

THE PHOTODISSOCIATION OF HNCS IN THE NEAR ULTRA-VIOLET

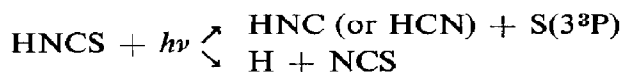
C. R. BOXALL* and J. P. SIMONS

Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT
(Gt. Britain)

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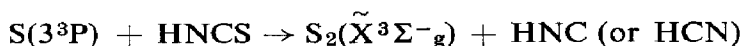
SUMMARY

The flash photolysis of HNCS has been studied in the vapour phase at wavelengths ≥ 190 nm. The principal primary products include S(3^3P), HNC or HCN, H, and NCS. NH and CS are not formed and S(3^1D) atoms are formed in low yield only. Thus the principal primary processes in the near u. v. are:



The photodissociation is compared with that of the isovalent molecules OCS and HNCO where the production of S(3^1D), or dissociation at the N–C bond are major primary processes and the reasons for the differences are discussed.

The reaction:



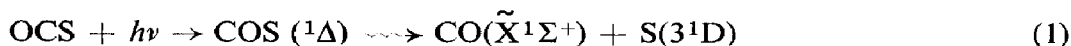
is very efficient with a rate coefficient $\geq 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

INTRODUCTION

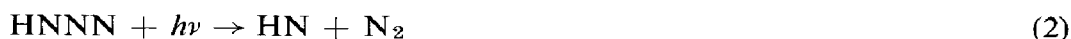
The spectroscopy and photochemistry of the isovalent series of molecules CO_2 , N_2O , HNCO, HN_3 , COS and CS_2 has attracted much interest¹. Correct assignment of their low-lying intravalency shell electronic transitions has been difficult because most of their associated absorption spectra are heavily predissociated but recently Rabalais *et al.*² have combined theory and observation to produce a self-consistent pattern which assigns all the known absorption bands to transitions involving $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ excitation. Detailed photochemical studies

* Present address: West Midlands Gas Board, Wharf Lane, Solihull, Warwicks. (Gt. Britain).

have been directed towards determination of the electronic states of the primary photoproducts and where possible, the energy distribution among them. Apart from CS₂ and possibly HNCO, the net spin appears to be conserved during the primary photochemical process. Excitation into the ¹Δ electronic state in N₂O^{1(d)} or CO₂^{1(e)} leads to formation of O(²D) atoms with near unit quantum efficiency and in COS the corresponding transition leads preferentially to the predissociation^{1(h),1(i)}



Flash photolysis of HN₃ and HNCO through quartz excites the molecules into the ¹A'' and ¹A' components of the ¹Δ state. The main primary process appears to be dissociation at the HN–NN or HN–CO bond^{1(l), 1(g)}:



but the initial spin state of the NH radical is uncertain. The absorbed energy is more than sufficient to excite the NH into the $\tilde{a}^1\Delta$ state but the singlet absorption has been detected only in HN₃³. However, HN ($\tilde{a}^1\Delta$) radicals are likely to be very reactive with respect to H atom abstraction from the parent molecule and might be very difficult to detect. The alternative primary process



is unimportant in HN₃ but may contribute in HNCO.

Flash photolysis of COS in the vacuum u.v. produces S(³S) atoms^{1(j)}, at wavelengths ~150 nm, probably *via* predissociation of the ¹Σ⁺ electronic state but predissociation *via* the same electronic state in CS₂ produces S(³P) atoms exclusively^{1(k)} despite the absorbed energy being sufficient to form S(³D) atoms and so conserve spin. Photodissociation within the singlet manifold must be too slow to compete against intersystem crossing into a triplet continuum:



The flash photolysis of HNCS has not been reported although the molecule has two diffuse absorption bands accessible in the quartz u.v. (λ_{max} at 240 nm and 197 nm), which have been assigned to the electronic transitions ¹A'' (¹Σ⁻) ← $\tilde{X}^1\text{A}'$ (mainly $\pi_{\text{N}} \rightarrow \pi^*_{\text{NCS}}$) and ¹A'' (¹Δ) ← $\tilde{X}^1\text{A}'$ (mainly $\pi_{\text{N,S}} \rightarrow \sigma^*_{\text{C-S}}$). By analogy with COS, predissociation at the C–S bond might have been expected to lead principally to HNC (or HCN) and S(³D). In fact the S atoms are produced almost entirely in the triplet ground state. This, and alternative primary processes in HNCS and related molecules is discussed in the present paper and a “rationale” for the observed behaviour is developed.

