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XCN (X = Cl, Br and I): a novel source of isocyanogen

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Abstract

Ambient light photolysis of gaseous BrCN, ClCN, and ICN results in the production of isocyanogen (NCNC) as the sole CN containing product. The flash vacuum pyrolysis of BrCN (1100°C and 10^{-5} mbar) generates NCNC, NCCN, HOCN, HNCO and the CN radical.

1. Introduction

Isocyanogen (**1**) and diisocyanogen (**2**) are formal isomers of cyanogen (**3**), and are of considerable chemical and astrophysical interest [1]. In principle all three cyanogen species can arise from the dimerisation of the cyanide radical (**4**):

$$\underset{\mathbf{4}}{2\ \mathrm{CN}^{\bullet}} \xrightarrow{\text{dimerisation}} \underset{\mathbf{1}}{\mathrm{NCNC}} + \underset{\mathbf{2}}{\mathrm{CNNC}} + \underset{\mathbf{3}}{\mathrm{NCCN}}$$

Scheme 1.

Over the past five years isocyanogen (**1**) and diisocyanogen (**2**) have been detected in the flash vacuum pyrolysis (FVP) of norbornadiene azine [2,3]; N-cyano-2,3-diphenylcyclopropeneimine [4], di-tert-butylcyclopropenonazine [5], as a result of the photolysis of, and potassium metal mediated dehalogenation of, tetrabromoformaldiazine [5], and in the microwave discharge of mixtures of acetylene and nitrogen [5]. We now wish to report the facile, one-step generation and characterisation of isocyanogen (**1**) from the gas phase photo-decomposition of cyanogen bromide, cyanogen chloride, cyanogen iodide, and the FVP of cyanogen bromide.

2. Results and discussion

In a typical experiment a gaseous mixture of cyanogen chloride/argon (1:30 or 1:1000) was placed in a 6 m pathlength gas cell and left exposed to ambient light. The IR spectrum was then recorded over a period of time (450 h). Figs. 1a–1d show the results of a typical experiment. At $t = 0$ min ClCN is the sole IR active species, however as the observations are continued a second IR active component grows, concurrent with the consumption of the IR bands previously assigned to ClCN ($\nu_{CN} = 2208$ cm^{-1}). This new species exhibits two main IR vibrations, $\nu_1 = 2302$ cm^{-1} and $\nu_2 = 2062$ cm^{-1}. Comparison of the IR spectra generated from the cyanogen halides with an authentic spectrum of isocyanogen

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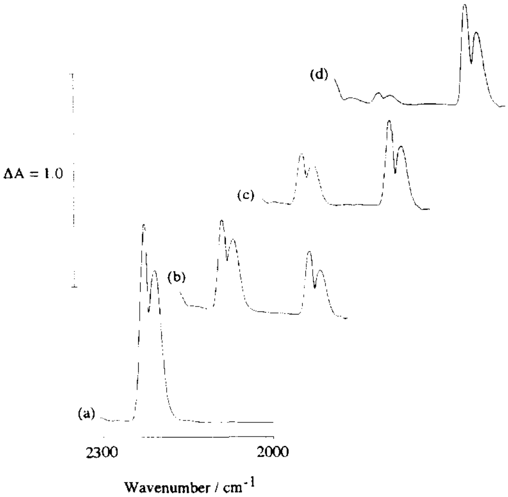

Fig. 1. Gas phase spectra of the daylight photolysis of ClCN (1:30 ClCN:Ar) in the region 2320–2000 cm^{-1} after (a) $t = 0$ min photolysis; (b) after $t = 175$ h; (c) after $t = 245$ h; and (d) after $t = 450$ h.

[3] conclusively demonstrated that the primary photo-decomposition product of BrCN, ClCN and ICN is isocyanogen. No other cyanide containing species was observed in this reaction.

