

## New Members of an Old Family: Isolation of IC(O)Cl and IC(O)Br and Evidence for the Formation of Weakly Bound Br $\cdots$ CO

Rosana M. Romano,<sup>†</sup> Carlos O. Della Védova,<sup>\*†‡</sup> Anthony J. Downs,<sup>§</sup> Yeny A. Tobón,<sup>†‡</sup> and Helge Willner<sup>||</sup>

CEQUINOR (UNLP–CONICET) and Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP–CIC–CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, (1900) La Plata, Argentina, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U.K., and FB C, Anorganische Chemie, Bergische Universität Wuppertal, Gaußstr. 20, D-42097 Wuppertal, Germany

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The photochemically induced reactions of a dihalogen, XY, with CO isolated together in an Ar matrix at about 15 K lead to the formation of carbonyl dihalide molecules XC(O)Y, where X and Y may be the same or different halogen atoms, Cl, Br, or I. In addition to the known compounds OCCl<sub>2</sub>, OCB<sub>2</sub>, and BrC(O)Cl, the carbonyl iodide chloride, IC(O)Cl, and carbonyl iodide bromide, IC(O)Br, compounds have thus been identified for the first time as products of the reactions involving ICl and IBr, respectively. The first product to be formed in reactions with Cl<sub>2</sub>, BrCl, or ICl is the ClCO $\cdot$  radical, which reacts subsequently with a second halogen atom to give the corresponding carbonyl dihalide [OCCl<sub>2</sub>, BrC(O)Cl, or IC(O)Cl]. The analogous reaction with Br<sub>2</sub> affords, in low yield, the unusually weakly bound BrCO $\cdot$  radical, better described as a van der Waals complex, Br $\cdots$ CO. The changes have been followed and the products characterized experimentally by their infrared spectra, and the spectra have been analyzed in light of the results afforded by ab initio (Hartree–Fock and Moeller–Plesset second-order) and density functional theory calculations.

### Introduction

One of the greatest chemical challenges consists of the preparation and isolation of relatively small but hitherto unknown molecules. Several strategies typically exist for this purpose. On the other hand, it is commonly presumed that the apparent nonexistence of a particular member of an otherwise well-defined series reflects the failure of conventional methods of synthesis to deliver that compound, although the literature too often falls short of such reports. This may well be the case with the carbonyl dihalide family XC(O)Y that includes phosgene.<sup>1,2</sup> In principle, there are 10 members of this family, but as depicted in Scheme 1, only

8 are known and they are either partially or fully characterized at the present time. The two missing members are IC(O)Cl and IC(O)Br.

Some of these molecules have been investigated in the context of the mechanisms of reactions leading to the destruction of ozone. Thus, it is known that various halogen-containing molecules can act as reservoirs of halogen atoms. Chlorine and bromine atoms are the prime movers in forming reactive radicals that enter into catalytic cycles for ozone destruction in the stratosphere, but the roles of fluorine and iodine atoms have also been investigated, and these have the potential to act as secondary radical sources in the earth's atmosphere.<sup>2–8</sup>

Although seemingly unrelated, an earlier study of the matrix photochemistry of (chlorocarbonyl)sulfonyl bromide,

\* Author to whom correspondence should be addressed. E-mail: carlosdv@quimica.unlp.edu.ar.

<sup>†</sup> CEQUINOR (UNLP–CONICET).

<sup>‡</sup> Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP–CIC–CONICET).

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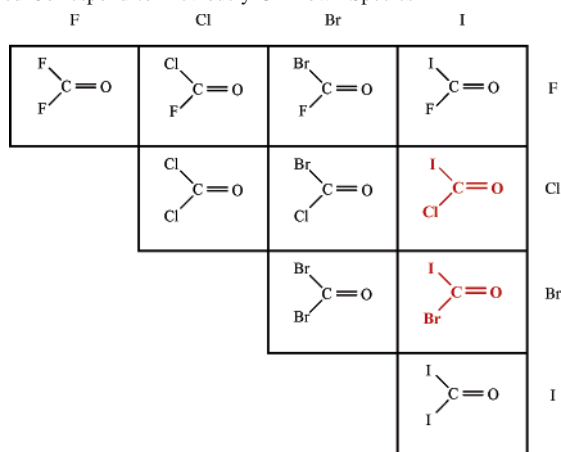
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**Scheme 1.** Members of the Carbonyl Dihalide Family. The Formulas in Red Correspond to Previously Unknown Species



ClC(O)SBr,<sup>9</sup> has served to point the way to a means of completing the carbonyl dihalide family. Broad-band UV–visible irradiation was then shown to lead not only to the partial transformation of the more stable syn form into the anti form of the molecule but also to the formation of its isomer BrC(O)SCI, as well as the photoevolution fragments BrCl, BrSCI, CO, and OCS. The mechanisms proposed<sup>9</sup> for the various processes imply active rather than passive roles for the stable products CO and OCS. Hence, it has already been shown, for example, that hitherto unknown compounds such as BrC(O)SBr can be formed under matrix conditions by the photoactivation of a dihalogen in the presence of OCS.<sup>10</sup>

Here, we report similar reactions involving a dihalogen and CO isolated together in an Ar matrix at about 15 K and show that broad-band UV–visible photolysis results in the formation of one or more carbonyl dihalides, XC(O)Y, where X and Y = Cl, Br, or I and may be the same or different atoms. Hence, carbonyl iodide chloride, IC(O)Cl, and carbonyl iodide bromide, IC(O)Br, two of the missing members of this well-known family of molecules, have finally been produced (by the reactions of CO with ICl and IBr, respectively). These and the known carbonyl dihalides OCCl<sub>2</sub>, OCB<sub>2</sub>, and BrC(O)Cl, formed in similar reactions involving the relevant halogen atoms, have been characterized experimentally by their infrared (IR) spectra and theoretically by the results of ab initio [Hartree–Fock (HF) and Moeller–Plesset second-order (MP2)] and density functional theory (DFT) calculations. As reported recently,<sup>11,12</sup> trapping XY and CO together in an Ar matrix results, prior to photolysis, only in the formation of a weakly bound adduct, XY⋯CO. The first product of photolysis when

either X or Y = Cl is the familiar radical ClCO<sup>•</sup>,<sup>13</sup> which subsequently takes up a second halogen atom to form the appropriate carbonyl dihalide XC(O)Cl (X = Cl, Br, or I). By contrast, the photoinduced reaction with Br<sub>2</sub> gives rise, initially, to the radical BrCO<sup>•</sup>, which has hitherto eluded detection; unlike its chloro counterpart, but in keeping with the results of earlier sophisticated quantum chemical calculations,<sup>14</sup> this is most aptly formulated as a weakly bound van der Waals complex, engaging CO to a Br<sup>•</sup> atom.