EXPERIMENTAL

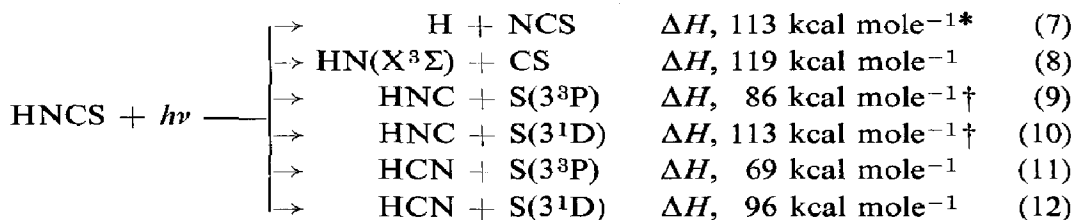
The flash photolysis apparatus was of a similar design to that described earlier⁴. Spectra were photographed on a quartz, Littrow spectrograph (Hilger, E742) using Ilford HP3 or Q2 plates.

HNCS was prepared under vacuum by dropping phosphoric acid on to solid KCNS and the gas was used directly. Preflushing of the reaction vessel and connecting tubing with the first gas samples prevented contamination by SO₂. The purity of the vapour was established by u.v. and i.r. absorption spectroscopy. He and Ar (Matheson) and N₂, H₂ and O₂ (British Oxygen) were dried by passage through refrigerated traps.

RESULTS AND DISCUSSION

Flash photolysis of HNCS under isothermal conditions in a large excess of Ar or N₂ at wavelengths \gtrsim 190 nm produced the following transient species detectable in absorption during or immediately after the flash, S₂($\tilde{X}^3\Sigma_g$), S₃, NCS; SH and S₂($\tilde{a}^1\Delta_g$) were present in very low concentrations only. In samples of HNCS contaminated with SO₂ transient spectra associated with CS, NS and SO could also be photographed. No features attributable to NH were detected under any conditions.

Primary processes that are energetically feasible at wavelengths \sim 190 nm (\equiv 150 kcal mole⁻¹) include:



Process (8) can be excluded immediately since CS and NH were not produced from pure samples of HNCS. The detection of S₂ and S₃ indicates the primary production of S atoms and this was confirmed by flashing HNCS in an atmosphere of O₂. The production of S₂ and SH was completely suppressed, SO and SO₂ being produced in their place (see Fig. 1): however, production of NCS was not significantly reduced (see Fig. 2). It follows that the secondary reaction:



is important but the alternative

* Assuming $D_{(\text{H}-\text{NCS})} = D_{(\text{H}-\text{NCO})}$.

† Assuming $\Delta H_f(\text{HNC}) - \Delta H_f(\text{HCN}) = \Delta H_f(\text{CH}_3\text{NC}) - \Delta H_f(\text{CH}_3\text{CN}) = 17 \text{ kcal mole}^{-1}$.

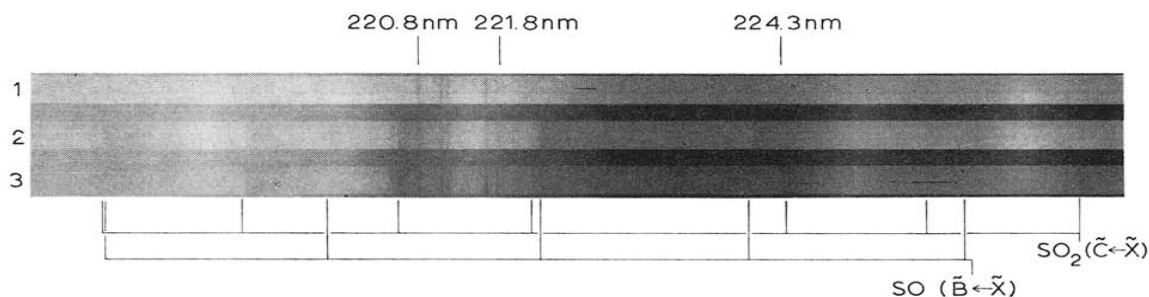


Fig. 1. Flash photolysis of an HNCS/O₂ mixture. 1, 2 and 3: before, during (32 μ sec delay) and after flash. $P_{\text{HNCS}} = 0.25$ Torr; $P_{\text{O}_2} = 300$ Torr; flash energy = 2 kJ.

