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# A Matrix Isolation Study of the Photochemically Induced Reactions of Ozone with Iodine Cyanide and Bromine Cyanide

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Ozone was co-deposited with ICN and, separately, with BrCN in argon matrixes at ca. 14 K, and the FTIR spectra were measured after each photolysis or warming cycle. The experiments were complemented by the analogous studies of ICN and BrCN separately in oxygen matrixes at ca. 14 K. Photolysis of matrixes containing $O_3$ and ICN led to the formation of bands attributed to an iodoso species, OICN, after only 30 min of irradiation ($\lambda > 650$ nm). UV−vis ($\lambda > 350$ nm) irradiation resulted in the appearance of bands attributed to iodoisocyanate, INCO. Subsequent Pyrex-filtered ($\lambda > 290$ nm) and quartz-filtered ($\lambda > 240$ nm) irradiation increased the yield of INCO and led to the formation of bands tentatively attributed to iodocarbonyl isocyanate, IC(O)NCO, and the acyclic dimer of iodoisocyanate, $I_2NC(O)NCO$. Bands attributed to an iodyl species, $O_2ICN$, were also detected. BrCN is clearly much less reactive than ICN with ozone and required several hours of UV irradiation before any new bands were observed; these are attributed to both bromoisocyanate, BrNCO, and bromocarbonyl isocyanate, BrC(O)NCO. No evidence was obtained for the formation of the halogen nitrile oxides ICNO and BrCNO in argon matrixes. The possible mechanisms of the reactions are discussed.

## Introduction

In the past decade or so, ozone has been extensively studied because of its significant role in atmospheric processes. Many matrix isolation studies have shown that ozone can interact and form weak complexes with small molecules ($CH_3I$,[1] HF,[2] $PH_3$,[3] $CF_3I$,[4] ICl,[5] and $C_2H_5I$[6]) and then undergo interesting photochemically induced reactions. Weak ozone complexes have the potential to alter atmospheric reaction rates and/or pathways, and they themselves are interesting subjects for experimental studies.

The present investigation involves the deposition of ozone with halogen cyanides in cryogenic matrixes and establishes the presence of weak complexes, $O_3\cdots ICN$ and $O_3\cdots BrCN$, between the precursors. Moreover, the matrix isolation technique is especially well-suited for the determination of whether different types of complexes such as $O_3\cdots XCN$ or $O_3\cdots NCX$ are present. The halogen cyanides are an interesting group of small molecules and may be considered analogous to diatomic interhalogen compounds due to the pseudohalide character of the cyanide moiety, −CN. The chosen precursors together contain the atmospherically important elements C, N, O, Br, and I, and thus, any photochemical reactions that occur between them may yield information relevant to the mechanisms of ozone depletion from the atmosphere and to interstellar chemistry.

## Experimental Section

Ozone was generated by Tesla coil discharge through either normal oxygen, oxygen-18, or a 1:1 mixture of each contained in a 10 cm Pyrex finger immersed in liquid nitrogen. Ozone was obtained in a blue condensed form and purified by multiple freeze−thaw cycles to remove any residual oxygen. British Oxygen Co. supplied the research-grade oxygen (>99.9%) and argon, while oxygen-18 (>97.7%) was supplied by Enritech Enrichment Technologies Ltd. Bromine cyanide and iodine cyanide were both purchased from Aldrich; bromine cyanide was used as supplied, but it was necessary to sublime iodine cyanide to obtain it in the form of pure white crystals.

In a typical experiment, the halogen cyanides were diluted separately at species-to-argon (S/Ar) ratios in the range of 1:6000−1:8000 by standard manometric procedures at room temperature. The precursor gas mixtures were then deposited for 6 h at rates of approximately 3 mmol $h^{-1}$ onto a cold (14 K) CsI window mounted in a Displex closed-cycle helium cryostat (Air Products DE 202 S). The vacuum shroud surrounding the cold window could be aligned for infrared transmission studies, gas deposition, or sample photolysis. Infrared spectra were recorded on a Bruker IFS 113v FT-IR spectrometer over the range of 500−4000 $cm^{-1}$ at a resolution of 0.5 $cm^{-1}$ using a germanium-coated KBr beam splitter and a MCT detector cooled with liquid nitrogen. The band wavenumbers observed are accurate to within ±0.2 $cm^{-1}$ for sharp bands. A DTGS detector was used to record spectra over the range of 600−200 $cm^{-1}$ at a resolution of 1 $cm^{-1}$. Spectra were recorded after each matrix irradiation or warming cycle to monitor any changes caused by these processes. The matrixes were irradiated for various periods with an Oriel xenon mercury lamp, and a 5 cm thick water filter was placed between the lamp and the sample to reduce the infrared output of the lamp. Filtered radiation in the visible and ultraviolet regions was selected with the following transmission filters: 8 mm thick deep red ($\lambda > 650$ nm), 2 mm thick green ($\lambda > 410$ nm), Corning 7 mm thick blue/green ($550 > \lambda > 350$ nm), Pyrex ($\lambda > 290$ nm), and quartz ($\lambda > 240$ nm). In this way, the wavelength selectivity of the product distribution could be established.

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**TABLE 1: Infrared Bands ($cm^{-1}$) of Iodine Cyanide, ICN, Trapped in a Variety of Matrixes at 14 K**

| Ar | $O_2$ | $^{16}O_3/Ar$ | $^{18}O_3/Ar$ | assignment |
|---|---|---|---|---|
| 2190.5 vw, sh[a] | | 2189.9 vw[a] | | |
| 2178.4 w, sh[a] | 2183.5 vw[a] | 2183.4 vw[a] | 2178.5 vw[a] | |
| 2174.5 vw, sh[a] | 2174.4 vw[a] | 2180.5 w[a] | 2174.1 vw[a] | |
| | 2173.2 vw[a] | 2178.1 w[a] | | |
| | | 2174.8 vw[a] | | |
| 2170.3 w | 2172.5 vvw | 2170.4 w | 2170.4 vw | $\nu_{C\equiv N}$ |
| | | 2153.5 w[d] | | |
| | | | 2149.2 vw | $\nu_1 + \nu_3$ ($^{16}O_3$) |
| | | | 2140.6 vw | ? |
| | | 2111.0 vw[d] | | |
| | | 2108.5 vw | | $2\nu_3$, $3\nu_2$ ($^{16}O_3$) ? |
| | | | 1996.4 vw[d] | |
| | | | 1993.7 vw | $2\nu_3$, $3\nu_2$ ($^{18}O_3$) ? |
| | | 1109.4 vw | | $\nu_1$ ($^{16}O_3$) |
| | | | 1043.2 w | $\nu_1$ ($^{18}O_3$) |
| | | 1039.6 mw | | $\nu_3$ ($^{16}O_3$) |
| | | 1033.9 w, sh[b] | | |
| | | 1028.6 w[b] | | |
| | | | 998.9 vw[b] | |
| | | | 989.6 vw[d] | |
| | | | 983.2 ms | $\nu_3$ ($^{18}O_3$) |
| | | | 972.7 vw, sh[b] | |
| | 725.2 vw | | | ? |
| | | 706.9 vvw[b] | | |
| | | 704.9 mw | | $\nu_2$ ($^{16}O_3$) |
| | | 698.7 w[b] | | |
| | | | 664.2 mw | $\nu_2$ ($^{18}O_3$) |
| | | | 653.7 w[b] | |
| 506.1 w[a] | | | | |
| 486.5 w | *c* | 486.5 vw | *c* | $\nu_{I-C}$ |
| 485.1 w[d] | | | | |
| 460.1 ms[a] | | | | |
| 456.1 ms[a] | | | | |

[a] Bands of ICN aggregates. [b] Complex bands of $O_3$. [c] Bands too weak to detect. [d] Bands due to matrix site effects.

Warming experiments were also carried out, but these brought about only very small changes to the relative intensities of the aggregate bands.

