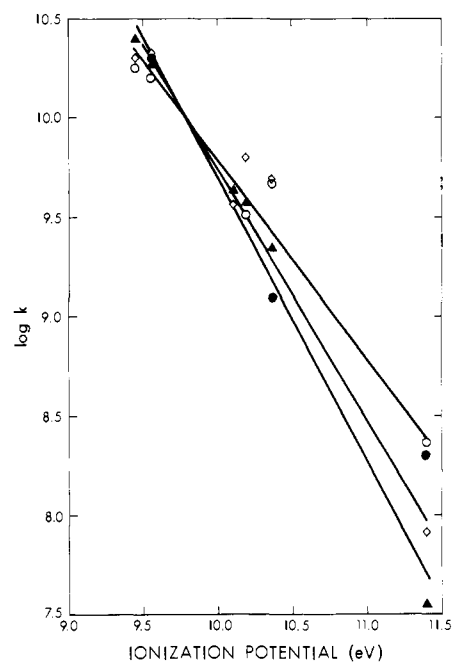
to the change in activation energy and plots of log k vs. the ionization potential of the alkynes for the S, CBr, and CCl reactions give approximate linear relations, Figure 3, as found before for electrophilic additions to alkenes. A strictly linear relationship would only be expected if the preexponential factors were constant within the series, which is not the case (vide infra).

The rate constants seem to be slightly lower and the activation energies slightly higher for the acetylene than the ethylene reaction in the case of the electrophiles S(^{3}P), O(^{3}P), CBr($\bar{X}^2\pi$), CCl($\bar{X}^2\pi$), and CF$_3$($\bar{X}^2\pi$). This may be related to the ionization potential differences of the substrate molecules.[44]

The activation energy of the porpyne reaction is significantly less than that of the acetylene reaction and from the assumed straight line relationship between ionization potential and activation energy, Figure 4, it is possible to estimate the activation energies of the alkylacetylenes for which ionization potential values are available. The activation energies obtained this way, along with the A factors computed from the measured rate constants, are also listed in Table IV. As seen from the results, the 2-alkynes, butyne-2 and pentyne-2, both have negative activation energies as was found before for the addition reaction of $S(^3P)$ atoms with the more reactive olefins, tri- and tetramethylethylene.

It was already pointed out above that $S(^3P)$ atoms do not react with C–H or C–C single bonds, and consequently the measured rate parameters refer to the interaction of $S(^3P)$ atoms with the acetylenic triple bonds. The molecular structure of the primary adduct C_2H_2S cannot be inferred from experiment since none of the C_2H_2S isomeric structures has a stable existence at room temperature. For the S+ acetylene adduct, six isomers can be written, of which **2** and **3**, according to a

1   2   3   4   5   6
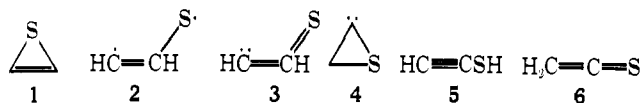
recent ab initio MO study,[16] can be considered as extreme representations of a single resonance hybrid structure since the computed C–C and C–S bonds are intermediate between single and double bond values. If it is assumed that the primary reaction follows a spin-allowed, least motion path, then, according to the results of the above MO computation, the primary reaction product with acetylene is the vibrationally excited ground triplet state thioformylmethylene, lying 31.2 kcal/mol below the $S(^3P)$ + C_2H_2 reactant state.[16] This is analogous to the reaction of $O(^3P)$ atoms with acetylenes[17-19] and the measured rate constants can be attributed to the reaction forming thioketocarbene. Thioformylmethylene and

$$S(^3P) + HC{\equiv}CH \longrightarrow \overset{..}{C}-C\overset{S}{\underset{H}{\diagup\diagdown}} \quad (T_0) \qquad (2)$$
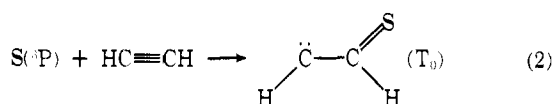
presumably thioketocarbenes in general have a triplet ground state which, with the amount of excess vibrational energy available from the addition, can isomerize to excited triplet thioketene ($\Delta H = +17.6$ kcal/mol, computed) which is collisionally relaxed to the ground state. Excited sulfur $^1D_2$ atoms from the photolysis of COS have been shown to react with acetylenes to yield (apart from solid polymeric materials) carbon disulfide, benzene, and thiophene or their derivatives as retrievable end products.[13-15] $S(^3P)$ atoms can yield the same principal products and energetically, the intervention of several transients are feasible, namely, $CH{\equiv}CSH(S_0)(\Delta H = -37.5$ kcal/mol), $CH_2{=}C{=}S$ $(S_0)(\Delta H = -36.5$ kcal/mol), $\overset{..}{C}HCHS$ $(T_0)(\Delta H = -31.2$ kcal/mol), $\overset{..}{C}HCHS$ (S_1)-$(\Delta H = -22.4$ kcal/mol), $CH_2{=}C{=}S$ $(T_1)(\Delta H = -13.6$ kcal/mol), a $(S_0)(\Delta H = -7.1$ kcal/mol), b $(S_0)(\Delta H = -6.8$

