The Reactions of $S(^1D)$ Atoms with Cyanogen and Acetylene

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THE reactions of ground state and excited-singlet state oxygen atoms with cyanogen have previously been reported.[1] The work described here was undertaken in order to investigate further the differences in reaction mechanisms between ground-state and excited-state atomic species. Suitable reactions for such studies, similar in many important respects to the previously studied atomic oxygen–cyanogen work, are those of atomic sulphur. Here again it is possible to produce either ground-state (^3P) or excited (^1D) atoms, by using carbon disulphide or carbonyl sulphide respectively as atomic sulphur sources.[2-4]

The apparatus and experimental technique have already been described.[1] As in the previous work on oxygen–cyanogen mixtures the conventional flash tube and reaction vessel assembly was used to study systems in which it was not desirable to dissociate the cyanogen directly in the photolytic flash and the concentric Spectrosil arrangement was used only when dissociation of the cyanogen was required.

Spectra obtained during the isothermal flash-photolysis of a carbonyl sulphide–cyanogen mixture (ratio 1 : 1) using the conventional flash tube showed the presence of the transient species S_2 and NCS in the reaction mixture. The observed NCS bands are listed in the Table. These same bands have also been observed by Holland *et al.*[5] The NCS absorption was observed to reach its maximum intensity at the shortest delay time used (15 μsec.) and then decay to zero after 2·5 msec. whereas the S_2 concentration did not build up appreciably until after 50 μsec., reached maximum intensity after about 2·5 msec., and then slowly decayed at the longer delay times. In all experiments the cyanogen–inert gas ratios were generally within the range 1 : 10 to 1 : 50.

TABLE

Band heads of the NCS *absorption spectrum observed during the flash photolysis of* C_2N_2–COS *mixtures. All the bands listed below were diffuse and degraded to the red*

Wavelength (in air) Å (±0·2 Å)	Relative intensity (visual estimate)
3860·5	5
3853·0	7
3828·8	5
3819·8	10
3730·6	3
3712·5	10
3702·5	5
3611·5	4
3558·9	5
3465·1	8

In contrast to these results, experiments on the isothermal flash photolysis of a carbon disulphide–cyanogen mixture (ratio 1 : 1), using the conventional flash tube, showed no indication of NCS absorption, the only transient species observed in this case being CS and S_2 both appearing strongly even at the shortest delay time.

The ultraviolet absorption spectrum of carbonyl sulphide consists of a region of continuous absorption from 2550 to 1600 Å,[6,7] and it has been shown[3,4] that photolysis by light in the wavelength range 2500—2290 Å results directly in the formation of a sulphur atom in the ${}^1D$-state according to reaction (1).

$$\mathrm{COS} \xrightarrow{h\nu} \mathrm{CO} + \mathrm{S}({}^1D) \tag{1}$$

When carbonyl sulphide–cyanogen mixtures are flash-photolysed in a conventional reaction vessel the only primary process operative is the photolytic dissociation of the COS according to reaction (1). The $S({}^1D)$ produced can then react with the cyanogen present according to equation (2) to give the observed NCS

$$\mathrm{S}({}^1D) + \mathrm{N{\equiv}C{-}C{\equiv}N} \rightarrow \mathrm{NCS} + \mathrm{CN}. \tag{2}$$

Reaction (2) is analogous to the reaction of $O({}^1D)$ with cyanogen resulting in the formation of the NCO radical.[1] However, in contrast to the oxygen analogue, no CN absorption was observed when 1 : 1 or 1 : 5 carbonyl sulphide–cyanogen mixtures were flashed in either the concentric Spectrosil or conventional reaction vessels. This indicates that CN radicals are removed rapidly from the reaction mixture since a relatively large concentration of these radicals is produced from cyanogen by the photolytic flash when the Spectrosil concentric set-up is used. The most probable reaction for this rapid removal of CN would be

$$\mathrm{CN} + \mathrm{COS} \rightarrow \mathrm{NCS} + \mathrm{CO} \tag{3}$$

and by analogy with the cyanogen–oxygen work already reported,[1] NCS and CN might be expected to react as follows:

