Inorg. Chem. **2007**, *46*, 4692–4703

Inorganic Chemistry Article

Formation of New Halogenothiocarbonylsulfenyl Halides, XC(S)SY, through Photochemical Matrix Reactions Starting from CS_2 and a Dihalogen Molecule XY (XY = Cl_2, Br_2, or BrCl)

Yeny A. Tobón,[†] Rosana M. Romano,[*,†] Carlos O. Della Védova,[†,‡] and Anthony J. Downs[§]

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, and Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U.K.

Received January 23, 2007

Isolation of a dihalogen molecule XY (XY = Cl_2, Br_2, or BrCl) with CS_2 in a solid Ar matrix at about 15 K leads, by broad-band UV–vis photolysis ($200 \leq \lambda \leq 800$ nm), to a variety of products depending on the natures of X and Y. These products have been identified on the basis of the IR spectra of the matrices. In addition to the familiar species $SCCl_2$, $ClCS^\bullet$, $Cl^\bullet\cdots SCS$, CCl_4, $\bullet CCl_3$, $:CCl_2$, SCl_2, $SCBr_2$, CBr_4, $\bullet CBr_3$, BrC(S)Cl, $BrCCl_3$, and :CBrCl, the following new molecules have also been identified as products of the various photoreactions: *syn*-ClC(S)SCl, *anti*-ClC(S)SCl, *syn*-BrC(S)SBr, *anti*-BrC(S)SBr, *syn*-ClC(S)SBr, *anti*-ClC(S)SBr, *syn*-BrC(S)SCl, *anti*-BrC(S)SCl, $ClC(S)S^\bullet$, $BrCS^\bullet$, and $Br^\bullet\cdots SCS$. The IR spectra of these hitherto unknown species have been interpreted with reference to the predictions of ab initio (HF and MP2) and density functional theory (DFT) calculations. The results are analyzed in relation to the reaction pathways accessed by matrix photolysis.

Introduction

Our research group in La Plata has been interested for some time in the matrix photochemistry of relatively small molecules. For example, carbonylsulfenyl compounds of the type XC(O)SY (X, Y = H, halogen, or an organic group) have been shown to possess a rich photochemistry involving a variety of reaction pathways which we have sought to elucidate. An earlier study of the matrix photochemistry of chlorocarbonylsulfenyl bromide, ClC(O)SBr,[1] has served in particular as a prototype for subsequent research. Broad-band UV−vis irradiation of ClC(O)SBr trapped in a solid Ar matrix was shown to result not only in partial transformation of the more stable syn conformer into the anti conformer of the parent molecule, but also in the formation of its isomer BrC(O)SCl, as well as the fragments BrCl, BrSCl, CO, and OCS. The photoreversibility of some of the changes suggested new synthetic options, exemplified by our recent reports of how the new molecules BrC(O)SBr[2] and IC(O)SBr[3] come to be formed upon photolysis of Ar matrixes containing, respectively, OCS/Br_2 and OCS/IBr mixtures. In these photolytically activated reactions between OCS and a dihalogen molecule, only the syn conformer of the carbonylsulfenyl product was detected. The corresponding anti form can be identified only upon irradiation of a matrix initially containing the more stable syn form (as with ClC(O)SCl[4] and ClC(O)SBr[1]).

Studies of the spectroscopic and conformational properties of thiocarbonylsulfenyl compounds have been motivated partly by the discovery that molecules containing the dithioester group afford an ideal resonance Raman probe for monitoring catalytic events within the active site of an enzyme.[5] Compounds of the type $RC(S)SR_1$ (R = CH_3; R_1 = CH_3 or CH_2CH_3) have been found to assume only the syn conformation.[6−8] Microwave spectra of dithioformic acid,

---

* To whom correspondence should be addressed. E-mail: romano@quimica.unlp.edu.ar.

[†] CEQUINOR (UNLP-CONICET).

[‡] Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET).

[§] Inorganic Chemistry Laboratory.

(1) Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5794−5801.

(2) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *Chem. Commun.* **2001**, 2638−2639.

(3) Tobón, Y. A.; Nieto, L. I.; Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A* **2006**, *110*, 2674−2681.

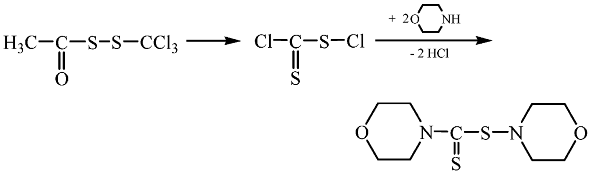
(4) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A* **2004**, *108*, 7179−7187.

(5) Lee, H.; Storer, H. C.; Carey, P. R. *Biochemistry* **1983**, *22*, 4781−4789.

10.1021/ic070119+ CCC: $37.00

HC(S)SH, have been interpreted, however, in terms of a conformational equilibrium between syn and anti forms, with the syn form predominating.[9]

To the best of our knowledge, no thiocarbonylsulfenyl halides of the type XC(S)SY (X, Y = the same or different halogen atoms) have hitherto been characterized experimentally. The chloride ClC(S)SCl has been proposed as an intermediate in the chemical reaction represented by eq 1.[10] However plausible this may be, direct evidence has yet to be advanced.



(1)

Here we report studies of some photochemical reactions involving a dihalogen molecule XY (Cl_2, Br_2, or BrCl) and CS_2 isolated together in an Ar matrix at about 15 K. Analysis of the FT-IR spectrum of such a matrix shows that broad-band UV−vis irradiation gives access to three primary reaction channels, as represented by eqs 2−4. Hence, in

$$S{=}C{=}S + XY \rightarrow XC(S)SY \qquad (2)$$

$$S{=}C{=}S + XY \rightarrow XC(S)Y + S \qquad (3)$$

$$S{=}C{=}S + XY \rightarrow \mathbf{:}CXY + 2S \qquad (4)$$

addition to the known thiocarbonyl dihalide XC(S)Y and the carbene **:**CXY, we have gained the first evidence for the halogenothiocarbonylsulfenyl halide XC(S)SY. Both the syn and anti rotamers of XC(S)SY are formed simultaneously. Various radicals are observed as intermediates. These include $ClC(S)S^\bullet$, $Br^\bullet\cdots SCS$, and $BrCS^\bullet$, each identified for the first time, as well as the known species $ClCS^\bullet$, $Cl^\bullet\cdots SCS$, and $\bullet CX_3$. Among the final products detected in these experiments are the tetrahalomethanes CCl_4, CBr_4, and $CBrCl_3$ and the sulfur dihalide SCl_2. Characterization of the new products by their IR spectra has been underpinned by the isotopic effects observed and by comparison with the results of appropriate quantum chemical calculations.

Experimental and Theoretical Methods

Commercial samples of Cl_2 and Br_2 (both from Aldrich) were used without further purification. CS_2 (again from Aldrich) was purified by repeated trap-to-trap condensation in vacuo. BrCl was produced by mixing equimolar amounts of Cl_2 and Br_2, leading to an equilibrium mixture of BrCl, Cl_2, and Br_2.[11] Gas mixtures of the dihalogen XY (Cl_2, Br_2, or BrCl), CS_2, and Ar, typically with the composition of XY/CS_2/Ar being between 2:1:200 and 0.5:1:200, were prepared by standard manometric methods. Each such mixture was deposited on a CsI window cooled to ∼15 K by a Displex closed-cycle refrigerator (Air Products, model CS202) using the pulsed-deposition technique.[12,13]

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 $\pm$ 0.1 cm^{-1}, using a Nicolet Magna-IR 560 FT-IR instrument equipped with either an MCTB or a DTGS detector (for the ranges of 4000−400 or 600−250 cm^{-1}, respectively). After deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV−vis radiation ($200 \leq \lambda \leq 800$ nm) 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 to minimize any heating effects. The IR spectrum of the matrix was then recorded at different times of irradiation, with close attention to the decay of absorptions due to the reactants and to the appearance and subsequent behavior of any new absorptions.

All of the quantum chemical calculations were performed using the Gaussian 98 program system[14] under the Linda parallel execution environment with two coupled PCs. HF, density functional theory (DFT), and MP2 methods were used in combination with a 6-31+G* basis set for C, S, and Cl atoms, and a LANL2DZ basis set,[15] including an effective core potential (ECP), for Br atoms. The ECP chosen is that proposed by Hay and Wadt[16] 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 geometric parameters. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary vibrational frequencies were found.

Results and Discussion

(i) Cl_2 + CS_2. A mixture of Cl_2, CS_2, and Ar, typically in the proportions 0.5:1:200 or 2:1:200, was deposited on the cooled CsI window. The IR spectrum of the resulting matrix, measured immediately after deposition, displayed only the IR absorptions characteristic of either free CS_2[17,18] or the weakly bound van der Waals complex $CS_2\cdots Cl_2$ described only very recently.[19]

---

(6) Herzog, K.; Steger, E.; Rosmus, P.; Scheithauer, S.; Mayer, R. *J. Mol. Struct.* **1969**, *3*, 339−350.
(7) Fausto, R.; Martins, A. G.; Teixeira-Dias, J. J. C.; Tonge, P. J.; Carey, P. R. *J. Mol. Struct*. **1994**, *323*, 59−69.
(8) Teixeira-Dias, J. J. C.; Fausto, R.; Batista de Carvalho, L. A. E. *J. Mol. Struct. (THEOCHEM)* **1992**, *262*, 87−103.
(9) Bak, B.; Nielsen, O. J.; Svanholt, H. *J. Mol. Spectrosc*. **1978**, *69*, 401−408.
(10) Senning, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 941−942.
(11) Mattraw, H. C.; Pachucki, C. F.; Hawkins, N. J. *J. Chem. Phys.* **1954**, *22*, 1117−1119.
(12) (a) Almond, M. J.; Downs, A. J. *Adv. Spectrosc*. **1989**, *17*, 1−511. (b) Dunkin, I. R. *Matrix-Isolation Techniques: A Practical Approach*; Oxford University Press: New York, 1998.
(13) Perutz, R. N.; Turner, J. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 452−461.
(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.
(15) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.
(16) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.
(17) Bahou, M.; Lee, Y. C.; Lee, Y. P. *J. Am. Chem. Soc*. **2000**, *122*, 661−667.
(18) Givan, A.; Loewenschuss, A.; Bier, K. D.; Jodl, H. J. *Chem. Phys.* **1986**, *106*, 151−159.
(19) Romano, R. M.; Picone, A. L.; Downs, A. J. *J. Phys. Chem. A* **2006**, *110*, 12129−12135.