a   b

kcal/mol), and a $(T_1)(\Delta H = +0.9$ kcal/mol). The values quoted were obtained from MO computations[16] as the differences in computed total energies and do not include the activation energy, 3 kcal/mol, of the $S(^3P)$ + C_2H_2 reaction. Consequently they all should be corrected by -3 kcal/mol.

The existence of the thiirene **1** and ethynylthiol **5** structures has been proven by their IR detection in the argon matrix isolated photolysate of 1,2,3-thiadiazoles[45-47] at 8 K and also
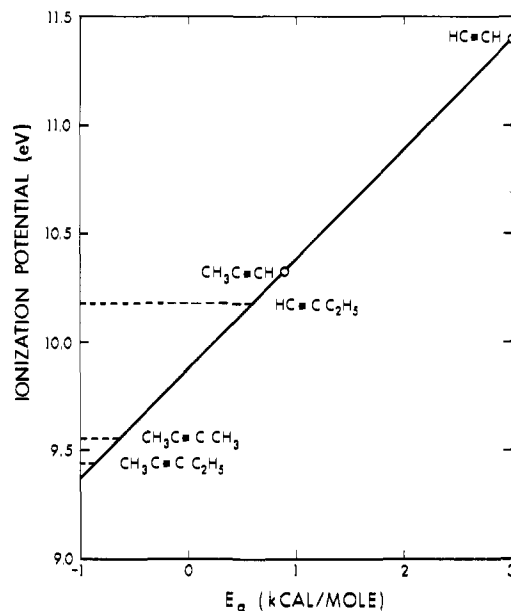
Figure 4. Empirical plot of ionization potential vs. Arrhenius activation energy.

by chemical trapping with perfluoro-2-butyne at room temperature in the gas phase.[47,48]
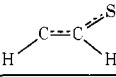
With substituted acetylenes, of course, the number of possible isomeric structures rapidly increases with the complexity of the substituent. With propyne the following formulas can be considered.
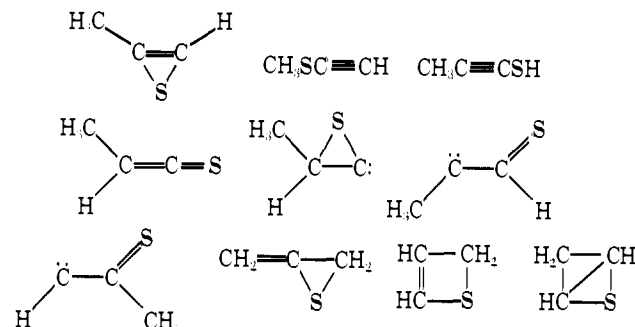
The preexponential factors of the acetylene reactions are markedly higher than for the olefin reactions and partially compensate in the rate constant for the higher activation energies. Szwarc et al.[43] have, in a qualitative fashion, attributed the high preexponential factors to the gain in entropy during passage from a linear reactant molecule to a nonlinear activated complex. The entropy of activation for the $S + C_2H_2$ reaction is -14.3 eu (standard state, 1 mol L^{-1}). The translational and vibrational contributions to the entropy of activation for the $S + C_2H_2$ and $S + C_2H_4$ reactions are virtually the same, but the rotational contribution in the C_2H_2 system is 3.3 times higher than in the C_2H_4 case. Since $A_{C_2H_2}/A_{C_2H_4}$ ~ 3 it can be concluded that the increase in the A factor in the C_2H_2 system is largely a consequence of the increase in the number of rotational modes in the activated complex as compared to the reactant state.