## Experimental Section

Commercial samples of ICl and IBr (Aldrich) were purified by repeated trap-to-trap condensation in vacuo, mainly to remove the I<sub>2</sub> impurity, the presence of which hampered photochemical studies by its inherently high absorption cross section throughout much of the visible and UV regions. Cl<sub>2</sub> and Br<sub>2</sub> (Aldrich) were used without further purification. BrCl was produced by mixing equimolar amounts of Cl<sub>2</sub> and Br<sub>2</sub>, leading to an equilibrium mixture of BrCl, Cl<sub>2</sub>, and Br<sub>2</sub>.<sup>15</sup> CO and Ar gases (BOC, research grade) were used without further purification.

Gas mixtures of the dihalogen or interhalogen molecules (XY), CO, and Ar, typically with the composition XY/CO/Ar = 1:1:200, were prepared by standard manometric methods. Each such mixture was deposited on a CsI window cooled to ca. 15 K by a Displex closed-cycle refrigerator (Air Products, model CS202), using the pulsed deposition technique.<sup>16,17</sup> Alternatively, a modified assembly was used in some experiments with IBr to overcome its low vapor pressure at ambient temperatures. In this case, the CO/Ar mixture was passed through a U trap containing IBr cooled to –45 °C before deposition on the CsI window, continuous deposition<sup>15</sup> being carried out at the rate of ca. 1–2 mmol h<sup>-1</sup>.

The IR spectrum of each matrix sample was recorded at a resolution of 0.5 cm<sup>-1</sup>, with 256 scans and a wavenumber accuracy of ±0.1 cm<sup>-1</sup>, using a Nicolet Magna-IR 560 FTIR instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000–400 cm<sup>-1</sup> and 600–250 cm<sup>-1</sup>, respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV–visible radiation (200 ≤ λ ≤ 800 nm) issuing from a Spectral Energy Hg–Xe arc lamp operating at 800 W. The output from the lamp was limited by a water filter to absorb infrared radiation and to minimize any heating effects. The IR spectrum of the matrix was then recorded at different times of irradiation to closely scrutinize any decay of the absorptions due to the reactants and the growth of absorptions due to the respective products.

All of the quantum chemical calculations were performed using the Gaussian 98 program system<sup>18</sup> under the Linda parallel execution environment using two coupled PCs. Different ab initio and DFT methods were tried, in combination with a 6-31+G\* basis set for C, O, and Cl atoms and a LANL2DZ basis set<sup>19</sup> including an effective core potential (ECP) for Br and I atoms. The ECP chosen is that proposed by Hay and Wadt,<sup>20</sup> which incorporates

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**Table 1.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-band UV–Visible Photolysis of an Ar Matrix Containing a Mixture of CO and Cl<sub>2</sub> at ca. 15 K

Ar matrix	assignment		wavenumbers reported
$\nu$ [cm <sup>-1</sup> ]	molecule	vibrational mode	previously
1877.1	CICO•	$\nu(\text{CO})$	1876.7 <sup>a</sup>
1845.2	OCCL <sub>2</sub>	$\nu_2 + \nu_5 + \nu_6$	1840.61 <sup>b</sup>
1840.8			1834.71 <sup>b</sup>
1839.1			1829.51 <sup>b</sup>
1834.9			
1829.8			
1818.3	OCCL <sub>2</sub>	$\nu(\text{CO}) (\nu_1)$	1815.58 <sup>b</sup>
1817.1			1814.78 <sup>b</sup>
1815.6			1814.26 <sup>b</sup>
1814.2			1813.56 <sup>b</sup>
1810.0			1810.12 <sup>b</sup>
1657.8	OCCL <sub>2</sub>	$2 \nu_5$	1652.00 <sup>b</sup>
1656.1			1650.98 <sup>b</sup>
1654.4			1650.56 <sup>b</sup>
1652.7			
1651.0			
1010.3	OCCL <sub>2</sub>	$\nu_2 + \nu_6$	1010.08 <sup>b</sup>
1004.2			1004.02 <sup>b</sup>
997.2			997.97 <sup>b</sup>
840.3	OCCL <sub>2</sub>	$\nu_{\text{as}}(\text{CCl}_2) (\nu_5)$	837.36 <sup>b</sup>
839.3			837.20 <sup>b</sup>
838.4			836.38 <sup>b</sup>
837.6			836.22 <sup>b</sup>
836.6			835.37 <sup>b</sup>
			835.23 <sup>b</sup>
810.0	OCCL <sub>2</sub>	$\nu_3 + \nu_6$	809.81 <sup>b</sup>
809.0			808.81 <sup>b</sup>
807.1			807.81 <sup>b</sup>
582.2	OCCL <sub>2</sub>	$\delta_{\text{oop}} (\nu_4)$	581.21 <sup>b</sup>
581.2			580.88 <sup>b</sup>
			580.56 <sup>b</sup>
570.3	OCCL <sub>2</sub>	$\nu_s(\text{CCl}_2) (\nu_2)$	568.29 <sup>b</sup>
569.3			564.75 <sup>b</sup>
565.7			561.12 <sup>b</sup>

<sup>a</sup> Reference 13. <sup>b</sup> Reference 24.

the mass velocity and Darwin relativistic effects. Representative levels of approximation are cited throughout this paper. Geometry optimizations were sought using standard gradient techniques by the simultaneous relaxation of all of the geometrical parameters. The calculated vibrational properties corresponded, in all cases, to potential energy minima for which no imaginary vibrational frequency was found. The wavenumbers of vibrational fundamentals calculated by HF methods were scaled by a factor of 0.9 to take account of their known overestimation of experimental (anharmonic) data.

