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Photochemical Reaction Channels of OCS with Cl₂, ICl, or IBr Isolated Together in an Argon Matrix: Isolation of *syn*-Iodocarbonylsulfenyl Bromide

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Received: October 25, 2005; In Final Form: December 7, 2005

The photolytically induced reactions of a dihalogen XY (= Cl₂, ICl, or IBr) with OCS isolated together in an Ar matrix at about 15 K lead to different photoproducts depending on the natures of X and Y. In addition to the known species ClCO•, OCCl₂, *syn*-ClC(O)SCl, *syn*-ClC(O)SSCl, IC(O)Cl, IC(O)Br, and *syn*-BrC(O)SBr, *syn*-iodocarbonylsulfenyl bromide, *syn*-IC(O)SBr, has thus been identified for the first time as a photoproduct of the reactions involving IBr. The first product to be formed in the reactions with Cl₂ or ICl is the ClCO• radical which reacts subsequently with halogen or sulfur atoms or other matrix guests to give the corresponding carbonyl dihalide (OCCl₂ and IC(O)Cl), *syn*-ClC(O)SCl or *syn*-ClC(O)SSCl. The analogous reaction with IBr affords *syn*-BrC(O)SBr, IC(O)Br, and *syn*-IC(O)SBr. The changes have been followed, the products characterized experimentally by IR measurements, and the spectra analyzed in the light of the results of appropriate theoretical calculations.

1. Introduction

In the pursuit of new species and elucidation of the photochemical reaction channels open to a dihalogen XY in the presence of OCS, we became interested in the specific cases where XY = Cl₂, ICl, or IBr. An earlier study of the matrix photochemistry of chlorocarbonylsulfenyl bromide, ClC(O)SBr,¹ has served as the basis for subsequent research. Broad-band UV–vis irradiation of ClC(O)SBr leads not only to partial transformation of the more stable *syn* into the anti form of the molecule but also to the formation of its isomer BrC(O)SCl, as well as the photoevolution of the fragments BrCl, BrSCl, CO, and OCS. The mechanisms proposed¹ 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 photoactivation of Br₂ in the presence of OCS.²

This experience has served to point the way to a means of completing the carbonyl dihalide family when the matrix photoreactions of IBr and ICl with CO were shown to afford IC(O)Br and IC(O)Cl, respectively.³ As reported recently,^{4,5} 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•,⁶ 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 Br₂ gives rise initially to the radical BrCO• which

had hitherto eluded detection; unlike its chloro counterpart, but in keeping with the results of earlier, sophisticated quantum chemical calculations,⁷ this is most aptly formulated as a weakly bound van der Waals complex engaging CO to a Br atom. All these antecedents are relevant to the current study, mainly because carbonyl sulfide, OCS, is dissociated into CO and S atoms upon broad-band UV–vis photolysis.⁸

Here, we report on some photolytically initiated reactions involving a dihalogen molecule XY (= Cl₂, ICl, or IBr) and OCS isolated together in a solid Ar matrix at about 15 K. Under broad-band UV–vis photolysis, the reaction pathways lead to the formation of one or more carbonyl dihalides, OCXY, and/or halogenosulfenylcarbonyl halides, XC(O)SY, where X, Y = Cl, Br, or I may be the same or different atoms. Hence, *syn*-iodocarbonylsulfenyl bromide, *syn*-IC(O)SBr, has finally been produced by the photoreaction of OCS with IBr; this is the first example of a molecule containing the hitherto unidentified IC(O)S– group. *syn*-IC(O)SBr as well as the known species ClCO•, OCCl₂, IC(O)Cl, *syn*-ClC(O)SCl, *syn*-ClC(O)SSCl, and IC(O)Br, formed in similar reactions involving the relevant halogen atoms, have been characterized experimentally by their IR spectra and theoretical calculations.

2. Experimental Section

Commercial samples of ICl and IBr (ex Aldrich) were purified by repeated trap-to-trap condensation in vacuo, mainly to remove I₂ impurity, the presence of which hampered photochemical studies by its inherently high absorption cross-section throughout much of the visible and UV regions. Cl₂ (again ex Aldrich) and OCS were used without any further purification. Gas mixtures of the dihalogen (XY), OCS, and Ar, typically with the composition XY/OCS/Ar = 0.5:1:200, 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

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refrigerator (Air Products, model CS202) using the pulsed deposition technique.^{9,10}

The IR spectrum of each matrix sample was recorded at a resolution of 0.5 cm⁻¹, with 256 scans and a wavenumber accuracy of ± 0.1 cm⁻¹, using a Nicolet Magna-IR 560 FTIR instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000–400 cm⁻¹ or 600–250 cm⁻¹, respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV–vis radiation ($200 \leq \lambda \leq 800$ 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 IR radiation and so minimize any heating effects. The IR spectrum of the matrix was then recorded at different times of irradiation and scrutinized closely for signs of decay of the absorptions due to the reactants and growth of absorptions due to the respective products. Experiments involving more selective photolysis were unsuccessful, the much reduced light flux resulting in little or no detectable change.

All of the quantum chemical calculations were performed using the Gaussian 98 program system¹¹ under the Linda parallel execution environment using two coupled PCs. HF, density functional theory (DFT), and MP2 methods were tried, in combination with a 6-31+G* basis set for C, O, and Cl atoms and a LANL2DZ basis set¹² including an effective core potential (ECP) for Br and I atoms. The ECP chosen is that proposed by Hay and Wadt¹³ which incorporates 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 simultaneous relaxation of all the geometrical parameters. The calculated vibrational properties correspond in all cases to potential energy minima for which no imaginary vibrational frequency was found.

3. Results and Discussion

(i) **Cl₂ + OCS.** A mixture of Cl₂, OCS, and Ar in different proportions, for example, 1:2:200, 1:1:200, or 2:1:200, formed a solid matrix at ca. 15 K which displayed only IR absorptions attributable to free OCS (at 2049.8 cm⁻¹);^{8,14} in addition, the presence of a weakly bound van der Waals complex OCS...Cl₂ was revealed by some changes in the patterns of the fundamental bands associated with the parent OCS molecule.

