Matrix Photochemistry of *syn*-(Chlorocarbonyl)sulfenyl Bromide, *syn*-ClC(O)SBr: Precursor to the Novel Species *anti*-ClC(O)SBr, *syn*-BrC(O)SCl, and BrSCl

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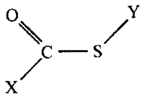
Abstract: The vapor of (chlorocarbonyl)sulfenyl bromide, ClC(O)SBr, was isolated in solid Ar, Kr, N_2, and Ar doped with 5% CO at 15 K, and the matrix was subsequently irradiated with broad-band UV−visible light ($200 \leq \lambda \leq 800$ nm), the changes being followed by reference to the IR spectrum of the matrix. The initial spectrum showed the vapor of ClC(O)SBr to consist of more than 99% of the syn form (with the C═O bond syn with respect to the S−Br bond) in equilibrium with less than 1% of the anti conformer. Irradiation caused various changes to occur. First, conformational randomization took place, leading to a roughly equimolar mixture of the two rotamers, and so affording the first spectroscopic characterization of an *anti*-ClC(O)S-containing compound. Simultaneously, the novel constitutional isomer *syn*-BrC(O)SCl was also formed. Continued photolysis resulted in the decay of all these species while revealing a third reaction channel, leading to the elimination of CO and the formation of the new triatomic sulfur halide BrSCl. The assignment of the IR bands to the different products was made on the basis of the usual criteria, taking account (i) of the effects of the naturally occurring isotopic pairs $^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$, (ii) of the vibrational properties of related molecules, and (iii) of the properties predicted for the relevant molecules by quantum chemical calculations.

Introduction

(Halogenocarbonyl)sulfenyl halides, XC(O)SY, where X and Y may be the same or different halogens, have been known since 1966, when Haas and Reinke reported the preparation of the first such compound, namely ClC(O)SCl.[1] Since then, several other members of the family have been characterized, e.g., FC(O)SCl,[1−4] FC(O)SBr,[5−7] and ClC(O)SBr.[7,8] The compounds are of interest on several counts.

(i) They are the obvious synthons for other compounds containing the −C(O)S− moiety, as attested, for example, by their roles in the preparation of the compounds XC(O)SNCO (X = F or Cl),[1] FC(O)SSCH$_3$,[7,9] FC(O)SNSO,[7,10,11] FC(O)SSC(O)F,[12] and FC(O)SCF$_3$.[13]

(ii) The molecules are planar, with two potential energy minima corresponding to the syn (**1**) and anti (**2**) conformers (where the labels relate to the relative orientation of the S−Y and C═O bonds). The two conformers can be distinguished by their vibrational spectra, notably through the ν(CO) mode, and numerous studies, both experimental and theoretical, have been carried out to assess their relative proportions and energies.[3−6] For all the molecules investigated to date, the syn conformation is favored over the anti one. However, the relative stabilities and barriers to rotation about the C−S bond vary substantially from compound to compound and also from one phase to another. Several interactions—both intramolecular, involving atoms, bonds, and lone pairs, and intermolecular—contribute



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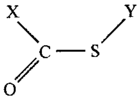

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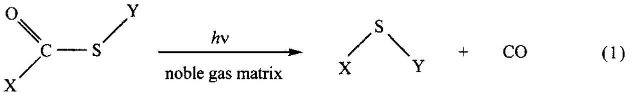
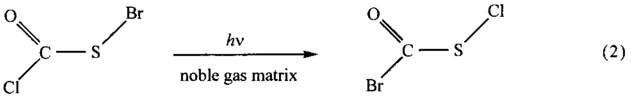
to this diversity of behavior, about which little can yet be predicted a priori.

(iii) Several of the compounds investigated display quite a rich photochemistry.[2,6] The most immediate effect of UV irradiation of FC(O)SBr isolated in a noble gas matrix is to bring about interconversion of the syn and anti forms.[6] More drastic action follows, though, for both FC(O)SCl[2] and FC(O)SBr[6] under these conditions, with the elimination of CO and the formation of the previously unknown mixed sulfur dihalides ClSF and BrSF (eq 1). Hence XC(O)SY compounds offer what appears to be a general route to sulfur(II) halides.[14]



Matrix isolation is a technique[15] that is particularly well suited to the study of (halogenocarbonyl)sulfenyl compounds. The combination of a rigid, inert host and low temperature enables the different conformers to be trapped and their thermal interconversion quenched (kT at 15 K = 0.12 kJ mol^{-1}). The sharply defined spectroscopic transitions of the trapped molecules facilitate the characterization of the distinct species and estimation of their relative proportions. As noted in the case of FC(O)SBr,[6] interconversion of the conformers can then be brought about by photolysis. If the picture may be complicated by photodecomposition, this can also be exploited for the access it gives to simple sulfur(II) compounds such as ClSF[2] or BrSF,[6] which are typically labile under normal conditions.

Here we report the results of experiments involving (chlorocarbonyl)sulfenyl bromide[7,8] isolated in solid Ar, Kr, N_2, or CO-doped Ar matrixes at ca. 15 K. The matrixes have been analyzed by reference to their IR spectra. Hence, the vapor of the compound has been shown to consist predominantly of the syn conformer. Irradiation with broad-band UV−visible light induces conformational randomization, leading to the first spectroscopic characterization of an *anti*-ClC(O)SY molecule. The photolysis also results in at least two further changes, namely isomerization to the new compound *syn*-BrC(O)SCl (eq 2) and photodecomposition with the elimination of CO and formation of the hitherto unknown BrSCl molecule (as in eq 1). Apart from BrSF, the only other sulfur halides known previously to feature S−Br bonds are SBr_2, S_2Br_2, S_xBr_2, S_2BrCl, and SF_5Br.[14] The different molecules have been identified and characterized (i) by their IR spectra, including the isotopic shifts due to the naturally occurring atomic pairs $^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$, (ii) by quantum chemical calculations and comparison of the vibrational properties thus forecast with the observed spectra, and (iii) by reference to the vibrational spectra of known cognate molecules.



Experimental Section

ClC(O)SBr was prepared by the reaction of FC(O)SBr with BCl_3 according to the published procedure[7,8] and was subsequently purified by repeated trap-to-trap distillation in vacuo. The matrix gases Ar, N_2, Kr, and CO were used as supplied (all BOC, research grade).