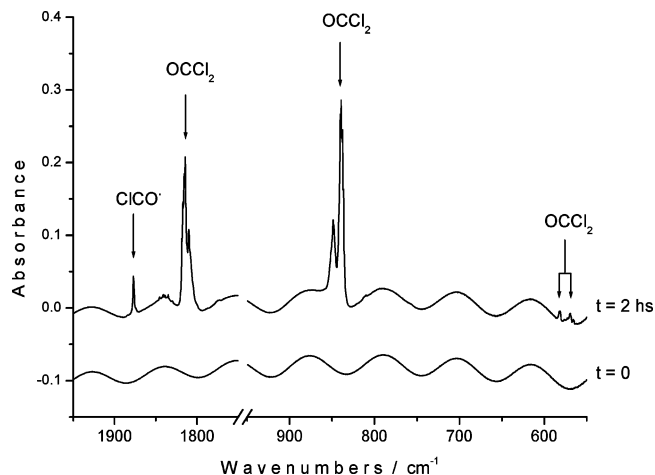
## Results and Discussion

To assist with the interpretation of the results of matrix experiments involving CO and the interhalogen molecules

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**Figure 1.** Fourier transform infrared spectra of an Ar matrix containing Cl<sub>2</sub> and CO (Cl<sub>2</sub>/CO/Ar = 1:1:200) (bottom) following deposition and (top) after 2 h of broad-band UV–visible photolysis.

ICl and IBr, we carried out similar experiments with CO, Cl<sub>2</sub>, and Br<sub>2</sub> or an equilibrium Cl<sub>2</sub>/Br<sub>2</sub> mixture (including BrCl as well as Cl<sub>2</sub> and Br<sub>2</sub>), which revealed the formation of known products. Accordingly, we consider first the results of these experiments.

(i) Cl<sub>2</sub> + CO. A mixture of Cl<sub>2</sub>, CO, and Ar, typically in the proportions 0.5:1:200, formed a solid matrix at ca. 15 K, which displayed only IR absorptions attributable to free CO (at 2138.2 cm<sup>-1</sup>)<sup>21</sup> and the weakly bound van der Waals complex OC••Cl<sub>2</sub> (at 2140.7 and 545.0/537.6 cm<sup>-1</sup>),<sup>11,12</sup> in addition to weak features arising from traces of H<sub>2</sub>O<sup>22</sup> and CO<sub>2</sub><sup>23</sup> impurities.

The subsequent irradiation of the matrix with broad-band UV–visible light (200 ≤ λ ≤ 800 nm) led, however, to drastic changes in the IR spectrum. Table 1 lists the wavenumbers of all of the new absorptions observed to develop under these conditions, together with literature data for both OCCL<sub>2</sub><sup>24</sup> and the CICO• radical<sup>13</sup> similarly isolated in Ar matrices. Four of these bands, centered near 1815, 838, 582, and 568 cm<sup>-1</sup>, are recognizable as the fundamentals  $\nu_1$ ,  $\nu_5$ ,  $\nu_4$ , and  $\nu_2$ , respectively, and four others, near 1838, 1654, 1004, and 809 cm<sup>-1</sup>, are recognizable as combinations or overtones of the OCCL<sub>2</sub> molecule<sup>24</sup> formed in what appeared to be a relatively efficient matrix reaction. All of them showed significant structures due, in part, to isotopic splitting (from <sup>35</sup>Cl/<sup>37</sup>Cl) and, in part, to matrix site effects.

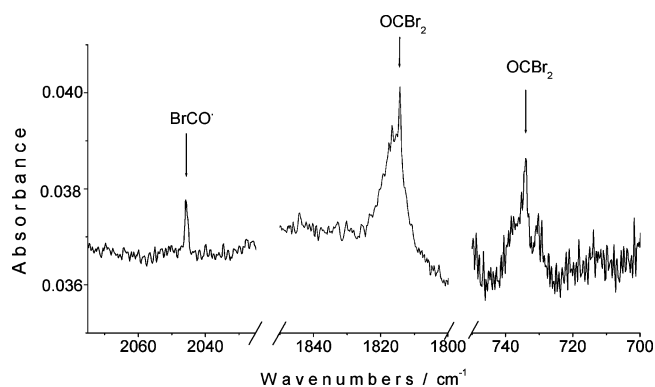
The first to appear, however, and plainly arising from a different product, was a band at 1877.1 cm<sup>-1</sup>, which, on the basis of evidence of its wavenumber, must arise from the chloroformyl radical CICO•. The other IR features characteristic of this species<sup>13</sup> were either masked by features due to OCCL<sub>2</sub> (at 570 cm<sup>-1</sup>) or were too weak to be detected

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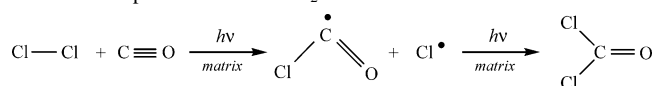
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**Figure 2.** Fourier transform infrared spectrum of an Ar matrix containing Br<sub>2</sub> and CO (Br<sub>2</sub>/CO/Ar = 1:1:200) after 2 h of broad-band UV–visible photolysis.

**Scheme 2.** Proposed Mechanism for the Formation of OCCl<sub>2</sub> in an Ar Matrix Doped with CO and Cl<sub>2</sub>



(near 330 cm<sup>-1</sup>). All of the new bands continued to grow, albeit at a rate that gradually tailed off, as a function of irradiation time. Figure 1 shows two different regions of the IR spectra of such a matrix, one immediately after deposition and the other after broad-band UV–visible irradiation for 2 h.

The intensities of the bands due to OCCl<sub>2</sub> and ClCO• varied with the photolysis time in a way suggesting that the radical is an intermediate stage in the formation of OCCl<sub>2</sub>, as represented in Scheme 2. By contrast, the spectra showed nothing to suggest that the OC••Cl<sub>2</sub> van der Waals complex plays a specific part in promoting the reaction, in that the relative intensities of the bands due to free CO and the complex remained more or less constant during the experiments. The results imply, therefore, that the reactions depend on the photodissociation of Cl<sub>2</sub> and the subsequent addition of the resulting Cl• atoms to either CO or ClCO•, with little contribution from the concerted addition of Cl<sub>2</sub> to CO.