Subsequent irradiation of the matrix with broad-band UV–vis light ($200 \leq \lambda \leq 800$ nm) led, however, to drastic changes in the IR spectrum. Table 1 lists the wavenumbers of all the new absorptions observed to develop under these conditions, together with the literature data for the OC...Cl₂ van der Waals complex,⁵ the free CO molecule,⁵ the ClCO• radical,⁶ OCCl₂,¹⁵ *syn*-ClC(O)SSCl,¹⁶ the OCCl₂...Cl₂ complex,¹⁷ *syn*-ClC(O)-SCl,¹⁸ and SCl₂;¹⁹ with the single exception of *syn*-ClC(O)-SSCl, for which literature data are scarce, all these products have previously been characterized by their IR spectra under comparable conditions. Four of the new bands, centered near 1810, 840/837, 581, and 572 cm⁻¹, are recognizable as the fundamentals ν_1 , ν_5 , ν_4 , and ν_2 , respectively, and two others, near 1841/1835 and 1010 cm⁻¹, as combinations or overtones of the OCCl₂ molecule.¹⁵ This was formed in what appeared to be a relatively efficient matrix reaction involving, first, the photoproduction of CO and S atoms from OCS⁸ and, second, the subsequent photoreaction of CO and Cl₂. All the bands showed a significant structure due in part to isotopic splitting (from ³⁵Cl/³⁷Cl) and in part to matrix site effects.⁹

First to appear after broad-band UV–vis photolysis, however, was a band centered near 2138 cm⁻¹ which on the evidence of

TABLE 1: Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV–Vis Photolysis of an Ar Matrix Containing a Mixture of OCS and Cl₂ at ca. 15 K

Ar matrix ν (cm ⁻¹)	assignment		wavenumber reported previously
	molecule	vibrational mode	
2140.6	OC...Cl ₂	ν (C=O)	2140.7 ^a
2137.9	free CO	ν (C=O)	2138.2 ^a
1877.1	ClCO•	ν (C=O)	1876.7 ^b
1840.6 } 1834.6 }	OCCl ₂	$\nu_2 + \nu_5 + \nu_6$	1840.61 } ^c 1834.71 }
1810.0	OCCl ₂	ν (C=O)	1810.12 ^c
1772.9	<i>syn</i> -ClC(O)SSCl	ν (C=O)	1795 ^d
1010.2	OCCl ₂	$\nu_2 + \nu_6$	1010.08 ^c
847.5	Cl ₂ /OCCl ₂	$\nu_{as}(\text{Cl}-\text{C}-\text{Cl})$	847.8 ^e
840.4 } 837.4 }	OCCl ₂	$\nu_{as}(\text{Cl}-\text{C}-\text{Cl})$ (ν_5)	837.36 } ^c 837.20 }
812.2	<i>syn</i> -ClC(O)SCl	$\nu_{as}(\text{Cl}-\text{C}-\text{S})$	812.4 ^f
803.8	<i>syn</i> -ClC(O)SSCl	$\nu_{as}(\text{Cl}-\text{C}-\text{S})$	795 ^d
581.2	OCCl ₂	δ_{oop} (ν_4)	581.21 } ^c 580.88 } 580.56 }
572.5	OCCl ₂	$\nu_s(\text{CCl}_2)$ (ν_2)	568.29 } ^c 564.75 } 561.12 }
547.9	<i>syn</i> -ClC(O)SSCl	$\nu_s(\text{Cl}-\text{C}-\text{S})$	
517.5	SCl ₂	$\nu_{as}(\text{Cl}-\text{S}-\text{Cl})$	517.5 ^g
515.8	SCl ₂	$\nu_s(\text{Cl}-\text{S}-\text{Cl})$	515.2 ^g
490.2	<i>syn</i> -ClC(O)SSCl	$\nu(\text{S}-\text{S})$	490 ^d
456.3 } 445.3 }	<i>syn</i> -ClC(O)SSCl	$\nu(\text{S}-\text{Cl})$	

^a Reference 5. ^b Reference 6. ^c Reference 15. ^d Reference 16 (liquid IR). ^e Reference 17. ^f Reference 18. ^g Reference 19.

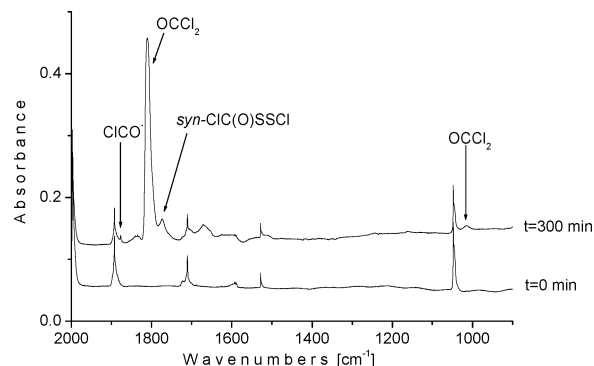


Figure 1. FTIR spectra in the 2000–900 cm⁻¹ region for an Ar matrix containing Cl₂ and OCS (Cl₂/OCS/Ar = 1:1:200) immediately after deposition (bottom) and after 5 h of photolysis (top).

its wavenumber must arise from the free CO molecule resulting, together with S atoms, from the photodissociation of OCS.⁸ As reported recently,^{4,5} the CO interacts with the Cl₂ molecules to form the weakly bound van der Waals complex OC...Cl₂. Figures 1 and 2 show two different regions of the IR spectra of such a matrix, first immediately after deposition and then after broad-band UV–vis irradiation for 5 h.