Gas mixtures of ClC(O)SBr in Ar, N_2, Kr, and Ar doped with 5% CO in the proportions ca. 1:1000, prepared by standard manometric methods, were deposited on a CsI window cooled to ca. 15 K by means of a Displex closed-cycle refrigerator (Air Products model CS202) using the pulsed deposition technique.[15,16] IR spectra of the matrix samples were recorded at a resolution of 0.5 cm^{-1}, with 256 scans and an 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 range 4000−400 or 600−250 cm^{-1}, respectively).

Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV−visible 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 IR radiation and so minimize any heating effects. Irradiation was carried out for different times, and the effects were assessed at each stage by measuring the IR spectrum of the matrix in order to monitor closely the evolution and/or decay of the various molecules. Visible photolysis experiments were also performed with radiation having wavelengths in the range 400−800 nm, but the only difference observed was a marked diminution in the rates of the different changes.

All the quantum chemical calculations were performed using the Gaussian 98 program package[17] under the Linda parallel execution environment using two coupled PCs. Different ab initio and density functional theory (DFT) methods were tried, in combination with different basis sets. Geometry optimizations were sought using standard gradient techniques by simultaneous relaxation of all the geometrical parameters. In all the cases cited, the vibrational properties corresponded to potential energy minima with no imaginary frequencies. The wavenumbers of the vibrational fundamentals calculated by Hartree−Fock (HF) methods were scaled by a factor of 0.9 to take account of the known overestimation that characterizes these methods.

Results and Discussion

1. Photochemical Behavior: Broad-Band UV−Visible Irradiation of ClC(O)SBr. The IR spectrum of ClC(O)SBr isolated in a solid Ne, Ar, or N_2 matrix at low temperatures has already been reported,[8] as have the IR spectra of the vapor and liquid and the Raman spectrum of the liquid. Assignment of the vibrational modes has been based on the presumed existence of only one conformer, namely the syn form, at ambient temperatures. The IR spectra recorded here for ClC(O)SBr isolated in an Ar, Kr, N_2, or CO-doped Ar matrix were entirely consistent with those previously described,[8] consisting primarily of four sets of bands corresponding to the four stretching fundamentals of the molecule, ν(C=O), ν_{as}(Cl−C−S), ν_s(Cl−C−S), and ν(S−Br). Table 1 lists the observed wavenumbers for each of the matrixes studied; values in bold type correspond to the most intense absorptions. Some bands were observed to display site splitting, whereas isotopic splitting could be discerned for the vibrational modes involving significant motion of the Cl or Br atom. In addition to the features listed in Table 1, the spectrum exhibited another band occurring at 557.3, 556.5, 558.8, or 558.2 cm^{-1} for an Ar, Kr, N_2, or CO-doped Ar matrix, respectively. This can be assigned to the CO out-of-plane bending mode on the evidence (i) of a similar band at 562 cm^{-1}

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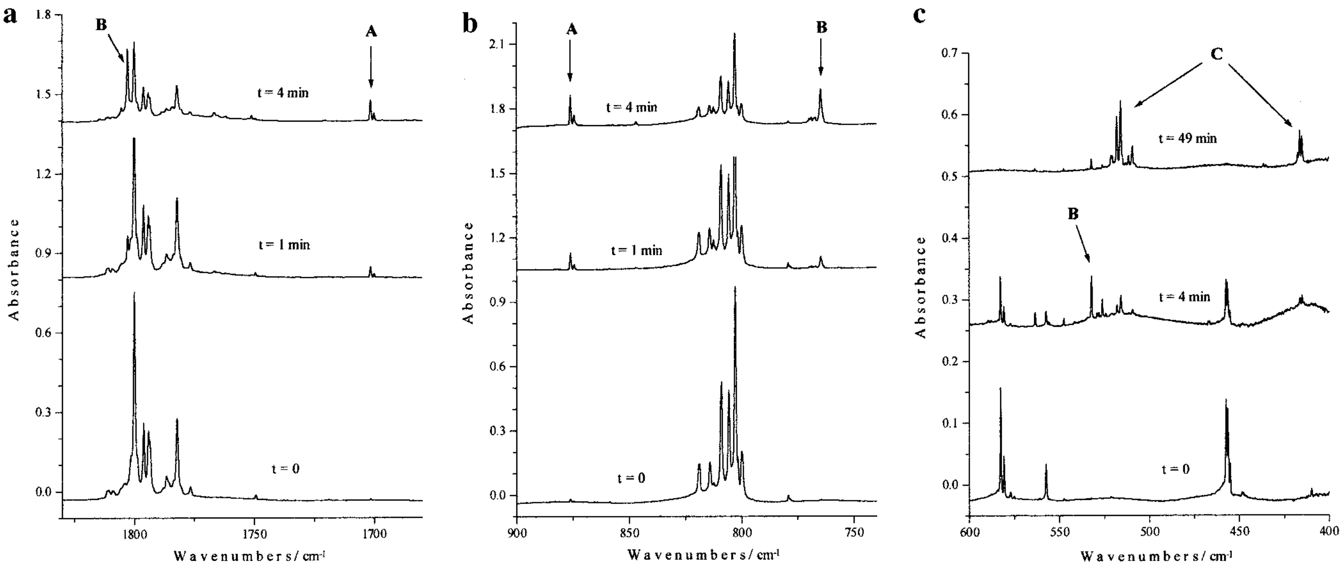

Figure 1. FTIR spectra of *syn*-ClC(O)SBr isolated in an Ar matrix (1:1000) at different irradiation times.