Table 1. Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV−vis Photolysis of an Ar Matrix Containing a Mixture of CS_2 and Cl_2 at $\sim$15 K

Ar matrix	assignment		wavenumbers reported previously
ν (cm^{-1})	molecule	vibrational mode	ν [cm^{-1}]
1481.5	Cl$^{\bullet}\cdots$SCS	ν_{as}(S=C=S)	1468^{a}
1189.1	ClCS$^{\bullet}$	ν(C=S)	1189.3^{b}
1145.5	*syn*-ClC(S)SCl	ν(C=S)	this work
1145.0			
1144.3			
1143.4			
1129.7	$SCCl_2$	ν(C=S) (ν_1)	1130.0
1123.9			1123.8^{c}
1088.5	*anti*-ClC(S)SCl	ν(C=S)	this work
1084.7			
914.6	ClC(S)S$^{\bullet}$	ν(C=S)	this work
898.1	$\bullet CCl_3$	ν_{as}(CCl_3) (ν_3)	898.4^{d}
889.4	*anti*-ClC(S)SCl	ν_{as}(Cl−C−S)	this work
884.9			
812.0	$SCCl_2$	($\nu_2 + \nu_5$)	810.0^{c}
808.8	*syn*-ClC(S)SCl	ν_{as}(Cl−C−S)	this work
788.6	CCl_4	ν_{as}(C−Cl) (n_3)	789.1
787.4			787.9
786.4			786.7
			785.8
			784.6^{e}
785.4	$SCCl_2$	ν_{as}(^{35}Cl−C−^{35}Cl) (ν_4)	785.0^{c}
783.7	$SCCl_2$	ν_{as}(^{37}Cl−C−^{35}Cl) (ν_4)	782.6^{c}
778.2	$SCCl_2$	ν_{as}(^{37}Cl−C−^{37}Cl) (ν_4)	776.8^{c}
767.0	CCl_4	($\nu_1 + \nu_4$)	767.4
764.8			765.9
763.9			764.5
761.6			762.1
			761.1
			759.5
			758.0^{e}
746.5	:CCl_2	ν_{as}(Cl−C−Cl)	745.7^{f}
540.0	*syn*-ClC(S)SCl	ν(S−Cl)	this work
520.6	SCl_2	ν_s(^{35}Cl−S−^{35}Cl)	520.2^{g}
517.1	SCl_2	ν_{as}(^{35}Cl−S−^{35}Cl)	517.5^{g}
516.2	*anti*-ClC(S)SCl	ν(S−Cl)	this work
511.9			
514.7	SCl_2	ν_s(^{35}Cl−S−^{37}Cl)	515.2^{g}
513.3	SCl_2	ν_{as}(^{35}Cl−S−^{37}Cl)	512.8^{g}
503.4	*syn*-ClC(S)SCl	ν_s(Cl−C−S)	this work
498.1	$SCCl_2$	ν_s(^{35}Cl−C−^{35}Cl) (ν_2)	499.5^{c}
493.2	$SCCl_2$	ν_s(^{37}Cl−C−^{35}Cl) (ν_2)	495.25^{c}
449.3	*anti*-ClC(S)SCl	ν_s(Cl−C−S)	this work
445.6	*anti*-ClC(S)SCl	$\delta_{oop}{}^{h}$	this work
414.3	*syn*-ClC(S)SCl	$\delta_{oop}{}^{h}$	this work
411.5			

[a] Ref 20 (Raman spectrum of CCl_4 solution). [b] Ref 26. [c] Ref 22. [d] Ref 27. [e] Ref 23. [f] Ref 25. [g] Ref 24. [h] δ_{oop} = out-of-plane deformation.

Subsequent irradiation of the matrix with broad-band UV−vis light ($200 \leq \lambda \leq 800$ nm) led, however, to drastic changes in the spectrum. Decay of the bands from the complex $CS_2\cdots Cl_2$ was accompanied by the appearance and growth of new bands from a variety of products, as listed in Table 1. The first of these bands to appear after 1 min of irradiation occurred near 1481, 1145, and 1088 cm^{-1}, that is, in a region generally characteristic of ν(C=S) vibrations. The development of a new band at 1481.5 cm^{-1} with a shift of −46.6 cm^{-1} with respect to free CS_2 suggests the formation of a molecular complex by the interaction of CS_2 with a Cl$^{\bullet}$ atom released through photodissociation of Cl_2. Such a complex, Cl$^{\bullet}\cdots$SCS, has already been studied extensively,[20,21] but the vibrational wavenumbers reported were derived not from the IR but from Raman spectra of solutions of CS_2 in CCl_4 at 1 M concentration. Several theoretical studies were then performed, revealing that the most stable structure is one with the Cl$^{\bullet}$ atom linked to an S atom to give a Cl$\cdots$S=C bond angle of $\sim$107º.[20] The other two features appearing in the ν(C=S) region, near 1145 and 1088 cm^{-1}, will be shown (quode vide) to be the most intense absorptions of the new chlorothiocarbonylsulfenyl chloride molecules *syn*-ClC(S)SCl and *anti*-ClC(S)SCl, respectively.

Continued broad-band UV−vis photolysis resulted in the development of yet more new bands. Among these, features centered near 1130/1124, 812, 785/784/778, and 498/493 cm^{-1} could be recognized as the ν_1, ($\nu_2 + \nu_5$), ν_4, and ν_2 vibrational transitions of the $SCCl_2$ molecule.[22] A set of bands near 789/787/786 cm^{-1} could also be identified with the ν_3 fundamental of CCl_4;[23] a multiplet at 767/765/764/762 cm^{-1} could be identified with the ($\nu_1 + \nu_4$) combination mode of this molecule. Other familiar products were SCl_2, the carbene **:**CCl_2, and the radicals ClCS$^{\bullet}$ and $\bullet CCl_3$ recognizable by bands at 513−521,[24] 746.5,[25] 1189.1,[26] and 898.1 cm^{-1},[27] respectively.

Furthermore, the spectrum showed the growth of some new bands that could not be attributed to any known species. For example, a family of bands arising from a single product, based on the evidence of a common growth pattern, was observed near 1145/1144/1143, 809, 540, 503, and 414/411 cm^{-1}. The wavenumbers give strong circumstantial evidence of a molecule incorporating the Cl−C=S and S−Cl fragments.[22,24,26] In addition, quantum chemical calculations predict vibrational properties for the hitherto unknown molecule *syn*-ClC(S)SCl in persuasive agreement with the observed pattern of IR absorptions (see Table 2). Another family composed of bands centered near 1088/1085, 889/885, 516/512, 449, and 446 cm^{-1} could then be assigned to the rotational isomer *anti*-ClC(S)SCl, a conclusion again supported by the results of theoretical calculations (see Table 2).

After 15 min of irradiation, an absorption at 914.6 cm^{-1} became discernible. This differed in its growth from the bands attributed to the ClC(S)SCl molecules, and its likely origin invited further quantum chemical calculations. There is no wholly satisfactory consensus between the predictions of the HF, DFT (B3LYP), and MP2 methods (see Supporting Information), but the B3LYP method, in combination with a 6-31+G* basis set, gives grounds for believing that the band could be carried by the hitherto unknown ClC(S)S$^{\bullet}$ radical.

---

(20) Wang, D.; Li, Y.-L.; Ho, W. S.; Leung, K. H.; Phillips, D. L. *J. Org. Chem*. **2002**, *67*, 747−752.

(21) Sumiyoshi, T.; Nakayama, M.; Fujiyoshi, R.; Sawamura, S. *Rad. Phys. Chem*. **2006**, *75*, 20−25.

(22) Hauswirth, W.; Willner, H. *Spectrochim. Acta, Part A* **1979**, *35*, 263−269.

(23) King, S. T. *J. Chem. Phys*. **1968**, *49*, 1321−1330.

(24) Bielefeldt, D.; Willner, H. *Spectrochim. Acta, Part A* **1980**, *36*, 989−995.

(25) (a) Andrews, L. *J. Chem. Phys*. **1968**, *48*, 979−982. (b) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys*. **1970**, *53*, 2688−2701.

(26) Schallmoser, G.; Wurfel, B. E.; Thoma, A.; Caspary, N.; Bondybey, V. E. *Chem. Phys. Lett*. **1993**, *201*, 528−534.

(27) Rogers, E. E.; Abramowitz, S.; Jacox, M. E.; Milligan, D. E. *J. Chem. Phys*. **1970**, *52*, 2198−2204.

Table 2. Experimental and Calculated IR Spectra of *syn*-Chlorothiocarbonylsulfenyl Chloride, *syn*-ClC(S)SCl, and *anti*-Chlorothiocarbonylsulfenyl Chloride, *anti*-ClC(S)SCl[a]

syn-ClC(S)SCl				*anti*-ClC(S)SCl				
Ar matrix	theoretical calculations			Ar matrix	theoretical calculations			vibrational mode
ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	
1145.5 1145.0 1144.3 1143.4 } (100)	1117.4 (100)	1145.1 (100)	1188.9 (100)	1088.5 1084.7 } (100)	1078.0 (100)	1079.3 (100)	1148.8 (100)	ν(C=S)
808.8 (48)	801.5 (37)	723.1 (46)	802.5 (67)	889.4 884.9 } (58)	873.0 (42)	869.5 (74)	900.5 (93)	ν_{as}(Cl−C−S)
540.0 (25)	547.0 542.1 } (11)	520.4 515.7 } (20)	561.0 555.5 } (18)	516.2 511.9 } (9)	528.0 523.3 } (11)	458.9 454.5 } (19)	524.7 519.8 } (25)	ν(S−^{35}Cl) ν(S−^{35}Cl)
503.4 (7)	497.8 (5)	500.5 (2)	521.3 (4)	449.3 (13)	472.3 (6)	477.0 (8)	495.1 (14)	ν_s(Cl−C−S)
414.3 411.5 } (5)	455.0 (<1)	458.9 (1)	435.9 (2)	445.6 (17)	458.5 (<1)	458.8 (23)	432.2 (1)	δ_{oop}[b]
	320.7 (<1)	315.5 (1)	334.0 (1)		311.3 (1)	313.5 (2)	326.8 (1)	δ(Cl−C=S)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses. [b] δ_{oop} = out-of-plane deformation