Once formed by interaction of the photoproducts CO and Cl₂, the products OCCl₂ and ClCO• gave absorptions whose intensities varied with photolysis time, as previously reported,³ in a way suggesting that the radical is an intermediate stage in the formation of OCCl₂ (see Figure 3). The results imply that the reactions depend on the photodissociation of Cl₂ and the subsequent addition of the resulting Cl• atoms variously to either S atoms, CO, or ClCO•, with little contribution from concerted addition of Cl₂ to CO.

To distinguish the bands corresponding to the different species formed in the matrix, and help determine the sequence of the

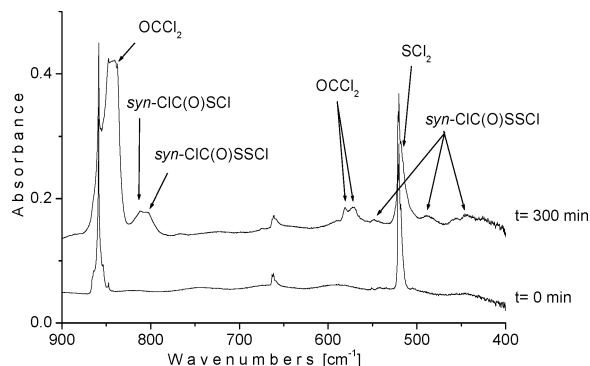
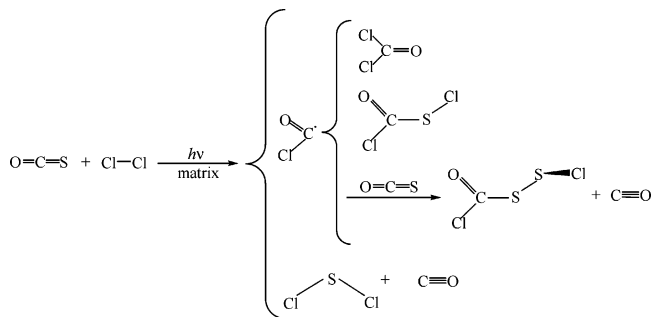


Figure 2. FTIR spectra in the 900–400 cm^{-1} region for an Ar matrix containing Cl_2 and OCS ($\text{Cl}_2/\text{OCS}/\text{Ar} = 1:1:200$) immediately after deposition (bottom) and after 5 h of photolysis (top).

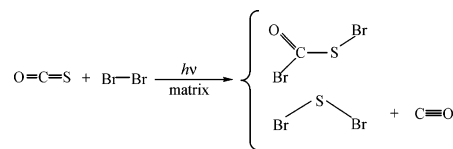
changes, the integrated intensities of the new bands have been plotted as a function of irradiation time, as depicted in Figure 3. Besides the bands belonging to OCCl_2 , SCl_2 , CO, and CICO^* , a new set of bands with a common growth pattern and wavenumbers near 1773, 804, 548, 490, and 456 cm^{-1} was tentatively assigned, respectively, to the $\nu(\text{C}=\text{O})$, $\nu_{\text{as}}(\text{Cl}-\text{C}-\text{S})$, $\nu_{\text{s}}(\text{Cl}-\text{C}-\text{S})$, $\nu(\text{S}-\text{S})$, and $\nu(\text{S}-\text{Cl})$ normal modes of *syn*- $\text{CIC}(\text{O})\text{SSCl}$. This assignment is based on comparisons with the IR spectra reported for $\text{CIC}(\text{O})\text{SSCl}$ as a liquid film¹⁶ and in CDCl_3 solution,¹⁹ although no more than three fundamentals were then identified. The other two bands, not reported previously, are in accordance with the results of theoretical calculations, as revealed in Table 2. The calculated vibrational spectrum corresponds to a *syn* structure for the molecule that was found to be the energy minimum over the potential energy surfaces.²¹

The yield of OCCl_2 , the major product formed in these experiments, was found to increase as the concentration of Cl_2 increases. An excess of Cl_2 relative to the OCS leads to an increased yield of *syn*- $\text{CIC}(\text{O})\text{SCI}$, SCl_2 , and *syn*- $\text{CIC}(\text{O})\text{SSCl}$. A remarkable difference is thus revealed between the matrix photochemistry of the system Cl_2/OCS and that of the system

SCHEME 1: Products Formed after Broad-Band UV–Vis Photolysis of an Ar Matrix Containing a Mixture of Cl_2 and OCS at ca. 15 K



SCHEME 2: Products Formed after Broad-Band UV–Vis Photolysis of an Ar Matrix Containing a Mixture of Br_2 and OCS at ca. 15 K



Br_2/OCS .² Whereas with Br_2 , *syn*- $\text{BrC}(\text{O})\text{SBr}$ is formed as a major product, the photochemical changes evolve rather differently with Cl_2 (see Schemes 1 and 2).

(ii) **ICI + OCS.** Similar studies were carried out with matrixes formed by mixtures of ICl, OCS, and Ar, typically in the proportion 2:1:200. The IR spectrum of such a matrix measured immediately after deposition was dominated by the absorptions of OCS,^{8,14} with evidence of some perturbation due to the interaction of OCS with ICl to form one or more van der Waals complexes $\text{OCS} \cdots \text{ICl}$. Irradiation with broad-band UV–vis light led to significant changes, as illustrated in Figure 4 for three different regions of the spectrum. Table 3 lists the wavenumbers of the absorptions seen to develop in these conditions, as well as the proposed assignments. As in the experiment with Cl_2 , the reaction is initiated by the photodissociation of OCS to give CO and S atoms.⁸ The subsequent