$$\mathrm{NCS} + \mathrm{CN} \rightarrow \mathrm{NCN} + \mathrm{CS}. \tag{4}$$

Reaction (4) would not be as favoured as the oxygen analogue due to the lower dissociation energy of CS [D(CS) = 166 kcal./mole] compared with that of CO [D(CO) = 256 kcal./mole]. The fact that no NCN absorption was observed with carbonyl sulphide–cyanogen mixtures may be due either to the small rate constant of reaction (4) or the predominance of reaction (3) resulting in the rapid removal of the CN radicals produced in (2). No evidence was found for the production of NCO by the direct reaction between CN and COS according to (5),

$$\mathrm{CN} + \mathrm{COS} \rightarrow \mathrm{NCO} + \mathrm{CS} \tag{5}$$

since no NCO or CS absorption was observed in any of these experiments. In any case, reaction (5) would not be as favoured on thermal grounds as reaction (3) since D(S–CO) = 76 kcal./mole whereas D(SC–O) = 148 kcal./mole.

The absorption of light by carbon disulphide in the region 3600—2800 Å gives rise to the transition ${}^3A_2 \leftarrow {}^1\Sigma_g^+$ and is known to produce electronically excited CS_2 molecules.[2] The second absorption system of CS_2, occurring at wavelengths below 2200 Å, is probably due to the transition ${}^1B_2 \leftarrow {}^1\Sigma_g^+$. Photodissociation in this spectral region produces ground-state sulphur atoms directly, according to (6).[3,8]

$$\mathrm{CS_2}({}^1\Sigma_g^+) \rightarrow \mathrm{CS}({}^1\Sigma) + \mathrm{S}({}^3P) \tag{6}$$

When carbon disulphide–cyanogen mixtures were flash-photolysed using a conventional reaction vessel the only effect of the photolytic flash would be the photolysis of the carbon disulphide according to reaction (6) and the most important experimental fact is that no NCS absorption was ever observed during these experiments. It must therefore be concluded that $S({}^3P)$, like $O({}^3P)$, does not react with cyanogen to any appreciable extent under the isothermal conditions used here.

From these experiments it can be seen that $S({}^1D)$ behaves in the same fashion as its oxygen counterpart $O({}^1D)$, in preferentially undergoing an insertion-type reaction with cyanogen, according to (7),

$$\mathrm{S}({}^1D) + \mathrm{N{\equiv}C{-}C{\equiv}N} \rightarrow \mathrm{N{\equiv}C{-}S{-}C{\equiv}N} \rightarrow \mathrm{NCS} + \mathrm{CN} \tag{7}$$

followed by break-up of the insertion complex to NCS and CN. The ground-state sulphur atom does not seem able to react in this way, to give an insertion intermediate, probably because of a combination of energetic and spin considerations.

A similar series of experiments to those described above was carried out using acetylene as the substrate instead of cyanogen. The experimental conditions were identical to those used in the cyanogen work, isothermal conditions being maintained by use of inert gas. The acetylene was not affected directly by the flash. At the shortest delay time used, very strong CS absorption was detected in the COS–C_2H_2 experiments, together with weak S_2 bands. The CS had reached its maximum strength at 7·5 μsec. and decayed very slowly over a period of several msec.

The possibility that the CS could have come from CS_2 impurity in the carbonyl sulphide was checked by flashing a sample of the COS itself. No CS could be detected in these experiments showing that the sample had no appreciable CS_2 content. In any case the strength of the observed CS bands in the experiments with acetylene was such that a very high impurity content would have been necessary to account for them.

The interesting result obtained here can be explained if $S(^1D)$ reacts in a similar way with acetylene as it does with cyanogen, *i.e.*, by insertion according to (8)

$$S(^1D) + H\text{–}C{\equiv}C\text{–}H \rightarrow HCS + CH \qquad (8)$$

followed by break-up of the HCS radical

$$HCS \rightarrow H + CS \qquad (9)$$

It was not possible to detect any absorption due to CH in these experiments, but this would have been difficult under the conditions used.

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