

Short Communication

Reaction of $\text{CN}(\text{X}^2\Sigma^+)$ with OCS and formation of SCN

MICHAEL C. ADDISON, ALAN J. LEITCH, CONSTANTINE FOTAKIS and ROBERT J. DONOVAN

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

(Received June 13, 1978)

The reaction between $\text{CN}(\text{X}^2\Sigma^+)$ and OCS has been investigated using both time-resolved spectrophotometry and flash spectroscopy. The reaction is shown to be fast ($k \geq 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and to lead to the formation of SCN.

1. Introduction

Reactions involving CN radicals are of considerable importance in combustion and flame chemistry. However, by comparison with radicals such as OH, relatively little systematic effort has been made to study either their chemistry or their kinetics under controlled laboratory conditions. The most recent studies are those by Schacke *et al.* [1], Bullock and Cooper [2] and Boden and Thrush [3].

We report here direct observations on the reaction between CN and OCS which is shown to yield the SCN radical.

2. Experimental

Two independent pieces of equipment were employed for this work. Firstly a conventional apparatus for flash photolysis with flash spectroscopy in the visible and ultraviolet regions ($\lambda > 200 \text{ nm}$) was used to study the formation of SCN; this equipment has been described elsewhere [4]. Secondly an apparatus for time-resolved spectrophotometry of CN radicals was employed to make detailed kinetic studies [5]; only a brief description will be given here. $\text{CN}(\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+)$ emission was excited using a microwave discharge through a flowing mixture of 1% CH_4 in N_2 ($P = 266 \text{ N m}^{-2}$), in a manner similar to that described by Boden and Thrush [3]. This emission was focused through the reaction vessel ($l = 40 \text{ cm}$), which was surrounded by a coaxial flash lamp, and onto the entrance slit of a monochromator (Hilger Monospek 1000). The variation in light intensity as a function of time at the exit slit of the monochromator ($\lambda = 388 \text{ nm}$) was monitored with an EMI 9781B photomultiplier.

The latter was wired so that only the first six dynodes were utilized, the seventh and subsequent dynodes acting as the anode; this allowed high incident light levels to be used and thus optimized the signal to noise ratio. The output from the photomultiplier was fed to a fast analogue to digital converter with an integral memory (Datalab DL905) and then (optionally) to a signal averager (Datalab DL4000). Data could be inspected on a visual display and transferred to an *XY* plotter for analysis. A typical single shot recording of the CN radical formation and decay is shown in Fig. 1. Flash energies of 125 J were found to be adequate for the present studies.

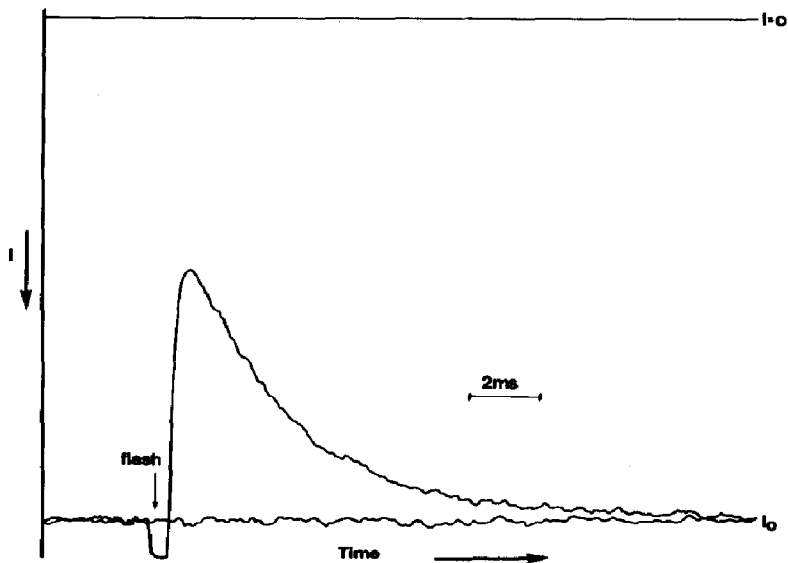


Fig. 1. Formation and decay of CN ($X^2\Sigma^+$) following the photolysis of $(CN)_2$: $P_{(CN)_2} = 23.7 \text{ N m}^{-2}$, $P_{N_2} = 1.24 \text{ kN m}^{-2}$; $\lambda = 388 \text{ nm}$; flash energy = 125 J.

Boden and Thrush [3] have discussed the problems associated with using an emission source for which the rotational temperature does not match that of the absorbing species. In the present work we adopted an empirical approach and determined a curve of growth for the CN radical under our experimental conditions. The reaction vessel was divided into sections of known length so that the path length of the absorbing layer could be changed in a systematic manner. Our results show that absorption by CN can be treated in terms of a modified Beer-Lambert expression, $OD = \ln(I_0/I) = \alpha(c l)^\gamma$, where γ was found to equal 0.6.