This reaction is wavelength dependant, occurring only when light of $200 < \lambda < 580$ nm is utilised. Isocyanogen proved surprisingly stable in the gas phase surviving $t > 450$ h, it has however resisted our attempts at argon matrix isolation (this requires the condensation of the NCNC gas mixture through a metal line onto a spectroscopic window at 12 K). As has been previously reported, contact with metals dramatically reduces the stability of isocyanogen [1]. We are presently investigating the nature of the isocyanogen decomposition products.

Experiments in which the cyanogen halides were pyrolysed and the products matrix isolated were carried out concurrently [3]. Favourable results were obtained only with cyanogen bromide. Thus, a 1 : 1000 mixture of BrCN : argon was passed through the pyrolysis oven, the pyrolsylate condensed onto a barium fluoride target at 12 K and the IR spectrum recorded over a 200–1250°C FVP range. BrCN proved remarkably stable surviving FVP conditions of 1000°C and 10^{-5} mbar, however at 1100°C several new IR bands are detected. Those occurring in the 2320–2000 cm^{-1} region are of particular interest (Fig. 2), they are assigned as follows: 2049 (CN

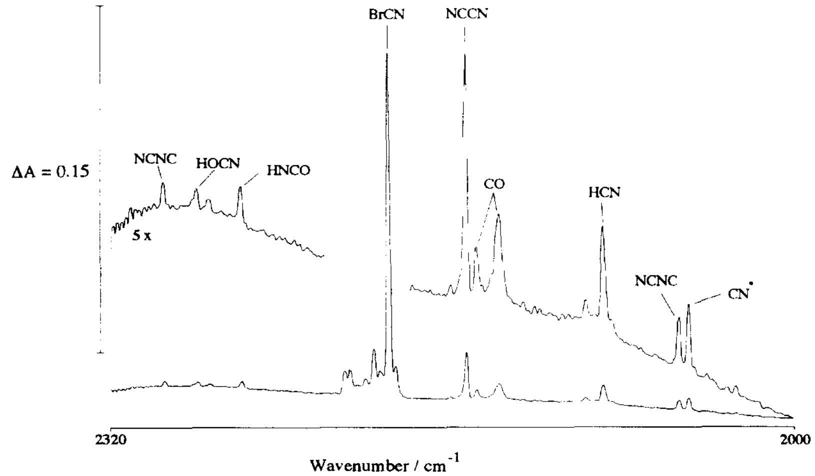

Fig. 2. Infrared spectrum in the spectral region 2320–2000 cm^{-1} at 14 K after pyrolysis of BrCN at 1100°C and 10^{-5} mbar, IR bands are assigned as shown.

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[3] The FVP apparatus employed a 10 cm length (0.8 cm inner diameter) quartz tube in housings flanged to a Leybold–Heraeus closed-cycle liquid He cryostat for Ar matrix isolation (10^{-5} mbar). FTIR spectra were recorded at 1 cm^{-1} resolution on a Perkin-Elmer 1720X spectrometer. Gas phase spectra were obtained using a 6 m multi-pass (Infrared Analysis (USA)) gas cell.

radical) [6,7], 2054 (ν_2 NCNC) [2,3], 2090 (HCN) [8], 2154 (ν_2 NCCN) [9], 2259 (HNCO) [10], 2279 (HOCN) [11] and 2294 cm^{-1} (ν_1 NCNC) [2,3].

The multitude of CN containing products is a direct result of the cleavage of the C–Br bond at 1100°C resulting in the highly reactive CN radical, which participates in bimolecular reactions prior to condensation at 12 K. The IR spectrum, even at 1100°C is dominated by BrCN (ν_{CN} 2190 cm^{-1}, also present are multiple bands assignable to BrCN in differing matrix sites), thus the actual quantity of BrCN pyrolysed is minute. Higher FVP temperatures were not investigated as radiant heating of the cold window prevented matrix isolation and hence complicated product identification.