## Results and Discussion

**Deposition of the Precursors, ICN, BrCN, and Ozone.** The infrared spectra of ICN and BrCN isolated separately in argon matrixes (ICN/Ar = 1:1500−1:8000 and BrCN/Ar = 1:4000−1:8000) and oxygen matrixes (ICN/$O_2$ = 1:6000 and BrCN/$O_2$ = 1:5000) have been recorded (Tables 1 and 2). In both cases, the ICN and BrCN band wavenumbers were found to be in close agreement with those reported elsewhere for these species in the gas phase[7−9] and various matrixes.[10,11] Increasing the concentration of either ICN or BrCN resulted in the appearance of additional bands; some were slightly blue-shifted from the band attributed to the C≡N stretch, while others appeared on either side of that attributed to the X−C stretch. These concentration-dependent bands are due to small aggregates of the halogen cyanide, sustained by the conditions of the matrix. Only at species-to-argon ratios in the region of 1:10000 was it possible to detect solely XCN monomer bands (Figure 1). Ultraviolet ($\lambda > 240$ nm) photolysis of Ar matrixes containing BrCN produced no new bands; yet in this situation with ICN, a new band appeared at 2057.2 $cm^{-1}$, with a shoulder at 2059.0 $cm^{-1}$ (Figure 1). These bands have also been observed by Fraenkel et al.,[10] who assigned them to the $\nu_{C\equiv N}$ of INC, the photoisomer of ICN. The fact that the $\nu_{C\equiv N}$ of ICN is ∼120 $cm^{-1}$ higher than that of INC suggests that the C≡N bond in ICN has more triple bond character than that in INC. This is also typical of other XCN/XNC pairs.[12]

The infrared spectra of either ICN or BrCN co-deposited with ozone in argon matrixes (ICN/$O_3$/Ar = 1:2:8000 and BrCN/$O_3$/Ar = 1:1.5:8000) exhibited bands that resembled those in the infrared spectra of ICN, BrCN, and ozone[13,14] isolated separately in argon (Tables 1 and 2). However, in the ICN/$O_3$/Ar experiment, weak bands with small wavenumber shifts from the ozone fundamental bands appeared at 1033.9, 1028.6, 706.9, and 698.7 $cm^{-1}$ and were destroyed by visible irradiation ($\lambda > 650$ nm and $\lambda > 410$ nm). These weak, shifted bands are attributed to the molecular complex $O_3$···ICN since they are comparable with those reported for $O_3$···I−Z complexes detected elsewhere[1,4−6] and since, upon irradiation with visible light, bands belonging to OI−CN are observed. Although the complex could alternatively be of the type ICN···$O_3$, the lack of shifts in $\nu_{C\equiv N}$ and lack of any new bands that could be attributed to ICNO militate against this possibility. The interaction between ozone and ICN in the matrix is sufficient to change the photochemical behavior of ozone, allowing oxygen−oxygen bond cleavage to occur with visible radiation. By contrast, isolated ozone will only photodissociate effectively after ultraviolet irradiation (200−310 nm). Similar weak bands detected in the BrCN/$O_3$/Ar matrix are attributed to ozone molecules which occupy different matrix sites rather than to an $O_3$···BrCN complex; this is because the intensities of the ozone bands were unaffected by photolysis with radiation of wavelengths longer than 290 nm. In other experiments in which ozone has been deposited with a bromine-containing compound, there was likewise no evidence for complex formation.[15,16] In addition to the precursor bands, others attributable to small quantities of matrix-isolated water and carbon dioxide were also detected.

Samples of isotopic ozone, $^{18}O_3$, and mixed isotopic ozone, $^{16}O_{3-x}{}^{18}O_x$, have also been condensed with the halogen cyanides in argon matrixes, and the appropriate spectroscopic data are listed in Tables 1 and 2.

**TABLE 2: Infrared Bands ($cm^{-1}$) of Bromine Cyanide, BrCN, Trapped in a Variety of Matrixes at 14 K**

| Ar | $O_2$ | $^{16}O_3$/Ar | $^{18}O_3$/Ar | assignment |
|---|---|---|---|---|
| 2763.4 w | | | | $\nu_{Br-C} + \nu_{C\equiv N}$[a] |
| 2761.7 w | | | | |
| 2536.0 vw | | | | $\delta_{BrCN} + \nu_{C\equiv N}$[a] |
| 2533.3 w | | | | |
| 2211.2 w[b] | | | | |
| 2208.8 w[b] | | | | |
| 2197.6 w[b] | | 2196.3 vw[b] | | |
| 2190.6 mw | 2194.4 wm | 2190.7 mw | 2190.7 wm | $\nu_{C\equiv N}$ |
| 2187.4 vw[c] | 2192.7 w[c] | | | |
| | | 2149.1 w | | $\nu_1 + \nu_3$ ($^{16}O_3$) |
| | | | 2140.6 vw | ? |
| | | 2110.7 ms[c] | | |
| | | 2108.6 ms | | $2\nu_3$, $3\nu_2$ ($^{16}O_3$) ? |
| | | | 1996.1 ms[c] | |
| | | | 1993.9 ms, sh | $2\nu_3$, $3\nu_2$ ($^{18}O_3$) ? |
| | | 1106.2 wm | | $\nu_1$ ($^{16}O_3$) |
| | | | 1043.7 wm | $\nu_1$ ($^{18}O_3$) |
| | | 1045.1 vs | | $\nu_3$ ($^{16}O_3$) |
| | | 1037.7 vs[c] | | |
| | | 1035.9 s[c] | | |
| | | 1034.7 s[c] | | |
| | | | 973.6 vs, br | $\nu_3$ ($^{18}O_3$) |
| | | 704.2 ms | | $\nu_2$ ($^{16}O_3$) |
| | | | 665.4 ms | $\nu_2$ ($^{18}O_3$) |
| | | | 652.4 vw[c] | |
| 576.8 vvw[b] | | | | |
| 575.0 vw | *d* | *d* | *d* | $\nu_{Br-C}$ |
| 573.4 vw[b] | | | | |

[a] BrCN in the gas phase[7] has fundamentals at 580, 368, and 2187 $cm^{-1}$ for $\nu_{Br-C}$, $\delta_{BrCN}$, and $\nu_{C\equiv N}$, respectively. [b] Bands of BrCN aggregates. [c] Bands due to matrix site effects. [d] Bands too weak to detect.

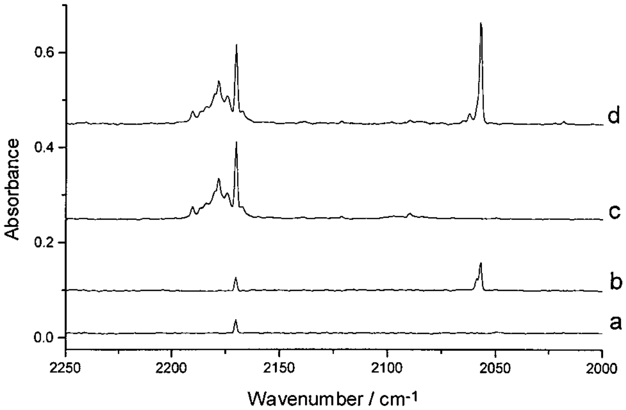


**Figure 1.** Infrared spectra of argon matrixes containing ICN after (a) deposition (ICN/Ar = 1:10000), (b) UV photolysis ($\lambda > 240$ nm) for 30 min (ICN/Ar = 1:10000), (c) deposition (ICN/Ar = 1:1500), and (d) UV photolysis ($\lambda > 240$ nm) for 30 min (ICN/Ar = 1:1500).

**Photolysis of ICN/$O_3$ Matrixes.** Deposition of argon matrixes containing ICN and ozone and their subsequent photolysis cycles using radiation of different wavelengths created a number of new species, as made evident by the emergence of new bands. Different photoproducts resulted, depending on the threshold wavelength for formation.

