

THE REACTION OF S(3³P_J) AND S(3¹D₂) WITH ACETYLENE

D. J. LITTLE and R. J. DONOVAN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ
(Gt. Britain)

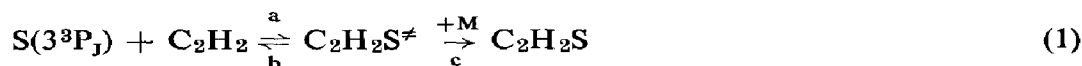
(Received October 20, 1972)

SUMMARY

The absolute rate for the addition of S(3³P_J) to acetylene (at 295K) is determined as $[5.0 \pm 0.5] \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (in the presence of 20 kN m⁻² of argon). The rate of the analogous reaction for S(3¹D₂), relative to the rate for quenching of this state by CO₂ is also determined, $k_{\text{C}_2\text{H}_2}/k_{\text{CO}_2} = 2.5 \pm 0.4$. Both S(3³P_J) and S(3¹D₂) are shown to react less rapidly with triple carbon bonds than with double bonds. The observation of CS radicals in the systems used to study these addition reactions, using flash photolysis, is shown to result from the photoexcitation of acetylene, rather than fragmentation of the addition product.

INTRODUCTION

In continuation of our investigation of reactions involving electronically excited atoms, and their comparison with reactions of ground state atoms, we here present a study of the reactions of S(3³P_J) and S(3¹D₂) with acetylene. The reaction of S(3³P_J) with C₂H₂ has previously been investigated using flash photolysis with kinetic mass spectrometry, and the unstable addition product, C₂H₂S (lifetime ~ 2 sec), observed¹:



In a separate study, Strausz *et al.*² have determined Arrhenius parameters for the addition of S(3³P_J) to a range of unsaturated molecules, relative to those for addition to ethylene, using end-product analysis techniques. In those cases where the primary addition product was unstable, which included the acetylenes studied, relative rate parameters were determined by the suppression in the yield of episulphide formed in the competing reaction. Using the previously reported absolute rate³ for the addition of S(3³P_J) to C₂H₄ at 300K, a value for the absolute rate of

reaction (1a) may be obtained. The present work thus provides an independent check on the rate data of refs. 2 and 3.

The reaction of S(3^1D_2) with acetylene has been investigated using kinetic absorption spectroscopy in the ultra-violet⁴, and the formation of the CS radical, attributed to fragmentation following insertion into the triple bond⁴:



However, the most reliable thermochemical data suggest that fragmentation to yield CS is endothermic¹. The alternative fragmentation process:



also appears to be endothermic¹; however, the uncertainties in the thermochemical data make it difficult to exclude reaction (2d) entirely.

We here re-examine reactions (1) and (2) and present quantitative rate data.

EXPERIMENTAL

The experimental arrangement for flash photolysis with time resolved atomic absorption in the vacuum ultra-violet has been described elsewhere⁵. A 1 m concave grating vacuum monochromator (Hilger and Watts E766) was employed to isolate the 182.04 nm emission line of sulphur. The atomic emission lamp was similar in construction to that previously described⁵, except that sulphur replaced the tellurium; the lamp was powered by a microwave generator (E.M.S. "Microtron 200"). Flash energies of 600 J were found to be adequate and resulted in low levels of photolysis; however, reaction mixtures were discarded after each flash. Care was taken to minimize the time for which reaction mixtures were exposed to the emission from the atomic lamp. A large excess ($>10^3$ fold excess) of inert diluent gas (generally argon) was used for all reaction mixtures, to maintain isothermal conditions, and rate data are reported for 295K.

An entirely separate apparatus was employed for the experiments in which the NS radical was used as a spectroscopic marker. This was of conventional design for flash spectroscopy in the region of 200–600 nm, and has been described previously⁶.

Materials

C_2H_2 : British Oxygen Co (BOC), cylinder grade acetylene was purified by passage through traps at 195K, degassed by repeated trapping at 77K, and fractionally distilled from 77K.

CO₂: BOC "grade X" was used directly from pyrex break-seal flasks.

SF₆: Matheson cylinder grade gas was trapped at 77K and degassed by bulb to bulb distillation.

Ar Matheson "ultra high purity" grade was taken directly from the cylinder.

N₂: BOC "white spot" grade nitrogen was passed through traps at 77K, before use.

N₂O and OCS were prepared as described previously⁶.