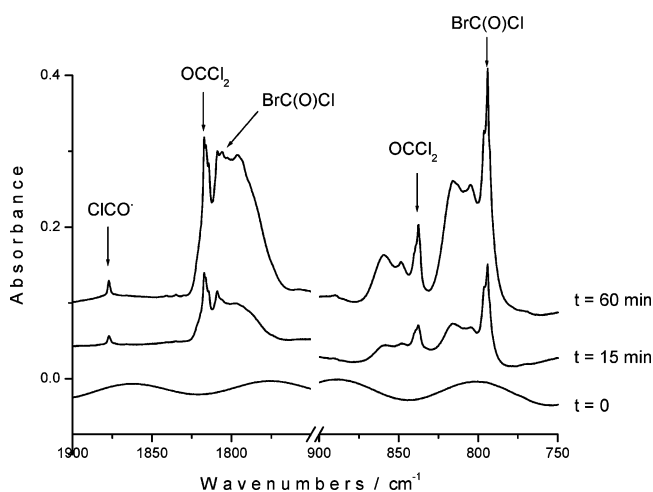
**(ii) Br<sub>2</sub> + CO.** Similar studies were carried out with matrixes formed by mixtures of Br<sub>2</sub>, CO, and Ar, typically in the proportions 1:1:200. The IR spectrum of the matrix immediately after deposition was dominated by two absorptions, one at 2138.2 cm<sup>-1</sup> due to free CO<sup>21</sup> and the other at 2144.1 cm<sup>-1</sup> due, in keeping with an earlier report,<sup>11,12</sup> to the OC••Br<sub>2</sub> van der Waals complex.

The exposure of such a matrix to broad-band UV–visible light produced only slight changes in the IR spectrum. Nevertheless, as illustrated in Figure 2, three new absorptions were observed to develop, all with very low intensities. These were located at 2045.7, 1816.6/1814.3, and 734.0 cm<sup>-1</sup> (see Table 2). The second and third absorptions can be identified with the ν(CO) and ν<sub>as</sub>(CBr<sub>2</sub>) fundamentals of OCBBr<sub>2</sub>, which, on the basis of evidence of an earlier report,<sup>25</sup> are responsible for the two most intense IR bands of this molecule isolated in an Ar matrix. With the product being formed in such low

**Table 2.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-band Photolysis of an Ar Matrix Containing a Mixture of CO and Br<sub>2</sub> at ca. 15 K

Ar matrix ν [cm <sup>-1</sup> ]	assignment		wavenumbers reported previously
	molecule	vibrational mode	
2045.7	BrCO•	ν(CO)	2082 <sup>a</sup>
1816.6	OCBr <sub>2</sub>	ν(CO) (ν <sub>1</sub> )	1816.0 <sup>b</sup>
1814.3			
734.0	OCBr <sub>2</sub>	ν <sub>as</sub> (CBr <sub>2</sub> ) (ν <sub>4</sub> )	734.4 <sup>b</sup>

<sup>a</sup> Calculated at the MP2 level of theory with aug-cc-pVDZ basis sets. Reference 14. <sup>b</sup> For OCBBr<sub>2</sub> isolated in an Ar matrix. Reference 25).



**Figure 3.** Fourier transform infrared spectra of an Ar matrix containing BrCl, Br<sub>2</sub>, Cl<sub>2</sub>, and CO (initial proportions Br<sub>2</sub>/Cl<sub>2</sub>/CO/Ar = 2:2:1:200) following deposition and after 15 and 60 min of broad-band UV–visible photolysis.

yields, we may reasonably suppose that the other bands are too weak to be detected.

The weak, sharp band at 2045.7 cm<sup>-1</sup> must originate in a different species, and an analogy with the Cl<sub>2</sub>/CO experiments suggests the bromoformyl radical BrCO•, which, to the best of our knowledge, has not been observed previously. In that case, BrCO• would be quite unlike ClCO•, with a ν(CO) wavenumber only 93 cm<sup>-1</sup> lower than that of free CO [compared with ClCO• for which ν(CO) is 262 cm<sup>-1</sup> lower than that in the parent molecule]. This suggests, in turn, only a weak interaction between the Br atom and the CO, which is, indeed, comparable with that in a monocarbonyl derivative of a noble transition metal [e.g., PdCO, PtCO, and AuCO, for which ν(CO) = 2045,<sup>26</sup> 2052,<sup>27</sup> and 2039<sup>28</sup> cm<sup>-1</sup>, respectively]. Hence, the product would appear to be more aptly described not as a bromoformyl radical but as a van der Waals complex in which the Br• atom is partnered by CO, or even as bromine carbonyl. This unexpected finding agrees well with the results of earlier high-level ab initio calculations,<sup>14</sup> which concluded that the lowest energy form of the BrCO• radical can be qualitatively described in just such a way, with a quasilinear structure, a Br•••C bond no shorter than 3.09 Å (cf. 1.86 Å for ClCO•),

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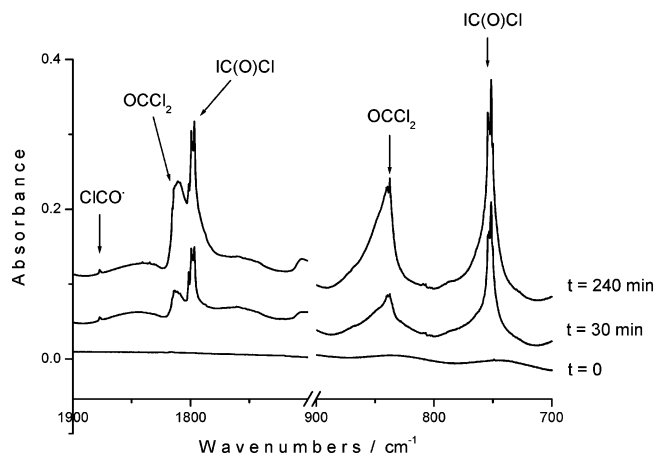
**Table 3.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV–Visible Photolysis of an Ar Matrix Containing a Mixture of CO, BrCl, Cl<sub>2</sub>, and Br<sub>2</sub> at ca. 15 K