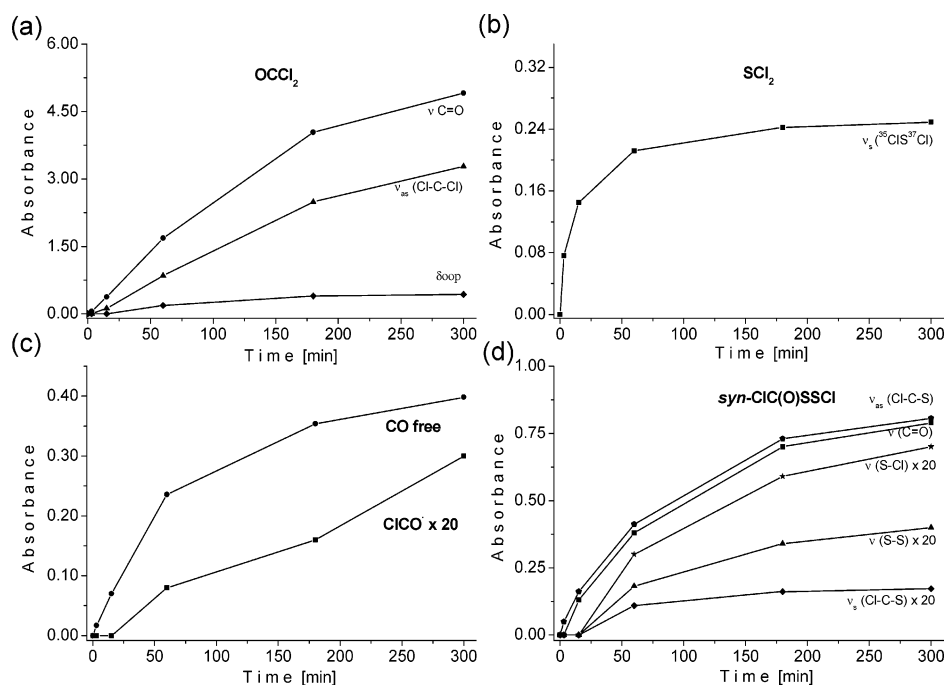
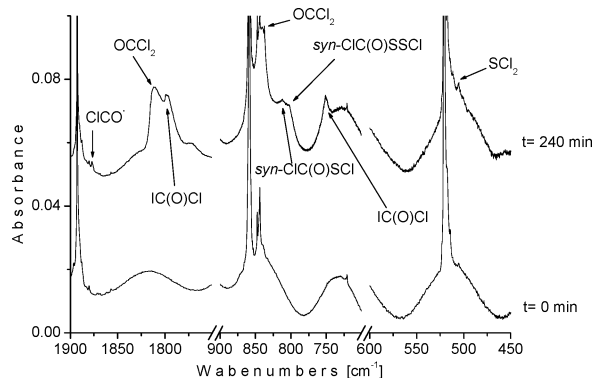


Figure 3. Plots as a function of irradiation time of the intensities of the bands assigned to (a) OCCl_2 , (b) SCl_2 , (c) CO and CICO^* , and (d) *syn*- $\text{CIC}(\text{O})\text{SSCl}$ in the IR spectrum of a matrix with the initial composition $\text{Cl}_2/\text{OCS}/\text{Ar} = 1:1:200$.

TABLE 2: Comparison of the Wavenumbers and Intensities of the IR Bands Due to the Photoproduct Believed to Be *syn*-ClC(O)SSCl with Previous Reports and with the Results of Theoretical Calculations with Different Models^a

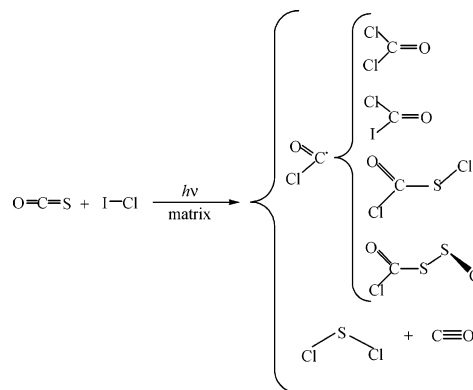
vibrational mode	Ar matrix IR (cm ⁻¹)	CDCl ₃ soln ^b	film ^c	HF/6-31+G* ^d	B3LYP/6-31+G* ^d	MP2/6-31+G* ^d
$\nu(\text{C}=\text{O})$	1772.9 (97)	1780	1795	1840.2 (65)	1866.3 (57)	1795.3 (43)
$\nu_{\text{as}}(\text{Cl}-\text{C}-\text{S})$	803.8 (100)	780	795	854.3 (100)	796.1 (100)	857.7 (100)
$\delta(\text{Cl}-\text{C}-\text{S})$				574.5 (2)	567.0 (1)	574.1 (1)
$\nu_{\text{s}}(\text{Cl}-\text{C}-\text{S})$	547.9 (1)			566.1 (13)	554.1 (3)	593.6(24)
$\nu(\text{S}-\text{S})$	490.2 (2)		490	523.3 (2)	495.4 (<1)	536.8 (1)
$\nu(\text{S}-\text{Cl})$	456.3 (4)			494.0 (7)	450.1 (13)	497.8 (9)
$\delta(\text{O}=\text{C}-\text{S})$	445.3 (?)			436.5 (1)	414.3 (4)	441.5 (2)

^a Relative intensities given in parentheses. ^b Reference 20. ^c Reference 16. ^d Wavenumbers scaled by a factor of 0.9.

**Figure 4.** FTIR spectra of an Ar matrix containing ICl and OCS (ICl/OCS/Ar = 0.5:1:200) immediately after deposition (bottom) and after 240 min of photolysis (top).**TABLE 3: Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV-Vis Photolysis of an Ar Matrix Containing a Mixture of OCS and ICl at ca. 15 K**

