

Gas-phase reactions of halogenated radical carbene anions with sulfur and oxygen containing species

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ABSTRACT

The reactivities of mono- and dihalocarbene anions ($\text{CHCl}^{\bullet-}$, $\text{CHBr}^{\bullet-}$, $\text{CF}_2^{\bullet-}$, $\text{CCl}_2^{\bullet-}$, and $\text{CBrCl}^{\bullet-}$) were studied using a tandem flowing afterglow-selected ion flow tube instrument. Reaction rate constants and product branching ratios are reported for the reactions of these carbene anions with six neutral reagents (CS_2 , COS , CO_2 , O_2 , CO , and N_2O). These anions were found to demonstrate diverse chemistry as illustrated by formation of multiple product ions and by the observed reaction trends. The reactions of $\text{CHCl}^{\bullet-}$ and $\text{CHBr}^{\bullet-}$ occur with similar efficiencies and reactivity patterns. Substitution of a Cl atom for an H atom to form $\text{CCl}_2^{\bullet-}$ and $\text{CBrCl}^{\bullet-}$ decreases the rate constants; these two anions react with similar efficiencies and reactivity trends. The $\text{CF}_2^{\bullet-}$ anion displays remarkably different reactivity; these differences are discussed in terms of its lower electron binding energy and the effect of the electronegative fluorine substituents. The results presented here are compared to the reactivity of the $\text{CH}_2^{\bullet-}$ anion, which has previously been reported.

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1. Introduction

Simple halogen substituted carbenes (CXY , where $\text{X} = \text{F}, \text{Cl}$, and Br and $\text{Y} = \text{H}, \text{F}, \text{Cl}$, and Br) have singlet ground states [1–3]. In solution, these molecules are highly reactive and undergo characteristic reactions such as insertion into single bonds and cycloaddition to double bonds [4,5], making them useful synthetic organic chemistry reagents. In the atmosphere, these compounds are likely photofragments of chlorofluoro compounds and other halons [6–10]; the role of halogenated compounds in ozone depletion has been well documented [11–14]. In addition, the reactions of halocarbenes are important to the plasma chemistry of halogenated compounds [15] and to organometallic chemistry [16–18].

There has been an extensive effort, both experimentally and theoretically, aimed at determining the fundamental physical properties of halocarbenes. These studies have been employed to determine the electronic and molecular structure of the ground and first excited state, vibrational frequencies, ionization energies, electron affinities, and the singlet–triplet splittings [1–3,19–46]. Additionally, heats of formation, gas-phase acidities, and bond dissociation energies have been determined either directly or indi-

rectly through gas-phase ion–molecule bracketing experiments and collision-induced dissociation threshold energy measurements [47–52].

While halogen substituted neutral carbenes have been extensively investigated, only a few studies have addressed the chemistry of the corresponding anions. Addition of an electron to a halocarbene forms a π -radical anion [1–3]. In solution, radical anions are of interest since these species are often reactive intermediates. In the gas-phase, the chemistry of radical anions has important implications for reactions in the upper atmosphere [53], negative ion chemical ionization mass spectrometry [54,55], and electron capture detectors [56].

The majority of the studies involving $\text{CXY}^{\bullet-}$ anions have focused on electron and proton transfer reactions [50–52]; these studies have provided valuable thermodynamic information about the corresponding neutral carbenes. Beyond this, Born et al. [50,57] have investigated the reactivity of a series of monohalocarbene anions with methyl halides, organic esters, and aliphatic alcohols. Their results show that reactions with methyl halides proceed solely by an $\text{S}_{\text{N}}2$ mechanism, while the reactions with the esters proceed by competing $\text{S}_{\text{N}}2$ and $\text{B}_{\text{AC}}2$ mechanisms [57]. The reactions with the alcohol series (ROH) indicate that, in addition to proton transfer, an $\text{S}_{\text{N}}2$ reaction to produce X^- also occurs. This $\text{S}_{\text{N}}2$ process must occur within the $[\text{RO}^- + \text{CH}_2\text{X}]$ complex before the initial products separate [50]. Recently, we investigated the reactions of $\text{CHCl}^{\bullet-}$ with a series of chloromethanes [58]. These reactions primarily occur via substitution and proton transfer. Additionally, however,

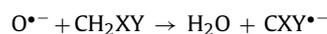
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isotopic labeling studies indicate that carbene anions can undergo an insertion–elimination mechanism, where the anion inserts into a C–Cl bond to form an unstable intermediate, which eliminates either $\text{Cl}_2^{\bullet-}$ or Cl^- and Cl^\bullet .