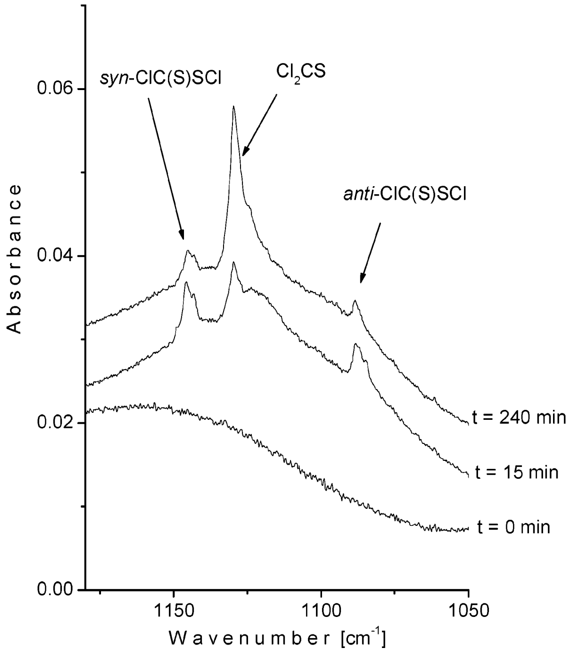


Figure 1. FT-IR spectra of an Ar matrix containing Cl_2 and CS_2 ($Cl_2/CS_2/Ar$ = 0.5:1:200) in the region of 1180−1050 cm^{-1} immediately after deposition (bottom), after 15 min of photolysis (middle), and after 240 min of photolysis (top).

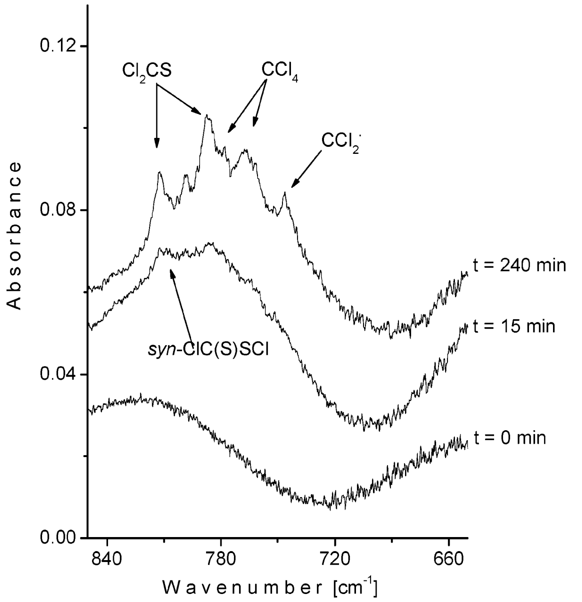


Figure 2. FT-IR spectra of an Ar matrix containing Cl_2 and CS_2 ($Cl_2/CS_2/Ar$ = 0.5:1:200) in the region of 850−650 cm^{-1} immediately after deposition (bottom), after 15 min of photolysis (middle), and after 240 min of photolysis (top).

Scheme 1. Possible Mechanism for the Formation of the syn and anti Forms of ClC(S)SCl in an Ar Matrix at ~15 K

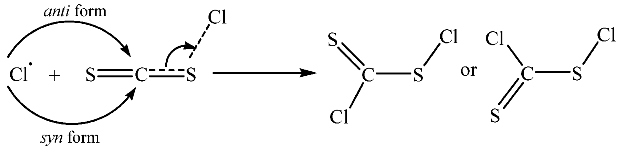


Table 1 lists the wavenumbers of all the new absorptions observed to develop in the photochemical reaction occurring between CS_2 and Cl_2 when isolated together in an Ar matrix. Literature data is also included for the Cl•···SCS complex,[20] the ClCS•[26] and •CCl_3[27] radicals, and :CCl_2,[25] $SCCl_2$,[22] CCl_4,[23] and SCl_2;[24] with the exception of the Cl•···SCS complex (quode vide), these data relate to species similarly isolated in Ar matrixes. Figures 1 and 2 show two different regions of the IR spectra of an Ar matrix doped with CS_2 and Cl_2, with traces recorded immediately after deposition and again after broad-band UV−vis irradiation.

Photolysis of matrix-isolated CS_2 to bring about either photodissociation to CS and S atoms or ionization to give the CS_2^+ radical cation, reported previously,[28] occurs only under the action of vacuum-UV radiation. None of the IR spectra recorded for photolyzed matrixes initially containing CS_2 isolated together with Cl_2 gave any hint of an absorption in the neighborhood of 1280 cm^{-1} that could be attributed to the CS molecule.[29] Hence, although the photoproducts included numerous species that could be formed only with the rupture of one or both C=S bonds of the CS_2 parent, that is, ClCS•, $SCCl_2$, :CCl_2, •CCl_3, and CCl_4, there is no

---

(28) (a) Fournier, J.; Lalo, C.; Deson, J.; Vermeil, C. *J. Chem. Phys.* **1977**, *66*, 2656−2659. (b) Bondybey, V. E.; English, J. H.; Miller, T. A. *J. Chem. Phys.* **1979**, *70*, 1621−1625.

(29) Taylor, G. W.; Setser, D. W.; Coxon, J. A. *J. Mol. Spectrosc.* **1972**, *44*, 108−117 and references cited therein.

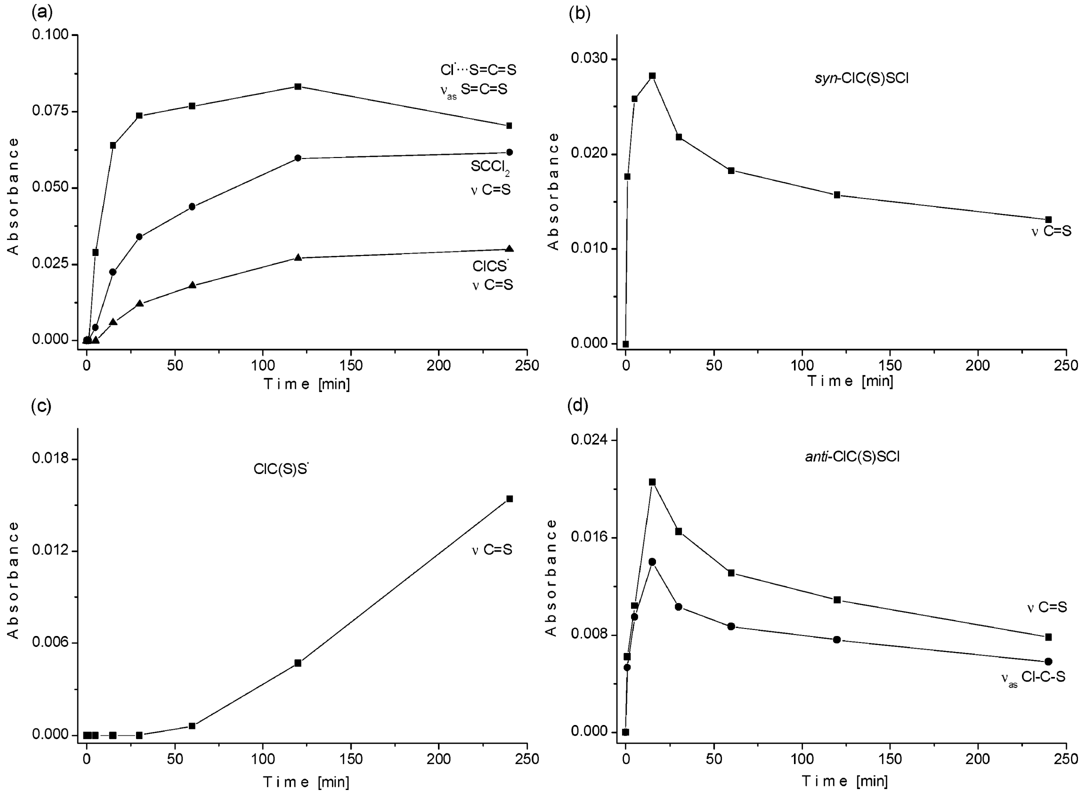


Figure 3. Plots as a function of irradiation time of the intensities of the bands assigned to (a) $Cl^{\bullet}\cdots SCS$, $SCCl_2$, and $ClCS^{\bullet}$, (b) *syn*-ClC(S)SCl, (c) $ClC(S)S^{\bullet}$, and (d) *anti*-ClC(S)SCl in the IR spectrum of an Ar matrix initially containing Cl_2, CS_2, and Ar in the proportion of 0.5:1:200.

reason to believe that photodissociation of CS_2 alone plays a significant part in the photochemistry displayed by matrix-isolated mixtures of CS_2 and Cl_2. Instead, it would appear that Cl_2 or $Cl^{\bullet}$ atoms act through coordination or, at the very least, close proximity to photosensitize the CS_2. Therefore, almost certainly, species such as $ClCS^{\bullet}$ and $SCCl_2$ evolve primarily from the complexes $Cl_2\cdots SCS$ and $Cl^{\bullet}\cdots SCS$, with $Cl^{\bullet}$ and S atoms being formed simultaneously. It is likely, too, that the chlorocarbon products are formed in a similar way from complexes such as $ClCS^{\bullet}\cdots Cl^{\bullet}$ or $Cl^{\bullet}\cdots SCCl_2$, although no positive evidence of these intermediates was apparent. Both the $Cl^{\bullet}$ and S atoms are relatively immobile in a solid Ar matrix at $\sim$15 K,[30] even if the extra energy supplied by the photolyzing radiation may be sufficient to mobilize them to some extent. The photochemistry observed is therefore likely to be dominated by the interactions between molecules or between molecules and atoms that are already held close together within a common matrix cage.

The formation of both syn and anti forms of the chlorothiocarbonylsulfenyl chloride, ClC(S)SCl, is apparent from the earliest stages of irradiation. There is no evidence to suggest that one rotamer is formed first and converted into the other upon continued photolysis (cf., the behavior of chlorocarbonylsulfenyl chloride, ClC(O)SCl[4]). The highly reactive complex $Cl^{\bullet}\cdots SCS$ is most likely to be the precursor to the syn and anti forms of ClC(S)SCl (as suggested in Scheme 1).