Ar matrix ν (cm ⁻¹)	assignment molecule	vibrational mode	wavenumber reported previously
2156.8 } 2154.6 } 2145.0	OC...ICl	$\nu(\text{C}=\text{O})$	2157.0 } ^a 2154.0 } 2145.6 } ^a
	OC...CII	$\nu(\text{C}=\text{O})$	2144.2 } ^a
2140.8	OC...Cl ₂	$\nu(\text{C}=\text{O})$	2140.7 ^a
2138.1	free CO	$\nu(\text{C}=\text{O})$	2138.2 ^a
2136.6	CO...CII	$\nu(\text{C}=\text{O})$	2136.5 ^a
2128.4	CO...ICl	$\nu(\text{C}=\text{O})$	2128.4 ^a
1876.9	ClCO•	$\nu(\text{C}=\text{O})$	1876.7 ^b
1815.2 } 1814.1 } 1810.3 }	OC(Cl) ₂	$\nu(\text{C}=\text{O})$	1815.58 } ^c 1814.78 } 1814.26 } 1813.56 } 1810.12 } ^d
1799.1 } 1796.7 }	IC(O)Cl	$\nu(\text{C}=\text{O})$	1801.5 } ^d 1799.2 } 1796.7 }
1772.4	<i>syn</i> -ClC(O)SSCl	$\nu(\text{C}=\text{O})$	1795 ^e
840.3	OC(Cl) ₂	$\nu_{\text{as}}(\text{Cl}-\text{C}-\text{Cl})$	837.36 } ^c 837.20 } 836.38 } 836.22 } 835.37 } 835.23 }
812.3	<i>syn</i> -ClC(O)SCl	$\nu_{\text{as}}(\text{Cl}-\text{C}-\text{S})$	812.4 ^f
802.8	<i>syn</i> -ClC(O)SSCl	$\nu_{\text{as}}(\text{Cl}-\text{C}-\text{S})$	795 ^e
751.3	IC(O)Cl	$\nu_{\text{as}}(\text{I}-\text{C}-\text{Cl})$	754.2 } ^d 753.1 } 751.4 } 750.1 }
517.2	SCl ₂	$\nu_{\text{as}}(^{35}\text{Cl}-\text{S}-^{35}\text{Cl})$	517.5 ^g

^a Reference 5. ^b Reference 6. ^c Reference 15. ^d Reference 3. ^e Reference 16 (liquid IR). ^f Reference 18. ^g Reference 19.

SCHEME 3: Products Formed after Broad-Band UV-Vis Photolysis of an Ar Matrix Containing a Mixture of ICl and OCS at ca. 15 K

interaction of CO and ICl gives products, which display IR bands in the $\nu(\text{C}=\text{O})$ region at 2157/2155, 2145, 2141, 2138, 2137, and 2128 cm⁻¹. As described previously,⁵ these can be attributed to the species OC...ICl, OC...CII, OC...Cl₂, free CO, CO...CII, and CO...ICl, respectively. The appearance of not only the adduct OC...Cl₂ but also the radical ClCO• and OC(Cl)₂ merits some comment.

As in the experiments with Cl₂, bands characteristic of OC(Cl)₂ (near 1815 and 840 cm⁻¹)¹⁵ and the ClCO• radical (1876.9 cm⁻¹)⁶ were clearly in evidence. In the absence of Cl₂ in the initial deposit, the intermediacy of Cl• atoms is plainly indicated by the evolution of these products and of the adduct OC...Cl₂. New bands belonging, on the evidence of a common growth pattern, to a single product were also observed near 1799 and 751 cm⁻¹. The wavenumbers and evidence of ³⁵Cl/³⁷Cl isotopic splitting suggest a molecule incorporating a Cl-C=O fragment, and the most plausible conclusion is that it is the carbonyl iodide chloride, IC(O)Cl.³

Once again, the primary reaction involves UV photodissociation of OCS into CO and S atoms;⁸ there is then competition between the halogen atoms generated by the dissociation of ICl and the S atoms to add to the CO either to form species such as OC(Cl)₂, IC(O)Cl, *syn*-ClC(O)SCl, *syn*-ClC(O)SSCl, and ClCO• or to regenerate OCS (see Scheme 3). No trace of the molecules ClC(O)SI, IC(O)SCl, ISCl, or SI₂ came to light in the spectra.

Figure 5 shows how the various bands grow as a function of irradiation time. Thus, bands originating in OC(Cl)₂, IC(O)Cl, free CO, ClCO•, and *syn*-ClC(O)SSCl show similar behavior in the way they evolve with time. This analysis seems therefore to confirm our interpretation, including the formation of the disulfide species *syn*-ClC(O)SSCl. No photolability signs of *syn*-ClC(O)SSCl have been found so far.

(iii) **IBr + OCS.** Similar experiments were carried out with Ar matrices doped with IBr and OCS, typically in the proportions IBr/OCS/Ar = 0.5:1:200. The most prominent features in