Table 1. Experimental FTIR Wavenumbers of *syn*-ClC(O)SBr and Comparison with the Standard Method HF/6-31+G*

matrix	ν(C=O)	ν_{as}(Cl–C–S)	ν_s(Cl–C–S)	ν(S–Br)
Ar	**1800.0**	819.0	**582.5**	**457.3**
	1796.1	814.1	580.7	456.4
	1794.2	809.0		
	1782.3	805.6		
		802.8		
		800.0		
Kr	1807.7	**810.2**	589.2	**461.7**
	1805.7	806.9	**584.6**	
	1801.1	803.3	582.8	
	1799.0	801.5		
	1797.0			
	1794.2			
	1792.9			
	1789.8			
	1784.5			
	1781.0			
	1779.3			
N_2	1795.2	817.5	589.5	**463.0**
	1794.0	815.0	**588.2**	462.3
		812.0	586.3	
		810.4		
		808.2		
Ar + 5% CO	1799.2	809.3	**582.4**	**456.0**
	1797.2	**804.7**		
	1795.5			
	1783.9			
	1783.0			
HF/6-31+G* [a]	1836.1	855.7	573.6	467.1
		854.8	571.3	466.3

[a] Scaled by a factor of 0.9.

in the IR spectrum of ClC(O)SCl isolated in an Ar matrix and which has been assigned to this mode[18] and (ii) of the vibrational properties anticipated for *syn*-ClC(O)SBr by the quantum chemical calculations (see below). There were also very weak absorptions occurring near 1700 and 880 cm^{-1}, the significance of which became apparent as the experiments proceeded.

Exposure of the matrix to broad-band UV–visible radiation (200 ≤ λ ≤ 800 nm) resulted in major changes in the IR spectrum, as illustrated, for instance, in the case of an Ar matrix with results measured at different irradiation times (see Figure 1). Similar behavior was displayed by all the other matrixes. The IR bands originating in *syn*-ClC(O)SBr decreased in intensity with irradiation time, with the simultaneous appearance and growth of sundry new bands. It is clear from the analysis of the spectra shown in Figure 1 that more than one product is formed on photolysis. To distinguish the bands corresponding to the different species and help determine the identity of each product, the integrated intensities of the more prominent bands have been plotted as a function of irradiation time, as depicted in Figure 2 for a typical experiment involving an argon matrix. Figure 2a illustrates the decay with time of the absorptions associated with the stretching fundamentals of *syn*-ClC(O)SBr. Ten new bands were then observed to develop; in an Ar matrix these have the following wavenumbers: 1802.9, 1701.5/1700.0, 876.1/874.4, 764.7, 563.3, 547.5/541.4, 532.0/526.0, 517.8/515.6/511.3/509.2, 467.0/466.2, and 416.0/414.8 cm^{-1}. Prolonging the photolysis causes eight of these bands subsequently to decay, whereas the other two—near 515 and 415 cm^{-1}—continue to grow. Hence, it becomes clear that the new bands are carried by three distinct products **A**, **B**, and **C**.

There are two main reasons for believing that not one but two products (**A** and **B**) are responsible for the eight bands which grow and then decay on continued photolysis. First, as shown in Figure 2b,c, the decay of the bands near 1701 and 876 cm^{-1} (associated with **A**) follows a pattern different from that of the bands near 1803, 765, 563, and 532 cm^{-1} (associated with **B**). Second, the two bands belonging to **A** could be discerned in the original spectrum of the matrix prior to irradiation (see above), albeit with very low intensities, whereas those due to **B** could be detected only after irradiation. The intensities of the two weaker bands near 547 and 467 cm^{-1} were more difficult to quantify but appeared to track those of the 1701 and 876 cm^{-1} absorptions and therefore to originate in **A**.

Figure 2d traces the intensities of the absorptions near 515 and 415 cm^{-1} which continue to grow on photolysis, tending asymptotically to limiting values in a way that complements the decay of the original *syn*-ClC(O)SBr molecule. These must clearly be associated with a new photostable product **C**.

Three other absorptions merit some comment. One of these, occurring near 2140 cm^{-1} and readily identifiable with the formation of free CO,[19] was observed to appear and otherwise to track the buildup of the photoproduct **C**. The second, occurring near 2050 cm^{-1} and accompanied by a much weaker

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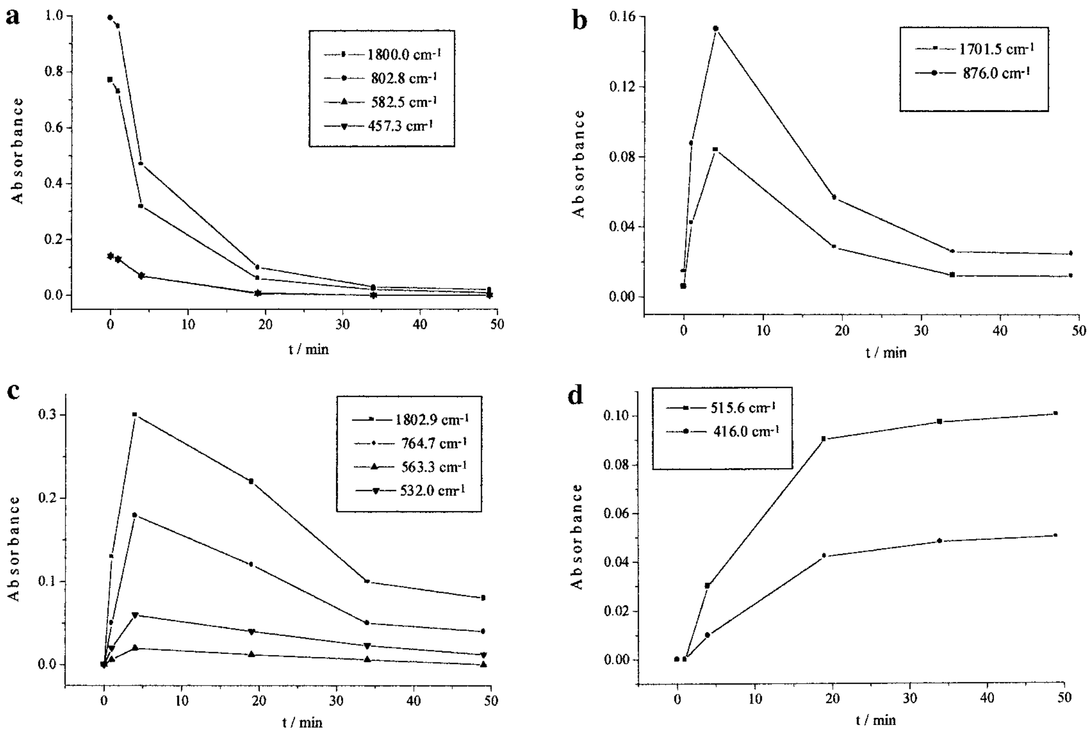