To help determine the sequence of the changes, the integrated intensities of some of the new bands have been monitored as a function of irradiation time, with the results depicted in Figure 3. This brings to light significant aspects of the growth or decay of the species in question. Thus, the syn and anti forms of ClC(S)SCl start to decay after 15 min of broad-band UV−vis irradiation, whereas the radicals $ClC(S)S^{\bullet}$ and $ClCS^{\bullet}$ start to grow. As indicated above, the $ClCS^{\bullet}$ radical is unlikely to be formed directly from CS_2; a more plausible precursor is $ClC(S)S^{\bullet}$, making $ClCS^{\bullet}$ a photoevolution product from *syn*- and *anti*-ClC(S)SCl. It was found that the relative yields of $SCCl_2$ and *syn*- and *anti*-ClC(S)SCl increased as the concentration of Cl_2 decreased. By contrast, an excess of Cl_2 relative to CS_2 led to an increased yield of CCl_4. The inference to be drawn is that an excess of CS_2 favors reaction network 1, whereas an excess of Cl_2 favors network 2 outlined in Scheme 2.

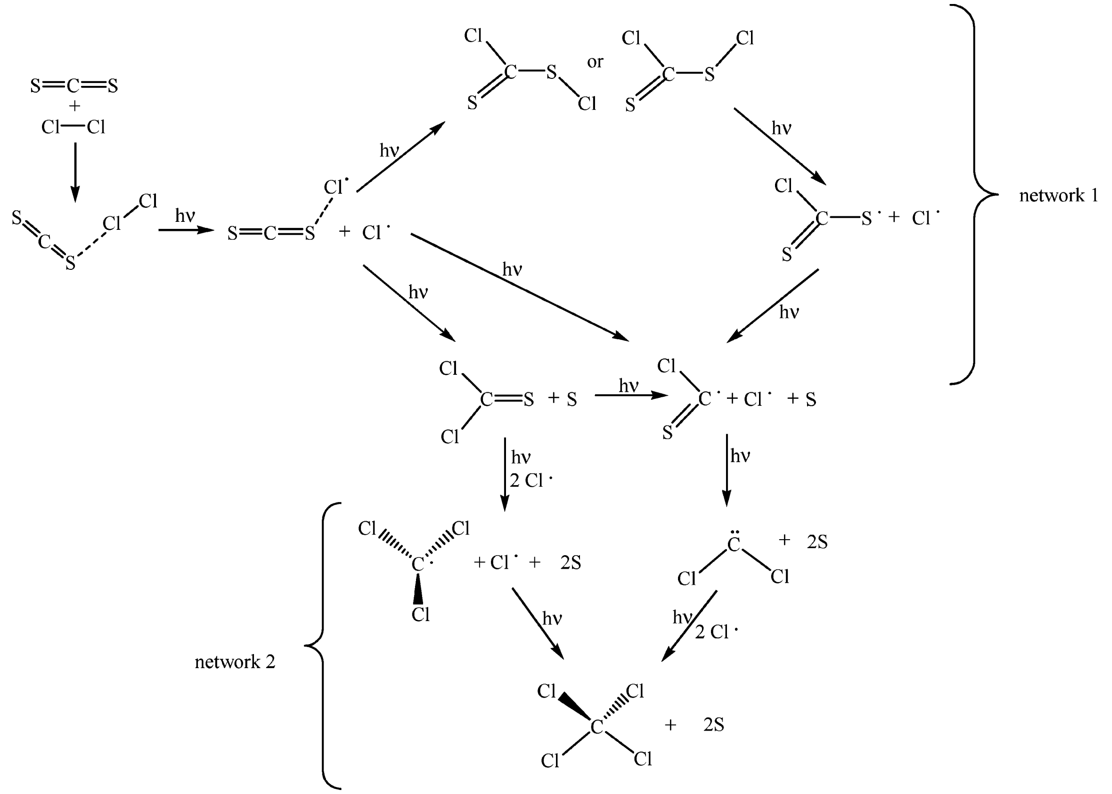
The geometric and vibrational properties of the species *syn*-ClC(S)SCl and *anti*-ClC(S)SCl have been simulated by ab initio (HF, MP2) and DFT (B3LYP) methods in combination with a 6-31+G* basis set, with the results presented in Table 2. The most intense IR absorptions predicted by the calculations are in good agreement with the features observed for the new products. In view of the calculated wavenumbers and IR intensities, there was significantly less chance of locating any of the other fundamental bands under the conditions prevailing in our experiments. The calculated geometric parameters are presented as Supporting Information.

(ii) $Br_2 + CS_2$. Similar studies were carried out with matrixes formed by mixtures of Br_2, CS_2, and Ar, typically

---

(30) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *Chem. Rev.* **2002**, *102*, 4191−4241 and references cited therein.

Scheme 2. Possible Mechanisms of the Photochemical Reactions Occurring in an Ar Matrix Doped with Cl_2 and CS_2 at ~15 K



in the proportions 2:1:200 or 1:1:200. The IR spectrum of the matrix recorded immediately after deposition was dominated by the absorptions of CS_2,[17,18] made more complicated by the presence of both the free CS_2 molecule and the van der Waals complex $Br_2 \cdots CS_2$.[19] The exposure of such a matrix to broad-band UV−vis light produced significant changes in the spectrum, as illustrated in Figures 4−6. Table 3 lists the wavenumbers, as well as the proposed assignments, of the absorptions that developed in these conditions, together with literature data for the singlet molecules $SCBr_2$[22] and CBr_4[31] and the •CBr_3 radical.[27,31]

As in the experiments with Cl_2, the reactions are presumably initiated primarily by the photodisociation of Br_2 to give $Br^•$ atoms. Two new bands in the $\nu_{as}(CS_2)$ region at 1499.4 and 1493.7 cm^{-1} were observed to develop after irradiation with shifts of −28.7 and −30.8 cm^{-1}, respectively, compared with free CS_2. In the light of the precedent set by the complex formed between $Cl^•$ and CS_2, an analogous complex between $Br^•$ and CS_2 would be the obvious carrier of these bands. Because we found no prior information about such a complex, we have performed calculations to determine the optimized geometry and vibrational properties of the complex

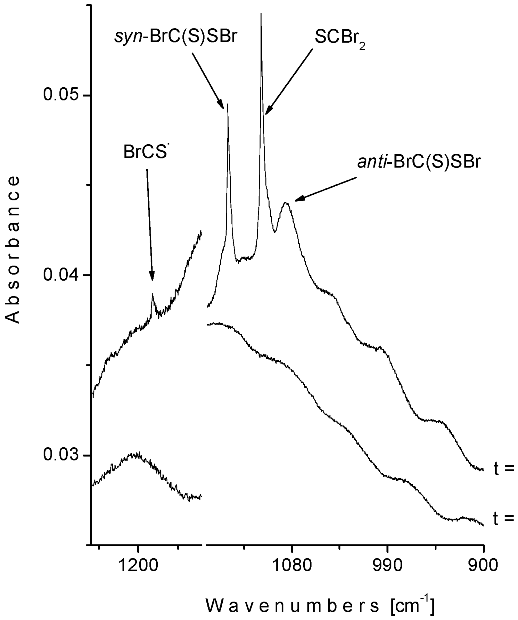


Figure 4. FT-IR spectra of an Ar matrix containing Br_2 and CS_2 ($Br_2/CS_2/Ar$ = 2:1:200) in the region of 1230−900 cm^{-1} immediately after deposition (bottom) and after 240 min of photolysis (top).

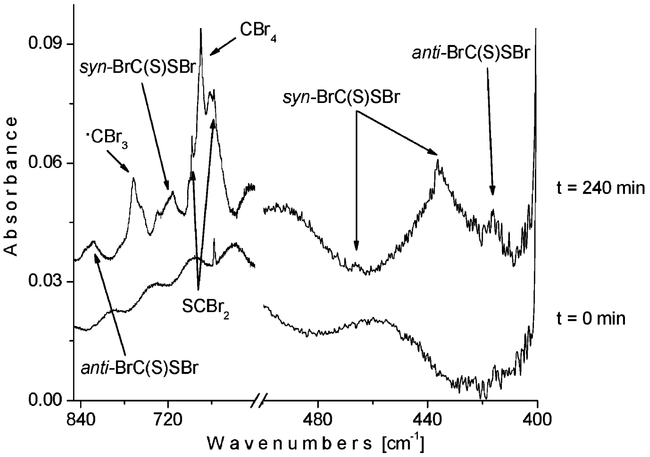


Figure 5. FT-IR spectra of an Ar matrix containing Br_2 and CS_2 ($Br_2/CS_2/Ar$ = 2:1:200) in the region of 850−400 cm^{-1} immediately after deposition (bottom) and after 240 min of photolysis (top).

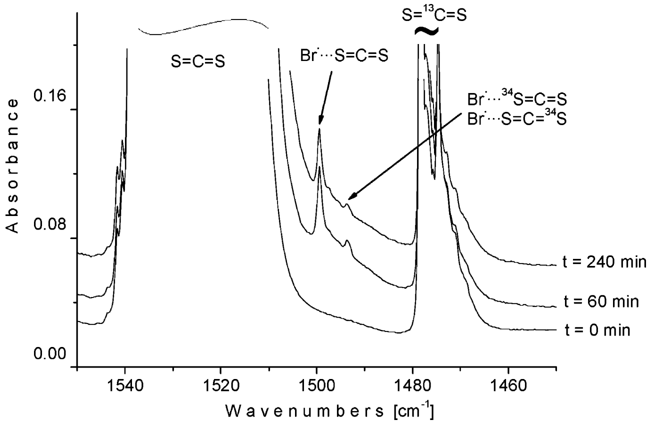


Figure 6. FT-IR spectra of an Ar matrix containing Br_2 and CS_2 ($Br_2/CS_2/Ar = 2:1:200$) in the region of 1550−1450 cm^{-1} immediately after deposition (bottom), after 60 min of photolysis (middle), and after 240 min of photolysis (top).