RESULTS

Ground state sulphur atoms S(3³P₁) were produced by the flash photolysis of OCS in the presence of a 1.5×10^3 fold excess of argon⁷. ($P_{\text{OCS}} = 13.3 \text{ N m}^{-2}$; $P_{\text{Ar}} = 20 \text{ kN m}^{-2}$). The decay of S(3³P₁) was monitored by observing the attenuation of resonance radiation at 182.04 nm; Signal-to-noise ratios were similar to those shown in Fig. 1 of ref. 7. The first order rate coefficients determined by plotting $\ln \ln I_0/I$ against time are presented in Fig. 1. The second order rate constant determined from Fig. 1 (corrected for the non-linear Beer-Lambert relation), was found to be $k_1 = (5.0 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (295K;

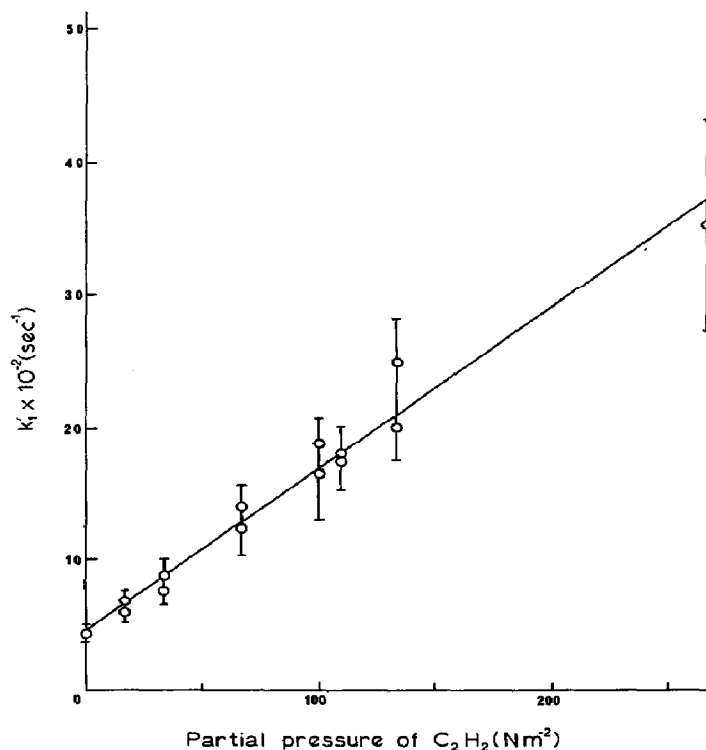


Fig. 1. Plot of first order rate coefficients (k_1') against partial pressure of C₂H₂.

$P_{Ar} = 20 \text{ kN m}^{-2}$; error for two standard deviations). The Beer-Lambert factor (γ) in the relation:

$$\ln \ln (I_0/I) = \text{O.D.} = \epsilon (cl)\gamma$$

was determined by comparing the attenuation of resonance radiation at 182.04 nm when half of the reaction vessel was blanked off, with that observed when the entire vessel was exposed to the flash; γ was determined to be 0.75 ± 0.07 under the present conditions⁸. The rate of reaction (1) was only determined for one value of the total pressure; however, this was chosen to be close to the high pressure limiting rate (the high pressure limiting rate should certainly lie within the experimental uncertainty of the present determination)⁹.

The rate for reaction (2) relative to that for quenching of $S(3^1D_2)$ by CO_2 was determined using the NS radical as a spectroscopic marker⁶. The Stern-Volmer type plots, derived using the marker technique, are shown in Fig. 2, from which the ratio $k_{C_2H_2}/k_{CO_2}$ was determined as 2.5 ± 0.4 .

The CS radical was observed *via* the strong (0,0) band of the $A \leftarrow X$ system, following the flash photolysis of OCS^{10} in the presence of C_2H_2 as reported previously⁴. In these experiments we employed SF_6 as the diluent gas so that no significant quenching of $S(3^1D_2)$ would result; however, when CO_2 was added to the reactant mixture, in ratios up to 20:1 ($CO_2 : C_2H_2$, which would result in $\sim 90\%$ of the $S(3^1D_2)$ being quenched), no reduction in the yield of CS could be detected. Similar results were obtained when a 10^3 fold excess of N_2 over C_2H_2 was used; under these conditions $\sim 99\%$ of the $S(3^1D_2)$ atoms would be quenched to the