In this study we evaluate the gas-phase reactivity of simple substituted carbene anions with a series of oxygen and sulfur containing neutral reagents (CS_2 , COS , CO_2 , O_2 , CO , and N_2O). In past studies from our laboratory, we have found that this series of neutral reagents can provide insight into the structure of an anion as well as form interesting product ions from diverse chemistry [59–67]. Additionally, the reactivity of methylene anion, $\text{CH}_2^{\bullet-}$, has been studied with this neutral series [65], which allows for direct comparison to the results presented here. In this work we have measured reaction rate constants as well as product ion branching ratios. Additionally, we suggest reaction mechanisms, which account for the observed product ions. Since there is very little thermochemical information available in the literature for these systems, electronic structure calculations are employed to evaluate the reaction exothermicities for several proposed pathways.

2. Experimental

The reactivities of mono- and dihalocarbene anions ($\text{CHCl}^{\bullet-}$, $\text{CHBr}^{\bullet-}$, $\text{CF}_2^{\bullet-}$, $\text{CCl}_2^{\bullet-}$, and $\text{CBrCl}^{\bullet-}$) were studied using a tandem flowing afterglow-selected ion flow tube instrument (FA-SIFT), which has previously been described [68]. Reactant ions were formed in a flowing afterglow source from the $\text{H}_2^{\bullet+}$ abstraction reactions of $\text{O}^{\bullet-}$ [69,70]:



Ions of a single isotopomer were mass-selected and injected into a reaction flow tube where they were thermalized to 302 ± 2 K by collisions with He buffer gas (0.5 torr, $\sim 10^4$ cm s⁻¹). Despite injecting the reactant ions with minimal energy, X^- ions produced from collision-induced dissociation were also present in the reaction flow tube; the presence of these additional ions was considered in the data analysis below.

Measured flows of neutral reagents were introduced into the reaction flow tube through a manifold of inlets and the reactant and product ions were analyzed by a quadrupole mass filter coupled to an electron multiplier. Reaction rate constants were determined by changing the neutral reagent inlet position, thereby varying the reaction distance and time, while monitoring the change in reactant ion intensity. Product branching fractions were measured at each neutral inlet and averaged together; secondary reactions in general do not occur for these systems. Efforts were made to minimize mass discrimination, however, it was necessary to estimate the relative detection sensitivities when calculating product branching ratios. The relative detection sensitivity was estimated by examining a series of exothermic ion–molecule reactions where only one ionic product was formed. For reactions of $\text{CBrCl}^{\bullet-}$, we were unable to cleanly separate the $\text{CBrCl}^{\bullet-}$ anion from the CHBrCl^- anion in the

injection process. The presence of this additional ion does not interfere with measurements of the overall reaction rate constant since $\text{CBrCl}^{\bullet-}$ can be resolved and monitored with the mass detection system. The presence of CHBrCl^- , however, does complicate the determination of the product branching ratios. For this same reason, the $\text{CBr}_2^{\bullet-}$ anion was not included in this study. Additionally the $\text{CHF}^{\bullet-}$ anion was not studied since it occurs at the same mass as $\text{O}_2^{\bullet-}$, which is also present in the ion source.

The error reported for the reaction rate constants is one standard deviation of at least three measurements. The uncertainty in the reaction rate constants due to systematic error is $\pm 20\%$ and the uncertainty in the product branching ratios is $\pm 30\%$. Helium buffer gas (99.995%) was purified by passage through a liquid nitrogen-cooled molecular sieve trap. Neutral reagents were purchased from commercial sources and used without further purification. The reactions of $\text{CXY}^{\bullet-}$ with COS indicate that the neutral sample contains a trace amount of H_2S impurity; as a result, the measured rate constants represent an upper bound value. The reported reaction efficiencies are the measured rate constant divided by the calculated collision rate constant ($\text{eff} = k/k_{\text{col}}$). Collision rate constants were calculated from parameterized trajectory collision rate theory [71].

Electronic structure calculations were performed using the G3 composite technique [72] provided in the Gaussian 03 suite of programs [73]. The electronic energy, harmonic frequencies, and rotational constants were determined for the optimized geometries of the reactants and products of the fluorinated and chlorinated reactions. These results were used to evaluate the exothermicities of the proposed mechanisms; a more detailed investigation to include the reaction intermediates and transition states is beyond the scope of this work. The exothermicities of the brominated reactions are not provided since the G3 method does not include fourth row elements. The Cartesian coordinates and energies for the optimized geometries of the reactants and products are provided in the [Supplementary Information](#).