Ar matrix $\nu$ [cm <sup>-1</sup> ]	assignment		wavenumbers reported previously
	molecule	vibrational mode	
1877.1	CICO•	$\nu$ C=O	1876.7 <sup>a</sup>
1840.9	OCCL <sub>2</sub>	$\nu_2 + \nu_5 + \nu_6$	1840.61 <sup>b</sup>
1834.9			1834.71 <sup>b</sup>
1829.8			1829.51 <sup>b</sup>
1817.1	OCCL <sub>2</sub>	$\nu$ C=O ( $\nu_1$ )	1815.58 <sup>b</sup>
1816.2			1814.78 <sup>b</sup>
1814.3			1814.26 <sup>b</sup>
1809.0			1813.56 <sup>b</sup>
			1810.12 <sup>b</sup>
1805.9	BrC(O)Cl	$\nu$ C=O	1828 <sup>c</sup>
1802.7			
1796.2			
1653.2	OCCL <sub>2</sub>	$2 \nu_5$	1652.00 <sup>b</sup>
1652.5			1650.98 <sup>b</sup>
			1650.56 <sup>b</sup>
1010.0	OCCL <sub>2</sub>	$\nu_2 + \nu_6$	1010.08 <sup>b</sup>
			1004.02 <sup>b</sup>
			997.97 <sup>b</sup>
890.0	complex ?		
859.5	complex ?		
848.5			
840.3	OCCL <sub>2</sub>	$\nu_{as}$ CCl <sub>2</sub> ( $\nu_5$ )	837.36 <sup>b</sup>
839.3			837.20 <sup>b</sup>
837.6			836.38 <sup>b</sup>
			836.22 <sup>b</sup>
			835.37 <sup>b</sup>
			835.23 <sup>b</sup>
815.9	complex ?		
804.8			
796.4	BrC(O)Cl	$\nu$ CCl	806 <sup>c</sup>
794.1			
792.6			
743.7	OCBr <sub>2</sub>	$\nu_{as}$ CBr <sub>2</sub> ( $\nu_4$ )	734.4 <sup>d</sup>
734.4			
582.2	OCCL <sub>2</sub>	$\delta$ oop ( $\nu_4$ )	581.21 <sup>b</sup>
			580.88 <sup>b</sup>
			580.56 <sup>b</sup>
568.5	OCCL <sub>2</sub>	$\nu_s$ CCl <sub>2</sub> ( $\nu_2$ )	568.29 <sup>b</sup>
			564.75 <sup>b</sup>
			561.12 <sup>b</sup>
546.6	BrC(O)Cl	$\delta$ oop	547 <sup>c</sup>
546.0			
545.1			
515.0	BrC(O)Cl	$\nu$ BrC	517 <sup>c</sup>
510.0			

<sup>a</sup> Reference 13. <sup>b</sup> Reference 24. <sup>c</sup> Gaseous molecule. References 2 and 29. <sup>d</sup> Reference 25.

and a binding energy on the order of only 1 kcal mol<sup>-1</sup>. The calculated  $\nu$ (CO) wavenumber is 2082 cm<sup>-1</sup>, with shifts of -62 and +165 cm<sup>-1</sup> relative to free CO and CICO•, respectively, at the same level of theory. There is, thus, satisfactory agreement with the corresponding experimental values of 2045.7, -93, and +169 cm<sup>-1</sup>.

The inefficiency of the photochemical reactions, in this case, made it impossible to meaningfully investigate either the decay of the reactants or the buildup of the products. There is no reason, however, to suppose that the reactions with Br<sub>2</sub> differ significantly from those with Cl<sub>2</sub>. The marked difference in yields must then reflect the reduced mobility of Br• compared to Cl• atoms in an Ar matrix, so that the photodissociation of Br<sub>2</sub> is largely hindered by the low probability of escape of a Br• atom from the matrix site of its formation.



**Figure 4.** Fourier transform infrared spectra of an Ar matrix containing ICl and CO (ICl/CO/Ar = 1:1:200) following deposition and after 30 and 240 min of broad-band UV–visible photolysis.

(iii) **BrCl + Cl<sub>2</sub> + Br<sub>2</sub> + CO.** Gaseous mixtures of Cl<sub>2</sub> and Br<sub>2</sub> give rise to an equilibrium between these two molecules and the interhalogen BrCl,<sup>15</sup> the components of which cannot be separated. When a gaseous mixture of Cl<sub>2</sub>, Br<sub>2</sub>, CO, and Ar, typically in the initial proportions 2:2:1:200, was deposited at ca. 15 K, the IR spectrum of the resulting matrix showed not only the absorption at 2138.2 cm<sup>-1</sup> characteristic of free CO but also three further absorptions in this region centered at 2148.3, 2144.3, and 2140.8 cm<sup>-1</sup>. As reported earlier,<sup>11,12</sup> these can be ascribed to the loosely bound 1:1 adducts OC•••BrCl, OC•••Br<sub>2</sub>, and OC•••Cl<sub>2</sub>, respectively. Bands associated with free and complexed BrCl were also observed near 430 cm<sup>-1</sup>.<sup>12</sup>

Figure 3 depicts parts of the IR spectra recorded for the matrix before and after broad-band UV–visible photolysis, whereas Table 3 summarizes the details of the absorptions associated with the various photoproducts. To the four guest species (BrCl, Cl<sub>2</sub>, Br<sub>2</sub>, and CO) initially present in one form or another were added, by photolysis, several different products. This gave rise to a relatively complex pattern of IR absorptions, reflecting both the overlapping of features due to different species [e.g., in the  $\nu$ (CO) and  $\nu$ (CCl) regions of the spectrum] and significant broadening of the individual features caused by the occupation of different sites made more numerous by the profusion of species now present in the matrix. The most prominent bands could be attributed, on the basis of the outcome of experiments involving Cl<sub>2</sub> and the results of earlier studies, to the species CICO•<sup>13</sup> and OCCL<sub>2</sub><sup>24</sup> and to the mixed carbonyl dihalide BrC(O)Cl, the IR spectrum of which has been reported previously<sup>29</sup> only for the gaseous molecule. In light of the experiments with Br<sub>2</sub>, it came as no surprise that Br•••CO could not be detected, while the appearance of a weak band near 740 cm<sup>-1</sup> gave the only clear sign that small amounts of OCBr<sub>2</sub> were also produced. The more intense  $\nu$ (CO) band of this molecule, expected at about 1816 cm<sup>-1</sup>, was inevitably obscured by the corresponding feature of OCCL<sub>2</sub> (centered near 1815 cm<sup>-1</sup>). Weak bands at 890, 859.5/848.5, and 815.9/804.8 cm<sup>-1</sup> that also developed upon photolysis could not

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**Table 4.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV–Visible Photolysis of an Ar Matrix Containing a Mixture of CO and ICl at ca. 15 K

