The Photochemistry of *C*-Nitroso-compounds. Part 7.[1] Nitrosyl Cyanide (1-Aza-2-nitrosoethyne)

By **Colin M. Keary, Brian G. Gowenlock,*** and **Josef Pfab,** Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS

The gas-phase photolysis of nitrosyl cyanide (1-aza-2-nitrosoethyne) has been studied using 589 nm radiation. The gaseous products are nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide and the solid products include cyanogen isocyanate. A mechanism is proposed to account for the reaction products. The experimental hazards associated with nitrosyl cyanide purification and reactions are emphasised.

THE properties of electrophilic *C*-nitroso-compounds (of which nitrosyl cyanide is a good example) have recently been reviewed by Kirby.[2] A small number of papers and theses have given details of other properties of this interesting molecule. The bond lengths and angles have been obtained from microwave spectroscopy,[3] the i.r. spectrum of the gas has been recorded,[4] and a shock-tube study of the gas-phase decomposition has been reported.[5] Studies of the electronic absorption spectra have been made [6] and the molecule proposed as a useful monopropellant chemical laser system.[6] A brief study of the thermal decomposition has been carried out [7] and we have published [8] a measurement of *D*(NC–NO). It appeared to us that a study of the photolysis would show interesting parallels with those for other *C*-nitroso-compounds. A parallel study [9] on fluorescent fragments produced in the vacuum u.v. photolysis of this compound has also been made in our laboratories. It was evident from the dienophilic character,[2] the NO bond length,[3] the NO stretching frequency [4] and the electronic absorption spectrum [3] that the molecule is a *C*-nitroso-compound and that comparisons with nitrosyl halides are not immediately useful. We are of the opinion that the established name of nitrosyl cyanide could perpetuate this misleading comparison and prefer to recall its character as a *C*-nitroso-compound by use of the systematic organic name of 1-aza-2-nitrosoethyne.

EXPERIMENTAL

Nitrosyl cyanide was prepared by the method of Dickinson *et al.*[3] using several cycles of condensation–evaporation of nitrosyl chloride onto freshly prepared dry silver cyanide. The product is a mixture of nitrosyl cyanide with nitrosyl chloride and some more volatile impurities (or decomposition products). Following some experience with a low temperature fractional distillation column [10] which is subject to greater risk consequent upon explosion damage, purification was usually made by repeated trap-to-trap distillation until negligible i.r. absorption from nitrosyl chloride was evident in the product.

---

[1] Part 6, D. Forrest, B. G. Gowenlock, and J. Pfab, *J.C.S. Perkin II*, 1977, 12.

[2] G. W. Kirby, *Chem. Soc. Rev.*, 1977, **6**, 1.

[3] R. Dickinson, G. W. Kirby, J. G. Sweeny, and J. K. Tyler, *J.C.S. Chem. Comm.*, 1973, 241.

[4] E. A. Dorko and L. Buelow, *J. Chem. Phys.*, 1975, **62**, 1869.

[5] E. A. Dorko, P. H. Flynn, U. Grimm, K. Scheller, and G. W. Mueller, *J. Phys. Chem.*, 1977, **81**, 811.

[6] L. Buelow, Thesis, Air Force Institute of Technology, Ohio, 1974.

[7] J. D. Illige, Thesis, University of California, Berkeley, 1976 (*Chem. Abs.*, 1977, **86**, 132, 629w; *Diss. Abs.*, 1977, **37**, 4454-B).

[8] B. G. Gowenlock, C. A. F. Johnson, C. M. Keary, and J. Pfab, *J.C.S. Perkin II*, 1975, 351.

[9] C. A. F. Johnson, V. Freestone, and J. Giovanacci, *Ber. Bunsengesellschaft Phys. Chem.*, 1977, **81**, 218.

[10] J. Dobson, Thesis, University of Indiana, 1967.

Commercial samples of nitrogen, oxygen, helium, carbon monoxide, carbon dioxide, nitrosyl chloride, nitrous oxide, nitric oxide, and nitrogen dioxide were used and purified by fractionation where necessary. A sample of perfluorocyclohexane was provided by Dr. R. G. Plevey.