The first new band detected, at 760.6 $cm^{-1}$, was weak and formed after visible irradiation ($\lambda > 650$ nm) (Table 3). The band intensified upon filtered photolysis at $\lambda > 410$ nm but was destroyed upon UV−vis ($\lambda > 350$ nm) irradiation (Figure 2). In the $^{18}O$-enriched ozone spectrum, $\nu_{I-^{16}O}$ occurs at 760.2 $cm^{-1}$ and $\nu_{I-^{18}O}$ at 722.2 $cm^{-1}$, with an isotopic shift of 38.0 $cm^{-1}$. Bands in this region are therefore assigned to the I−O stretch of the iodoso species OI−CN on the bases of the band wavenumbers and the $^{18}O$ isotopic shift, both of which compare well with those obtained for other iodoso species isolated in argon, viz., $CH_3$−IO (723.7 $cm^{-1}$, $^{18}O$ shift of 35.6 $cm^{-1}$),[1] $CF_3$−IO (732.3 $cm^{-1}$, $^{18}O$ shift of 26.3 $cm^{-1}$),[4] and Cl−IO (779.1 $cm^{-1}$, $^{18}O$ shift of 27.8 $cm^{-1}$).[5] The predicted isotopic shift for a harmonic I−O vibration is 37.4 $cm^{-1}$, suggesting that $\nu_{I-O}$ of OI−CN is essentially uncoupled to any nearby vibrational modes. Note that $\nu_{I-O}$ of OI−CN (760.6 $cm^{-1}$) falls between that of the fluorine- and chlorine-containing iodoso species, illustrating the point that the CN group behaves as a pseudohalide with properties between those of F and Cl. A doublet of bands belonging to the $^{16}O$ and $^{18}O$ isotopomers of OI−CN was detected in the mixed-ozone experiment; no intermediate components were observed, thus confirming that there is a contribution from only a single oxygen atom to the vibrational mode. There was no detectable shift to any of the $\nu_{C\equiv N}$ bands, nor were any new bands detected which could be indicative of the formation of either free IO or free CN.

**TABLE 3: Infrared Bands ($cm^{-1}$) Formed after Visible ($\lambda >$ 650 nm) Irradiation of Matrixes Containing ICN and Ozone and Attributed to OICN**

| $^{16}O_3$/Ar | $^{18}O_3$/Ar | $^{16}O_{3-x}{}^{18}O_x$/Ar | assignment |
|---|---|---|---|
| 760.6 w | | 760.2 vw | $\nu_{I-^{16}O}$ |
| | 727.6 w[a] | | |
| | 726.2 vw[a] | | |
| | 721.0 w | 722.2 vw | $\nu_{I-^{18}O}$ |

[a] Bands due to matrix site effects.

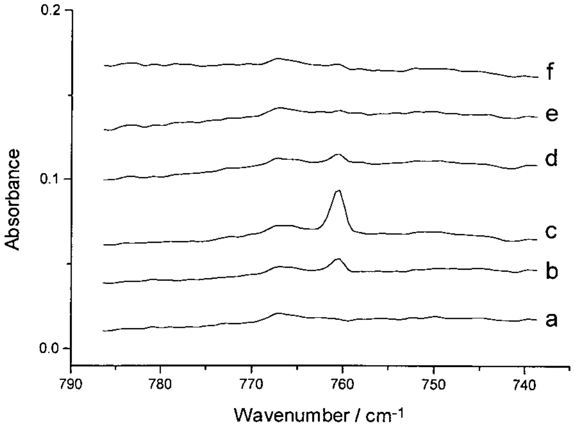


**Figure 2.** Infrared spectra showing the $\nu_{I-O}$ region for an argon matrix containing ICN and ozone, taken after (a) deposition, (b) $\lambda > 650$ nm photolysis, (c) $\lambda > 410$ nm photolysis, (d) $\lambda > 350$ nm photolysis, (e) Pyrex-filtered ($\lambda > 290$ nm) photolysis, and (f) quartz-filtered ($\lambda >$ 240 nm) photolysis.

A group of bands started to appear after irradiation at wavelengths longer than 410 nm and continued to grow upon UV−vis ($\lambda > 350$ nm) and UV irradiation ($\lambda > 290$ and 240 nm); they were attributed to iodoisocyanate INCO (Table 4), with the bands at 2196.9, 1273.2, and 591.6 $cm^{-1}$ being assigned to the N═C stretch, the C═O stretch, and the −NCO out-of-plane bend, respectively. The I−N stretch escaped detection but should have appeared just below 500 $cm^{-1}$; it should thus occur beyond the range of the MCT detector but must have been too weak to be detected in the range of the DTGS detector. Extra bands also appeared alongside the fundamentals, owing either to additional sites in the matrix or to aggregates of INCO. Analogous bands at lower wavenumbers appeared in the spectra of ICN/$^{18}O_3$/Ar matrixes under identical photolytic conditions and were attributed to the formation of $INC^{18}O$. When $^{18}O_3$ is

**TABLE 4: Infrared Bands ($cm^{-1}$) Detected after Photolysis ($\lambda > 350$ nm) of Matrixes Containing ICN and Ozone and Attributed to INCO**

| $^{16}O_3$/Ar | $^{18}O_3$/Ar | $^{16}O_{3-x}{}^{18}O_x$/Ar | assignment |
|---|---|---|---|
| | | 2198.0 ms, sh[a] | |
| 2196.9 ms | | 2197.1 s | $\nu_{N=C}$ ($-NC^{16}O$) |
| 2192.5 mw, sh[a] | | 2195.5 ms, sh[a] | |
| | | 2178.1 mw, sh[a] | |
| | 2177.0 mw | 2177.0 ms | $\nu_{N=C}$ ($-NC^{18}O$) |
| | 2175.6 w[a] | 2175.5 mw, sh[a] | |
| | 2148.3 vw | | ? |
| 2149.0 vw | 2147.7 vw | 2147.7 vw | ? |
| 1275.1 vvw, sh[a] | | 1277.6 vvw[a] | |
| | | 1274.5 vvw[a] | |
| 1273.2 vw | | 1272.9 vw | $\nu_{C=O}$ ($-NC^{16}O$) |
| | | 1250.8 vw[a] | |
| | | 1249.0 vvw[a] | |
| | | 1247.2 vw[a] | |
| | | 1245.0 vvw[a] | |
| | 1226.8 vw[a] | 1226.6 vvw[a] | |
| | 1226.0 vw[a] | 1225.8 vvw[a] | |
| | 1224.7 vw | 1224.7 vw | $\nu_{C=O}$ ($-NC^{18}O$) |
| 596.1 vw[a] | | | |
| 593.9 vw[a] | | | |
| 591.6 w | | | $\gamma_{NC^{16}O}$ (o−o−p)[b] |
| 586.3 vw[a] | | | |
| 583.0 vw[a] | | | |
| 580.4 vw[a] | | 578.7 vw, sh[a] | |
| 577.0 w[a] | | 577.5 vw, sh[a] | |
| | | 576.8 vw[a] | |
| | | 576.6 vw, sh[a] | |
| | | 575.6 vw, sh[a] | |
| | 572.8 vw[a] | 572.5 vw, sh[a] | |
| | 571.9 vw | 571.6 vw | $\gamma_{NC^{18}O}$ (o−o−p) |
| | 567.7 vw[a] | | |
| | 561.8 vw[a] | | |

[a] Bands due to matrix site effects or aggregates. [b] $\delta_{NC^{16}O}$ (i−p) and $\delta_{NC^{18}O}$ (i−p) bands are obscured by $CO_2$ impurity bands at ca. 667 $cm^{-1}$.