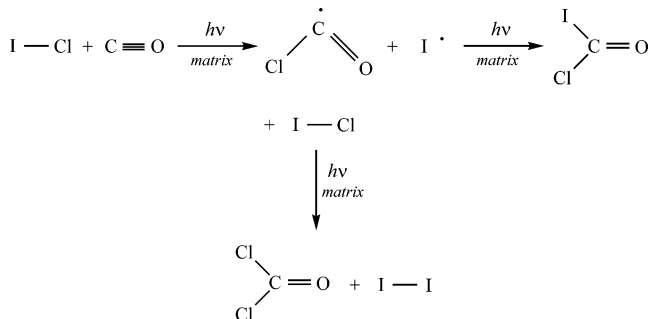
Ar matrix	assignment		wavenumbers reported
$\nu$ [cm <sup>-1</sup> ]	molecule	vibrational mode	previously
1877.2	CICO*	$\nu(\text{CO})$	1876.7 <sup>a</sup>
1840.7	OCCL <sub>2</sub>	$\nu_2 + \nu_5 + \nu_6$	1840.61 <sup>b</sup>
1834.7			1834.71 <sup>b</sup>
1829.1			1829.51 <sup>b</sup>
1815.4	OCCL <sub>2</sub>	$\nu(\text{CO}) (\nu_1)$	1815.58 <sup>b</sup>
1813.9			1814.78 <sup>b</sup>
1810.7			1814.26 <sup>b</sup>
1808.9			1813.56 <sup>b</sup>
			1810.12 <sup>b</sup>
1801.5	IC(O)Cl	$\nu(\text{CO})$	
1799.2			
1796.7			
1010.3	OCCL <sub>2</sub>	$\nu_2 + \nu_6$	1010.08 <sup>b</sup> 1004.02 <sup>b</sup> 997.97 <sup>b</sup>
840.3	OCCL <sub>2</sub>	$\nu_{\text{as}}(\text{CCl}_2) (\nu_5)$	837.36 <sup>b</sup> 837.20 <sup>b</sup> 836.38 <sup>b</sup> 836.22 <sup>b</sup> 835.37 <sup>b</sup> 835.23 <sup>b</sup>
839.3			809.81 <sup>b</sup>
837.5			808.81 <sup>b</sup>
836.6			807.81 <sup>b</sup>
809.1	OCCL <sub>2</sub>	$\nu_3 + \nu_6$	
807.2			
754.2	IC(O)Cl	$\nu \text{ CCl}$	
753.1			
751.4			
750.1			
581	OCCL <sub>2</sub>	$\delta_{\text{oop}} (\nu_4)$	581.21 <sup>b</sup> 580.88 <sup>b</sup> 580.56 <sup>b</sup>
569	OCCL <sub>2</sub>	$\nu_{\text{s}}(\text{CCl}_2) (\nu_2)$	568.29 <sup>b</sup> 564.75 <sup>b</sup> 561.12 <sup>b</sup>
504	IC(O)Cl	$\delta_{\text{oop}}$	
502			
486	IC(O)Cl	$\nu \text{ Cl}$	

<sup>a</sup> Reference 13. <sup>b</sup> Reference 24.

be ascribed to any specific product or products but probably reflect complexation on the part of at least one of the main products.

(iv) **ICl + CO.** Experiments with a gaseous mixture of ICl and CO in different proportions with an excess of Ar gave matrixes that initially displayed IR bands in the  $\nu(\text{CO})$  region at 2157.0/2154.0, 2145.6/2144.2, 2138.2, 2136.5, and 2128.4 cm<sup>-1</sup>. As described previously,<sup>12</sup> these can be attributed to the species OC...ICl, OC...ClI, free CO, CO...ClI, and CO...ICl, respectively. Additional bands near 370 cm<sup>-1</sup> due to free<sup>30</sup> or complexed<sup>12</sup> ICl could also be observed. The fact that there was no hint of the adduct OC...Cl<sub>2</sub> appeared to rule out the presence of Cl<sub>2</sub> as a significant impurity.

Irradiation with broad-band UV–visible light led to significant changes in the spectrum, as illustrated for two regions in Figure 4. Table 4 lists the wavenumbers of the absorptions seen to develop in these conditions as well as the proposed assignments. As in the experiments with Cl<sub>2</sub>,

**Scheme 3.** Proposed Mechanism for the Formation of IC(O)Cl and OCCL<sub>2</sub> from the Matrix Photochemical Reaction of Iodine Monochloride and Carbon Monoxide**Table 5.** Geometric Parameters Calculated with Different Theoretical Approximations for Carbonyl Iodide Chloride, IC(O)Cl<sup>a</sup>

geometric parameter	HF	B3LYP	MP2
$r(\text{C}=\text{O})$	1.1575	1.1810	1.1985
$r(\text{C}-\text{Cl})$	1.7445	1.7727	1.7502
$r(\text{C}-\text{I})$	2.1446	2.1740	2.1456
$\angle \text{Cl}-\text{C}=\text{O}$	122.9	123.2	122.7
$\angle \text{I}-\text{C}=\text{O}$	122.7	123.3	123.2
$\angle \text{I}-\text{C}-\text{Cl}$	114.4	113.5	114.1

<sup>a</sup> Calculations used a 6-31+G\* basis set for C, O, and Cl and a LANL2DZ pseudopotential for I. Distances ( $r$ ) are measured in angstroms, and angles ( $\angle$ ) are measured in degrees.

bands characteristic of OCCL<sub>2</sub><sup>24</sup> and the CICO\* radical<sup>13</sup> were clearly in evidence. In the absence of Cl<sub>2</sub> in the initial deposit, the intermediacy of Cl\* atoms is plainly indicated by the evolution of these products. New bands belonging, on the basis of evidence of a common growth pattern, to a single product were also observed near 1799, 752, 503, and 486 cm<sup>-1</sup>. The wavenumbers and signs of <sup>35</sup>Cl/<sup>37</sup>Cl isotopic splitting suggest a molecule incorporating a Cl–C=O fragment, and the obvious conclusion is that it is the hitherto unknown carbonyl iodide chloride, IC(O)Cl. The presence of the CICO\* radical, together with the formation of both IC(O)Cl and OCCL<sub>2</sub>, suggests that the reaction may occur following the two-channel mechanism represented in Scheme 3.