3. Product identification

In order to confirm the identity of the primary decomposition product of the cyanogen halides, i.e. isocyanogen, an authentic sample was synthesised by the method of van der Does and Biekelhaupt [2]. Preliminary comparisons of the gas phase IR spectra of both samples were in excellent agreement in the main region of interest (Fig. 3). However the slow infusion of atmospheric gases into our gas cell complicated the identification of all the previously assigned gas phase bands. Thus confirmation of the presence of isocyanogen by low temperature IR spectroscopy was attempted. Consequently samples (containing IR bands previously assigned to isocyanogen) were condensed onto a spectroscopic window at 14 K. Surprisingly we were unable to detect any IR bands that could be assigned to isocyanogen. This was true for both samples, with the major IR band being detected at 2049 cm^{-1} (close to that reported for CN radical) [6,7]. We had on previous occasions matrix-isolated isocyanogen according to the method of van der Does and Bickelhaupt [2] (FVP of norbornadiene azine at 600°C) [4], both samples (that from the cyanogen halides and that from norbornadiene) only gave rise to a single IR active

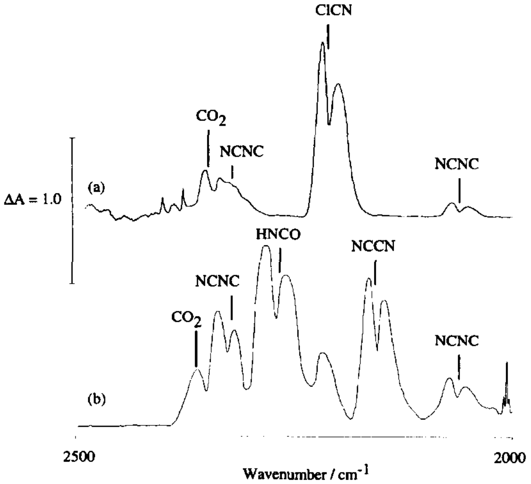

Fig. 3. Gas phase infrared spectra in the region 2320–2000 cm^{-1} after (a) ambient light photodecomposition of ClCN; and (b) after FVP of norbornadiene azine at 600°C and 1×10^{-3} mbar.

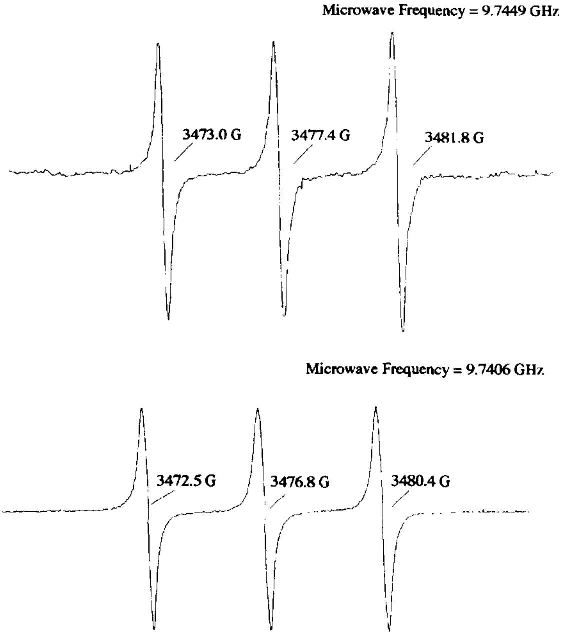

Fig. 4. ESR spectra recorded at 14 K; (a) deposition of gas phase sample arrising from the ambient light photodecomposition of ClCN, and (b) deposition of an authentic sample of NCNC generated by the FVP of norbornadiene azine at 600°C and 1×10^{-3} mbar.

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[4] When the pyrolysis of norbornadiene azine was carried out with a metal thermocouple present within the pyrolysis zone the quantities of isocyanogen detected were significantly reduced, with the concomitant increase in the intensity of the IR band at 2049 cm^{-1}.

