14 May 1982

OCS FORMATION IN THE REACTION OF OH WITH CS2

B M.R. JONES, J.P. BURROWS, R.A. COX and S.A. PENKETT Environmental and Medical Sciences Division, AERE, Harwell, Oxon OX11 ORA, UK

Received 13 March 1982

A steady-state system involving photolysis of HONO as a source of OH was used to investigate the reaction of OH with CS₂ at 1 atm and 295 K. In the presence of O₂ (>40 Torr) a rapid reaction of OH with CS₂ occurs giving OCS. At lower O₂ concentrations, OCS formation ceases. In air the overall rate constant for OH + CS₂ \rightarrow OCS was (1.7 ± 0.9) × 10⁻¹² cm³ molecule⁻¹ s⁻¹.

1. Introduction

Information on the rate constant and the products of the reaction of OH radicals with carbon disulphide (CS_2) ,

$$OH + CS_2 \rightarrow products,$$
 (1)

is important for an understanding of the fate of CS_2 in the atmosphere. Following the discovery that CS_2 is present in the atmosphere [1] and the recognition that CS_2 oxidation may provide a source of atmospheric OCS [2], a number of investigations of this reaction have been reported.

Direct measurements of k_1 have all used the flash photolysis technique with resonance fluorescence to detect OH. Two earlier studies gave values of k_1 near 300 K of 7 X 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ [3] and (1.9 ± 0.3 X 10⁻¹³ cm³ molecule⁻¹ s⁻¹ [4]. In the latter work it was suggested that reaction (1) proceeded via an addition complex yielding ultimately OCS and HS as products, since the alternative abstraction reaction to give HOS is endothermic by 96 kJ mol⁻¹. A more recent study, in which complications arising from photoexcitation of CS₂ by the flash were minimised by using a CS₂ filter, has indicated that the previous values were far too high. An upper limit of 1.5×10^{-15} cm³ molecule⁻¹ s⁻¹ was obtained at 297 K and it was suggested that reaction of OH with CS₂ photolysis products was the cause of the rapid OH decay rates which were attributed to reaction (1) in earlier work.

Support for only a very slow reaction between OH

and CS₂ to produce OCS comes from the work of Iyer and Rowland [5] who found negligible production of $O^{14}CS$ from $^{14}CS_2$ in the presence of OH generated from H₂O₂ photolysis at 254 nm. On the other hand Cox and Sheppard [6] have reported measurements of the relative rates of decay of CS₂ and C₂H₄ in the presence of OH generated by photolysis of HONO in synthetic air. The experiments were complicated by apparent contributions to decay due to reaction of O(³P) with CS₂ and direct photolysis but after correction for these a value of $k_1 = (4.3 \pm 1.6) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ was obtained. Observation of OCS and SO₂ as products was also reported.

In view of the apparent disagreement between the conclusions from the study under atmospheric conditions and the more recent flash photolysis work, we have conducted a more detailed investigation of reaction (1) using HONO photolysis as a source of OH. The results which are reported here show that reaction of OH with CS₂ occurs quite rapidly in an N₂ + O₂ diluent at 1 atm pressure and that the rate as measured from the formation of OCS product, is strongly dependent on the O₂ mole fraction.

2. Experimental

The reaction of OH with CS_2 was studied by photolysis of mixtures of CS_2 (5.3-6300 ppbv)[‡] and HONO

^{\pm} 1 ppbv = 2.4 × 10¹⁰ molecules cm⁻³ at 1 atm pressure and 298 K.

0 009-2614/82/0000-0000/\$ 02.75 @ 1982 North-Holland

(1-2 ppm) in N₂ or N₂ + O₂ diluent contained in a 200 & bag fabricated from FEP Teflon (Dupont) at 1 atm pressure and ambient temperature (295 ± 3 K). The bag was surrounded by 20 fluorescent "blacklights" (Philips TL 20/08, 310 < λ < 410, λ_{max} = 350 nm) and 6 "sunlamps" (Westinghouse FS40; 280 < λ < 450, λ_{max} = 315 nm). Photolysis of the HONO in the mixture results in a steady-state concentration of OH radicals which at small conversions is governed by the reactions [7]

$$HONO + h\nu \rightarrow OH + NO, \tag{2}$$

$$OH + HONO \rightarrow H_2O + NO_2. \tag{3}$$

Reaction mixtures were prepared by flowing N_2 (high purity) and O_2 (breathing grade) into the bag. Known concentrations of CS_2 were obtained by injection of a measured quantity of CS_2 (BDH Analar Grade) into the diluent prior to its entry to the bag, and HONO was introduced by diverting the diluent over a freshly prepared solution containing NaNO₂ in 10% H₂SO₄. The reactions were followed by gas chromatographic analysis of CS_2 , OCS and SO₂ during photolysis. Gaseous aliquots were withdrawn from the bag at intervals, and after chromatographic separation the sulphur compounds were detected using a sensitive flame photometric detector. Full details of the analytical system and its calibration will be described elsewhere. OCS could be measured more accurately than CS_2 or SO_2 , and rate measurements were based on the build-up of OCS during photolysis. HONO, NO and NO₂ were measured by chemiluminescence with O₃ using a commercial NO_x analyser (TECO model 12A) using previously described techniques [7,8].