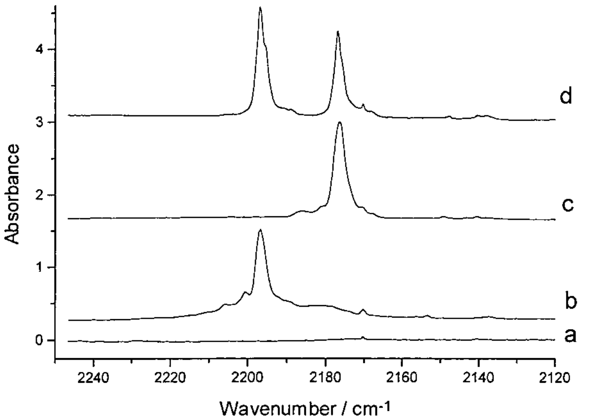


**Figure 3.** Infrared spectra in the 2240−2120 $cm^{-1}$ range for argon matrixes containing ICN and ozone after (a) deposition, (b) $\lambda > 350$ nm photolysis (ICN/$^{16}O_3$/Ar), (c) $\lambda > 350$ nm photolysis (ICN/$^{18}O_3$/Ar), and (d) $\lambda > 350$ nm photolysis (ICN/$^{16}O_{3-x}{}^{18}O_x$/Ar).

replaced by a $^{16}O_3/^{18}O_3$ mixture, many doublets appear which incorporate the $^{16}O$ and $^{18}O$ isotopomer bands in the experiments with pure isotopic ozone ($^{16}O_3$ and $^{18}O_3$) (Table 4 and Figure 3). These features suggest that only a single oxygen atom is present in the photoproduct, which further supports the attribution of bands to an INCO species. The wavenumbers of these INCO bands compare extremely well with those obtained for halogen isocyanate molecules, XNCO (X = Cl, Br, or I), in the vapor state.[17] The $^{18}O$ shift observed for the $\nu_{N=C}$ (of the −NCO moiety) of BrNCO vapor[18] is 22.1 $cm^{-1}$ and clearly relates to that observed in this work for INCO, viz., $\nu_{N=C} =$ 2196.9 $cm^{-1}$ (INC$^{16}$O), $\nu_{N=C} = 2177.0$ $cm^{-1}$ (INC$^{18}$O), and $^{18}O$ shift = 19.9 $cm^{-1}$. The wavenumbers of the −NCO group vibrations are very similar for each of the halogen isocyanates, and hence, changing the halogen atom, X, does not significantly change the electronic structure. The formation of $\nu_{N=C}$ bands at the expense of ozone bands can be seen in Figure 4.

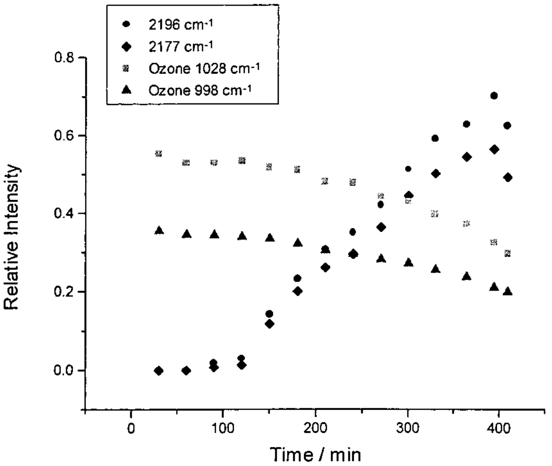


**Figure 4.** IR absorbance for the new $\nu_{N=C}$ bands of INC$^{16}$O and INC$^{18}$O at 2196 and 2177 $cm^{-1}$, respectively, and for the depleting ozone ($\nu_3$) bands at 1028 and 998 $cm^{-1}$ as a function of photolysis time.

The wavenumbers of the fundamentals of halogen nitrile oxides have been determined previously;[19,20] thus, $\nu_{C\equiv N}$, $\nu_{N-O}$, and $\delta_{CNO}$ occur at ~2260−2220, ~1345−1305, and ~465−420 $cm^{-1}$, respectively. The formation of iodonitrile oxide ($I-C\equiv N \rightarrow O$) upon photolysis might also have been expected, but no bands attributable to this species were detected in the IR spectra. However, it is possible that ICNO could exist in the matrix as a transition-state intermediate, leading to the formation of the more stable iodoisocyanate INCO (this is discussed further in the section on the photochemical pathway).

Further photolysis of ICN/$O_3$ matrixes with Pyrex-filtered radiation ($\lambda > 290$ nm) gave rise to new bands in the carbonyl region of the infrared spectrum (Table 5), the intensities of which continued to increase after subsequent quartz-filtered ($\lambda > 240$ nm) irradiation (Figure 5). In fact, several very weak and weak bands assigned to $\nu_{C=O}$ appeared in the spectrum between 1787.9 and 1779.3 $cm^{-1}$, and they are due to different carbonyl species occupying different matrix sites. Upon $^{18}O$ substitution, many carbonyl bands appeared between 1742.2 and 1736.9 $cm^{-1}$ with $^{18}O$ isotopic shifts of ca. 42 $cm^{-1}$. In the mixed-ozone experiment, both sets of bands were detected, indicating that only one $^{16}O$ atom or one $^{18}O$ atom is present in the molecule. The majority of these $\nu_{C=O}$ bands are attributed to an iodocarbonyl isocyanate species, IC(O)NCO, on the basis of similarities with analogous fluorocarbonyl isocyanate, chlorocarbonyl isocyanate, and bromocarbonyl isocyanate species studied elsewhere.[21−24] Comparing the $\nu_{C=O}$ values (Table 5) for IC(O)NCO (1787.9−1779.3 $cm^{-1}$) and BrC(O)NCO (1814.2 and 1807.4 $cm^{-1}$) with the gas-phase values for *trans*-FC(O)NCO (1879 $cm^{-1}$),[21] *trans*-ClC(O)NCO (1817 $cm^{-1}$),[21] and matrix-isolated *trans*-BrC(O)NCO (1813 $cm^{-1}$),[24] we see that the wavenumbers of $\nu_{C=O}$ bands for XC(O)NCO species decrease in the following order: X = F > Cl > Br > I. Halogen carbonyl isocyanates exist in either a cisoid or a transoid conformation whereby the −NCO group adopts either a cis or trans orientation with respect to the carbonyl group. The $\nu_{C=O}$ vibration of the known cisoid conformers occurs 20−30 $cm^{-1}$ below that of transoid ones. This shows evidence for the presence of one

**TABLE 5: Infrared Bands (cm$^{-1}$) Formed after Pyrex-Filtered ($\lambda$ > 290 nm) Photolysis of ICN/O$_3$ Matrixes at 14 K**