The expected properties of this molecule have been simulated by ab initio (HF and MP2) and DFT calculations. Table 5 lists the geometric parameters evaluated in this way, and Table 6 lists the corresponding wavenumbers and IR intensities of the six vibrational fundamentals. With a planar skeleton conforming to C<sub>s</sub> symmetry and a relatively narrow I–C–Cl angle near 114°, the predicted structure holds no surprises. Moreover, the IR spectrum is expected to contain four bands in the region 400–1900 cm<sup>-1</sup>, with wavenumbers and relative intensities in good agreement with those of the four features belonging to the new photoproduct. The two fundamentals expected to occur at lower wavenumbers escaped detection presumably either (i) because of a low intensity in IR absorption combined with a reduced sensitivity of detection at this end of the spectrum (e.g., near 310 cm<sup>-1</sup>) or (ii) because of falling below the threshold to detection in the present experiments (e.g., near 200 cm<sup>-1</sup>).

Separate studies of the reactions induced by the UV–visible photolysis of OCS in the presence of ICl in an Ar

(30) (a) Wight, C. A.; Ault, B. S.; Andrews, L. *J. Mol. Spectrosc.* **1975**, *56*, 239–250. (b) Hawkins, M.; Andrews, L.; Downs, A. J.; Drury, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 3076–3082.

**Table 6.** Vibrational Wavenumbers (in  $\text{cm}^{-1}$ ) and IR Relative Intensities (in Parentheses) Calculated for Carbonyl Iodide Chloride, IC(O)Cl<sup>a</sup>

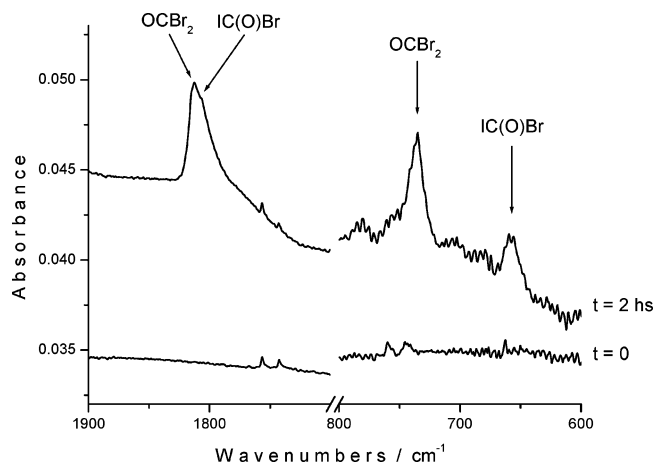
vibrational mode	HF <sup>b</sup>	B3LYP	MP2	Ar matrix	assignment
$\nu_1$	1853.1 (90)	1879.9 (76)	1797.7 (62)	1801.5 (80) 1799.2 (80) 1796.7 (80)	$\nu(\text{CO})$
$\nu_2$	778.3 (100)	746.7 (100)	800.9 (100)	754.2 (100) 753.1 (100) 751.4 (100) 750.1 (100)	$\nu \text{CIC}$
$\nu_3$	509.4 (1)	508.3 (<1)	522.9 (<1)	504 (<1) 502 (<1)	$\delta_{\text{oop}}(\text{CO})$
$\nu_4$	489.7 (2)	484.8 (2)	507.2 (2)	486 (<1)	$\nu \text{CI}$
$\nu_5$	313.6 (<1)	308.7 (1)	324.2 (<1)		$\delta(\text{CICO})$
$\nu_6$	200.1 (<1)	203.6 (<1)	217.3 (<1)		$\delta(\text{ICCl})$

<sup>a</sup> Calculated for the optimum geometries specified in Table 5. <sup>b</sup> Scaled by a factor of 0.9.

matrix have revealed<sup>31</sup> the formation of a number of products, including IC(O)Cl, identifiable by their IR spectra. A primary reaction, in this case, involves the UV photodissociation of OCS into CO and S atoms;<sup>32,32</sup> there is then a competition between the halogen atoms generated by the dissociation of ICl and the S atoms to add to the CO, resulting in either the formation of species such as OCCl<sub>2</sub>, IC(O)Cl, and ClCO• or the regeneration OCS.

(v) **IBr + CO.** Similar experiments were carried out to isolate IBr and CO together in an Ar matrix, typically in the proportions IBr/CO/Ar = 1:2:400. The most prominent features in the IR spectrum of the initial deposit were confined to the  $\nu(\text{CO})$  region. They included, in addition to the absorption of free CO, two pairs of bands, a stronger one at 2154.1/2150.8  $\text{cm}^{-1}$  and a weaker one at 2145.5/2143.2  $\text{cm}^{-1}$  that can be ascribed<sup>12</sup> to the adducts OC••IBr and OC••BrI, respectively. The subsequent irradiation of such a matrix with broad-band UV–visible light produced only minor changes in the spectrum, interpreted elsewhere<sup>12</sup> in terms of the formation of the less stable molecular pairs CO••IBr and CO••BrI; the only other products were formed in amounts so small that positive identification was hindered.

To increase the concentration of IBr in the matrix, a CO/Ar mixture was passed over IBr at  $-45^\circ\text{C}$ , and a matrix was formed by the continuous deposition of the resulting gas mixture. This had the desired effect of intensifying all of the IR bands reflecting the presence of IBr in the initial deposit. The exposure of the matrix to UV–visible light then caused new bands to appear at 1814, 1806, 779, 735, and 658  $\text{cm}^{-1}$ , which were still weak but reproducible (see Figure 5 and Table 7). An examination of how the bands grow as a function of irradiation time indicated two distinct products. One, associated with the 1814, 779, and 735  $\text{cm}^{-1}$  features, is readily identified on the basis of the results of our experiments with Br<sub>2</sub> and those of earlier studies<sup>25</sup> with OCB<sub>2</sub>. The second product, responsible for the shoulder at 1806  $\text{cm}^{-1}$  and the weak band correlating with it at 658  $\text{cm}^{-1}$ , is then most likely to be the mixed carbonyl dihalide IC(O)Br. None of the experiments gave any sign of the band at 2045.7  $\text{cm}^{-1}$  associated with the Br•••CO radical, but with

**Figure 5.** Fourier transform infrared spectra of an Ar matrix containing IBr and CO following deposition and after 2 h of broad-band UV–visible photolysis.**Table 7.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-band UV–Visible Photolysis of an Ar Matrix Containing CO and IBr at ca. 15 K

Ar matrix	assignment		wavenumbers reported previously
$\nu$ [ $\text{cm}^{-1}$ ]	molecule	vibrational mode	
1814	OCBr <sub>2</sub>	$\nu(\text{CO})$	1816.0 <sup>a</sup>
1806	IC(O)Br	$\nu(\text{CO})$	
779	OCBr <sub>2</sub>	$\nu_2 + \nu_5$	778.6 <sup>a</sup>
735	OCBr <sub>2</sub>	$\nu_{\text{as}}(\text{CBr}_2)$	734.4 <sup>a</sup>
658	IC(O)Br	$\nu \text{CBr}$	

<sup>a</sup> Reference 25.