Table 3. Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV−vis Photolysis of an Ar Matrix Containing a Mixture of CS_2 and Br_2 at ~15 K

Ar matrix	assignment		wavenumbers reported previously
ν (cm^{-1})	molecule	vibrational mode	ν (cm^{-1})
1499.4	$Br^\bullet\cdots S{=}C{=}S$	$\nu_{as}(^{32}S{=}C{=}^{32}S)$	this work
1493.7	$Br^\bullet\cdots S{=}C{=}S$	$\nu_{as}(^{34}S{=}C{=}^{32}S)$	this work
1190.6	$BrCS^\bullet$	$\nu(C{=}S)$	this work
1140.4	*syn*-BrC(S)SBr	$\nu(C{=}S)$	this work
1138.9			
1108.8	$SCBr_2$	$\nu(C{=}S)$ (ν_1)	1109.0[a]
1107.6			
1086.8	*anti*-BrC(S)SBr	$\nu(C{=}S)$	this work
1084.1			
823.2	*anti*-BrC(S)SBr	$\nu_{as}(Br{-}C{-}S)$	this work
767.0	$\bullet CBr_3$	$\nu_{as}(CBr_3)$ (ν_3)	773[b]
713.4	*syn*-BrC(S)SBr	$\nu_{as}(Br{-}C{-}S)$	this work
691.3	$SCBr_2$	$\nu_{as}(Br{-}C{-}Br)$ (ν_4)	688.5[a]
686.8			
674.7	CBr_4	$\nu_{as}(C{-}Br)$ (ν_3)	675[b]
663.1	$SCBr_2$	$\nu_{as}(Br{-}^{13}C{-}Br)$ (ν_4)	664.2[a]
466.1	*syn*-BrC(S)SBr	$\nu_s(Br{-}C{-}S)$	this work
436.2	*syn*-BrC(S)SBr	$\nu(S{-}^{79}Br)$	this work
434.7		$\nu(S{-}^{81}Br)$	
416.8	*anti*-BrC(S)SBr	$\nu(S{-}^{79}Br)$	this work
415.9		$\nu(S{-}^{81}Br)$	

[a] Ref 22. [b] Ref 31.

Table 4. Experimental and Calculated Wavenumbers and Wavenumber Shifts (in cm^{-1}) for the $\nu_{as}(S{=}C{=}S)$ Fundamental of the Complex $Br^\bullet\cdots S{=}C{=}S$

species	B3LYP/6-31+G*		Ar matrix	
	$\nu_{as}(S{=}C{=}S)$	$\Delta\nu(S{=}C{=}S)$	$\nu_{as}(S{=}C{=}S)$	$\Delta\nu(S{=}C{=}S)$
$Br^\bullet\cdots S{=}C{=}S$	1521.0	−28.2	1499.4	−28.7
$Br^\bullet\cdots ^{34}S{=}C{=}S$	1517.7	−27.9	1493.7	−30.8
$Br^\bullet\cdots S{=}C{=}^{34}S$	1516.7	−28.9		
$Br^\bullet\cdots ^{34}S{=}C{=}^{34}S$	1513.7	−28.3		

$Br^\bullet\cdots SCS$. The results of these calculations give wavenumber shifts for the $\nu_{as}(S{=}C{=}S)$ fundamental in satisfactory agreement with the experimental shifts. The more intense band then corresponds to the predominant isotopomer $Br^\bullet\cdots ^{32}S{=}C{=}^{32}S$, while the weaker one, toward lower energy, corresponds to the less abundant isotopomer $Br^\bullet\cdots ^{32}S{=}C{=}^{34}S$. The results are listed in Table 4, and the relevant portion of the spectrum is illustrated in Figure 6.

The continuation of photolysis resulted in the appearance of more new bands. Two of these, centered near 1109/1108 and 691/687 cm^{-1}, are recognizable as the fundamentals ν_1 and ν_4, respectively, of the $SCBr_2$ molecule.[22] A third band occurring near 675 cm^{-1} can be identified as the ν_3 fundamental of CBr_4,[31] while a fourth close to 767 cm^{-1} is attributed to the $\bullet CBr_3$ radical.[27,31]

In addition, the spectrum showed the growth of new bands that could not be attributed to any known species. One group of such bands, with centers near 1140/1139, 713, 466, and 436/435 cm^{-1}, with a common growth/decay pattern, can be plausibly assigned to the hitherto unknown molecule *syn*-BrC(S)SBr on the basis of the wavenumbers and pattern of the $^{79}Br/^{81}Br$ isotopic splitting. Similarly, another group, with band centers at ~1087/1084, 823, and 417/416 cm^{-1} can be identified with the corresponding anti isomer. As in the experiments with Cl_2, both the syn and anti rotamers appear to be formed simultaneously in the matrix.

Yet another band also appeared weakly on photolysis. This, occurring at 1190.6 cm^{-1}, was distinguished by a growth pattern quite unlike that of any other band. The wavenumber value implies that it arises from a species containing a C=S group. After careful analysis of the different species that might be formed in primary or secondary photochemical processes, including some computational tests, this band seems most likely to belong to the hitherto unknown radical $BrCS^\bullet$. There was no sign that the $BrC(S)S^\bullet$ radical, a likely precursor to $BrCS^\bullet$, is produced (cf. $ClC(S)S^\bullet$).

Failure to detect this last species, the carbene **:**CBr_2[31] or either SBr or SBr_2[32] marks points of departure from the experiments with Cl_2, although the relevant features could well be masked by more intense absorptions from other products. A further difference emerges with the discovery that the relative yields of the various photoproducts in the Br_2 experiments are *not* affected by the proportions of the primary reagents. Enhanced yields of all the products were observed as the concentration of Br_2 was increased. It may be that the greater bulk of Br_2 limits to one the number of dihalogen molecules that can be accommodated within the same immediate reaction sphere as the CS_2, with only energetic $Br^\bullet$ atoms having the power to add to the primary reactions. By contrast, more than one dihalogen molecule may be admitted to this sphere in the case of Cl_2, with a probability that increases as the square of the Cl_2 concentration. Taking account of the species observed and their behavior with increasing irradiation time (as revealed in Figure 7), we are led to propose the reaction paths for the system Br_2/CS_2 set out in Scheme 3.

The syn and anti forms of BrC(S)SBr are generated presumably by the addition of a $Br^\bullet$ atom to the $Br^\bullet\cdots SCS$ complex but are themselves photolabile and decompose upon continued irradiation to furnish the $BrCS^\bullet$ radical, as depicted

---

(31) Andrews, L.; Carver, T. G. *J. Chem. Phys.* **1968**, *49*, 896−902.

(32) *Sulphur*; Gmelin Handbook of Inorganic Chemistry Suppl. Vol. 2; Springer-Verlag: Heidelberg, Germany, 1978.

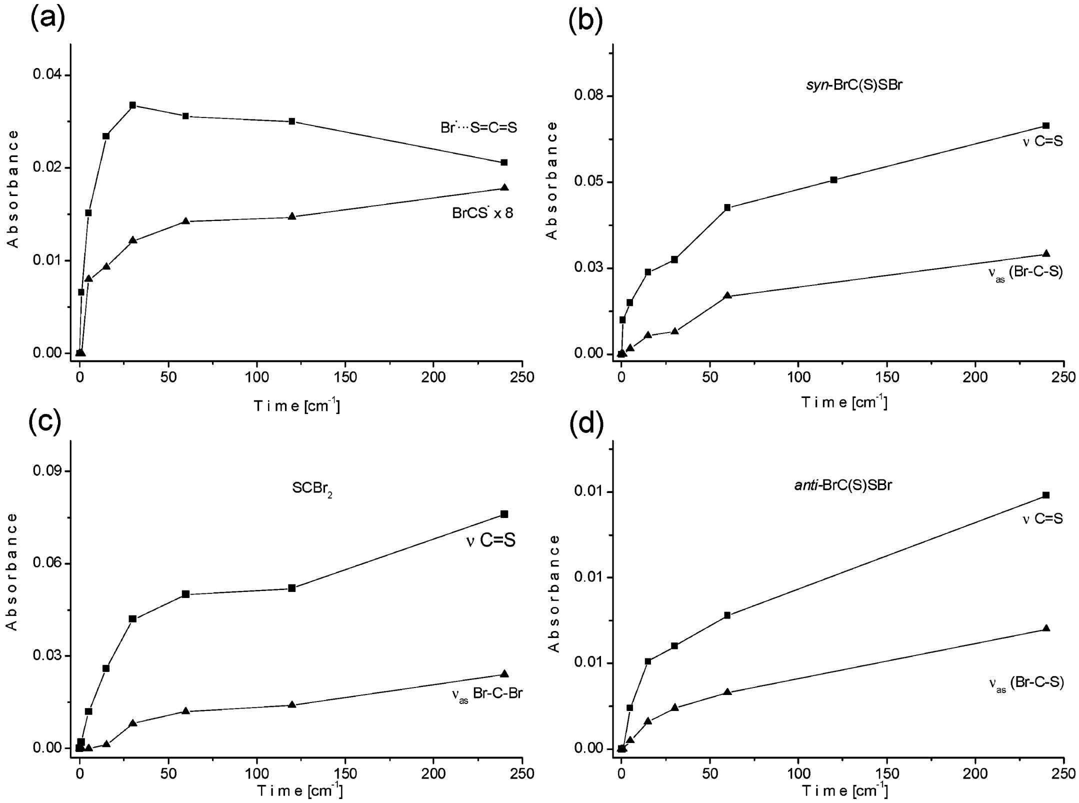


Figure 7. Plots as a function of irradiation time of the intensities of the bands assigned to (a) $Br^{\bullet}\cdots SCS$ and $BrCS^{\bullet}$, (b) *syn*-BrC(S)SBr, (c) $SCBr_2$, and (d) *anti*-BrC(S)SBr in the IR spectrum of an Ar matrix initially containing Br_2, CS_2, and Ar in the proportion of 2:1:200.