3. Results and discussion

Photolysis of mixtures containing HONO and CS₂ led to decay of CS₂ ($\approx 12\%$ in a typical 30 min irradiation) and the appearance of an equivalent amount of OCS and SO₂. Thus the overall stoichiometry for CS₂ oxidation is given by

$$\operatorname{CS}_2 + \frac{3}{2}\operatorname{O}_2 \to \operatorname{OCS} + \operatorname{SO}_2. \tag{4}$$

The formation of OCS and the disappearance of CS₂ during the photolysis of CS₂-HONO mixtures is illustrated in fig. 1. The upper curve shows data obtained with 20% O₂ in the N₂ + O₂ diluent, i.e. as in air. A rapid production of OCS occurs in the first 10 min of



Fig. 1. Formation of OCS and decay of CS₂ during photolysis of CS₂-HONO mixtures in N₂ + O₂ diluent at 1 atm pressure and 295 K. OCS on left-hand ordinate; CS₂ on right-hand ordinate. Initial concentrations of CS₂ and O₂ given in the figure.

Volume 88, number 4

photolysis with an equivalent decay of CS_2 shown by the broken line. After 10 min the rate d [OCS]/dt falls off rather rapidly. This is consistent with the involvement of OH in the oxidation of CS_2 , since the steady state of OH declines as HONO is photolysed and the products NO and NO₂, which react rapidly with OH via the reactions

$$OH + NO + M \rightarrow HONO + M,$$
 (5)

$$OH + NO_2 + M \rightarrow HONO_2 + M$$
 (6)

build up. Since the rate of reaction (1) was normally small compared to reactions (3), (5) and (6), the steady state of OH could be determined approximately from the expression

$$[OH]_{ss} = \frac{k_2 [HONO]}{k_3 [HONO] + k_5 [NO] + k_6 [NO_2]}, \quad (1)$$

where k_5 and k_6 are appropriate for 1 atm pressure. Initially, when [NO] and [NO₂] are small compared with [HONO], [OH]_{ss} is independent of [HONO], with a value of $\approx 8 \times 10^7$ molecule cm⁻³ at full photolytic light intensity, falling to $\approx 2 \times 10^7$ molecule cm⁻³ after 30 min photolysis.

The lower OCS formation curve in fig. 1 shows data obtained with only 0.15 Torr O_2 present. Here d[OCS]/ dt is essentially zero during the first few minutes of photolysis, rising to a steady value at longer reaction times. Since [OH]_{ss} is not expected to be influenced by O_2 it is clear that OH radical initiation of CS₂ oxidation is inhibited at low $[O_2]$. OCS formation at longer reaction times can be satisfactorily accounted for by reaction of CS₂ with ground-state O atoms, produced by photolysis of NO₂ formed in reaction (2):

$$NO_2 + h\nu \to NO + O(^{3}P), \tag{7}$$

$$O(^{3}P) + CS_{\gamma} \rightarrow \text{products} (\text{including OCS}).$$
 (8)

This mechanism for OCS formation is much less important at higher O_2 concentration since the $O(^{3}P)$ steady-state concentration is maintained at a low value by its reaction with O_2 :

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M.$$
 (9)

Experiments conducted with NO2 but no HONO pres-

Table 1

Initial CS2 (ppbv)	О₂ (Топ)	k ^I (10 ^{−5} s ^{−1})	k_1 (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	
 5.7	150	i.4	1.7	
19.9	150	1.5	2.0	
52.2	150	0.86 a)	2.0	
52.5	150	0.62 ^{b)}	1.7	
93.6	150	0.54 b,c)	1.6	
6300	150	1.5	2.0	
52.3	-	< 0.01	< 0.01	
52.5	0.15	< 0.01	< 0.01	
52.3	1.5	< 0.04	< 0.04	
51.8	15	0.08	0.10	
51 6	38	0 28	0.32	
52.2	76	0.45	0.70	
52.4	150	1.2	1.6	
52.3	380	1.7	2.1	

Rate constants for reaction of OH with CS2 based on OCS formation during photolysis of CS2-HONO mixtures

a) Using 3/4 light intensity including shorter-wavelength "sunlamps", all other experiments used "blacklamps" only.

b) Using 1/2 light intensity.

c) Surface/volume ratio increased by a factor of 2.

Volume 88, number 4

ent showed that at 150 Torr O_2 , OCS production from this source could only account for a few percent of the observed OCS formation in the initial stages of reaction.