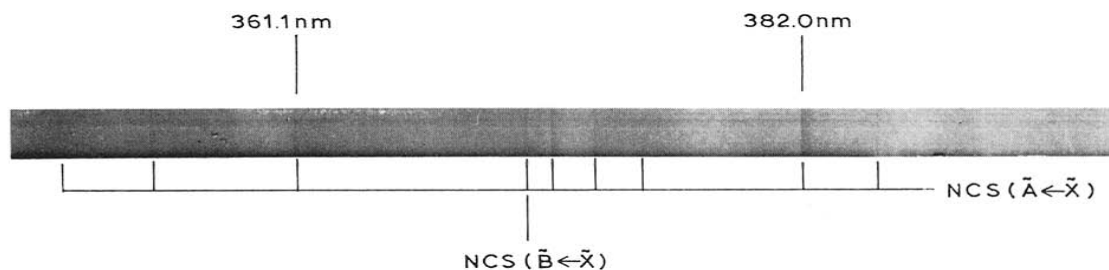


Fig. 2. Flash photolysis of HNCS/O₂ mixture: delay 32 μ sec. $P_{\text{HNCS}} = 14$ Torr; $P_{\text{O}_2} = 600$ Torr; flash energy = 2 kJ.



which is endothermic by 30 kcal mole⁻¹ for S(3³P) atoms, is not. Almost all the NCS observed must have been produced in the primary step (7).

Since most of the S₂ was detected in the triplet ground state it appeared likely that S(3³P) atoms were involved in reaction (13), though the diluent gases, Ar or N₂, might either deactivate some of the S atoms initially produced in the 3¹D state, before their collision with undissociated HNCS and/or promote collisional relaxation of S₂ (a¹Δ_g) molecules. However, substitution of He which is a most inefficient quencher⁵ for S(3¹D) produced no observable change in the spectral intensities or the rates of appearance of either triplet S₂ or SH (see Fig. 3). That S atoms were in fact, produced very largely in the 3³P ground state was confirmed by flashing HNCS in an atmosphere of H₂, with which S(3¹D) atoms react very efficiently⁵: reaction with S(3³P) is endothermic by 22 kcal mole⁻¹. If singlet S atoms were important primary products the presence of a large excess of H₂ should suppress the transient absorption of S₂ at short delay times and enhance that of SH. In practice that of SH was only slightly enhanced and there was no discernible reduction in the intensity of the triplet S₂ band system (see Fig. 4). The primary process(es) (10) or (12) can only make a minor contribution, with almost all of the S atoms being produced in the spin forbidden steps (9) and/or (11). (HNC is expected to have a singlet ground state.)

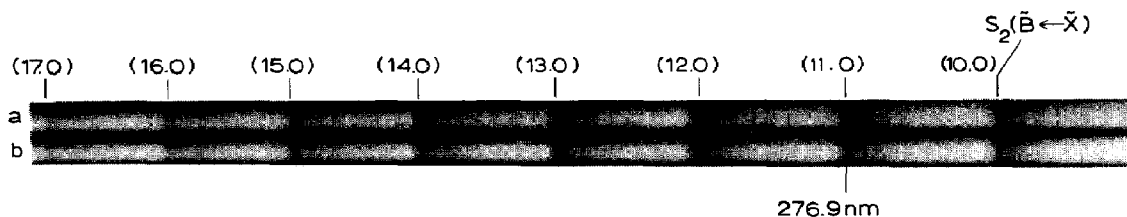


Fig. 3. Flash photolysis of HNCS in He and Ar: delay 32 μ sec. (a) $P_{\text{HNCS}} = 2$ Torr; $P_{\text{He}} = 50$ Torr. (b) $P_{\text{Ar}} = 50$ Torr; flash energy = 0.9 kJ.