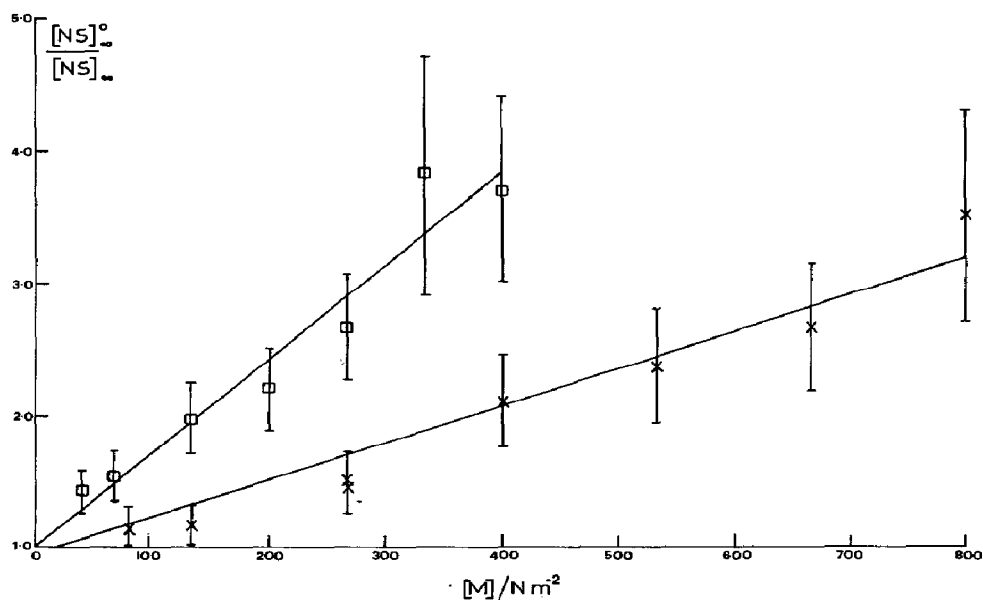


Fig. 2. Plot of $[NS]_{\infty}^0/[NS]_{\infty}$ against pressure of added gas $[M]$. $M = C_2H_2$ (\square), CO_2 (\times).

S(3³P_J) state⁶. Thus only if S(3¹D₂) and S(3³P_J) reacted with C₂H₂ to produce CS, could the previously proposed mechanism⁴ be substantiated. As the production of CS from reaction (1) is strongly endothermic, we conclude that CS is not produced by the direct reaction of sulphur atoms with acetylene.

Furthermore, the addition of excess ethylene to reaction mixtures should result in the removal³ of S(3³P_J); we observed no decrease in the yield of CS when ethylene was added to the reaction mixtures containing acetylene. If ethylene and OCS, in the presence of excess argon, are photolyzed a small yield of CS is observed but this is negligible in comparison with that produced when acetylene is added. The yield of CS in the presence of acetylene was found to vary with flash energy, while doubling the flash energy resulted in a less than two fold increase in [CS] (due account being taken of the Beer-Lambert factor for the 258 nm band¹¹). This could be due to strong absorption by the species giving rise to CS, such that non-uniform light absorption across the reaction vessel occurred. Acetylene is known to be a strong absorber for $\lambda < 200$ nm and we conclude that the most likely source of CS is the reaction of photoexcited acetylene (or a photolysis fragment) with OCS. In view of the complexities of such reactions we have not investigated it further.

DISCUSSION

The reaction of O(2³P_J) with C₂H₂ is of considerable importance in a number of combustion processes and has been the subject of numerous investigations^{12,13}. However, it is only recently that reliable rate data for the primary reaction have been established^{12,13}. The application of sensitive techniques, whereby the atomic reactant is monitored directly (*i.e.*, using spectroscopic techniques), has allowed the rate of the primary reaction to be investigated, without the complications of competing side reactions which arise from the free radicals produced following the fragmentation of the addition product. The addition of O(2³P_J) to C₂H₂ at high pressures ($P > 50$ MN m⁻²) or in an argon matrix¹⁴ (20K) leads to the formation of CH₂CO and not the oxirene, which thus indicates the high kinetic and thermodynamic instability of the initial addition product. In the gas phase the high exothermicity of the reaction leads to extensive fragmentation *via* a number of reaction channels including chemi-ionization¹². The dominant fragmentation process, however, produces CH₂ and CO, and the subsequent reaction of CH₂ with O(2³P_J) yields further amounts of vibrationally excited CO¹². The production of CO with a vibrational population inversion has been suggested as the basis for a "free burning laser"¹⁵.