Photolyses were carried out in a reaction vessel fitted with an electromagnetically operated paddle wheel stirrer, a Pyrex window and connections to the preparative line, a glass spiral manometer, and a gas sampling valve. All taps were greaseless. The vacuum line was covered with black adhesive tape to exclude light and to retain glass fragments in the event of an explosion. The photolysis lamp was an Atlas Sox 35 W low pressure sodium lamp emitting the sodium doublet at 589 nm. Schott–Mainz neutral density filters were employed where necessary.

Gas analyses were performed using a Taylor–Servomex gas chromatograph equipped with a microcatharometer type MK 158 with helium as carrier gas. Columns used were (1) Chromosorb with 10% triacetin (glycerol triacetate), 8 ft × 1/4 in copper, operated at 75°, (2) molecular sieve 5A (30—60 mesh), 9 ft × 1/4 in stainless steel, operated at room temperature, and (3) Porapak Q (80—100 mesh), 12 ft × 1/4 in stainless steel, operated at room temperature.

It should be noted that nitrosyl cyanide is a hazardous compound with high explosion risk. It is recommended that it be handled in very small quantities with avoidance of the condensed states where possible.

RESULTS

Identification of Products of Photolysis.—G.c. analysis using the three columns given above showed that the only volatile products of photolysis were nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide. It was also shown that cyanogen, nitric oxide, nitrogen dioxide, and oxygen were not formed in the photolysis. During the photolyses, a yellow involatile solid was deposited in the reaction vessel. Identification was attempted by i.r. analysis, the gas being photolysed in a cell fitted with CaF_2 windows. Prior to photolysis the i.r. spectrum was similar to that recorded by Dorko and Buelow.[4] As photolysis proceeded the characteristic C≡N and N=O stretching bands (doublets) both diminished and finally disappeared and absorption in the range 2 200—2 350 cm^{-1} increased as the photolysis proceeded. Pumping the vessel subsequent to photolysis did not remove the absorbing material. The main bands repeatedly observed in this region are compared with those obtained by Mayer [11] for the strongest bands in the spectrum of yellow amorphous polymeric solid cyanogen isocyanate (sample at −196°) and for the gaseous monomer (200°). The agreement is enheartening and suggests that our products contain this compound. Other physical properties of our solid are similar to those reported by Mayer.

Photolysis products (ν/cm^{-1})	2 085	2 210	2 240	2 270	2 320	2 335	2 390
NCNCO solid (ν/cm^{-1})	2 083w	2 212m		2 270vs		2 345s	2 410w
NCNCO gas (ν/cm^{-1})	2 110w	2 230sh		2 272vs	2 284vs	2 330vs	2 400sh

Comparison of the i.r. spectra of our products with those recorded for carbonyl cyanide [12] and azodinitrile [13] imply the absence of these two compounds from our products except in very minor amounts indeed. A mass spectrometric analysis of the solid extracted from the reaction vessel and subject to possible oxidation suggested the presence of NCN and NCO fragments. It is noted that if gaseous nitrosyl cyanide is allowed to remain in a blackened vessel for 16 h a small amount of decomposition occurs and both i.r. and g.c. analysis showed the presence of nitrogen dioxide, a product not found on photolysis, and also small quantities of nitrogen.

Variation of Photolysis Conditions.—(a) *Pressure variation of nitrosyl cyanide.* The relative pressures of products formed on photolysis for 2 h at room temperature (complete photolysis) are shown in Table 1. There was no discernible pressure change during photolysis and it seems probable that the remaining gas is cyanogen isocyanate which slowly polymerised at the walls of the reaction vessel. The gaseous products that have been quantitatively analysed by g.c. are formed in the approximate ratio $N_2 : CO : CO_2 : N_2O = 5 : 2 : 4 : 3$. The mass balance deficiency has the approximate value $C_{1.5-3}N_{3-4}O$ corresponding approximately to C_2N_2O for cyanogen isocyanate.

TABLE 1

Variation of products formed with change of pressure of NOCN

Pressure of NOCN (mmHg)	Pressure of products (mmHg)			
	N_2	CO	CO_2	N_2O
9	2.3	1.0	1.9	1.3
19	4.8	2.0	4.0	2.5
21.4	5.5	2.1	4.5	3.3
34	8.0	3.2	6.3	4.5

(b) *Time variation of product yields.* The data presented in Figure 1 show the relative yields of the four identifiable gaseous products as a function of photolysis time. The relative product ratios remain constant within experimental error over the period 23—120 min.