Scheme 3. Possible Mechanisms of the Photochemical Reactions Occurring in an Ar Matrix Doped with Br_2 and CS_2 at ~15 K

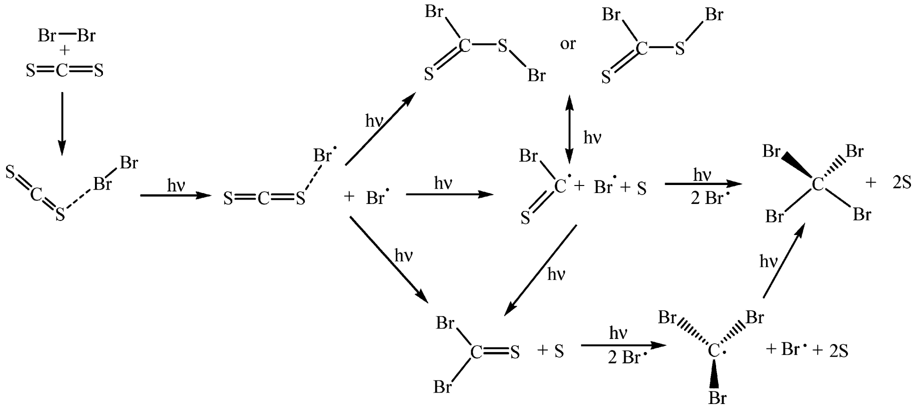


Table 5. Experimental and Calculated IR Spectra of *syn*-Bromothiocarbonylsulfenyl Bromide, *syn*-BrC(S)SBr, and *anti*-Bromothiocarbonylsulfenyl Bromide, *anti*-BrC(S)SBr[a]

syn-BrC(S)SBr				*anti*-BrC(S)SBr				
Ar matrix	theoretical calculations			Ar matrix	theoretical calculations			vibrational mode
ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	
1140.4 1138.9 (100)	1104.0 (100)	1148.5 (100)	1192.7 (100)	1086.8 1084.1 (100)	1057.0 (100)	1061.0 (100)	1122.0 (91)	ν(C=S)
713.4 (44)	732.6 (32)	665.5 (34)	703.7 (35)	823.2 (41)	822.9 (39)	833.0 (76)	843.0 (100)	ν_{as}(Br−C−S)
466.1 (4)	456.7 (<1)	461.2 (4)	462.2 (6)		373.7 (4)	374.1 (9)	345.8 (11)	ν_s(Br-C-S)
	456.8 (<1)	456.7 (1)	433.5 (2)		467.6 (<1)	471.6 (1)	426.4 (2)	δ_{oop}[b]
436.2 434.7 (15)	449.5 448.5 (9)	430.7 429.1 (18)	396.1 394.7 (9)	416.8 415.9 (11)	459.5 458.7 (6)	414.5 413.7 (27)	400.0 399.3 (20)	ν(S−^{79}Br) ν(S−^{81}Br)
	250.5 (<1)	237.6 (1)	237.2 (2)		259.5 (<1)	259.8 (1)	262.1 (3)	δ(Br−C=S)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses. [b] δ_{oop} = out-of-plane deformation.

in Scheme 3. This change opens the way to several secondary channels. Thus, BrC(S)SBr dissociates first to give $BrCS^{\bullet}$, together with the S and $Br^{\bullet}$ atoms. The highly reactive $BrCS^{\bullet}$ radical may then recombine with these atoms, still held in the same matrix cage, to regenerate BrC(S)SBr, or it may add only a $Br^{\bullet}$ atom to form $SCBr_2$.

Table 6. Experimental and Calculated IR Spectra of the Bromothiocarbonyl Radical, $BrCS^{\bullet}$[a]

Ar matrix	theoretical calculations			vibrational mode
ν [cm^{-1}]	HF	B3LYP	MP2	
1190.6	1019.8 (100)	1195.4 (100)	1683.4 (100)	ν(C=S)
	491.3 (84)	491.1 (24)	416.0 (7)	ν(C−Br)
	254.4 (<1)	262.0 (<1)	241.7 (2)	δ(Br−C=S)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses.

Table 7. Wavenumbers (in cm^{-1}) and Assignments of the IR Absorptions Appearing after Broad-Band UV−vis Photolysis of an Ar Matrix Containing a Mixture of CS_2, Cl_2, Br_2, and BrCl at ∼15 K

Ar matrix	assignment		wavenumbers reported previously
ν (cm^{-1})	molecule	vibrational mode	ν (cm^{-1})
1499.4	$Br^{\bullet}\cdots S=C=S$	ν_{as}(^{32}S=C=^{32}S)	this work
1493.8	$Br^{\bullet}\cdots S=C=S$	ν_{as}(^{34}S=C=^{32}S)	this work
1481.7	$Cl^{\bullet}\cdots S=C=S$	ν_{as}(S=C=S)	1468[a]
1188.8	$ClCS^{\bullet}$	ν(C=S)	1189.3[b]
1190.0	$BrCS^{\bullet}$	ν(C=S)	this work
1144.8	*syn*-ClC(S)SCl	ν(C=S)	this work
1143.4	*syn*-BrC(S)SCl	ν(C=S)	this work
1139.9	*syn*-BrC(S)SBr	ν(C=S)	this work
1129.9	$SCCl_2$	ν(C=S) (ν_1)	1130.0 1123.8[c]
1128.6	*syn*-ClC(S)SBr	ν(C=S)	this work
1120.0	BrC(S)Cl	ν(C=S)	1106[d]
1108.7	$SCBr_2$	ν(C=S) (ν_1)	1109.0[c]
1104.2	*anti*-ClC(S)SBr	ν(C=S)	this work
1088.7	*anti*-ClC(S)SCl	ν(C=S)	this work
1054.7	*anti*-BrC(S)SCl	ν(C=S)	this work
914.5	$ClC(S)S^{\bullet}$	ν(C=S)	this work
883.6	*anti*-ClC(S)SBr	ν_{as}(Cl−C−S)	this work
808.7	*syn*-ClC(S)SCl	ν_{as}(Cl−C−S)	this work
801.2	*syn*-ClC(S)SBr	ν_{as}(Cl−C−S)	this work
785.4	$SCCl_2$	ν_{as}(Cl−C−Cl) (ν_4)	785.0[c]
777.7	$BrCCl_3$	ν_{as}(CCl_3)	777.8[e]
751.6	*syn*-BrC(S)SCl	ν_{as}(Br−C−S)	this work
738.6	**:**CBrCl	ν_{as}(Br−C−Cl)	739[f]
737.6	BrC(S)Cl	ν_{as}(Br−C−Cl)	742[d]
724.7	$BrCCl_3$	ν_s(CCl_3)	725.7 723.9[e]
713.8	*syn*-BrC(S)SBr	ν_{as}(Br−C−S)	this work
691.3	$SCBr_2$	ν_{as}(Br−C−Br) (ν_4)	688.5[c]
556.0	*syn*-ClC(S)SBr	ν_s(Cl−C−S)	this work
528.2	*syn*-BrC(S)SCl	ν(S−Cl)	this work
518.9	*anti*-BrC(S)SCl	ν(S−Cl)	this work
472.3	*syn*-BrC(S)SCl	ν_s(Br−C−S)	this work
466.9			
453.4	*syn*-ClC(S)SBr	ν(S−^{79}Br)	this work
451.9		ν(S-^{81}Br)	
436.2	*syn*-BrC(S)SBr	ν(S−^{79}Br)	this work
434.7		ν(S-^{81}Br)	

[a] Ref 20. [b] Ref 26. [c] Ref 22. [d] Ref 34 (IR spectrum of the liquid). [e] Ref 23. [f] Ref 31.

The geometric and vibrational properties of the new species *syn*-BrC(S)SBr, *anti*-BrC(S)SBr, $BrCS^{\bullet}$, and the $Br^{\bullet}\cdots SCS$ complex have been simulated by ab initio and DFT methods using a 6-31+G* basis set for the C and S atoms and a LANL2DZ basis set,[15] including an effective core potential (ECP), for the Br atoms, with the results set out in Tables 4−6. The most intense IR absorptions predicted by the calculations tally well with the features observed for the new products in the matrix spectra. The geometric parameters are presented as Supporting Information.

(iii) BrCl + CS_2. Gaseous mixtures of Cl_2 and Br_2 give rise to an equilibrium mixture including these two species and the interhalogen BrCl,[11] the components of which cannot be separated. When a gaseous mixture of Cl_2, Br_2, CS_2, and Ar, typically in the initial proportions 2:2:1:200, was deposited on a CsI window at ∼15 K, the IR spectrum of the resulting matrix showed only the absorptions characteristic of free CS_2,[17,18] BrCl (near 420 cm^{-1}),[33] and the van der Waals complex ClBr···SCS, which was reported only very recently.[19]

Subsequent irradiation of the matrix with broad-band UV−vis light led to significant changes in the spectrum; new bands appeared and grew, notably at the expense of the bands from the complex ClBr···SCS. The first to appear were bands around 1499 and 1482 cm^{-1}, which were recognized readily from the experiments with Br_2 and Cl_2 as separately arising from the molecular complexes formed by the interaction of a $Br^{\bullet}$ or $Cl^{\bullet}$ atom with a CS_2 molecule. As in the experiments previously described, therefore, the first step involves photodissociation of the dihalogen to give $Cl^{\bullet}$ and $Br^{\bullet}$ atoms which bind loosely to CS_2 in the formatio of the van der Waals complexes $Cl^{\bullet}\cdots SCS$ and $Br^{\bullet}\cdots SCS$, respectively.