Figure 2. Plot of the intensities of the bands in the FTIR spectra of *syn*-ClC(O)SBr isolated in an Ar matrix (1:1000) vs irradiation times.

band near 850 cm^{-1}, clearly arose from the molecule OCS.[20] This was observed with modest intensity even before irradiation, suggesting slight thermal decomposition of the ClC(O)SBr, but gained significantly in intensity as photolysis proceeded in a way that appeared to complement the decay of **A** and/or **B**. The evolution of OCS suggests BrCl as a coproduct of the photodissociation, and indeed at the conclusion of photolysis a very weak multiplet absorbing at 436.3/434.8 cm^{-1} could be discerned (see Figure 1). The IR spectrum of matrix-isolated BrCl has not been reported previously, but the wavenumbers of the observed features, and particularly the evidence of ^{79}Br/^{81}Br splitting amounting to 1.5 cm^{-1}, are wholly consistent with the vibrational properties reported previously for this molecule.[21] At this point of the experiment, all traces of the parent compound, **A**, and **B** had been extinguished, leaving as the only significant features the IR absorptions associated with the molecule **C**, CO, OCS, and BrCl.

Experiments were also carried out with ClC(O)SBr trapped in an Ar matrix doped with 5% CO. Earlier matrix studies of the fluorocarbonyl derivatives FC(O)SCl[2] and FC(O)SBr[6] have shown that CO is not merely a photoproduct but can play an active role in the photochemically induced reactions of these molecules, as evidenced by the formation of the molecules ClC(O)F and BrC(O)F, together with OCS, in experiments involving CO matrixes. Through the formation of the radicals XCO$^•$, where X is a halogen, CO also provides a means of detecting free halogen atoms generated in the course of matrix reactions.[22] It was of interest, therefore, that the experiments with CO-doped Ar matrixes gave results which, apart from marginal changes in the patterns and wavenumbers of the IR bands, did not differ from those achieved with an undoped matrix. Hence, there was no evidence suggesting the formation of additional products, such as ClCO$^•$ [23] or ClC(O)Br,[24] or any active participation of CO in the matrix photochemistry. In this respect, ClC(O)SBr evidently differs from FC(O)SCl[2] and FC(O)SBr,[6] at least with regard to some of the photochemical channels favored by its photodecomposition under matrix conditions.

As part of the exercise of identifying the products **A**–**C**, we have considered a number of possible species that might, in principle, result from unimolecular decomposition of ClC(O)SBr under the action of UV–visible light. The relevant vibrational frequencies are listed in Table 2.

In no case, however, did the observed IR spectra give any hint of absorptions suggesting the presence of any of these molecules.

Photoproduct A: *anti*-ClC(O)SBr. The IR bands of the intermediate species **A** plotted in Figure 2b, together with the two weaker bands near 567 and 467 cm^{-1}, will be shown to arise from the rotational conformer *anti*-ClC(O)SBr, which has not been identified previously. In Table 3, the wavenumbers of the bands in the four different matrixes are presented. These bands were present in the spectrum of each matrix as formed initially by co-deposition of ClC(O)SBr vapor at ambient temperature with an excess of the relevant matrix gas, but with intensities less than 1% of those associated with the corresponding features of the *syn*-ClC(O)SBr conformer. The wavenumber and intensity pattern of the bands then give good grounds for believing that **A**, the carrier of these bands, is the anti conformer. If it is assumed that the extinction coefficients of the ν(CO) fundamental are the same for the syn and anti species, it follows that the vapor at ambient temperatures contains less than 1% of the anti conformer. However, broad-band UV–visible irradiation of the matrix-isolated sample causes the proportion of the anti conformer to increase with respect to that of the syn conformer until roughly equimolar quantities of the two are present. A similar conformational randomization has been

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Table 2. Some Possible Formal Species Derived from Several Combination of the Atoms Forming the ClC(O)SBr Molecule

molecule	wavenumbers (cm^{-1})	ref
$C^{35}Cl$ (N_2 matrix)	876	*a*
$C^{37}Cl$ (N_2 matrix)	870	*a*
BrClO (Ar matrix)	940.9, 932.7	*b*
ClBrO (Ar matrix)	819.9, 817.5	*b*
CCl_2 (Ar matrix)	745.7, 719.5	*c*
CBr_2 (Ar matrix)	640.5, 595.0	*d*
CClBr (Ar matrix)	739 ± 1, 612 ± 1	*c*
ClO (matrix)	850.7	*e*
ClBrCO (gas)	1828, 806, 547, 517, 372, 240	*f*
Cl_2CO (gas)	1827, 849, 580, 569, 440, 285	*f*
Br_2CO (gas)	1828, 757, 512, 425, 350, 181	*f*
OCCl (matrix)	1880, 570, 281	*g*
SBr (matrix)	518	*h*
$S^{35}Cl$ (matrix)	617	*h*
$S^{37}Cl$ (matrix)	612	*h*

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Table 3. Experimental FTIR Wavenumbers of *anti*-ClC(O)SBr and Comparison with the Standard Method HF/6-31+G*

matrix	$\nu(C{=}O)$	$\nu_{as}(Cl{-}C{-}S)$	$\nu_s(Cl{-}C{-}S)$	$\nu(S{-}Br)$
Ar	**1701.5**	**876.1**	**547.5**	**467.0**
	1700.0	874.4	541.4	466.2
Kr	1704.0	880.3	**547.0**	**473.5**
	1702.6	878.8		
	1700.7	877.4		
		876.4		
		874.8		
N_2	1708.8	884.8	553.0	**473.0**
	1706.9	**883.1**	**552.1**	
	1705.3	881.0		
	1697.8			
Ar + 5% CO	**1700.6**	876.0	**545.5**	**474.1**
	1699.1	**875.1**	540.4	472.7
		873.7		
HF/6-31+G* [a]	1802.9	905.1	565.5	475.6
		904.1		475.0

[a] Scaled by a factor of 0.9.

observed previously in studies of the matrix-isolated (fluorocarbonyl)sulfenyl compounds FC(O)SCl,[3] FC(O)SBr,[6] FC(O)SSC(O)F,[12] and FC(O)SNSO,[10] for which the initial proportion of the anti form varies between 10 and 20%.