The secondary kinetic isotope effect measured in the S + acetylene reaction, and reported earlier in the literature[29] for the O + acetylene reaction, was small and equal to unity within experimental error. For the S + ethylene reaction the secondary isotope effect, measured k_H/k_D, was inverted and had a value[49] of 0.88. Theoretical analysis[49] within transition state theory shed illuminating light on the reaction path and structure of the transition state, and indicated that the source of the secondary isotope effect is the creation of new, isotopically

Table V. Calculation of Isotope Effect for the S + C_2H_2/C_2D_2 Reaction[a]

Vibrational frequencies, cm^{-1} Acetylene[b]	$\overset{H}{\underset{H}{}}C\!\!=\!\!C\overset{\cdots S}{}$	EXC	ZPE
3373	3100	1.000	1.122
1974	1600	0.998	1.096
3282	3020	1.000	1.109
613	920	1.022	0.884
613	840	1.018	0.912
730	1100	1.028	0.832
730	940	1.021	0.869

[a] MMI × EXC × ZPE = 1.152 × 0.795 = 0.998. [b] Reference 53.

sensitive normal modes in the reaction during passage from the reactant state to the activated complex.

A similar computation was carried out here for the S + acetylene reaction. In terms of absolute rate theory the rate constant is given by the expression

$$k = \chi \frac{kT}{h} \frac{Q^{\ddagger}}{Q} e^{E_a/RT}$$

where χ is the transmission coefficient, Q is the partition function, E_a is the activation energy, and $\ddagger$ signifies the transition state.

Separating the partition function Q into its translational, rotational, and vibrational components, the rate constant ratio for the isotopically substituted molecule realtive to the unsubstituted molecule can be written as derived by Bigeleisen and Wolfsberg:[50]

$$\frac{k_1}{k_2} = \left[\frac{\left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}} \right)^{1/2} \left(\frac{M_2}{M_1} \right)^{3/2}}{\left(\frac{I_{A_2}{}^{\ddagger} I_{B_2}{}^{\ddagger} I_{C_2}{}^{\ddagger}}{I_{A_1}{}^{\ddagger} I_{B_1}{}^{\ddagger} I_{C_1}{}^{\ddagger}} \right)^{1/2} \left(\frac{M_2{}^{\ddagger}}{M_1{}^{\ddagger}} \right)^{3/2}} \right]$$

$$\times \left[\frac{\prod_i^{3N-6} \left[\frac{1 - \exp(-u_{1i})}{1 - \exp(-u_{2i})} \right]}{\prod_i^{3N_{\ddagger}-7} \left[\frac{1 - \exp(-u_{1i}{}^{\ddagger})}{1 - \exp(-u_{2i}{}^{\ddagger})} \right]} \right]$$

$$\times \left[\frac{\exp\left[\sum_i^{3N-6} (u_{1i} - u_{2i})/2 \right]}{\exp\left[\sum_i^{3N_{\ddagger}-7} (u_{1i}{}^{\ddagger} - u_{2i}{}^{\ddagger})/2 \right]} \right]$$

where I is the principal moment of inertia, M is the molecular mass, and $u_i = hc\omega_i/kT$, where ω_i is a normal vibrational frequency. This equation can be rewritten in an abbreviated form as

$$k_1/k_2 = (MMI)(EXC)(ZPE)$$

where MMI represents the translational and rotational energy contributions, EXC the vibrational energy, and ZPE the zero point energy contributions.

The transition state for the S + C_2H_2 reaction is assumed to be a structure close to the geometry of thioformylmethylene.[16]

$$\overset{H}{\underset{H}{}}C\!\!=\!\!C\overset{\cdots S}{}$$
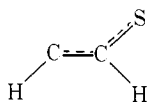
It is interesting to note here that contrary to the present case, the addition of monovalent atoms to acetylene gives the trans isomer of the vinyl radical as in the addition[51] of HBr to C_2H_2, and that the lowest triplet state of acetylene[52] also has a trans geometry.
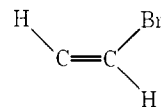
Acetylene has 3 × 4 − 5 = 7, whereas the activated complex has 3 × 5 − 6 = 9 normal vibrational frequencies. The two new frequencies in the activated complex, C–S stretching and C–C–S bending, are not sensitive to deuterium substitution and therefore do not generate isotope effects. The isotope effect is thus probably doe to changes in the acetylene frequencies on going over to the transition state, Assignment of vibrational frequencies in the activated complex can be done by assuming appropriate frequencies in the activated complex on the basis of comparison with acetylene, ethylene, propylene, and ethane by fitting them to the activation entropies derived from the measured preexponential factors. These, together with the computed isotope effect for each vibration, are given in Table V.