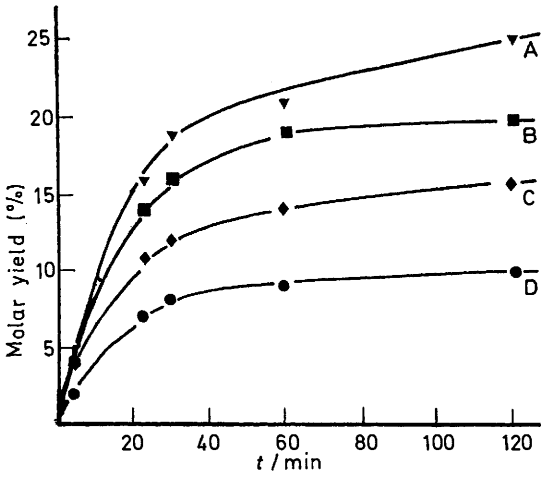


FIGURE 1 Product yields as a function of time of irradiation: A, nitrogen; B, carbon dioxide; C, nitrous oxide; D, carbon monoxide

(c) *Intensity variation of product yields.* The data

---

[11] E. Mayer, *Monatsh.*, 1970, **101**, 834.

[12] A. Tramer and K. L. Wierzchowski, *Bull. Acad. polon. Sci.*, 1957, **5**, 411.

[13] B. Bak and P. Jansen, *J. Mol. Structure*, 1972, **11**, 25.

presented in Figure 2 show the relative yields of the four identifiable gaseous products as a function of light intensity. The relative product ratios are relatively insensitive to changes of light intensity.

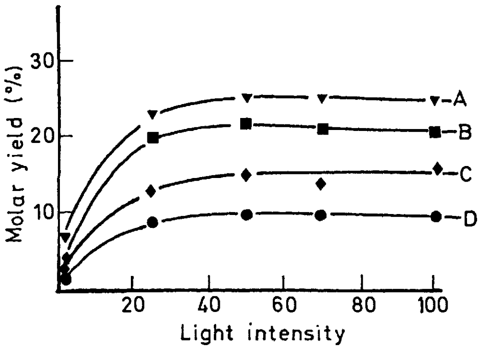


FIGURE 2. Product yields as a function of incident light intensity: A, nitrogen; B, carbon dioxide; C, nitrous oxide; D, carbon monoxide

(d) *Addition of quenching gases.* The effect of added helium and perfluorocyclohexane on the reaction products is shown in Table 2.

TABLE 2

Variation of products formed with [additive]/[NOCN] ratios

Pressure of NOCN (mmHg)	[Additive]/ [NOCN]	Pressure of products (mmHg) N_2	CO	CO_2	N_2O
21.4		5.5	2.1	4.5	3.3
27.2	10 [a]	6.0	2.3	5.2	4.4
25.0	30 [a]	4.5	1.7	4.5	5.0
20.0	1 [b]	4.9	2.0	3.4	3.3
26.0	10 [b]	4.1	0.4	1.6	2.8

[a] He. [b] C_6F_{12}.

(e) *Addition of oxygen.* Figure 3 shows the relative yields of the four gaseous products as a function of O_2 : NOCN ratio. It is evident that the relative yields of carbon dioxide and nitrous oxide are enhanced under these conditions.

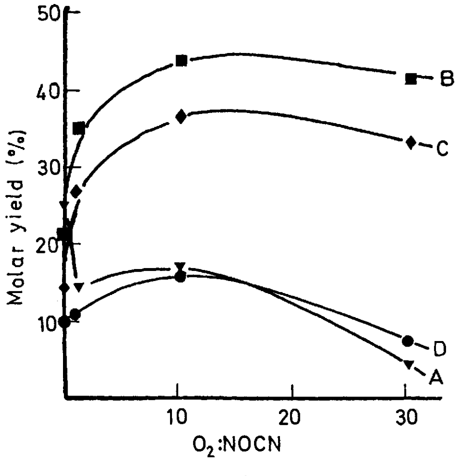


FIGURE 3. Product yields as a function of O_2 : NOCN ratio: A, nitrogen; B, carbon dioxide; C, nitrous oxide; D, carbon monoxide

(f) *Dark reaction of nitrosyl cyanide with nitric oxide.* A sample of nitrosyl cyanide was admitted to the reaction vessel and the pressure recorded (14 mmHg). It was then condensed at liquid nitrogen temperature and *ca.* 60 mmHg of nitric oxide admitted to the reaction vessel and the condensed NOCN immediately allowed to vaporise. An orange solid (presumably polymeric) was formed and apparently all NOCN was consumed. The relative yields of gaseous product were $N_2 : CO : CO_2 : N_2O = 4.5 : 1 : 1 : 1$. Repetition of the reaction within a gas i.r. cell led to a dark yellow liquid, an initial appearance of a yellow solid and a violent explosion.