3. Results and discussion

An intense spectrum of the SCN radical [6] was observed in absorption ($\lambda = 346 - 382 \text{ nm}$) when either $(CN)_2$ or ClCN was photolysed in the presence of OCS; typical conditions were $P_{(CN)_2} = 1.3 \text{ kN m}^{-2}$, $P_{OCS} = 0.23 \text{ kN m}^{-2}$ and a flash energy of 10^3 J . The decay of SCN was rapid ($\tau \approx 50 \mu\text{s}$) and led to the prompt formation of S_2 . Possible reactions which could

lead to SCN formation in this system are CN reacting with OCS or $S(^1D)$ reacting with $(CN)_2$. The latter was ruled out by repeating the experiments in the presence of a large excess of N_2 which is known to quench $S(^1D)$ efficiently [7]; no significant change in the SCN yield was observed in the presence of excess N_2 . Reaction of $S(^3P)$ with $(CN)_2$ is very unlikely on thermochemical grounds, however. We also eliminated this possibility by adding various pressures of C_2H_6 to the system. It was found that addition of C_2H_6 gave a marked reduction in the yield of SCN. This would be expected if CN is the precursor of SCN, as CN is known to react rapidly with C_2H_6 ($k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [2]. Removal of $S(^3P)$ by C_2H_6 would be negligible and it cannot therefore be the precursor of SCN.

By using the SCN spectrum as a "spectroscopic marker" [7], a rate constant for CN + OCS relative to that for CN + C_2H_6 was obtained as $k_{OCS} \approx 4k_{C_2H_6}$. This agrees with the lower limit for k_{OCS} (presented later) when compared with the known value [2] for $k_{C_2H_6}$.

Detailed kinetic studies of CN using time-resolved spectrophotometry proved to be more difficult than expected with OCS. From Fig. 1 it can be seen that the time scale for removal of CN in a $(CN)_2 + N_2$ mixture is relatively long and thus the "dead time" associated with the firing of the flash lamp is of little consequence under these conditions. Addition of a reagent which removes CN increases the rate of decay and a rate coefficient at a given partial pressure of reagent can be obtained, provided pseudo first order kinetics are maintained. For pseudo first order decay kinetics the reagent should be in a tenfold (or greater) excess over the CN radical concentration. We have estimated the $[CN]$ produced in our system as about $8 \times 10^{12} \text{ cm}^{-3}$; this necessitates reagent concentrations of not less than 10^{14} cm^{-3} . However, for fast reactions the amount of reagent which can be added is limited by the dead time of the detector.

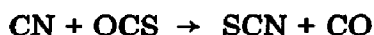
The use of this technique is therefore constrained by the dead time of the detector, on the one hand, and by the need to maintain pseudo first order kinetics on the other. It is well suited to measuring rate constants in the range $1 \times 10^{-11} - 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reaction of CN with OCS is one of the fastest reactions that we have attempted to study and thus only a limited range of OCS partial pressures could be used. The signal to noise ratio is lower and hence the kinetic data are subject to larger uncertainties when such fast reactions are studied. To help alleviate this problem signal averaging was employed. The first order rate coefficients determined for various pressures of OCS are presented in Table 1: the second order rate constant derived from these data and corrected for γ was found to be $(3.8 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The stated error is for 2σ but is based only on an analysis of random errors in the rate measurements; it does not allow for systematic errors associated with departure from pseudo first order kinetics. In view of the limitations discussed above we prefer to quote a lower limit for the rate constant as $k_{OCS} > 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The reaction of CN with OCS has thus been shown to be rapid, leading to the formation of SCN:

TABLE 1

Rate data for the removal of CN by OCS (295 K)

P_{OCS} (N m^{-2})	First order rate coefficient (s^{-1})
0	660 ± 120
6.7×10^{-2}	1070 ± 260
0.133	1350 ± 360



A lower limit for the C-S bond strength in SCN can be derived as not less than $306.4 \text{ kJ mol}^{-1}$, based on the known bond energy [8] of OCS.

Acknowledgments

We are indebted to Professor C. Kemball for his encouragement and laboratory facilities and to the S.R.C. for equipment grants and support for M.C.A. and A. J. L. We also thank Dr. C. Morley for helpful discussions and Shell Research Limited for partial support of A.J.L. under the S.R.C./C.A.S.E. scheme.

- 1 H. Schacke, H. Gg. Wagner and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, 81 (1977) 670.
- 2 G. E. Bullock and R. Cooper, *J. Chem. Soc. Faraday Trans. 1*, 68 (1972) 2185.
- 3 J. C. Boden and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, 305 (1968) 107.
- 4 H. M. Gillespie and R. J. Donovan, *Chem. Phys. Lett.*, 37 (1976) 468.
- 5 A. J. Leitch, Ph.D. Thesis, University of Edinburgh, to be published (1978).
- 6 R. Holland, D. W. G. Style, R. N. Dixon and D. A. Ramsay, *Nature (London)*, 182 (1958) 336.
- 7 D. J. Little, A. Dalglish and R. J. Donovan, *Faraday Discuss. Chem. Soc.*, 53 (1972) 211.
- 8 S. W. Benson, *Chem. Rev.*, 78 (1978) 23.