| $^{16}$O$_3$/Ar | $^{18}$O$_3$/Ar | $^{16}$O$_{3-x}$$^{18}$O$_x$/Ar | assignment |
|---|---|---|---|
| 2205.6 w | | 2205.6 vw | |
| | | 2202.3 vw | |
| 2200.5 ms | | 2200.9 mw | $\nu_{\mathrm{N=C}}$ ($-$NC$^{16}$O) |
| | | 2182.8 vw | |
| | 2180.9 mw | 2181.3 w | $\nu_{\mathrm{N=C}}$ ($-$NC$^{18}$O) |
| 2137.6 vw | | | $\nu_{\mathrm{C\equiv O}}$ (CO) |
| 1787.9 w | | 1787.9 w | $\nu_{\mathrm{C=^{16}O}}$[a] |
| 1786.1 w, sh | | | |
| 1785.0 vw, sh | | 1785.8 mw | |
| 1783.7 vw, sh | | 1784.2 w | |
| 1780.8 vw | | 1780.8 vw | |
| 1779.3 w | | 1779.3 vw | |
| | 1742.2 vw, sh | 1741.0 w, sh | $\nu_{\mathrm{C=^{18}O}}$[a] |
| | 1741.2 vw | 1740.0 w | |
| | 1740.2 vw, sh | 1739.0 vw, sh | |
| | 1739.0 vw | 1737.9 vw, sh | |
| | 1738.1 vvw | 1736.9 vw, sh | |
| | 1736.9 vw | 1734.6 vw | |
| | | 1733.5 vw | |
| | | 1279.6 vw, sh | |
| 1278.3 w | | 1278.4 vw | $\nu_{\mathrm{C=O}}$ ($-$NC$^{16}$O) |
| | 1230.6 vw | 1231.0 vvw | $\nu_{\mathrm{C=O}}$ ($-$NC$^{18}$O) |
| 833.3 vw | | | $\nu_{\mathrm{NC}}$ (NCN) ? |
| 832.5 vvw, sh | | | |
| 828.0 vvw | | 828.3 vvw | |
| 825.5 vvw | | 825.3 vvw | |
| | | 823.8 vvw | |
| | | 822.0 vvw | |
| | | 815.6 vw, sh | $\nu_{\mathrm{I^{16}O_2\,(asym)}}$[b] |
| 814.8 vw | | 814.8 vw, sh | |
| 813.4 vw | | 813.8 vw | |
| | | 812.5 vw | |
| | | 804.0 vvw | $\nu_{\mathrm{I^{16}O^{18}O\,(asym)}}$[b] |
| | | 801.7 vw, sh | |
| | | 800.6 vw | |
| | | 798.8 vw, sh | |
| | | 798.0 vw, sh | |
| | 787.6 vw | | $\nu_{\mathrm{I^{18}O_2\,(asym)}}$[b] |
| | 786.2 vw, sh | | |
| | 784.0 vw | | |
| 777.8 vvw | | | $\nu_{\mathrm{I^{16}O_2\,(sym)}}$ |

[a] Carbonyl bands attributable to IC(O)NCO, I$_2$NC(O)NCO, CO(NCO)$_2$, or $-$C=O···I$_2$ complexes. [b] Bands attributed to O$_2$ICN; such bands arise from matrix site effects and/or the formation of aggregates.

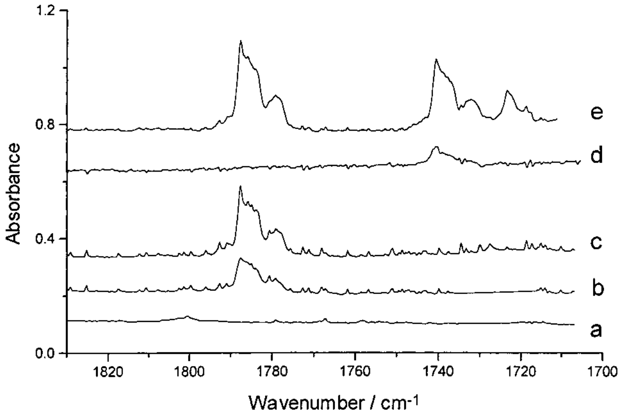


**Figure 5.** Infrared spectra of the carbonyl region of argon matrixes containing ICN and ozone after (a) deposition, (b) $\lambda$ > 240 nm photolysis for 30 min (ICN/$^{16}$O$_3$/Ar), (c) $\lambda$ > 240 nm photolysis for 12 h (ICN/$^{16}$O$_3$/Ar), (d) $\lambda$ > 240 nm photolysis for 30 min (ICN/$^{18}$O$_3$/Ar), and (e) $\lambda$ > 240 nm photolysis for 12 h (ICN/$^{16}$O$_{3-x}$$^{18}$O$_x$/Ar).

**TABLE 6: Infrared Bands (cm$^{-1}$) Detected after Prolonged Quartz-Filtered ($\lambda$ > 240 nm) Irradiation of ICN/O$_3$ Matrixes at 14 K**

| $^{16}$O$_3$/Ar | $^{16}$O$_{3-x}$$^{18}$O$_x$/Ar | O$_2$ | assignment |
|---|---|---|---|
| | | 2195.7 vw | $\nu_{\mathrm{N=C}}$ (IC(O)NCO) |
| | | 2189.4 vw | $\nu_{\mathrm{N=C}}$ (INCO) |
| | | 2138.7 w | $\nu_{\mathrm{C\equiv O}}$ (CO) |
| 2064.8 vvw, sh[a] | | | |
| 2062.7 vw[a] | | | |
| 2059.1 w | *b* | 2061.3 vw | $\nu_{\mathrm{C\equiv N}}$ (INC) |
| 2057.2 w[a] | | | |
| | | 1808.7 vw | $\nu_{\mathrm{C=^{16}O}}$[c] |
| | | 1807.6 w | |
| | | 1806.5 vw | |
| | | 1804.3 vw | |
| | 1723.6 w | 1793.0 vw | $\nu_{\mathrm{C=^{16}O}}$[d] |
| | 1722.4 w | 1789.4 vw | |
| | 1718.9 vw | 1784.5 vw, sh | |
| | | 1781.6 vw | |
| | 1717.6 vw | 1775.6 vw | |
| | | 1273.4 vw | $\nu_{\mathrm{C=O}}$ ($-$NC$^{16}$O) (IC(O)NCO) |
| | | 1272.3 wm | $\nu_{\mathrm{C=O}}$ ($-$NC$^{16}$O) (INCO) |
| | | 1268.6 vw[a] | |
| | | 843.6 vw | $\nu_{\mathrm{I^{16}O_2\,(asym)}}$ (O$_2$ICN) |
| | | 841.8 vvw | |
| | | 840.0 vw | |
| | | 834.2 vw | |

[a] Bands due to matrix site effects. [b] Bands in this region are obscured by precursor bands. [c] Carbonyl bands attributable to IC(O)NCO, I$_2$NC(O)NCO, CO(NCO)$_2$, or $-$C=O···I$_2$ complexes. [d] Bands are due to the cisoid conformer of IC(O)NCO.

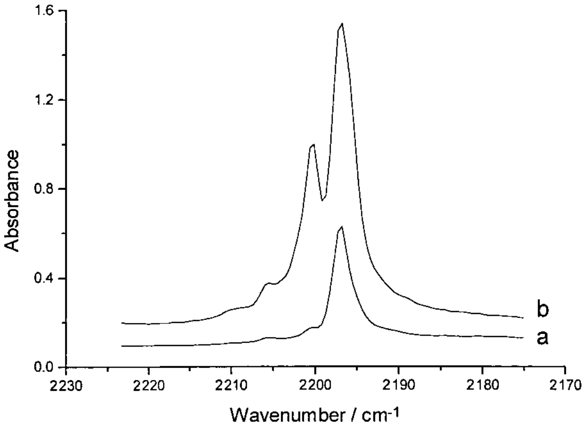


**Figure 6.** Infrared spectra of an ICN/$^{16}$O$_3$/Ar matrix after (a) $\lambda$ > 350 nm photolysis showing the $\nu_{\mathrm{N=C}}$ band of INCO and (b) $\lambda$ > 240 nm photolysis showing another $\nu_{\mathrm{N=C}}$ band, this time belonging to IC(O)NCO.

isomer in the matrix, namely, the transoid. However, in one experiment (ICN/$^{16}$O$_{3-x}$$^{18}$O$_x$/Ar), prolonged quartz irradiation for 12 h led to the appearance of bands around 1723−1717 cm$^{-1}$, showing a ~20 cm$^{-1}$ shift from those of the transoid conformer, and are thus attributed to the cisoid conformer (Table 6 and Figure 5). Durig et al. showed that the transoid conformer is the more stable of the two,[22,23] a conclusion which is consistent with the formation and assignment of bands in these experiments. The bands at 2200.5 and 1278.3 cm$^{-1}$ are assigned to $\nu_{\mathrm{N=C}}$ and $\nu_{\mathrm{C=O}}$ ($-$NCO) of IC(O)NCO, respectively, since as photolysis times increase, they continue to grow relative to those at 2196.9 and 1273.2 cm$^{-1}$ of INCO, respectively (Table 5 and Figure 6). The $^{18}$O counterparts for $\nu_{\mathrm{N=C}}$ and $\nu_{\mathrm{C=O}}$, attributed to IC($^{18}$O)NC$^{18}$O, appeared at 2180.9 and 1230.6 cm$^{-1}$, respectively. These NCO bands first appeared after Pyrex-filtered photolysis and continued to grow upon quartz-filtered irradiation. The characteristic $\nu_{\mathrm{C-N}}$ band of IC(O)NCO could not be detected in these experiments because strongly absorbing ozone bands appear in the same region.