DISCUSSION

This study is admittedly incomplete. Many preparations and other experiments, *e.g.* the NO–NOCN reaction were attended with explosions. In an attempt to make a more complete study of the effect of additives on the photolysis a preparation led to a violent detonation of *ca.* 2 ml of the liquid during fractionation at −40° with personal injury to the investigator and consequently the direct experiments were terminated at that stage. There are however certain novel features in the reaction schemes necessary to explain our results and to harmonise them with those of other workers [4-8] which we consider of importance.

An earlier study [14] of the gas-phase photolysis of a *C*-nitroso-compound suggests that the primary photochemical process is (A) followed by subsequent attack

$$\text{R-NO} \overset{h\nu}{\rightleftharpoons} \text{RNO}^* \longrightarrow \text{R} + \text{NO} \qquad \text{(A)}$$

of the products of photolysis on the substrate molecule at the −N=O functional group and production of R-containing and R(−H)-containing molecules. The products of photolysis of nitrosyl cyanide suggest that such a scheme is insufficient to account for the products and consequently it is necessary to consider reactions which remove the CN radical *via* oxidation pathways. In addition, the production of cyanogen isocyanate suggests the formation of NCN and/or NCO intermediates. It is also apparent that the gaseous products are thermodynamically favoured and consequently the activation energies of the reaction steps proposed are of crucial importance for a reaction system operating at room temperature. Comparison with the thermal decomposition studies carried out at 75° [7] and flash photolytic studies [15] can also be useful.

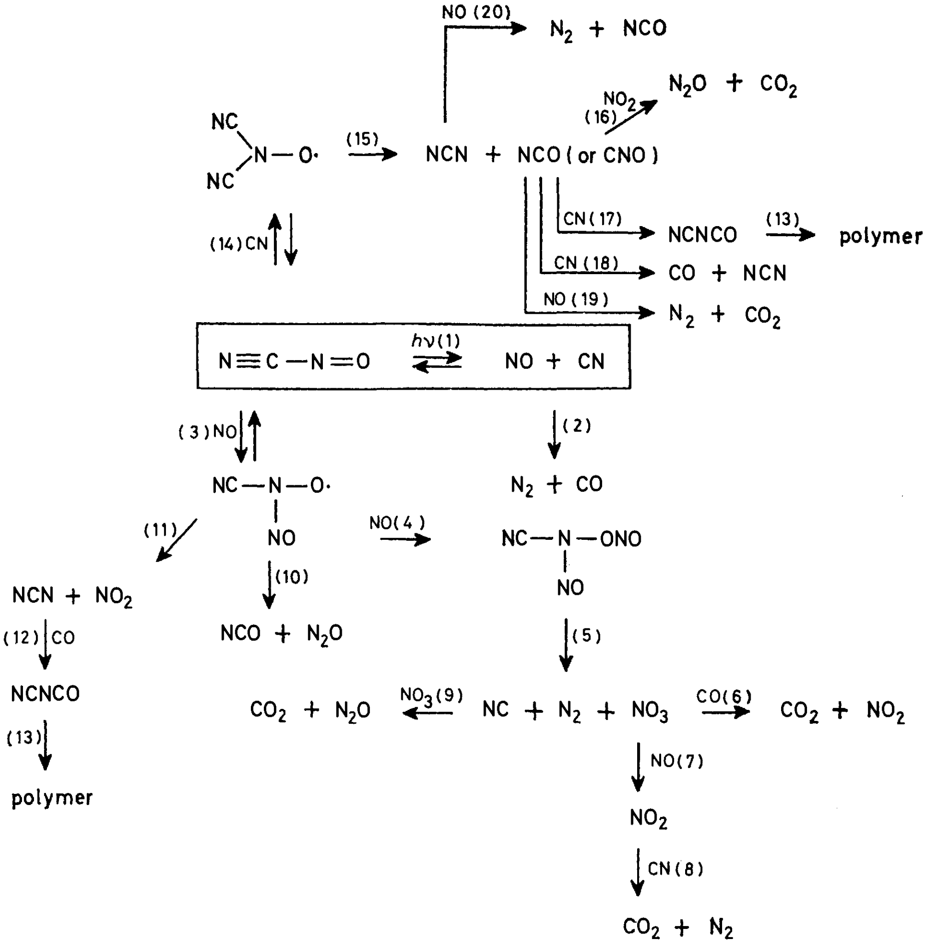
A tentative reaction mechanism (Scheme) is given which utilises the known ability of a *C*-nitroso-compound to scavenge free radicals and nitric oxide and which includes exothermic oxidation pathways. Reaction (1) is the expected primary photochemical process, involving the breaking of the weak C–N bond. Either or both of the products may be vibrationally excited. Reaction (2) has been proposed previously [15] and its high exo-