The MMI factor in the expression for k_H/k_D is computed to be 1.152 and from the EXC and ZPE contributions k_H/k_D = 0.998, which agrees with the measured value of unity.

The absolute rate parameters of the reactions of $O(^3P)$ atoms with acetylene and propyne are similar to those reported here for $S(^3P)$ atoms. The rate constant for the S + C_2H_2 reaction is about three times higher than for the O + C_2H_2 reaction and the difference appears to be due entirely to the correspondingly higher A factor of the former reaction. For the propyne reaction, the activation energy is higher and the A factor is slightly lower for the O atom than for the S atom. Generally speaking, inasmuch as can be deduced from the scattered data coming from different laboratories and obtained by different measuring techniques, both the acetylene and olefin reactions of O atoms have somewhat lower A factors and slightly higher activation energies than S atom reactions. This is especially true for the less substituted molecules.

The preexponential factors vary with the molecular structure of the alkynes and exhibit a gradually declining trend with increasing substitution and size of substituents. The values decrease from 10.53 (measured) for the acetylene reaction to 9.64 (estimated) for reaction with 2-pentyne, Table IV. This trend is similar to that observed in the reactions of $S(^3P)$ atoms with olefins and seems to point to the increasing steric hindrance exerted by the substituents.

Returning again to the $O(^3P)$ atom reactions, it should be mentioned that the reaction products are CO, alkenes, and unsaturated ketones[17-19] formed in pressure-dependent yields as well as polymer and the results of the O + C_4H_6 reaction were found to be consistent with the mechanism[19] of Scheme I, where * signifies excess vibrational energy.

The intervention of oxirene (c) was definitely ruled out.[17,19]

c

Scheme I
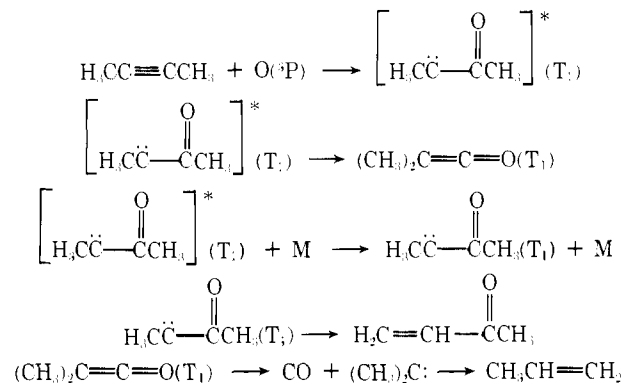
On the other hand, it has been conclusively demonstrated that in the photolytic Wolff rearrangement-decomposition sequence of diazo ketones the ketocarbene-ketene rearrangement involves vibrationally excited singlet ketocarbenes and ground singlet state oxirenes to various degrees. The triplet state of ketocarbenes seems to play no role in these systems.[17,54-58]

In matrix isolation studies of the $O(^3P) + C_2H_2$ reaction the spectrum of ketene has been observed[59] but there were no absorptions which could be assigned to oxirene.

Further studies are in progress.

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Induction and Inhibition of Chemical Oscillations by Iodide Ion in the Belousov-Zhabotinskii Reaction

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Abstract: Initial addition of iodide ion to the oscillatory bromate-cerium-malonic acid system produces a variety of phenomena, depending on the initial iodide concentration. At moderately high and low $[I^-]$, the onset of oscillations is delayed, while very high $[I^-]$ totally suppresses oscillation. In an intermediate range of iodide concentration, oscillations which are qualitatively different from the halide-free oscillations appear with a shorter than normal induction period. These oscillations are later superceded by the ordinary, halide-free oscillations. Our observations may be accounted for by a mechanism involving (a) the direct reduction of Ce(IV) to Ce(III) by iodide, (b) the iodide-catalyzed production of glyoxylic acid, which gives rise to the induced oscillations, and (c) eventual oxidation of iodide to iodate by bromate.

The study of chemical systems which exhibit nonmonotonic[2] and, in particular, oscillatory behavior[3] has grown in the past decade from consideration of a few curious lecture demonstrations to a major area of chemical research. Oscillating reactions have yielded important insights into kinetic[4] and thermodynamic[5] problems, and provide alluring analogues of