Continued photolysis gave rise to new bands in other regions of the spectrum. Two of these bands, occurring at ∼1120 and 738 cm^{-1}, can be identified as the ν(C=S) and ν_{as}(Br−C−Cl) modes of the thiocarbonyl dihalide BrC(S)-Cl, a compound first synthesized by Diderrich and Haas in 1976.[34] The spectrum of the liquid was then reported, although no assignment of the bands was proposed. Theoretical calculations support, and offer an interpretation of the earlier, as well as the present, results with the assignments given in Tables 7 and 10. The spectrum of the photolyzed matrix also revealed the presence of the carbene **:**CBrCl[31] and the tetrahalomethane $BrCCl_3$.[23] The first was recognizable by a band at 738.6 cm^{-1} and the second by the bands

Table 8. Experimental and Calculated IR Spectra of *syn*-Chlorothiocarbonylsulfenyl Bromide, *syn*-ClC(S)SBr, and *anti*-Chlorothiocarbonylsulfenyl Bromide, *anti*-ClC(S)SBr[a]

syn-ClC(S)SBr				*anti*-ClC(S)SBr				vibrational mode
Ar matrix	theoretical calculations			Ar matrix	theoretical calculations			
ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	
1128.6 (100)	1113.8 (100)	1142.2 (100)	1188.1 (100)	1104.2 (100)	1074.5 (100)	1077.2 (100)	1141.9 (80)	ν(C=S)
801.2 (80)	794.6 (43)	717.7 (50)	786.8 (68)	883.6 (90)	869.9 (45)	863.9 (80)	903.9 (100)	ν_{as}(Cl−C−S)
556.0 (1)	501.2 (3)	500.2 (7)	520.6 (7)		486.0 (1)	476.8 (7)	497.1 (6)	ν_s(Cl−C−S)
	466.4 (<1)	467.3 (1)	443.6 (1)		468.0 (<1)	469.2 (1)	436.4 (1)	δ_{oop}[b]
453.4 451.9 (5)	462.2 461.3 (4)	453.9 452.6 (9)	420.6 419.8 (5)		439.3 438.5 (9)	409.2 408.4 (26)	485.3 384.6 (14)	ν(S−^{79}Br) ν(S−^{81}Br)
	309.5 (<1)	304.1 (1)	315.0 (<1)		301.8 (<1)	303.0 (2)	307.9 (4)	δ(Cl−C=S)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses. [b] δ_{oop} = out-of-plane deformation.

Table 9. Experimental and Calculated IR Spectra of *syn*-Bromothiocarbonylsulfenyl Chloride, *syn*-BrC(S)SCl, and *anti*-Bromothiocarbonylsulfenyl Chloride, *anti*-BrC(S)SCl

syn-BrC(S)SCl				*anti*-BrC(S)SCl				
Ar matrix	theoretical calculations			Ar matrix	theoretical calculations			vibrational mode
ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	
1143.4 (100)	1108.8 (100)	1153.0 (100)	1191.9 (100)	1054.7 (100)	1058.5 (100)	1065.4 (100)	1130.2 (100)	ν(C=S)
751.6 (50)	741.9 (27)	675.5 (33)	716.7 (37)		822.2 (35)	833.6 (70)	835.6 (77)	ν_{as}(Br−C−S)
528.2 (10)	534.7 529.6 } (13)	497.4 491.3 } (20)	542.4 536.0 } (17)	518.9 (50)	525.2 520.1 } (14)	457.4 452.8 } (42)	521.2 514.7 } (32)	ν (S−^{35}Cl) ν(S−^{37}Cl)
472.3 (3)	462.7 (2)	468.9 (9)	472.4 (8)		386.1 (4)	384.4 (9)	373.3 (10)	ν_s(Br−C−S)
472.3 466.9 }	463.4 (<1)	464.5 (1)	430.5 (2)		459.6 (<1)	464.3 (1)	427.2 (2)	δ_{oop}[b]
	255.6 (<1)	242.7 (2)	243.3 (2)		275.8 (1)	275.9 (2)	288.1 (2)	δ(Br−C=S)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses. [b] δ_{oop} = out-of-plane deformation.

Table 10. Experimental and Calculated IR Spectra of Thiocarbonyl Chloride Bromide, BrC(S)Cl

Ar matrix	reported values[b]	theoretical calculations			
ν (cm^{-1})	ν (cm^{-1})	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*	vibrational mode
1120.0 (100)	1106	1117.9 (100)	1124.0 (100)	1167.8 (100)	ν(C=S)
737.6 (90)	742	785.7 (53)	724.7 (80)	769.8 (91)	ν_{as}(Br−C−Cl)
		487.2 (<1)	498.7 (1)	454.5 (1)	δ_{oop}[c]
		434.9 (3)	433.5 (6)	433.5 (9)	ν_s(Br−C−Cl)
		261.8 (<1)	263.2 (<1)	262.8 (1)	δ(Cl−C=S)
		237.6 (<1)	243.6 (<1)	250.3 (<1)	δ(Br−C−Cl)

[a] Wavenumbers in cm^{-1}; relative intensities given in parentheses. [b] Ref 34 (liquid phase). [c] δ_{oop} = out-of-plane deformation.

at 777.7 and 724.7 cm^{-1}. Table 7 lists not only the wavenumbers and suggested origins of all the new absorptions observed to develop under these conditions but also relevant literature data for the species Cl$^•$···SCS,[20] ClCS$^•$,[26] **:**CBrCl,[31] BrCCl$_3$,[23] SCCl$_2$,[22] and SCBr$_2$,[22] similarly isolated in Ar matrixes, as well as for liquid BrC(S)Cl.[34]

The spectrum confirmed that BrC(S)Cl is not the only thiocarbonyl dihalide to be formed because the absorptions characteristic of SCCl$_2$[22] and SCBr$_2$[22] also appear upon photolysis. In addition, bands corresponding to the syn forms of both ClC(S)SCl and BrC(S)SBr could be discerned, although the yields were low. The presence of the anti form of each species could be inferred only by the perception of weak shoulders on the bands from the syn form. Very weak bands which appeared only after irradiation for 2 h were identifiable as the radicals ClCS$^•$,[26] BrCS$^•$, and ClC(S)S$^•$.

Moreover, the spectrum included new bands not attributable to any known species. One group of such bands with centers near 1129, 801, 556, and 453/452 cm^{-1} can be ascribed to the hitherto unknown molecule *syn*-ClC(S)SBr, while another group with centers near 1143, 752, 528, and 472/467 cm^{-1} can be attributed to *syn*-BrC(S)SCl. These identities were endorsed by the evidence of splitting attributed to the isotopic pairs $^{79/81}$Br and $^{35/37}$Cl displayed by certain bands and also by the results of quantum chemical calculations (see Table 8). Four weak bands centered near 1104, 1055, 884, and 519 cm^{-1} were seen as candidates for absorptions of the anti forms of ClC(S)SBr and BrC(S)SCl. With the aid of further theoretical calculations, it was possible satisfactorily to assign all four absorptions. Thus, the bands at 1104.2 and 883.6 cm^{-1} can be linked to *anti*-ClC(S)SBr, and those at 1054.7 and 518.9 cm^{-1} can be linked to *anti*-BrC(S)SCl. The antisymmetric Br−C−S stretching fundamental of *anti*-BrC(S)SCl was masked presumably by intense absorptions in the region of 840−700 cm^{-1} resulting from other molecules; the theoretical calculations predict a wavenumber of about 830 cm^{-1} for this mode. Figures 8 and 9 illustrate two different regions of the IR spectrum of such a matrix.

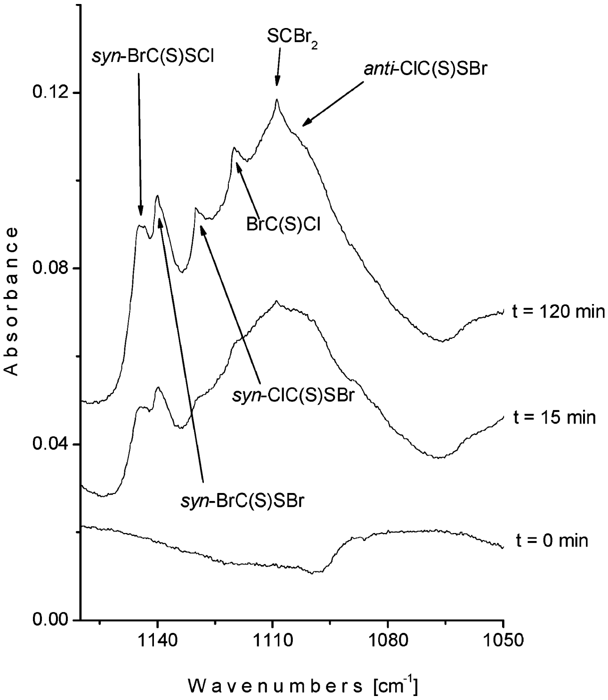


Figure 8. FT-IR spectra of an Ar matrix containing Cl$_2$, Br$_2$, and CS$_2$ (Br$_2$/Cl$_2$/CS$_2$/Ar = 2:2:1:200) in the region of 1150−1050 cm^{-1} immediately after deposition (bottom), after 15 min of photolysis (middle), and after 120 min of photolysis (top).

---

(33) Wight, C. A.; Ault, B. S.; Andrews, L. *J. Mol. Spectrosc.* **1975**, *56*, 239−250.
(34) Diderrich, G.; Haas, A. *Chem. Ber.* **1976**, *109*, 3432−3440.

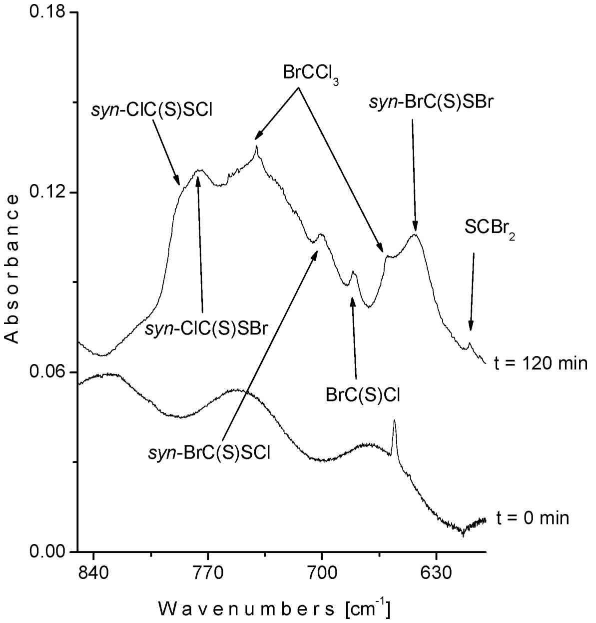


Figure 9. FT-IR spectra of an Ar matrix containing Cl_2, Br_2, and CS_2 ($Br_2/Cl_2/CS_2/Ar = 2:2:1:200$) in the region of 850−600 cm^{-1} immediately after deposition (bottom) and after 120 min of photolysis (top).

The behavior of certain bands as a function of irradiation time, as shown in Figure 10, suggests that, as with the systems Cl_2/CS_2 and Br_2/CS_2, the photolytic processes are mediated by the complexes Cl•···SCS and Br•···SCS. The evidence of the species observed and of their response to continued irradiation leads us to propose the reaction scheme summarized in Scheme 4.