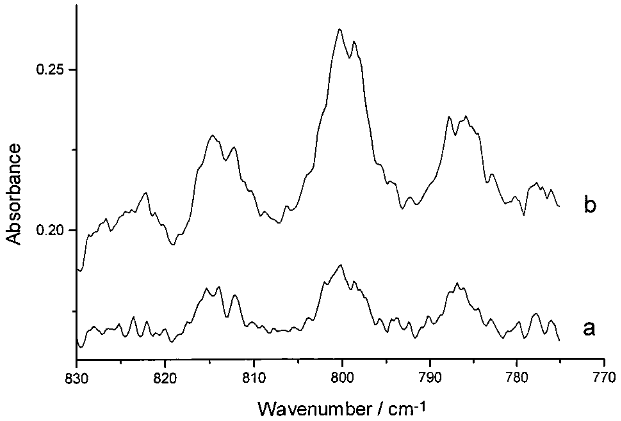


**Figure 7.** Infrared spectra of an ICN/$^{16}O_{3-x}{}^{18}O_x$/Ar matrix after (a) Pyrex-filtered photolysis ($\lambda$ > 290 nm) and (b) quartz-filtered photolysis ($\lambda$ > 240 nm), showing $\nu_{IO_2}$ isotopomer bands in a 1:2:1 ratio.

Other new bands, growing very slowly after Pyrex-filtered irradiation and much more rapidly after quartz-filtered irradiation, were situated between 833.3 and 777.8 cm$^{-1}$ ($^{16}O_3$ experiments) and between 804.6 and 784.0 cm$^{-1}$ ($^{18}O_3$ experiments) (Table 5). Those occurring very weakly at 814.8 and 813.4 cm$^{-1}$ are assigned to the asymmetric $-IO_2$ stretch of an iodyl species, Z$-IO_2$; the $^{18}$O counterparts occurred between 787.6 and 784.0 cm$^{-1}$. There is good agreement between the wavenumbers of $\nu_{IO_2}$ bands for Z$-IO_2$ and those for other iodyl species.[1,4−6,25] Moreover, a triplet of bands in a 1:2:1 ratio appeared in the 1:1 mixed-ozone experiment, which indicates that two symmetrically placed oxygen atoms contribute to $\nu_{IO_2}$ (Figure 7). Bands belonging to the symmetric stretch of the $-IO_2$ unit were too weak to be detected in the $^{18}$O experiments. Although it is possible that the bands in this region could alternatively belong to the $-$C(O)I deformation of IC(O)NCO—cf. fluorocarbonyl isocyanate[22] and chlorocarbonyl isocyanate[23]—the presence of a 1:2:1 triplet in the ICN/$^{16}O_{3-x}{}^{18}O_x$ experiment and the fact that no such bands appear in this region for BrCN/$O_3$ experiments make such an assignment unlikely. Extremely weak bands appearing between 833.3 and 825.5 cm$^{-1}$ are tentatively assigned to the NC stretch (NCN) of carbonyl diisocyanate CO(NCO)$_2$, cf. in the gas phase (831 and 827 cm$^{-1}$) and as a liquid (824 cm$^{-1}$).[26] Furthermore, the $\nu_{NC}$ (NCN) bands could also arise from the dimer I$_2$NC(O)NCO, once produced by Birkenbach et al. as a result of INCO polymerization.[27] These bands also appeared in the mixed-ozone experiment but were too weak for detection in the $^{18}O_3$ experiments. The presence of CO(NCO)$_2$ or I$_2$NC(O)NCO could be responsible for some of the many carbonyl bands in the IR spectra ($\nu_{C=O}$ of CO(NCO)$_2$ occurs at 1772 cm$^{-1}$).[26] Warming the matrix caused the intensities of some $\nu_{C=O}$ bands of IC(O)NCO to increase slightly at the expense of the $\nu_{N=C}$ bands of INCO, indicating a thermally induced route from the isocyanate to the carbonyl isocyanate.

In cases where the concentration of ICN was high, a weak band at 2059.1 cm$^{-1}$ was formed after prolonged UV photolysis and assigned to the $\nu_{C\equiv N}$ of INC (Table 6). Thus, any uncomplexed ICN in ICN/$O_3$ matrixes will photoisomerize to form INC in the same way as ICN isolated in argon.

Prolonged quartz-filtered ($\lambda$ > 240 nm) photolysis of ICN deposited in solid oxygen rather than in ozone/Ar matrixes was required before any new bands were formed (Table 6), and these were assigned on the basis of their resemblance to those from the ICN/$O_3$ experiments. The oxygen matrix, like the ozone/Ar matrix, consequently acts as an oxygen atom source, but unlike the situation with ozone, no complex is formed; thus, very harsh photolysis conditions are required to form INCO, IC(O)NCO, and O$_2$ICN.

**TABLE 7: Infrared Bands (cm$^{-1}$) Formed after Quartz-Filtered ($\lambda$ > 240 nm) Irradiation of BrCN/$O_3$ Matrixes at 14 K**

| $^{16}O_3$/Ar | $^{18}O_3$/Ar | $^{16}O_{3-x}{}^{18}O_x$/Ar | assignment |
|---|---|---|---|
| | | 2223.9 vw | $\nu_{C\equiv N}$ (BrCNO) ? |
| | | 2202.7 vw[a] | |
| 2194.5 w, sh | | 2194.0 vw, sh | $\nu_{N=C}$ ($-NC^{16}O$) (BrC(O)NCO) |
| 2193.9 mw, sh[a] | | | |
| 2192.4 m, sh[a] | | 2192.4 w, sh[a] | |
| 2191.9 m | | 2191.9 wm | $\nu_{N=C}$ ($-NC^{16}O$) (BrNCO) |
| | 2172.9 w, sh[a] | | |
| | 2171.6 w | 2172.2 w | $\nu_{N=C}$ ($-NC^{18}O$) (BrC(O)NCO) |
| | 2170.3 m | 2170.4 wm | $\nu_{N=C}$ ($-NC^{18}O$) (BrNCO) |
| | 2169.6 mw, sh[a] | 2169.7 wm[a] | |
| 2138.6 vw | | | $\nu_{C\equiv O}$ (CO) |
| 1814.2 vw | | | $\nu_{C={}^{16}O}$ (BrC(O)NCO) |
| 1807.4 w[a] | | 1807.4 vw[a] | |
| | 1723.3 vw | 1723.3 vw | $\nu_{C={}^{18}O}$ (BrC(O)NCO) |
| 1299.4 vw[a] | | 1303.1 vw[a] | |
| 1292.6 vw[a] | | | |
| 1290.8 wm | | 1291.0 vw | $\nu_{C=O}$ ($-NC^{16}O$) (BrC(O)NCO) |
| 1280.1 wm[a] | | 1278.6 vw[a] | |
| 1272.8 w | | 1272.8 w | $\nu_{C=O}$ ($-NC^{16}O$) (BrNCO) |
| | 1252.5 w | 1255.6 vw | $\nu_{C=O}$ ($-NC^{18}O$) (BrC(O)NCO) |
| | 1231.2 w | 1232.1 vw | $\nu_{C=O}$ ($-NC^{18}O$) (BrNCO) |
| 800.9 vvw | | | $\nu_{Br-C}$ (BrC(O)NCO) ? |
| 784.7 vvw[a] | | | |
| 592.2 vw[a] | | | |
| 591.2 vw | *b* | *b* | $\gamma_{NCO}$ (o$-$o-p)[c] (BrNCO) |
| 587.0 vw[a] | | | |

[a] Bands are due to matrix site effects or to aggregates. [b] Bands are too weak to detect. [c] $\delta_{NC^{16}O}$ (i$-$p) and $\delta_{NC^{18}O}$ (i$-$p) bands are obscured by CO$_2$ impurity bands at ca. 667 cm$^{-1}$.