**Table 8.** Geometric Parameters Calculated with Different Theoretical Approximations for Carbonyl Iodide Bromide, IC(O)Br<sup>a</sup>

geometric parameter	HF	B3LYP	MP2
$r(\text{C}=\text{O})$	1.1543	1.1782	1.1946
$r(\text{C}-\text{Br})$	1.9265	1.9540	1.9819
$r(\text{C}-\text{I})$	2.1519	2.1795	2.1484
$\angle \text{Br}-\text{C}=\text{O}$	122.2	122.6	122.0
$\angle \text{I}-\text{C}=\text{O}$	122.9	123.4	123.4
$\angle \text{I}-\text{C}-\text{Br}$	114.9	114.0	114.6

<sup>a</sup> Calculations used a 6-31+G\* basis set for C and O and a LANL2DZ pseudopotential for Br and I. Distances ( $r$ ) are measured in Å, and angles ( $\angle$ ) are measured in degrees.

such low concentrations of the photoproducts, we attach no particular significance to this apparent omission.

The dimensions and vibrational properties of IC(O)Br have been calculated, again by ab initio and DFT methods, with the results set out in Tables 8 and 9. The most intense IR

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(32) (a) Hawkins, M.; Downs, A. J. *J. Phys. Chem.* **1984**, *88*, 1527–1533; 3042–3047. (b) Hawkins, M.; Almond, M. J.; Downs, A. J. *J. Phys. Chem.* **1985**, *89*, 3326–3334.

**Table 9.** Vibrational Wavenumbers (in  $\text{cm}^{-1}$ ) and IR Relative Intensities (in Parentheses) Calculated for Carbonyl Iodide Bromide,  $\text{IC(O)Br}^a$ 

vibrational mode	HF <sup>b</sup>	B3LYP	MP2	Ar matrix	assignment
$\nu_1$	1861.5 (90)	1889.9 (80)	1812.1 (79)	1806 (85)	$\nu(\text{CO})$
$\nu_2$	708.8 (100)	685.0 (100)	710.4 (100)	658 (100)	$\nu \text{ BrC}$
$\nu_3$	477.0 (1)	476.3 (<1)	486.3 (<1)		$\delta_{\text{oop}}(\text{CO})$
$\nu_4$	376.4 (1)	374.8 (1)	371.3 (3)		$\nu \text{ CI}$
$\nu_5$	307.2 (<1)	300.0 (1)	314.6 (1)		$\delta(\text{BrCO})$
$\nu_6$	143.4 (<1)	145.4 (<1)	152.0 (<1)		$\delta(\text{ICBr})$

<sup>a</sup> Calculated for the optimum geometries specified in Table 8. <sup>b</sup> Scaled by a factor of 0.9.

absorptions are predicted to occur near 1850 and 700  $\text{cm}^{-1}$ , in generally satisfactory agreement with the two bands observed for the second photoproduct. On the basis of evidence of their calculated wavenumbers and intensities, there was significantly less chance of locating any of the other fundamentals under the conditions prevailing in our experiments. Both  $\text{OCBr}_2$  and  $\text{IC(O)Br}$  are formed, presumably, by the addition to CO of the halogen atoms created by the photodissociation of  $\text{IBr}$ , the inefficiency of the reactions testifying to the immobilizing effect of the matrix cages on the  $\text{Br}^\bullet$  and  $\text{I}^\bullet$  atoms, with the regeneration of  $\text{IBr}$  being the predominant sequel to dissociation.

## Conclusions

Photoinduced reactions between CO and a dihalogen molecule,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{ICl}$ , or  $\text{IBr}$ , occurring in an Ar matrix at ca. 15 K have been shown to give rise to one or more carbonyl dihalide molecules,  $\text{XC(O)Y}$ , where X and Y = Cl, Br, or I. Hence, the mixed dihalides  $\text{IC(O)Cl}$  and  $\text{IC(O)Br}$  have been prepared and characterized at least partially by their IR spectra, with findings endorsed by the results of quantum chemical calculations. Once formed, the phosgene molecules are quite stable. As shown in Figures 4 and 5, they are formed efficiently after 2 h broad-band UV-visible photolysis.

The initial formation of van der Waals complexes of the type  $\text{OC}\cdots\text{XY}^{11,12}$  does not appear to have any specific influence on the photochemistry of the systems. The photodissociation of the dihalogen is evidently the essential means of initiation, with the addition of the halogen atoms to CO then being restricted in varying degrees by matrix cage effects, and potentially also by the photolability of the products. The intermediacy of halogen atoms is evidenced by the identification of the familiar  $\text{CICO}^\bullet$  radical<sup>13</sup> in experiments with chlorine-containing dihalogen molecules, as well as what is probably a first sighting of its bromo

counterpart,  $\text{BrCO}^\bullet$ , in experiments with  $\text{Br}_2$ . In keeping with a previous theoretical forecast,<sup>14</sup>  $\text{BrCO}^\bullet$  is noteworthy for a  $\text{Br}\cdots\text{C}$  bond because it is more closely related to a van der Waals complex, “bromine carbonyl” rather than “bromoformyl” being perhaps the more appropriate nomenclature for it.

To generate, in higher yields, molecules such as  $\text{BrC(O)Cl}$ ,  $\text{IC(O)Cl}$ ,  $\text{IC(O)Br}$ , and even  $\text{OCI}_2$ , the most promising approach would appear to be to trap out CO with the appropriate halogen atoms (formed externally to the matrix, either thermally or in a discharge) in a solid noble gas matrix. Hence, IR measurements might be expected to afford a fuller characterization of these compounds and, perhaps, also adduce evidence of iodine carbonyl  $\text{I}\cdots\text{CO}$ . Experiments along these lines are currently under way in our laboratories.

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