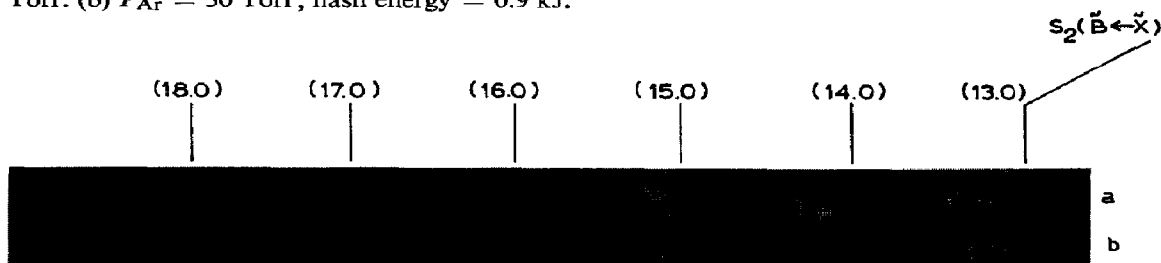


Fig. 4. Flash photolysis of HNCS in Ar and H_2 : delay 32 μ sec. (a) $P_{\text{H}_2} = 360$ Torr; (b) $P_{\text{Ar}} = 330$ Torr; flash energy = 2 kJ.

There was no measurable delay in the appearance of the absorption bands of S_2 , even when the partial pressure of HNCS was reduced to 0.25 Torr. This implies a rate coefficient for reaction (13) $\gtrsim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at $\sim 300\text{K}$; *cf.* the reactions:



$$k = 1.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$



$$k = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Since the reaction is exothermic releasing 32 kcal mole $^{-1}$ if HCN is formed directly or 15 kcal mole $^{-1}$ if HNC is the initial product, a mechanism involving "attractive release" should produce some vibrationally excited S_2 . In fact no vibrationally "hot" bands could be detected in absorption even at the peak of the photolysis flash and unless vibrational relaxation of S_2 is particularly efficient in this system an "attractive release" pathway can be excluded. The same conclusion was reached in the related reaction⁷:



Comparison of photodissociation in HNCS and related molecules

Table 1, which compares dissociation energies in HNCS and HNCO indicates why predissociation at the C-N bond is favoured in HNCO but is absent in HNCS. The dissociation path of lowest energy, which correlates with the primary products $\text{HCN} + \text{S}(3^3\text{P})$, requires that H atom migration accompanies the C-S bond cleavage. It is conceivable that this might occur since the NCS group would

TABLE 1

DISSOCIATION ENERGIES (kcal mole⁻¹) IN HNCO AND HNCS

H-NCO	113	HN(³ Σ ⁻) + CO	78	HNC—O	131
		HN(¹ Δ) + CO	115		
H-NCS	113(est)	HN(³ Σ ⁻) + CS	119	HNC + S(³ P)	86
		HN(¹ Δ) + CS	156	HNC + S(¹ D)	113
				HCN + S(³ P)	69
				HCN + S(¹ D)	96

bend at the C atom on electronic excitation*; if the excited molecule adopted a *trans* configuration H atom transfer might well be facilitated and attempts are being made to photograph any absorption bands in the vacuum u. v. which might be ascribed to HNC. SCF molecular orbital calculations place the lowest allowed electronic transitions at wavelengths ~140 nm.

When an HNCS/Ar mixture was flashed through a filter solution (CH₂Cl₂ in ethanol), which absorbed all wavelengths ≤ 225 nm the absorption bands of S₂($\tilde{X}^3\Sigma^-_g$) became much weaker and those of S₂($\tilde{a}^1\Delta_g$) disappeared completely (see Fig. 5). In contrast the transient absorption of NCS was only slightly reduced. Since the filter prevents excitation into the ¹A'' (¹Δ) state of HNCS the results suggest that: (i) H-NCS bond cleavage is more favoured from the ¹A'' (¹Σ⁻) state; (ii) HNC-S cleavage can occur from either the ¹A'' (¹Σ⁻) or ¹A'' (¹Δ) states; and (iii) the small proportion of S(³D) atoms arise from excitation into the ¹A'' (¹Δ) state, which is the more energetic of the two.