By comparison reaction (1a) is less exothermic and the only thermochemically favourable fragmentation process, is the reverse reaction (1b). Rearrangement of the initially formed thiirene to yield CH₂CS might be expected¹³ but Strausz *et al.*¹ favour the formation of the thiirene as the major product.

The absolute rate of reaction (1a) was only determined at one total pressure, which was chosen* such that the observed rate should be close to the high pressure limiting rate⁹, and equal to it within the experimental uncertainty. The observation of large quantities of C₂H₂S using kinetic mass spectrometry¹, where lower total pressures were employed, further substantiates this point. Using the previously reported relative Arrhenius parameters² for reaction (1a), together with the absolute rate for the addition of S(3³P_J) to ethylene³, a value for the absolute rate of reaction (1a) at 295K is obtained which is apparently a factor of three less than that determined here. No indication of the error limits for the relative Arrhenius parameters was given in ref. 2, and it is possible that the combined errors in activation energy and pre-exponential factor could account for this discrepancy. We note that the data for the acetylenes studied in ref. 2 were obtained by observing the depression in the yield of episulphide formed in a competing reaction, as the end product with acetylenes was unstable. This may have led to larger errors in the rate data for the acetylenes compared to the other molecules studied.

The rate of reaction (1a) is thus *slower* than that for the addition of S(3³P_J) to ethylene, and thus parallels the slower addition rates observed for O and H atoms with acetylene, relative to their addition to ethylene¹².

By comparing the data given in ref. 6 with those determined here, it can be seen that the rate of reaction of S(3¹D₂) with acetylene is also slower than the rate with ethylene. Thus it would appear to be a general rule, that the rate of atomic reactions with triple carbon bonds are slower than those with double bonds.

The data of ref. 2 and those reviewed in ref. 12, indicate that this is due to the higher activation energies for reactions involving triple bonds.

ACKNOWLEDGEMENTS

We thank Professor C. Kemball and Professor E. A. V. Ebsworth for encouragement and laboratory facilities. We also thank the S.R.C. for an equipment grant and the award of a studentship to D.J.L. The assistance of Miss R. Ramage with some of the preliminary experiments is gratefully acknowledged.

REFERENCES

- 1 O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle and H. E. Gunning, *J. Am. Chem. Soc.*, 89 (1967) 4805.
- 2 O. P. Strausz, W. B. O'Callaghan, E. M. Lown and H. E. Gunning, *J. Am. Chem. Soc.*, 93 (1971) 559.
- 3 R. J. Donovan, D. Husain, R. W. Fair, O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, 66 (1970) 1635.

* Any significant reduction in the total pressure could lead to a rise in temperature following the flash. The more sensitive technique of resonance fluorescence is more suitable for measurements at low pressures, as lower flash energies can be employed.

- 4 W. D. McGrath, T. Morrow and D. N. Dempster, *Chem. Commun.*, (1967) 516.
- 5 D. J. Little and R. J. Donovan, *J. C. S. Faraday Trans. II*, to be published.
- 6 R. J. Donovan, D. J. Little and A. Dalgleish, *Discuss. Faraday Soc.*, 53 (1972) 211.
- 7 D. J. Little and R. J. Donovan, *Chem. Phys. Lett.*, 13 (1972) 488.
- 8 γ was reported as 0.9 ± 0.1 in ref. 7; however, we have since changed the grating for one of lower resolution.
- 9 The high pressure limit for the addition of H to C₂H₂ has been established by K. Hoyermann, H.Gg. Wagner and J. Wolfrum, *Ber. Buns. Phys. Chem.*, 72 (1968) 1004.
- 10 The CS radical is also observed if care is not taken to remove traces of CS₂ impurity which is generally present in cylinder grade OCS. In the present experiments, the production of CS from this impurity was negligibly small.
- 11 I. W. M. Smith, *Trans. Faraday Soc.*, 64 (1968) 378.
- 12 H.Gg. Wagner and J. Wolfrum, *Angew. Chem. Int. Edn.*, 10 (1971) 604, and references therein.
- 13 H. E. Avery and S. J. Heath, *J. C. S. Faraday Trans. I*, 68 (1972) 512, and references therein.
- 14 I. Haller and G. C. Pimentel, *J. Am. Chem. Soc.*, 84 (1962) 2855.
- 15 Y. S. Liu, R. A. McFarlane and G. J. Wolga, *Chem. Phys. Lett.*, 14 (1972) 559.