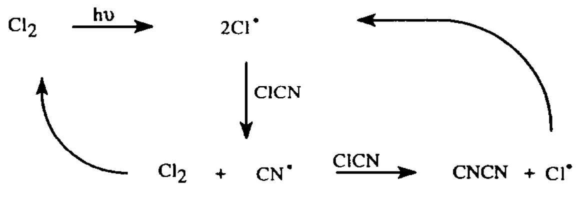
absorption in the nitrile region at 2049 cm^{-1}. The closeness of our observed IR absorption to that reported for the cyanide radical encouraged us to perform the same deposition experiment with ESR observation. In these case a 1 : 1 : 1 triplet centered on $g = 2.0016$ with a splitting of ≈ 4.4 G was observed (Fig. 4), strongly suggesting that isocyanogen was undergoing a metal-catalysed cleavage to the cyanide radical.

The similarity in behaviour and the observation of identical IR bands from the ambient light photolysis of the cyanogen halides and the above behaviour upon condensation onto a spectroscopic target at 14 K identifies the primary decomposition product of the cyanogen halides as isocyanogen.

4. Mechanism of isocyanogen formation

The mechanism of isocyanogen formation in the gaseous photo-decomposition is not fully understood. We have obtained evidence of low halogen concentrations and believe that these reactions occur via homolytic cleavage of the halide–halide bond initiating a radical chain reaction, Scheme 2.

We believe that the reaction is, at least in the first instance, radically driven on the following basis: (i) the reaction is light initiated with light of $200 < \lambda < 580$ nm, which overlaps the UV–visible absorptions of Br_2, Cl_2, and I_2; (ii) the photochemical reaction prevails even after the photolysis source is removed; (iii) the gas phase product, NCNC, is formally a CN radical dimer, which can arise from the homolytic cleavage of the carbon–halide bond; and (iv) the FVP of BrCN yields products consistent with the generation of the CN radical (followed by recombination and/or reaction with contaminants in the vacuum system, mainly CO and H_2O), indeed the IR absorption at 2049 cm^{-1} is assigned to the CN radical, as is the 1 : 1 : 1 triplet in the ESR spectrum (although we as yet have been unable to record a UV–visible spectrum of this species). The protracted nature of these reactions and the continued decomposition of the cyanogen halides even after the photolysis sources has been removed (Fig. 5) strongly suggests that there is also another mechanism involved. We are continuing our mechanistic examination of the processes involved in these reactions.



Scheme 2.

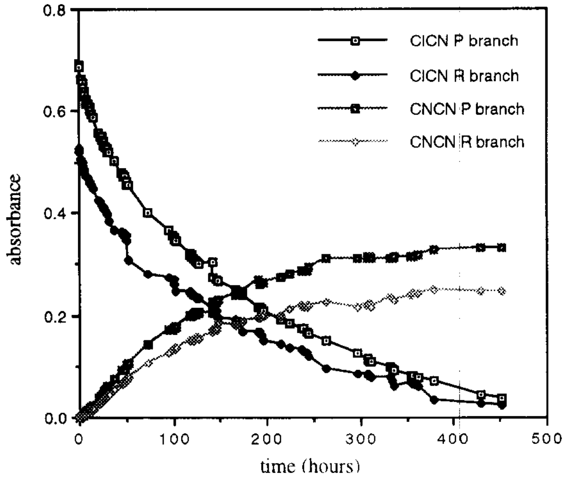


Fig. 5. Graphical representation of the gas phase decomposition of ClCN in a 6 m multipass gas cell accompanied by the concurrent growth of the IR absorptions assigned to isocyanogen (1).

Thus isocyanogen is generated from the ambient-light photolysis of BrCN, ClCN, and ICN. We believe that the generation of NCNC is radical-initiated. In addition the FVP of BrCN affords a convenient route into CN radical chemistry.

Acknowledgement

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