**Photolysis of BrCN/$O_3$ Matrixes.** Photolysis of argon matrixes containing BrCN and ozone using radiation with varying wavelengths ($\lambda$ > 650 nm, $\lambda$ > 410 nm, $\lambda$ > 350 nm, and $\lambda$ > 290 nm) did not produce any new bands; only after quartz-filtered irradiation ($\lambda$ > 240 nm) for longer than 60 min were any produced (Table 7). Of these, the medium bands at 2191.9 cm$^{-1}$ with $^{16}O_3$ and at 2170.3 cm$^{-1}$ with $^{18}O_3$ were assigned to the $\nu_{N=C}$ of BrNC$^{16}$O and BrNC$^{18}$O, respectively. Furthermore, only two bromoisocyanate isotopomer bands appeared in this region in the mixed-ozone ($^{16}O_{3-x}{}^{18}O_x$) experiment, thus confirming the contribution of only one oxygen atom to the vibrational mode, $\nu_{N=C}$, of $-$NCO (Figure 8). The observed $^{18}$O shift of 21.6 cm$^{-1}$ is in good agreement with that calculated for BrNC$^{16/18}$O (22 ± 2 cm$^{-1}$).[18] The $\nu_{N=C}$ value for BrNC$^{16}$O compares well with that for BrNCO in the gas phase (2198.0[17] and 2199 cm$^{-1}$, respectively),[18] in a neon matrix (2196.0 cm$^{-1}$),[18] in an argon matrix (2191.9 cm$^{-1}$),[18] and condensed on a KBr disk (2164 cm$^{-1}$).[28] In these cases, bromoisocyanate was prepared either by the reaction of bromine vapor with silver isocyanate, AgNCO,[28] or by the vacuum pyrolysis of tribromoisocyanuric acid, (BrNCO)$_3$.[29] Hence, the work presented here demonstrates for the first time the formation

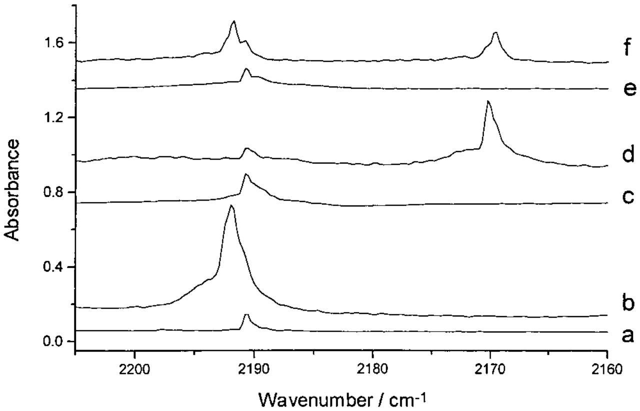


**Figure 8.** Infrared spectra in the 2205−2160 cm$^{-1}$ range for argon matrixes containing BrCN and ozone after (a) deposition (BrCN/$^{16}$O$_3$/Ar), (b) $\lambda > 240$ nm photolysis for 24 h (BrCN/$^{16}$O$_3$/Ar), (c) deposition (BrCN/$^{18}$O$_3$/Ar), (d) $\lambda > 240$ nm photolysis for 12 h (BrCN/$^{18}$O$_3$/Ar), (e) deposition (BrCN/$^{16}$O$_{3-x}$$^{18}$O$_x$/Ar), and (f) $\lambda > 240$ nm photolysis for 8 h (BrCN/$^{16}$O$_{3-x}$$^{18}$O$_x$/Ar).

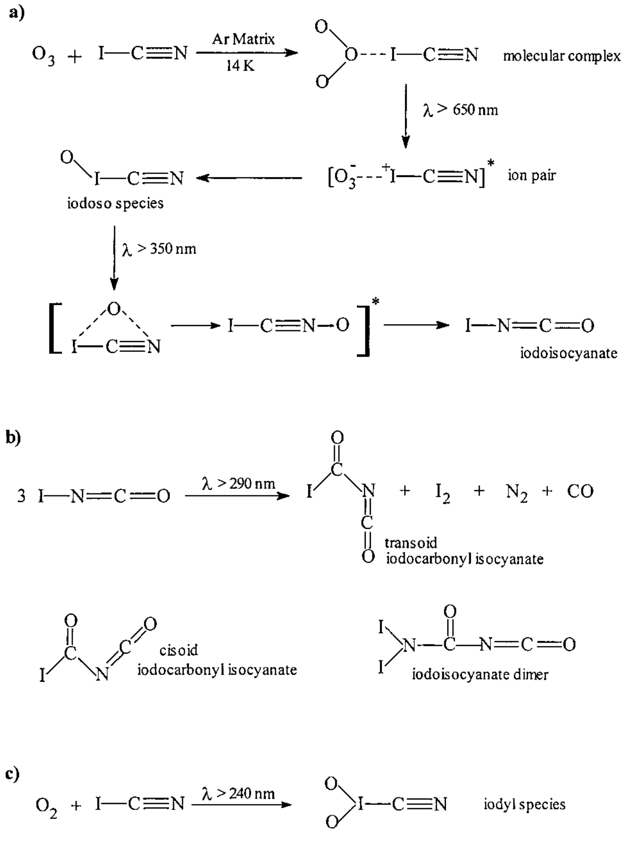
of BrNCO in solid matrixes using the photochemical reaction between ozone and bromine cyanide, BrCN.

Other bands that were detected after quartz-filtered photolysis of the matrix could also be attributed to BrNCO. These include very weak to weak-medium bands situated between 1299.4 and 1272.8 cm$^{-1}$ (the $^{18}$O counterparts occurring at 1252.5 and 1231.2 cm$^{-1}$) and assigned to the C=O stretch of BrNCO; the large number of such bands is due to the presence of different matrix sites and possible aggregates of bromoisocyanate (Table 7). Very weak bands around 591.2 cm$^{-1}$ are assigned to the out-of-plane bend, $\gamma_{\mathrm{NCO}}$; these bands compare well with those detected elsewhere for BrNCO.[17,18,28] However, in the $^{18}$O$_3$ and $^{16}$O$_{3-x}$$^{18}$O$_x$ experiments, $\gamma_{\mathrm{NCO}}$ bands were too weak to be detected. The Br−N stretch, $\nu_{\mathrm{Br-N}}$, expected to occur at ~500 cm$^{-1}$, was too weak to be detected.

In a mixed-ozone experiment, a very weak band at 2223.9 cm$^{-1}$ is cautiously assigned to $\nu_{\mathrm{C\equiv N}}$ of the bromonitrile oxide isomer, BrCNO. Its weakness and the fact that it did not appear in the other spectra suggest that the photoinduced formation of the isocyanate is the favored pathway.