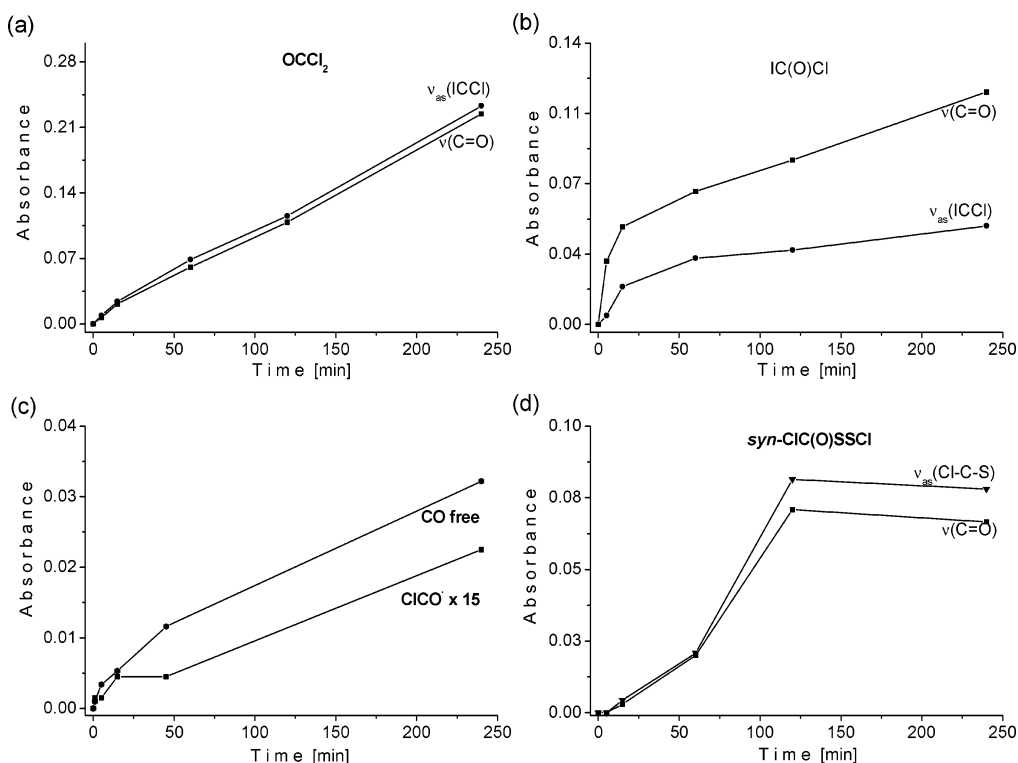


Figure 5. Plots as a function of irradiation time of the intensities of the bands assigned to (a) OCCl_2 , (b) IC(O)Cl , (c) CO and CICO^* , and (d) syn-CIC(O)SSCl in the IR spectrum of a matrix with the initial composition $\text{ICl/OCS/Ar} = 0.5:1:200$.

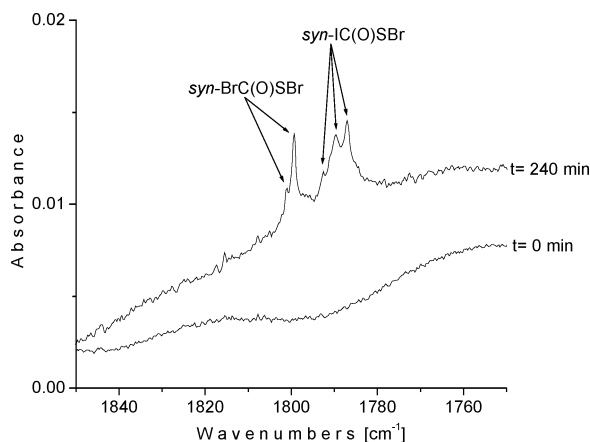


Figure 6. 1850–1750 cm^{-1} region of the FTIR spectra of an Ar matrix containing IBr and OCS ($\text{IBr/OCS/Ar} = 0.5:1:200$) immediately after deposition (bottom) and after 240 min of photolysis (top).

the IR spectrum of the initial deposit were again confined to the OCS regions.^{8,14} They showed, in addition to the absorptions characteristic of free OCS , some perturbation of these contours arising, we presume, from the presence of one or more adducts formed by OCS and IBr .⁵ Subsequent irradiation of such a matrix with broad-band UV–vis light produced several changes in the spectrum. These can be interpreted for the most part in terms of the formation of the known van der Waals complexes $\text{OC}\cdots\text{IBr}$, $\text{OC}\cdots\text{BrI}$, and $\text{CO}\cdots\text{IBr}$, together with free CO , IC(O)Br , syn-BrC(O)SBr , and SBr_2 . In addition, however, the spectrum witnessed the growth of new bands that can be attributed to the hitherto unknown molecule syn-IC(O)SBr ; this is noteworthy for incorporating, apparently for the first time, the IC(O)S- group (see Figures 6 and 7 and Table 4). Identification of the different products was aided by scrutiny of how the new bands grow as a function of irradiation time (Figures 8 and 9).

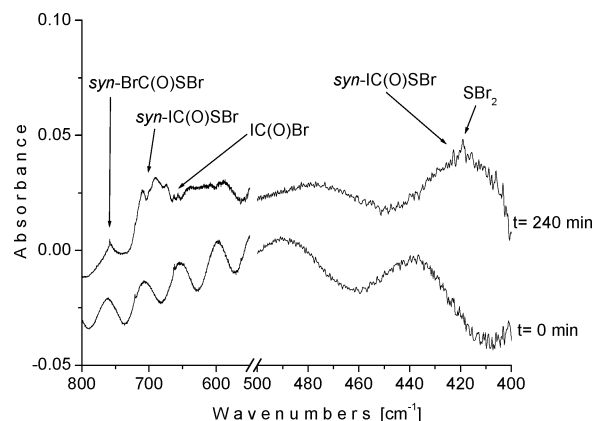


Figure 7. 800–400 cm^{-1} region of the FTIR spectra of an Ar matrix containing IBr and OCS ($\text{IBr/OCS/Ar} = 0.5:1:200$) immediately after deposition (bottom) and after 240 min of photolysis (top).

One such product, characterized by bands at 1801/1799 and 758 cm^{-1} , is readily identified on the basis of the results of earlier studies of the photoinduced matrix reaction between Br_2 and OCS as the sulphenyl bromide syn-BrC(O)SBr .² A second product, responsible for the band at 1805 cm^{-1} and a weak band correlating with it at 657 cm^{-1} , is then most likely to be the mixed carbonyl dihalide BrC(O)I .³ A third product, readily identified by its absorption at 419 cm^{-1} , is the triatomic molecule SBr_2 .²² On the basis of the results of our quantum chemical calculations, the set of bands occurring near 1790, 700, and 423 cm^{-1} is identified with the new molecule syn-IC(O)SBr . None of the experiments gave any sign of the band at 2045.7 cm^{-1} associated with the $\text{Br}\cdots\text{CO}$ radical,³ but with the generally rather low concentrations of photoproducts, we attach no particular significance to this apparent omission. Scheme 4 details some of the feasible reactions of the photo-reaction between IBr and OCS .