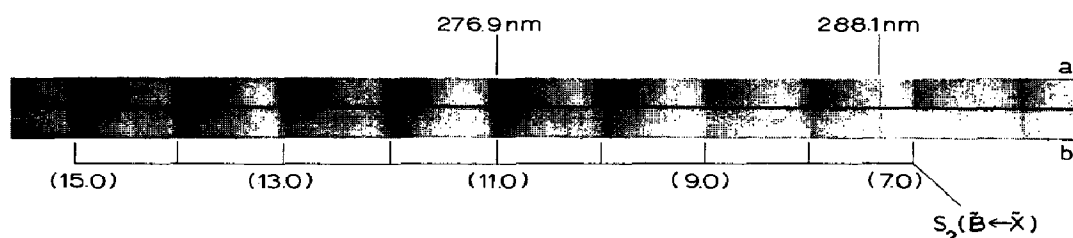


Fig. 5. Flash photolysis of HNCS in Ar: delay 32 μsec. $P_{\text{HNCS}} = 1$ Torr; $P_{\text{Ar}} = 420$ Torr; flash energy = 2 kJ. (a) No filter, $\lambda \geq 190$ nm; (b) filter, $\lambda \geq 225$ nm.

Table 2 compares the excess absorbed photon energies with the observed spin states of S atoms produced by photodissociation of N₂O, CO₂, HNCS, COS and CS₂ from a variety of electronic states. In general there is no correlation between the probability of spin conservation and the available excess energy. Thus the existence of a high density of vibronic states within the singlet manifold does

* Transient absorption from NCS radicals carrying one quantum of the bending vibration could be detected during the photolysis flash.

TABLE 2

SPIN CONSERVATION AND ITS BREAKDOWN IN THE PHOTODISSOCIATION OF HNCS, COS AND CS₂

	λ_{abs} , (nm)	Excess energy (kcal mole ⁻¹)	Spin state of O or S atom
N ₂ O(¹ Δ)	190	70	exclusively singlet
CO ₂ (¹ Δ_g)	147	21	exclusively singlet
OCS(¹ Δ)	220	30	principally singlet [S(³ D)~0.74 at 228.8–253.7 nm]
HNCS(¹ A' ⁻ ¹ Δ^-)	197	32	principally triplet
HNCS(¹ A' ⁻ ¹ Σ^-)	240	6	exclusively triplet
CS ₂ (¹ Σ_u^+)	190	21	exclusively triplet
CS ₂ (¹ Δ_g)	290	endothermic	

not necessarily preclude efficient intersystem crossing. If this is encouraged by the presence of an S atom then the behaviour of COS would seem to be anomalous. Perhaps the greater ease of intersystem crossing in HNCS and CS₂ is associated with their increased molecular dimensions compared with COS, which should reduce the singlet–triplet energy gap².

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REFERENCES

- (a) J. P. Simons, *Photochemistry and Spectroscopy*, Wiley, London, 1971; (b) P. Ausloos, *A. Rev. Phys. Chem.*, 22 (1971) 85; (c) K. F. Preston and R. F. Barr, *J. Chem. Phys.*, 54 (1971) 3347; (d) T. G. Slanger and G. Black, *J. Chem. Phys.*, 54 (1971) 1889; (e) G. Paraskevopoulos and R. J. Cvetanovic, *J. Am. Chem. Soc.*, 91 (1969) 7572; (f) H. Okabe, *J. Chem. Phys.*, 53 (1970) 3507; (g) B. A. Thrush, *Proc. Roy. Soc. (London)*, A 235 (1956) 143; (h) H. Okabe, *J. Chem. Phys.*, 49 (1968) 2726; (i) W. H. Breckenridge and H. Taube, *J. Chem. Phys.*, 53 (1970) 1750; (j) R. J. Donovan, *Trans. Faraday Soc.*, 65 (1969) 1419; (k) A. B. Callear, *Proc. Roy. Soc.*, A 276 (1963) 401.
- J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. McGlynn, *Chem. Rev.*, 71 (1971) 73.
- G. Herzberg, in R. Stoops (ed.), *Energy transfer in gases*, Interscience, New York, 1962, p. 9.
- C. R. Boxall, J. P. Simons and P. W. Tasker, *Discuss. Faraday Soc.*, 53 (1972) 182.
- R. J. Donovan and D. Husain, *Chem. Rev.*, 70 (1970) 489.
- I. W. M. Smith, *Trans. Faraday Soc.*, 64 (1968) 3183.
- I. W. M. Smith, *Discuss. Faraday Soc.*, 44 (1967) 194.