---

[14] J. R. Dickson and B. G. Gowenlock, *Annalen*, 1971, **745**, 152.

[15] N. Basco, J. E. Nicholas, R. G. W. Norrish, and W. H. J. Vickers, *Proc. Roy. Soc.*, 1963, **A272**, 147. N. Basco and R. G. W. Norrish, *Proc. Roy. Soc.*, 1975, **A283**, 291; N. Basco, *ibid.*, p. 302.

thermicity has led to the proposed use of nitrosyl cyanide as a monopropellant laser system.[5] This reaction is believed to be fast [16] and a theoretical study [17] suggests that it may proceed *via* a cyclic carbene intermediate. The addition reactions (3) and (14) are of basic importance for reactions of nitric oxide and radicals in the presence of an excess of a *C*-nitroso-compound. The sequence (4), (5), and (7) is similarly well documented for alkyl and aryl radicals. Reactions (6), (8), and (9) are presumably rapid at room temperature and account for product formation and absence of nitrogen dioxide and cyanogen. The decomposition reactions of the nitroxide radicals (10), (11), and (15) are proposed to account for routes to polymer formation and to other stable products. The Scheme requires further study.



SCHEME

It should be noted that almost all the reactions proposed are considerably exothermic and it is necessary to assume that in all cases the activation energies are low. The decomposition reactions of the nitroxide radicals are formally equivalent to terminal atom abstraction reactions from the nitrosyl cyanide *i.e.*, reactions (B)—(D). Room temperature elementary abstraction reactions of doubly and triply bonded atoms are relatively uncommon. Such abstractions have been proposed by Illige [7] to account for the distribution of labelled products in the gas-phase thermal decomposition of NOCN.[15]

$$NO + NCNO \longrightarrow N_2O + CNO \text{ (or NCO by rearrangement)} \quad [\mathit{cf.}\ (3) + (10)] \tag{B}$$

$$NO + NCNO \longrightarrow NO_2 + NCN \quad [\mathit{cf.}\ (3) + (11)] \tag{C}$$

$$CN + NCNO \longrightarrow NCO + NCN \quad [\mathit{cf.}\ (14) + (15)] \tag{D}$$

The formation of nitrosyl cyanide as an intermediate in photochemical and thermal reactions has been postulated from time to time.[15,18,19] We have attempted to repeat one of these studies namely the photolysis of nitric oxide–cyanogen mixtures in the range 220—360 nm but without success. Consequently we regard as unproven the report of the formation of the intermediate of considerable stability claimed to be nitrosyl cyanide. A

---

[16] D. W. Setser and B. A. Thrush, *Proc. Roy. Soc.*, 1965, **A288**, 275; J. C. Boden and B. A. Thrush, *ibid.*, 1968, **305**, 107.

[17] B. G. Gowenlock and L. Radom, submitted for publication in *Austral. J. Chem.*

[18] R. G. W. Norrish and F. F. R. Smith, *Trans. Faraday Soc.*, 1928, **24**, 620.

[19] J. P. Galvin and H. O. Pritchard, *J. Phys. Chem.*, 1964, **68**, 1035.

similar attempt[20] failed to produce any nitrosyl cyanide as evidenced by microwave spectroscopy.

We thank Drs. E. A. Dorko, J. K. Tyler, and W. L. Jolly for information relating to unpublished material and theses concerning nitrosyl cyanide. C. M. K. thanks the S.R.C. for a maintenance grant.

[7/987 *Received*, *9th June*, 1977]

---

[20] J. K. Tyler, personal communication.