The optimized geometries and vibrational properties of all the new species have been calculated by ab initio and DFT methods using a 6-31+G* basis set for Cl, C, and S atoms and a LANL2DZ basis set,[15] including an effective core potential (ECP), for Br atoms, with the results set out in Tables 8 and 9. The most intense IR absorptions predicted by the calculations anticipate the matrix features observed for the new products well. On the evidence of the calculated wavenumbers and IR intensities, there was significantly less chance of locating any of the other fundamentals under the experimental conditions described. The geometry and vibrational properties of the known molecule BrC(S)Cl have also been calculated in the absence of any previous attempt to determine its structure or to interpret its IR spectrum. The vibrational results are given in Table 10. The calculated geometric parameters of all these molecules are presented as Supporting Information.

Conclusions

Photoinduced reactions carried out in a solid Ar matrix at ∼15 K doped with CS_2 and a dihalogen molecule XY (Cl_2, Br_2, or BrCl) have been shown to give rise to one or more halothiocarbonylsulfenyl halide molecules, XC(S)SY. Thus, *syn*-ClC(S)SCl, *anti*-ClC(S)SCl, *syn*-BrC(S)SBr, *anti*-BrC(S)SBr, *syn*-ClC(S)SBr, *anti*-ClC(S)SBr, *syn*-BrC(S)SCl, and *anti*-BrC(S)SCl have each been identified and characterized

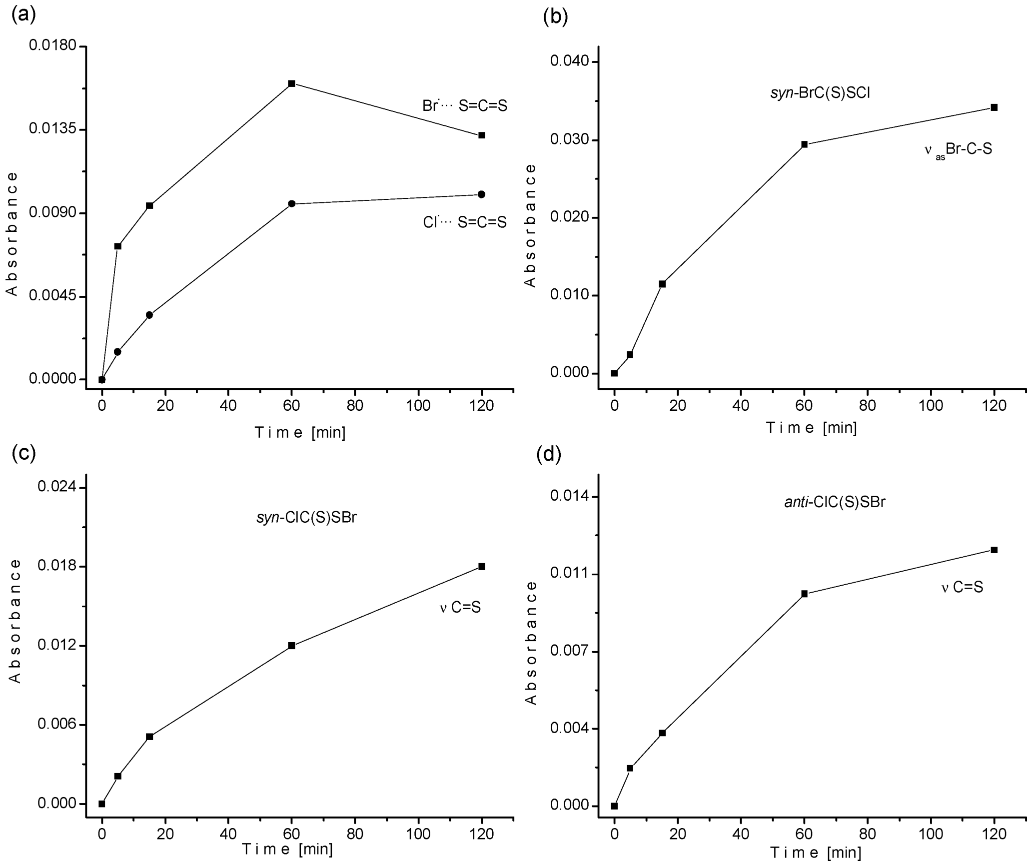


Figure 10. Plots as a function of irradiation time of the intensities of the bands assigned to (a) Br•···SCS and Cl•···SCS, (b) *syn*-BrC(S)SCl, (c) *syn*-ClC(S)SBr, and (d) *anti*-ClC(S)SBr in the IR spectrum of an Ar matrix initially containing CS_2, Cl_2, Br_2, and BrCl.

Scheme 4. Possible Scheme for the Photochemical Reactions Occurring in an Ar Matrix Doped with CS_2 and BrCl at ~15 K

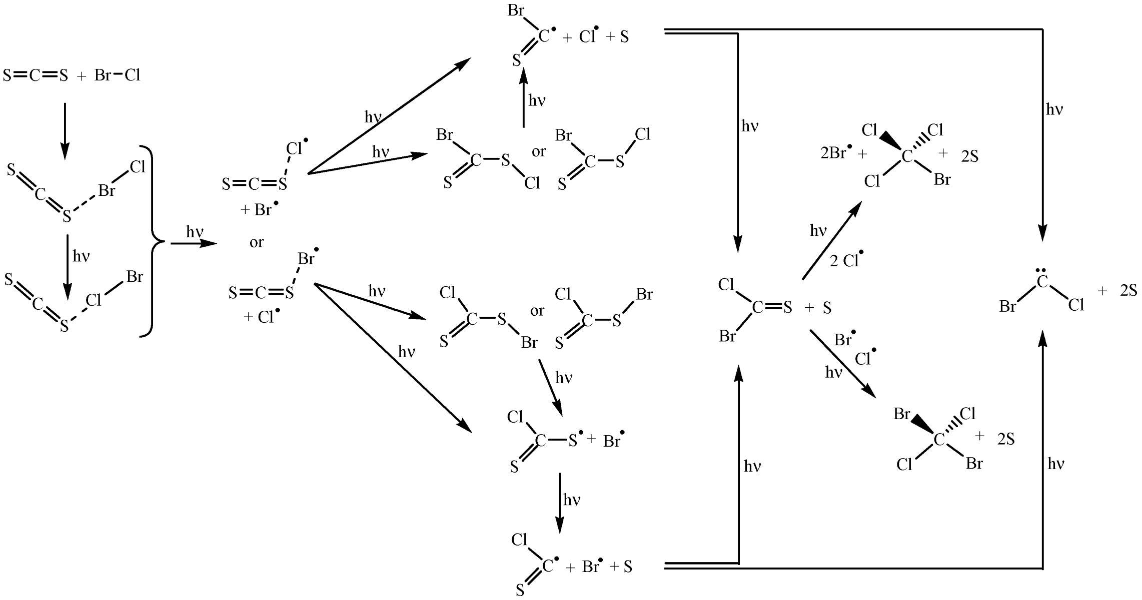


Table 11. Comparison of the Energy Difference and Energy Barrier between syn and anti Forms of Carbonylsulfenyl and Thiocarbonylsulfenyl Compounds of the Type XC(E)SY (X, Y = Cl or Br; E = O or S) Calculated with the B3LYP Method[a]

molecule	ΔE anti−syn (kcal mol^{-1})	energy barrier (kcal mol^{-1})
ClC(O)SCl	2.6	12.5
ClC(S)SCl	0.4	12.4
BrC(O)SBr	3.6	12.1
BrC(S)SBr	0.3	11.2
ClC(O)SBr	2.9	11.3
ClC(S)SBr	0.2	10.9
BrC(O)SCl	3.8	13.8
BrC(S)SCl	1.4	13.7

[a] Using a 6-31+G* basis set for C, S, and Cl atoms and a LANL2DZ basis set,[15] including an effective core potential (ECP), for Br atoms.

at least partially by their IR spectra, with findings endorsed by the results of appropriate quantum chemical calculations. Some radicals, namely, ClC(S)S•, Br•···SCS, and BrCS•, have also been detected and characterized for the first time as reactive intermediates of the reactions starting from Cl_2, Br_2, or BrCl.

The yields of the different photoproducts are liable to vary significantly with the proportions dihalogen/CS_2 present in the matrix. In the case of Cl_2, the amounts of $SCCl_2$ and *syn*- and *anti*-ClC(S)SCl formed were found to increase as the proportion of Cl_2 decreased, while an excess of Cl_2 relative to CS_2 led to an increased yield of CCl_4. In the reactions starting from Br_2, however, all of the products were formed in higher concentrations as the proportion of Br_2 to CS_2 increased.

Whereas the photochemical reactions involving CS_2 and a dihalogen molecule XY (Cl_2, Br_2, or BrCl) led to the simultaneous formation of the syn and anti forms of the respective halogenothiocarbonylsulfenyl halide molecule, XC(S)SY, the analogous reactions involving OCS yielded only the syn forms of the corresponding halogenocarbonylsulfenyl halide, XC(O)SY.[2,3] Theoretical calculations predict that the energy barrier for interconversion of the syn and anti rotamers is quite high and not very different for the carbonylsulfenyl and thiocarbonylsulfenyl derivatives (10−14 kcal mol^{-1}), although the energy difference between the minima is smaller in the thiocarbonylsulfenyl case (0.2−1.4 vs 2.6−3.8 kcal mol^{-1}). If a matrix containing *syn*-XC(O)SY is irradiated with broad-band UV−vis light, however, partial isomerization to the anti form occurs.[1,4] Table 11 compares the energy differences and energy barriers calculated for carbonylsulfenyl and thiocarbonylsulfenyl compounds by the B3LYP/6-31+G* method.

Acknowledgment. The authors acknowledge with thanks 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. thanks the DAAD, which generously sponsors the DAAD Regional Program of Chemistry of the Republic Argentina supporting Latin-American students to obtain their PhD in La Plata.

Supporting Information Available: Calculated optimized geometric parameters (i) of the *syn* and *anti* conformers of each of ClC(S)SCl, BrC(S)SBr, ClC(S)SBr, and BrC(S)SCl and (ii) of the radicals ClC(S)S•, BrCS•, and Br•···SCS. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070119+