The effect of variables on the rate of CS_2 oxidation was determined from the pseudo-first-order rate constant, k^1 , calculated from the equation

$$d[OCS]/dt = k^{I}[CS_{2}], \qquad (ii)$$

using the rate of OCS formation during the first few minutes of photolysis. The values of k^{1} are presented in table 1. The first set of k^{I} values were all obtained using 150 Torr of oxygen in the diluent. It will be seen that k^1 was independent of [CS₂] over the range 5.7-6300 ppbv, i.e. the reaction was first order with respect to CS_2 . k^{I} was independent of surface/volume ratio, directly proportional to light intensity and unaffected by the presence of shorter-wavelength radiation from the sunlamps, which increased the rate of photoabsorption by CS₂ by a factor of 4. Any possibility of reaction of CS^{*}, formed by excitation in the near UV band of CS₂, with OH can be discounted since k^{I} would have a second-power dependence on light intensity and should be greatly enhanced by sunlamp radiation. Reaction of CS, possibly produced by reaction of CS_2^* with O_2 , with OH can be discounted on the same basis.

The second set of k^{I} values in table 1 was obtained at constant [CS₂] but with varying [O₂]. k^{I} shows a steady increase with [O₂] above 8 Torr, but at lower [O₂] the rate was too small to be measured precisely.

The final column in table 1 shows the rate coefficient k_1 determined from k^1 and the initial [OH]_{ss} calculated from eq. (i) for each set of experimental conditions. The average value for the experiments with 150 Torr O₂ was 1.7×10^{-12} cm³ molecule⁻¹ s⁻¹ with an uncertainty of ±50% arising from the experimental error in rate determination and the uncertainty in the calculated value of [OH]_{ss}.

4. Discussion

The above results show clearly that the reaction of OH with CS₂ occurs relatively rapidly at 1 atm pressure provided sufficient O₂ is present. A possible mechanism which would explain this behaviour involves reaction of O₂ with a short-lived species formed by the addition of OH to CS₂:

OH + CS₂ (+ M)
$$\stackrel{k_a}{\neq}$$
 CS₂OH (+ M),

$$CS_2OH + O_2 \xrightarrow{\kappa_c} \text{products (including OCS).}$$

Simple competition between decomposition of the adduct, $k_{\rm h}$, and reaction with O_2 , k_c , should give a linear functional plot of $1/k_1$ versus $1/[O_2]$. The data from table 1 when analysed in this fashion exhibited curvature which indicates a more complex role of O2. Consequently, the lifetume of CS2OH could not be determined from a simple analysis. In the recent flash photolysis studies of reaction (1) at room temperature, with no O_2 present [9], no evidence for a rapid addition reaction between OH and CS2 could be observed on the millisecond time scale, even at the highest pressures employed. This would require a lifetime of $< 10^{-6}$ s for CS₂OH, i.e. $k_b \ge 10^6 \text{ s}^{-1}$. Since O₂ partial pressures of the order of 100 Torr ($\approx 3 \times 10^{18}$ molecules cm^{-3}) are required for effective competition between k_b and $k_c[O_2]$ to produce OCS, k_c needs to be of the order of 10^{-12} cm³ molecule⁻¹ s⁻¹. This is not an unreasonable value for the reaction of O_2 with a radical if reaction occurs by addition (cf. $k[CH_3 + O_2] \approx 2$ \times 10⁻¹² cm³ molecule⁻¹ s⁻¹ at 1 atm) or abstraction of a weakly bound H atom (cf. $k[HCO + O_2] = 5 X$ 10^{-12} cm³ molecule⁻¹ s⁻¹). Since the structure of the proposed CS₂OH intermediate is not defined, its possible reaction with O_2 cannot be specified. Nevertheless it can be concluded that the present results can be reconciled with the absence of any observable rapid reaction between CS₂ and OH in other experimental studies, if a mechanism involving reaction of O2 with a relatively short-lived CS₂OH adduct is operative. Further studies including investigation of the effect of temperature and total pressure on the CS₂ + OH reaction in the presence of O_2 are required to substantiate the proposed mechanism. The results of the present study show that oxidation of CS2 via reaction with OH radicals can provide a significant source of OCS in the atmosphere.

Acknowledgement

This work was supported by the UK Department of the Environment.

Volume 88, number 4

References

- [1] F.J. Sandalls and S.A. Penkett, Atm. Environ. 11 (1977) 197.
- [2] N.D. Sze and M.K.W. Ko, Nature 278 (1979) 731.
- [3] R. Atkinson, R.A. Perry and J.N. Pitts Jr., Chem. Phys. Letters 54 (1978) 14.
- [4] M.J. Kurylo, Chem. Phys. Letters 58 (1978) 238.
- [5] R. Subramonia Iyer and F.S. Rowland, Geophys. Res. Letters 7 (1980) 797.
- [6] R.A. Cox and D.W. Sheppard, Nature 284 (1980) 330.
- [7] R.A. Cox, J. Photochem. 3 (1974/5) 175.
- [8] D.H.F. Atkins and R.A. Cox, AERE Report R7615, HMSO (1973).
- [9] P.H. Wine, R.C. Shah and A.R. Ravishankara, J. Phys. Chem. 84 (1980) 2499.