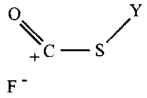
The four IR absorptions associated with **A** were each observed to display multiplet patterns attributable to either matrix or isotopic splitting. Thus, the bands near 875 and 545 cm^{-1} each display a doublet pattern with components bearing a roughly 3:1 intensity ratio and attributable, therefore, to $^{35}Cl/^{37}Cl$ splitting (the relevant shifts being 1.7 and 6.1 cm^{-1}, respectively, for an Ar matrix). Accordingly, these features are most plausibly attributed to the antisymmetric and symmetric Cl−C−S stretching fundamentals. The band near 467 cm^{-1} is also a doublet but with components of almost equal intensity and separated by only 0.8 cm^{-1}, features clearly signaling $^{79}Br/^{81}Br$ splitting associated with the $\nu(S{-}Br)$ fundamental.

The $\nu(C{=}O)$ mode is clearly responsible for the feature appearing at 1701.5/1700.0 cm^{-1} (in the spectrum of an Ar matrix), some 100 cm^{-1} to low frequency of the corresponding mode in the syn conformer. There are no real precedents for such a shift, comparisons with other (chlorocarbonyl)sulfenyl compounds being frustrated by the predominance of the syn conformer. To our knowledge, the literature contains no previous spectroscopic sighting of an *anti*-ClC(O)SY species. However, support for the low-frequency shift of the $\nu(C{=}O)$ mode in *anti*-ClC(O)SBr is provided by our quantum chemical calculations, although its magnitude is underestimated by some margin (quod vide).

Table 4. Comparison of the Difference between the CO Stretching Vibrational Mode for the Syn and Anti Conformers of Some Selected Sulphenylcarbonyl Compounds (XC(O)SY)

X	Y	$\nu(C{=}O)_{syn}$	$\nu(C{=}O)_{anti}$	$\Delta\nu(C{=}O)_{syn-anti}$	ref
H	H	1708	1713	−5	25
F	Cl	1843	1803	40	4
F	Br	1838	1800	38	5
F	CH_3	1845	1824	21	13
F	SCH_3	1822	1770	52	9
F	NSO	1850	1811	39	11

Table 4 lists values for $\nu(C{=}O)$ in the syn and anti conformers of XC(O)SY molecules previously characterized by experiment. For compounds of the type FC(O)SY, the proportion of the anti conformer in the vapor under ambient conditions is typically higher than in the case of ClC(O)SBr, and it is noteworthy that $\nu(C{=}O)$ in this conformer is between 21 (Y = CH_3[13]) and 52 cm^{-1} (Y = SCH_3[9]) to low frequency of $\nu(C{=}O)$ in the syn form. Overall, the wavenumbers show the expected trend with the sum of the electronegativities of the substituents X and SY attributable to the contribution of mesomeric forms such as **3**. This effect is also responsible, at least in part, for some of the structural differences between the syn and anti conformers.



3

In the case of the syn form, the overlap between the $\sigma^*(C{=}O)$ orbital and the lone-pair orbital on the S atom, lp(S), is also more effective than the corresponding overlap between the $\sigma^*(C{-}X)$ orbital and lp(S) in the anti form. Increasing the atomic number of the halogen X may be expected to amplify this discrimination. Thus, the anomeric effect described is expected to lead to a slightly higher bond order and shorter distance for the C−S bond of the syn form, as found by both experiment and theory in the limited number of cases investigated to date.[3,10,12] It is a natural consequence that some correlation should exist between the $\nu(C{=}O)$ wavenumber and molecular dimensions.

Photoproduct B: *syn*-BrC(O)SCl. The intermediate **B** we identify with the constitutional isomer of (chlorocarbonyl)sulfenyl bromide, namely BrC(O)SCl, formed by a change hitherto unprecedented in the chemistry of XC(O)SY compounds in which there is scrambling of the halogen atoms X and Y at the carbon and sulfur centers.

Table 5 lists the wavenumbers of the IR bands due to **B** in its different matrix environments. The absorption associated with the $\nu(C{=}O)$ mode comes very close to, and is practically overlaid by, the corresponding mode of *syn*-ClC(O)SBr. In an Ar matrix, for example, the main feature of **B** is only 2.9 cm^{-1} to high wavenumber of its counterpart in the parent compound. Elsewhere, the effects of isotopic splitting have played a major role in determining the identity of **B**. For example, the absorption near 532 cm^{-1} (in an Ar matrix) signals by its position and doublet pattern (intensity ratio roughly 3:1, splitting 6.0 cm^{-1})

Table 5. Experimental FTIR Wavenumbers of *syn*-BrC(O)SCl and Comparison with the Standard Method HF/6-31+G*

matrix	ν(C=O)	ν_{as}(Br−C−S)	ν_{s}(Br−C−S)	ν(S−Cl)
Ar	**1802.9**	**764.7**	**563.3**	**532.0** (S−^{35}Cl)
				526.0 (S−^{37}Cl)
Kr	1806.9	**774.3**	**569.5**	**537.2** (S−^{35}Cl)
	1804.7	763.1	564.7	531.0 (S−^{37}Cl)
	1803.7			
N_2	**1805.8**	777.9	**567.7**	**537.8** (S−^{35}Cl)
	1804.4	**770.6**		531.6 (S−^{37}Cl)
Ar + 5% CO	1828.7	**766.6**	**563.9**	**531.6** (S−^{35}Cl)
	1816.4			526.0 (S−^{37}Cl)
	1808.9			
	1802.7			
HF/6-31+G* [a]	1836.9	809.6	550.8	529.1 (S−^{35}Cl)
				523.9 (S−^{37}Cl)

[a] Scaled by a factor of 0.9.