Like the ICN/O$_3$ system, new bands also appeared in the carbonyl region after UV irradiation of BrCN/O$_3$/Ar matrixes. In this case, the $\nu_{\mathrm{C=O}}$ bands occurred at 1814.2 and 1807.4 cm$^{-1}$ (Table 7) and are attributed to the stable transoid conformer of bromocarbonyl isocyanate BrC(O)NCO. In the $^{18}$O$_3$ experiments, the $\nu_{\mathrm{C=O}}$ band for the isotopomer BrC($^{18}$O)NC$^{18}$O appeared at 1723.3 cm$^{-1}$, while in the mixed-ozone experiment, both isotopomer bands were present, at 1807.4 and 1723.3 cm$^{-1}$. The $\nu_{\mathrm{C=O}}$ values for BrC(O)NCO compare well with those for IC(O)NCO discussed earlier and with those for analogous species in the vapor phase studied elsewhere, viz., FC(O)NCO,[21,22] ClC(O)NCO,[21,22] and BrC(O)NCO.[24,30] Some new $\nu_{\mathrm{N=C}}$ bands were detected at 2194.5 and 2193.9 cm$^{-1}$ and are also attributed to BrC(O)NCO. These and analogous bands appear in the $^{18}$O-enriched matrixes and are listed in Table 7. Again, no bands could be assigned to the characteristic C−N stretch of the halogen carbonyl isocyanate due to the presence of ozone bands in the expected region. In one experiment, extremely weak bands were detected at 800.9 and 784.7 cm$^{-1}$ and are tentatively assigned to the Br−C stretch of BrC(O)NCO, due to their resemblance to the $\nu_{\mathrm{Br-C}}$ band at 775 cm$^{-1}$ for BrC(O)NCO in the gas phase[30] (none of the $\nu_{\mathrm{Br-C}}$ bands showed evidence for bromine isotopic structure). Alternatively, it is possible the bands in this region could also arise from a Br−O stretch ($\nu_{\mathrm{Br-O}}$), cf. spectra of Br−O bonded species in argon matrixes elsewhere (804 cm$^{-1}$).[31,32] However, no bands attributed to other isocyanates were detected, nor were any clearly identifiable bands found belonging to Z−BrO or Z−BrO$_2$ species, unlike the case with iodine cyanide and ozone. Furthermore, unlike the case with ICN and ozone, BrCN did not form a complex with ozone. Consequently, the BrCN/O$_3$ matrixes required intense UV irradiation for many hours before the precursors would react. Warming the matrix caused the intensities of $\nu_{\mathrm{N=C}}$ bands of BrNCO to decrease slightly and those of $\nu_{\mathrm{C=O}}$ bands of BrC(O)NCO to increase slightly.

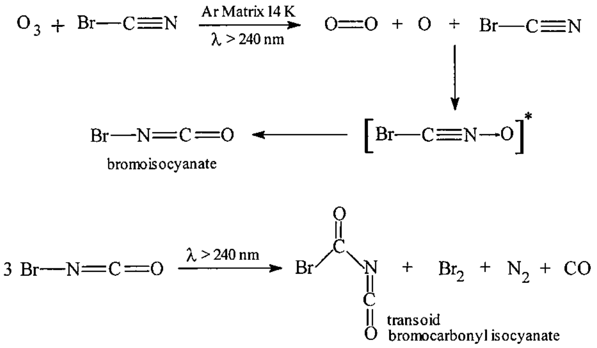
**SCHEME 1**



Photolysis of BrCN in solid oxygen matrixes did not result in reaction, even after tens of hours of intense UV irradiation. However, solid oxygen matrixes are not very transparent, thus adding to the difficulty of observing any possible new bands.

**Photochemical Pathway.** *ICN and O$_3$.* The first step in the photochemical interconversion (Scheme 1a) is the formation of a weak complex between ICN and ozone after co-deposition of the two precursors in solid argon. The complex is of the type O$_3$···ICN because an I−O bond forms first; after irradiation ($\lambda > 650$ nm) via a charge-transfer-type intermediate, the iodoso species OI−CN is produced. Photolysis with shorter-wavelength radiation ($\lambda > 350$ nm) results in the destruction of OI−CN and, at the same time, the formation of INCO, thus demonstrating a link between these two species. The photoinduced conversion of OI−CN into INCO is considered to take place by the formation of a cyclic intermediate to form the N−O bond of the ICNO intermediate, which then readily isomerizes into the isocyanate INCO. Such rearrangements can occur via the conversion of the nitrile oxide to an oxazirene, which converts into an acylnitrene and then rearranges to the isocyanate.[20] Other possible mechanisms are discussed elsewhere.[33] Previous studies[20,33,34] and the work presented here have been unable to generate −CNO in concentrations sufficient for infrared detec-

**SCHEME 2**



tion due to the efficient photoisomerization process in matrixes; the same radiation that produces −CNO results in the isomerization of the latter to −NCO.

Further Pyrex-filtered ($\lambda > 290$ nm) and quartz-filtered ($\lambda > 240$ nm) photolysis produced carbonyl bands belonging to the transoid conformer of iodocarbonyl isocyanate, IC(O)NCO (Scheme 1b). Only the transoid conformer is observed due to its stability being than that of the cisoid (cisoid bands were only observed after prolonged quartz-filtered irradiation in a single experiment). Upon photolysis of INCO, the reaction mechanism is believed to proceed by a series of radical interconversions,[35,36] forming other products such as $N_2$, $I_2$, and CO on route; these could complex with the carbonyl group and contribute to the large number of $\nu_{C=O}$ bands detected. The detection of CO in the matrix after photolysis is consistent with the proposed mechanism. There is a possibility that the dimer, $I_2NC(O)NCO$, is formed since bands are detected which tentatively may be assigned to $\nu_{NC}$ (NCN); these bands could also belong to carbonyl diisocyanate, $CO(NCO)_2$. At this stage, no evidence is available to distinguish between the two possibilities, although it is certain that more than one species is responsible for the many $\nu_{C=O}$ bands detected.

Production of the iodyl bands ($\nu_{IO_2}$) after Pyrex-filtered irradiation ($\lambda > 290$ nm) is believed to occur via the reaction between the isolated ICN and the excited molecular oxygen to form $O_2ICN$ (Scheme 1c). Molecular oxygen could also react with INCO (formed after $\lambda > 350$ nm irradiation) to form $O_2$-INCO, although the intensities of INCO bands were seen to increase after Pyrex-filtered photolysis rather than decrease, as would be the case if this reaction had occurred.

*BrCN and $O_3$.* Unlike the reaction between ICN and ozone, which is wavelength-dependent, that between BrCN and ozone is time-dependent (Scheme 2). There was no evidence for the formation of a complex between BrCN and ozone nor any to suggest that any Br−O bonds are formed. Extreme photolysis conditions ($\lambda > 240$ nm for many hours) were required to produce any new bands, with those that eventually formed belonging to bromoisocyanate, BrNCO. Initially, UV irradiation causes ozone to dissociate, forming oxygen atoms which then react with BrCN to form the intermediate BrCNO. Again, photoisomerization occurs at the same time as oxidation, and hence, only BrNCO is detected. Alternatively, cleavage of the Br−C bond could occur, and so, O, Br, and CN could recombine in the matrix cage, forming either BrCNO or BrNCO, the former then photoisomerizing to the isocyanate. However, the fact that no bands assignable to either BrOCN or BrONC were detected makes this pathway seem unlikely.

Carbonyl bands were also detected and are attributed to the stable transoid conformer of bromocarbonyl isocyanate, BrC(O)NCO, on the bases that a similar photoinduced reaction has been performed elsewhere[29] and that chlorocarbonyl isocyanate ClC(O)NCO is formed after the photolysis ($\lambda > 280$ nm) of chloroisocyanate ClNCO.[35,36] The reaction mechanism is considered to progress via a sequence of radical interconversions, with the formation of other products such as $N_2$, $Br_2$, and CO (bands attributed to CO were detected in some experiments). The carbonyl bands could also belong to the dimer of bromoisocyanate, $Br_2NC(O)NCO$, which has been identified earlier by Gottardi[29] after polymerization of BrNCO. However, the fact that carbon monoxide was observed suggests that the formation of BrC(O)NCO is the favored product.

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