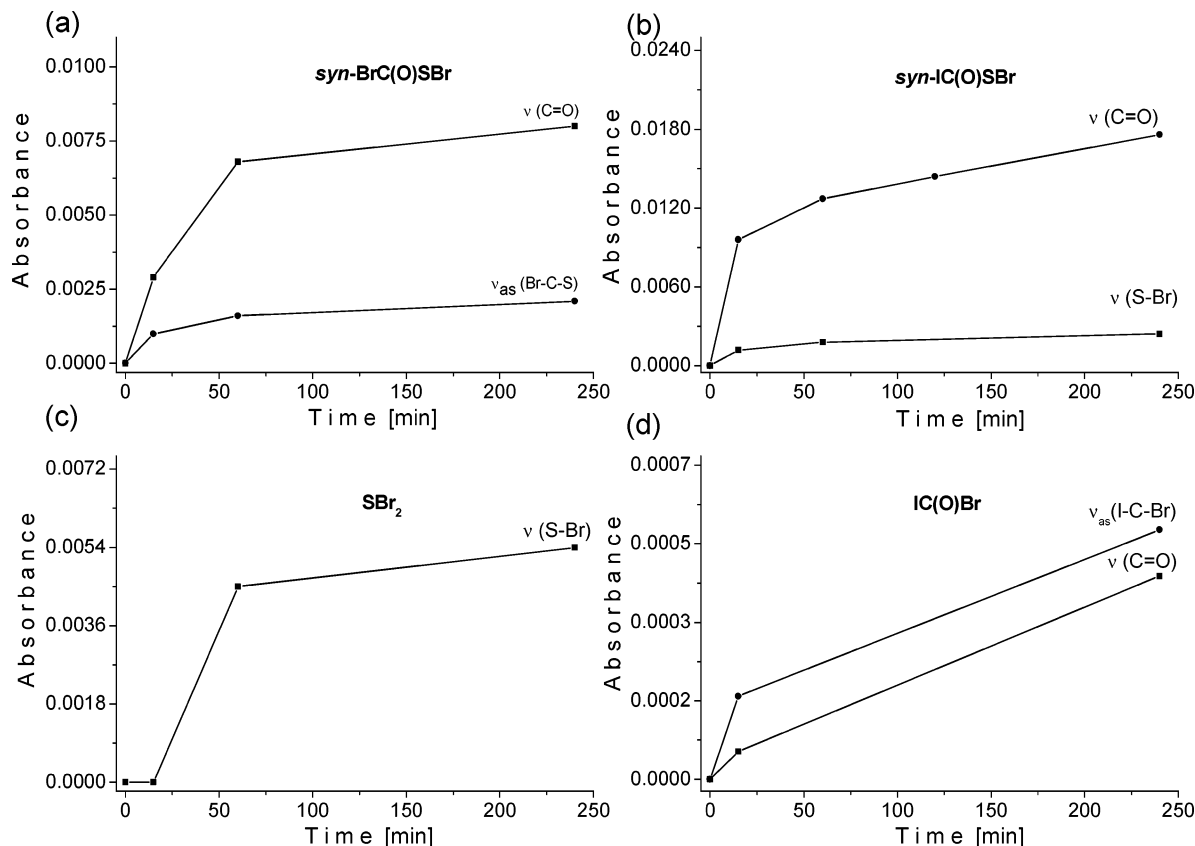


Figure 8. Plots as a function of irradiation time of the intensities of the bands assigned to (a) *syn*-BrC(O)SBr, (b) *syn*-IC(O)SBr, (c) SBr₂, and (d) IC(O)Br in the IR spectrum of a matrix with the initial composition IBr/OCS/Ar = 0.5:1:200.

TABLE 4: Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV-Vis Photolysis of an Ar Matrix Containing a Mixture of OCS and IBr at ca. 15 K

Ar matrix	assignment		wavenumber reported previously
ν (cm ⁻¹)	molecule	vibrational mode	
2150.8	OC...IBr	ν (C=O)	2150.8 ^a
2145.0	OC...BrI	ν (C=O)	2145.5 ^a
2138.0	free CO	ν (C=O)	2138.2 ^a
2136.4	CO...BrI	ν (C=O)	2136.5 ^a
1805.0	IC(O)Br	ν (C=O)	1806 ^b
1801.2 } 1799.4 }	<i>syn</i> -BrC(O)SBr	ν (C=O)	1801.0 } ^c 1799.4 }
1792.6 } 1789.9 } 1787.1 }	<i>syn</i> -IC(O)SBr	ν (C=O)	this work
758.3 } 709.4 }	<i>syn</i> -BrC(O)SBr	ν_{as} (Br-C-S)	758.2 ^b
699.2 } 689.8 } 674.3 }	<i>syn</i> -IC(O)SBr	ν_{as} (I-C-S)	this work
656.8	IC(O)Br	ν_{as} (I-C-Br)	658 ^b
422.7	<i>syn</i> -IC(O)SBr	ν (S-Br)	this work
419.2	SBr ₂	ν (S-Br)	418 ^d

^a Reference 5. ^b Reference 3. ^c Reference 2. ^d Reference 22.

The dimensions and vibrational properties of *syn*-IC(O)SBr have been calculated by ab initio, DFT methods, and perturbation theory in combination with a 6-31+G* basis set for C, O, and S and a LANDL2DZ pseudopotential for I and Br, with the results set out in Tables 5 and 6.

The most intense IR absorptions are predicted to occur near 1800, 700, and 420 cm⁻¹, in persuasive agreement with the features observed for the new photoproduct. On the evidence of the calculated wavenumbers and IR intensities, there was