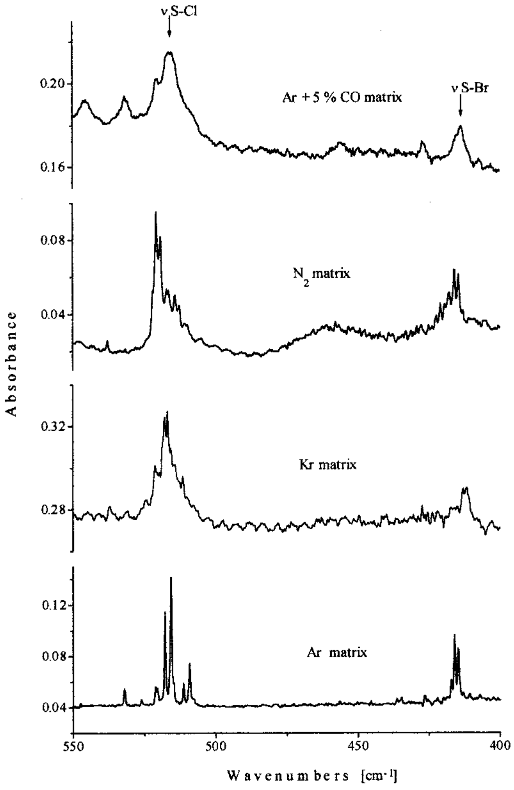


Figure 3. FTIR spectra of BrSCl isolated in different matrixes.

that it originates in what is largely a ν(S−Cl) vibration. Support for such an assignment comes from the corresponding mode of ClC(O)SCl, also isolated in an Ar matrix (547.5/541.5 cm^{-1}).[26] The wavenumbers of the other two bands carried by **B**—near 765 and 563 cm^{-1} in an Ar matrix—are then wholly consistent with the assignments given in Table 5, which are endorsed by the results of HF and other calculations (quod vide).

Photoproduct C: BrSCl. Characterized by just two IR absorptions at wavenumbers greater than 250 cm^{-1} (occurring near 515 and 415 cm^{-1} in an Ar matrix), product **C** appears to be linked in its formation with the release of free CO (see Figures 1 and 2). Typical spectra showing these features are illustrated in Figure 3, and the relevant wavenumbers are listed in Table 6.

Table 6. Experimental FTIR Wavenumbers of BrSCl and Comparison with the Standard Method HF/6-31+G*

matrix	ν(S−Cl)	ν(S−Br)
Ar	517.8 (S−^{35}Cl)	**416.0** (S−^{79}Br)
	515.6 (S−^{35}Cl)	414.8 (S−^{81}Br)
	511.3 (S−^{37}Cl)	
	509.2 (S−^{37}Cl)	
Kr	521.2	**413.0** (S−^{79}Br)
	519.6	411.8 (S−^{81}Br)
	517.8	
	516.8	
	515.6	
	511.4	
N_2	520.7	**416.0** (S−^{79}Br)
	519.2	414.6 (S−^{81}Br)
	517.1	
	514.2	
Ar + 5% CO	**515.2**	**413.7**
HF/6-31+G* [a]	509.6 (S−^{35}Cl)	418.8(ν S−^{79}Br)
	503.3 (S−^{37}Cl)	417.4 (ν S−^{81}Br)

[a] Scaled by a factor of 0.9.

The circumstances leading to the formation of the compound, allied to analogies with the behaviors of FC(O)SCl,[2] FC(O)SBr,[6] and ClC(O)SCl[26] under similar conditions, give us every reason to believe that **C** is the mixed sulfur(II) halide BrSCl. This conclusion is confirmed by the isotopic splitting displayed by the two bands and most readily apparent in experiments with an Ar matrix. Here the absorption near 515 cm^{-1} is seen to be a pair of overlapping doublets separated by 2.2 cm^{-1} and representing, no doubt, the occupation of two different matrix sites. Each doublet has components with intensities in the ratio ca. 3:1 and a spacing of 6.5 cm^{-1}. Further support for assignment to what is predominantly a ν(S−Cl) mode comes from the frequencies reported for the corresponding modes of ClSCl (524.1/517.5 cm^{-1})[26] and ClSF (543.2/537.0 cm^{-1}),[2] each isolated in an Ar matrix. By contrast, the band near 415 cm^{-1} appears as a doublet with components of comparable intensity and separated by 1.2 cm^{-1}, credentials entirely appropriate to its assignment to a ν(S−Br) fundamental. The corresponding mode of BrSF, also isolated in an Ar matrix, is reported to occur at 434/432 cm^{-1}.

The proposed assignments prove to be in excellent agreement with the results of HF and other calculations (see Table 6, for example). Such calculations also predict that the remaining fundamental of the triatomic BrSCl molecule occurs near 160 cm^{-1}, a wavenumber falling beyond the lower threshold of the present measurements (250 cm^{-1}).

Theoretical Calculations. With three new compounds identifiable only on the evidence of their IR spectra and unmistakable signs that the matrix photochemistry of ClC(O)SBr visits a number of reaction channels, quantum chemical calculations have played a vital part not only in checking the identities of the products **A**−**C**, but also in characterizing their structures, energies, and dynamics. Hence, we have sought information likely to have a bearing on the properties of compounds of the types XC(O)SY and XSY at large, and on the mechanisms of the photoinduced reactions in which they are featured.

Calculations were first directed to investigating the relative stabilities of syn and anti rotational conformers of ClC(O)SBr. The structures of these two forms were optimized using different theoretical models to confirm that each has a planar skeleton, as illustrated in Figure 4, corresponding to a true minimum on the potential surface. The energy differences calculated with the HF/6-31+G* method and with the DFT hybrid B3LYP/6-31+G* method predict the anti conformer to lie 3.58 and 2.83 kcal mol^{-1} above the more stable syn conformer; the MP2/6-31+G* theoretical model gives a value of 3.29 kcal mol^{-1}. On the basis of the theoretical thermodynamic functions at 298 K,

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(25) Della Védova, C. O. *J. Raman Spectrosc.* **1991**, *22*, 291−295.

(26) Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Green, T. M., unpublished results.