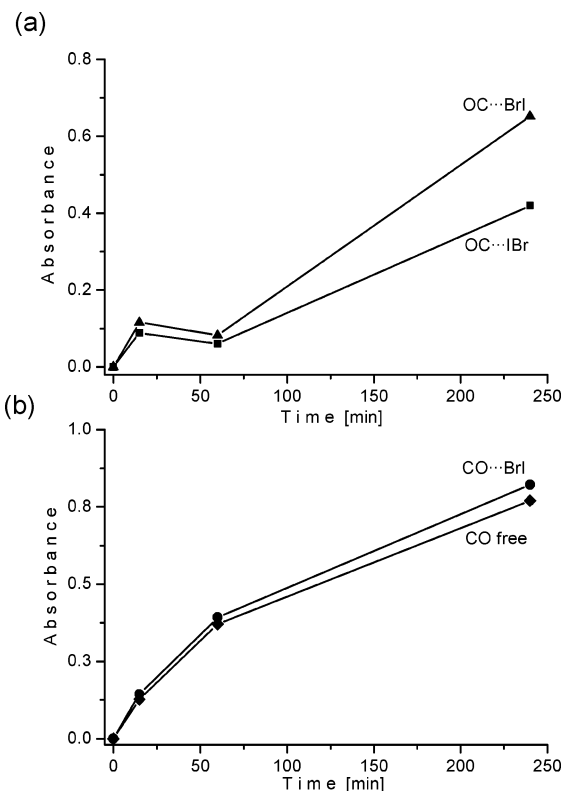
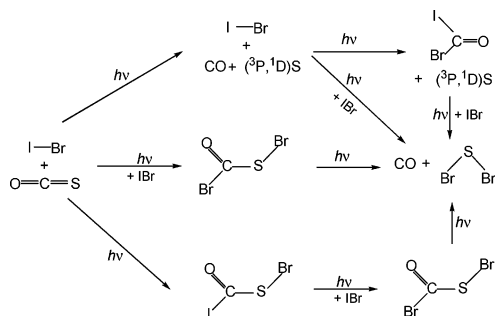


Figure 9. Plots as a function of irradiation time of the intensities of the bands due to the van der Waals complexes OC...BrI, OC...IBr, and CO...BrI and free CO in the IR spectrum of a matrix with the initial composition IBr/OCS/Ar = 0.5:1:200.

significantly less chance of locating any of the other fundamentals under the conditions prevailing in our experiments.

TABLE 5: Experimental and Calculated Values for *syn*-IC(O)SBr^a

Ar matrix		theoretical calculations		
ν (cm ⁻¹)	vibrational mode	HF/6-31+G* LANL2DZ	B3LYP/6-31+G* LANL2DZ	MP2/6-31+G* LANL2DZ
1792.6 1789.9 1787.1	$\nu(\text{C}=\text{O})$	1836.6 (100)	1871.9 (100)	1785.6 (100)
709.4				
699.2				
689.8 674.3	$\nu_{\text{as}}(\text{I}-\text{C}-\text{S})$	744.2 (84)	706.8 (62)	770.4 (95)
	$\nu_{\text{s}}(\text{I}-\text{C}-\text{S})$	522.8 (5)	537.0 (6)	554.7 (5)
	$\delta_{\text{oop}}(\text{I}-\text{C}-\text{S})$	504.4 (1)	499.0 (<1)	518.3 (<1)
422.7 (15)	$\nu(\text{S}-\text{Br})$	426.0 (7)	398.5 (14)	379.9 (6)

^a Relative intensities are given in parentheses.**SCHEME 4: Possible Mechanisms of the Photochemical Reaction between IBr and OCS in an Ar Matrix at ca. 15 K****TABLE 6: Geometrical Parameters for *syn*-IC(O)SBr Calculated with Different Theoretical Approximations Using a 6-31+G* Basis Set for C, O, and S and a LANL2DZ Pseudopotential for Br and I**

geometrical parameter	HF	B3LYP	MP2
$r(\text{C}=\text{O})$	1.1592	1.1833	1.2025
$r(\text{C}-\text{I})$	2.1842	2.2406	2.1941
$r(\text{C}-\text{S})$	1.7718	1.7654	1.7544
$r(\text{S}-\text{Br})$	2.1839	2.2337	2.2915
$\alpha(\text{I}-\text{C}-\text{S})$	109.0	104.9	107.4
$\alpha(\text{I}-\text{C}=\text{O})$	122.4	123.7	123.6
$\alpha(\text{O}=\text{C}-\text{S})$	128.6	131.4	129.1
$\alpha(\text{C}-\text{S}-\text{Br})$	102.1	103.3	102.4

4. Conclusions

Photoinduced reactions between OCS and a dihalogen molecule Cl₂, ICl, or IBr occurring in an Ar matrix at ca. 15 K have been shown to give rise to one or more carbonyl dihalide molecules OCXY, where X, Y = Cl, Br, or I, and to halogenocarbonylsulfonyl compounds of the type XC(O)SY. Hence, the molecule *syn*-IC(O)SBr has been prepared and characterized, at least partially, by its IR spectrum, with its identity being endorsed by the results of quantum chemical calculations.

The yields of the different photoproducts vary markedly with the nature of the halogen atoms X and Y. If at least one of these atoms is Cl, as in the case of Cl₂ or ICl, the most important reaction channel leads to the formation of OCXCl, with X = Cl or I. On the other hand, in the reactions of OCS with Br₂ or IBr, the dominant photoproduct is the corresponding sulfonyl-carbonyl compound BrC(O)SBr² or IC(O)SBr. The difference can be attributed to the intermediacy and relatively high stability of the ClCO[•] radical which is formed from OCS and XCl (X = Cl or I) under matrix conditions. This contrasts with the much more weakly bound complex formed between CO and a Br

atom³ (and presumably also an I atom), the low stability of which causes it to have little or no influence in directing the course of the matrix reactions between OCS and XBr (X = Br or I) that are set in train by broad-band UV-vis irradiation.

Acknowledgment. The authors acknowledge a British Council-Fundación Antorchas award for British-Argentine cooperation. C.O.D.V. and R.M.R. thank Jesus College Oxford, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Facultad de Ciencias Exactas, Universidad Nacional de La Plata for financial support. R.M.R. is also grateful to the Fundación Antorchas and to the Royal Society of Chemistry for a grant for international authors. In addition, A.J.D. is indebted to the EPSRC for support allowing the purchase of equipment, while Y.A.T. acknowledges a Deutscher Akademischer Austausch Dienst (DAAD) award. C.O.D.V. especially acknowledges the DAAD for its generous sponsorship of the DAAD Regional Program of Chemistry of the Republic of Argentina (supporting Latin-American students for a Ph.D. program in La Plata).

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