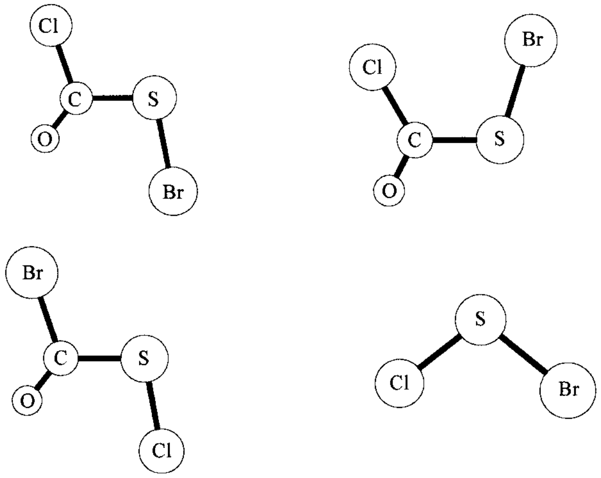


Figure 4. B3LYP/6-31+G* molecular models of *syn*-ClC(O)SBr, *anti*-ClC(O)SBr, *syn*-BrC(O)SCl, and BrSCl.

the free molecule is estimated to consist of the following fractions of the syn conformer at normal temperatures: 99.7% (HF/6-31+G*) and 99.1% (B3LYP/6-31+G*). These results are wholly in accord with the experimental findings based on the relative intensities of the ν(C=O) bands in the IR spectrum of the matrix-isolated vapor and imply that >99% of the vapor is made up of the syn conformer.

The IR spectra of the two conformers of ClC(O)SBr were simulated by the different methods, with the results placed in Supporting Information. The calculations agree that ν(C=O) for the anti conformer occurs at significantly lower wavenumber than does its counterpart for the syn conformer, but the calculated shifts of 39 (HF/6-31+G*) and 59 cm^{-1} (B3LYP/6-31+G*) fall somewhat short of the experimental value of nearly 100 cm^{-1}. Nevertheless, the product and sum rules confirm the trend in ν(C=O) calculated for the less stable conformer. The dimensions of the syn and anti forms as optimized by the different treatments are included in the Supporting Information.

A similar approach was adopted for the constitutional isomer **B**, i.e., BrC(O)SCl. The corresponding vibrational properties, also available as Supporting Information, anticipate well the IR spectrum observed for the photoproduct **B**. Hence, we note that ν(C=O) is, indeed, predicted to be very close to ν(C=O) for *syn*-ClC(O)SBr. Moreover, the relative intensities of the observed bands are well reproduced by the calculations. For example, the ν(C=O) mode is predicted and observed to give rise to the most intense IR band in the spectrum of *syn*-ClC(O)SBr. For *syn*-BrC(O)SCl, however, the most intense feature is predicted to arise not from this mode but from the ν_{as}(Br−C−S) fundamental (near 770 cm^{-1}), a prognosis wholly borne out in the spectrum due to **B**. The calculations took in both syn and anti conformers of BrC(O)SCl. Three aspects of the results are noteworthy. (i) The potential minimum of the anti conformer lies 3.78 (B3LYP/6-31+G*)−4.17 (HF/6-31+G*) kcal mol^{-1} above that of the syn form, suggesting that the energy difference for XC(O)SY molecules increases with the atomic number of X. (ii) On the evidence of the calculated vibrational properties, *anti*-BrC(O)SCl does not enter into the matrix photochemistry of ClC(O)SBr, IR bands attributable only to the syn form being detected. (iii) Exchanging the halogen substituents at carbon and sulfur makes little difference to the energy of the molecule, which rises by only 5.79 (HF/6-31+G*) or 3.75 kcal mol^{-1} (B3LYP/6-31+G*) when *syn*-ClC(O)SBr gives way to *syn*-BrC(O)SCl.

The much simpler triatomic molecule BrSCl, **C**, invites calculations at a range of levels (for the resulting geometrical parameters and vibrational wavenumbers, see Supporting Information). As expected, improved levels of approximation in the method of calculation need to be matched by more refined basis sets if they are to be used with significant advantage. Nevertheless, there is pleasingly close agreement between the calculated and observed wavenumbers and the ^{35}Cl/^{37}Cl and ^{79}Br/^{81}Br isotopic shifts for the two stretching fundamentals (see Table 6). On the basis of the QISD/6-31+G* calculations, which give the best account of the observed IR spectrum (ν(S−Cl) = 513 cm^{-1} and ν(S−Br) = 429 cm^{-1}), the dimensions of the BrSCl molecule are most probably as follows: r_e(S−Cl) = 2.05 Å, r_e(S−Br) = 2.21 Å, and ∠Cl−S−Br = 103°.

Conclusions and Possible Mechanisms

The vapor of (chlorocarbonyl)sulfenyl bromide has been shown by experiment and theory to consist of an equilibrium mixture of syn and anti conformers, with more than 99% of the former at ambient temperatures. Broad-band UV−visible irradiation of the matrix-isolated compound results in the following changes: (i) the syn and anti conformers interconvert in a randomization process that leads to a roughly equimolar mixture of the two; (ii) isomerization occurs to form *syn*-BrC(O)SCl with exchange of halogen substituents at the carbon and sulfur centers; and (iii) both forms of ClC(O)SBr and *syn*-BrC(O)SCl suffer photodecomposition which appears to follow two distinct reaction channels, one leading to CO and the mixed sulfur(II) halide, BrSCl, and the other to OCS + BrCl. The course and sequence of these changes have been traced through the IR spectrum of the matrix, and the various products have been identified and characterized by the wavenumbers and, in some cases, the intensity patterns of the relevant bands, as well as the effects of the naturally occurring ^{35}Cl/^{37}Cl and ^{79}Br/^{81}Br isotopes on certain features. HF and DFT methods have been used to estimate the geometries and energies of the new molecules and to simulate their IR spectra, with results giving persuasive support to the preceding interpretation of the experimental results.

Any attempt to give a mechanistic interpretation of the various changes must take into account the following aspects.

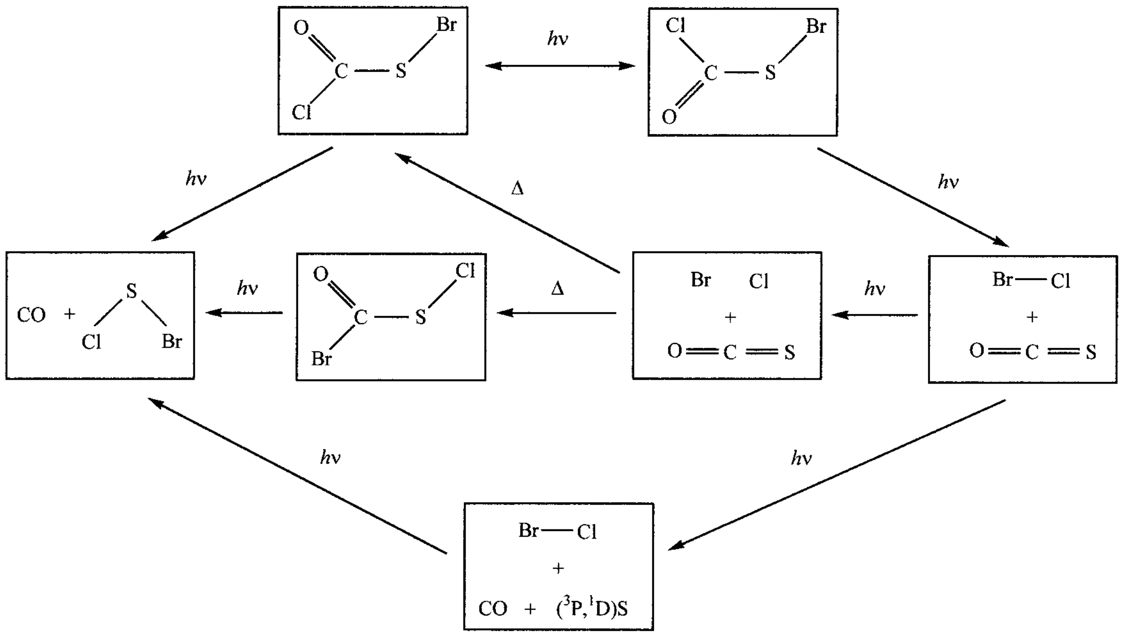
(i) The photolysis conditions were relatively unselective, the radiation spanning the wavelength range 200−800 nm, and the involvement of several photolabile products, as well as the photolabile precursor, makes it impossible to judge the nature of the photoactive transitions with any certainty. Attempts to restrict more closely the wavelength range served only to retard the changes to an unacceptable extent.

(ii) The matrix cage effect[15] may be expected to inhibit the separation of molecular and even atomic products, such as Cl and Br, following photodissociation.

(iii) There is no change in the pattern of behavior when an Ar matrix is doped with CO, and no sign of any extra products. The failure to detect any spectroscopic trace attributable to radicals of the type XCO$^{\bullet}$ appears to rule out the release of X atoms (X = Cl or Br) to the matrix at large as a significant part of the observed photochemistry.[22,23]

(iv) The IR spectra imply that syn ↔ anti randomization and isomerization of *syn*-ClC(O)SBr to *syn*-BrC(O)SCl are among the first changes to occur. After initial buildup, these products decay while there is a simultaneous growth of two of the four main products detectable by their IR spectra, viz., OCS and BrCl. In contrast, the other two products, BrSCl and CO, appear to form more or less continuously and in step with the decay of *syn*-ClC(O)SBr.

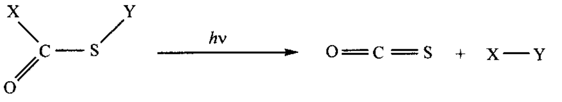
Scheme 1. Outline of Reactions Occurring, or Possibly Occurring, on Broad-Band UV−Visible Photolysis of Matrix-Isolated ClC(O)SBr



The photolytic interconversion of the two rotamers of ClC(O)SBr is entirely analogous to the behaviors of FC(O)SCl[2] and FC(O)SBr,[6] and we must suppose that the molecule gains access to a common excited electronic state. The minimum in the potential surface of this state must then lie almost directly above the maximum separating the two minima in the ground state surface, so that the return to the ground state allows the molecule roughly equal chances of adopting either the syn or anti conformation.

This process appears then to compete, as in the case of the FC(O)SX molecules,[2,6] with photodissociation of the *syn*-ClC(O)SBr molecule to eliminate CO and form BrSCl. Rough calculations based on the appropriate mean bond enthalpies and the known bond enthalpy of CO[27] indicate that reaction 1 is mildly endothermic, the enthalpy changes being +14, +14, and +7 kcal mol^{-1} for FC(O)SCl, FC(O)SBr, and ClC(O)SBr, respectively.

The proximal disposition of the Cl and Br substituents in *anti*-ClC(O)SBr suggests that photodecomposition of this molecule might proceed additionally or exclusively in accordance with eq 3. Calculations similar to those involving reaction 1 and based



(3)

on the reported atomization enthalpy of OCS[27] indicate that reaction 3 is endothermic for FC(O)SCl and FC(O)SBr but *exothermic* for ClC(O)SBr, the estimated enthalpy of the reaction being +31, +18, and −3 kcal mol^{-1}, respectively. Under the conditions of our experiments, the interhalogen product BrCl may be expected to dissociate into Br and Cl atoms, which are then confined to the same matrix cage as the OCS. Within this cage, regeneration of BrCl competes with addition of the atoms to OCS either to regenerate ClC(O)SBr or to form the constitutional isomer BrC(O)SCl, differing only a little in energy from the parent compound. Further photochemical opportunities arise from the photodissociation of OCS in accordance with eq 4 under the action of UV light.[20] Not only will this add to the

$$O{=}C{=}S \xrightarrow{h\nu} CO + (^{3}P,{}^{1}D)S \qquad (4)$$

CO reservoir, but the generation of S atoms—and particularly S atoms in the excited ^{1}D state—suggests a secondary route to BrSCl via eq 5. The various pathways are summarized in

$$S + BrCl \xrightarrow{h\nu} BrSCl \qquad (5)$$

Scheme 1, although further matrix studies are required to test the contribution made by some of them. For example, OCS clearly invites such studies to ascertain the part it plays in the photochemistry of (halogenocarbonyl)sulfenyl compounds.

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Supporting Information Available: Simulated IR spectra and the optimized dimensions of the syn and anti conformers of ClC(O)SBr; vibrational properties of BrC(O)SCl; calculated geometrical parameters and vibrational wavenumbers for triatomic molecule BrSCl (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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