3. Results and discussion

Table 1 displays the experimentally measured reaction rate constants for the reactions of $\text{CXY}^{\bullet-}$ with each neutral reagent; Table 2 presents product ion branching fractions. Fig. 1 is a plot of reaction efficiency as a function of anion basicity for the reactions of $\text{CXY}^{\bullet-}$ with CS_2 , COS , CO_2 , O_2 , and CO ; N_2O is excluded from this plot since it only reacts with $\text{CF}_2^{\bullet-}$. In this figure each trace represents a different neutral reagent and the data points are connected to guide the eye only. The reaction trends presented in this plot are not readily observed in Table 1 since the collision rate constants for the reactions of CO_2 and CS_2 are smaller than for COS . The $\text{CHCl}^{\bullet-}$ and $\text{CHBr}^{\bullet-}$ anions react with similar efficiencies and trends. As expected, replacing a hydrogen atom with a chlorine atom to form $\text{CCl}_2^{\bullet-}$ and $\text{CBrCl}^{\bullet-}$ substantially decreases the reaction efficiency. The reaction efficiencies and trends for the $\text{CCl}_2^{\bullet-}$ and $\text{CBrCl}^{\bullet-}$

Table 1
Reaction rate constants (10^{-10} cm³ s⁻¹) for the reactions of $\text{CXY}^{\bullet-}$ with CS_2 , COS , CO_2 , O_2 , CO , and N_2O

| Neutral reagent | $\text{CHCl}^{\bullet-}$ (384.8; 1.210) ^a | $\text{CHBr}^{\bullet-}$ (380.7; 1.454) | $\text{CF}_2^{\bullet-}$ (377.4; 0.180) | $\text{CCl}_2^{\bullet-}$ (364.2; 1.590) | $\text{CBrCl}^{\bullet-}$ (361; 1.84) |
|----------------------|--|---|---|--|---------------------------------------|
| CS_2 | 10.5 ± 0.7^b | 9.14 ± 0.22 | 10.7 ± 0.3 | 0.400 ± 0.080 | 0.162 ± 0.009 |
| COS^c | 6.87 ± 0.25 | 5.27 ± 0.14 | 5.02 ± 0.17 | 1.31 ± 0.03 | 0.850 ± 0.038 |
| CO_2 | 5.62 ± 0.17 | 5.13 ± 0.02 | $<0.070 \pm 0.002$ | <0.001 | <0.001 |
| O_2 | 2.11 ± 0.04 | 1.80 ± 0.05 | 2.65 ± 0.03 | 0.946 ± 0.025 | 0.748 ± 0.014 |
| CO | 1.42 ± 0.25 | 0.943 ± 0.013 | <0.001 | <0.001 | <0.001 |
| N_2O | <0.001 | <0.001 | 0.178 ± 0.030 | <0.001 | <0.001 |

^a The enthalpy of protonation in kcal mol⁻¹ and the electron binding energy in eV are given in parentheses; see Refs. [2,3,50,51].

^b Standard deviation of at least three measurements.

^c Reaction rate constants represent an upper bound value, see experimental section.

Table 2
Product ion distributions for the reactions of $\text{CXY}^{\bullet-}$ with CS_2 , COS , CO_2 , and O_2

| Neutral reagent | Product ions | $\text{CH}_2^{\bullet-}$ ^b (407.4; 0.6520) ^a | $\text{CHCl}^{\bullet-}$ (384.8; 1.210) | $\text{CHBr}^{\bullet-}$ (380.7; 1.454) | $\text{CF}_2^{\bullet-}$ (377.4; 0.180) | $\text{CCl}_2^{\bullet-}$ (364.2; 1.590) | $\text{CBrCl}^{\bullet-}$ ^c (361; 1.84) |
|----------------------|---|---|--|--|--|---|---|
| CS_2 | X^- | | 0.07 | 0.50 | | 1.00 | Cl^- , Br^- |
| | $\text{X}_2^{\bullet-}$ | | | | | | $\text{BrCl}^{\bullet-}$ |
| | $\text{S}^{\bullet-}$ | + | | | | | |
| | SH^- | + | | | | | |
| | $\text{CS}_2^{\bullet-}$ | + | | | | 1.00 | |
| | C_2HS^- | + | | | | | |
| | $\text{C}_2\text{S}_2^{\bullet-}$ | | 0.02 | 0.01 | | | + |
| | $\text{CXS}^{\bullet-}$ | | 0.18 | 0.37 | | | |
| | $\text{CYXS}^{\bullet-}$ | + | 0.73 | 0.12 | | | |
| Loss of e^- | + | | | | | | |
| COS | X^- | | 0.90 | 1.00 | | 0.94 | Cl^- , Br^- |
| | $\text{X}_2^{\bullet-}$ | | | | | | $\text{BrCl}^{\bullet-}$ |
| | $\text{S}^{\bullet-}$ | + | | | | | |
| | $\text{C}_2\text{OS}^{\bullet-}$ | | 0.03 | Trace | | | |
| | $\text{CXY}^{\bullet-}$ | + | 0.07 | | 1.00 | 0.06 | |
| Loss of e^- | + | | | | | | |
| CO_2 | X^- | | 0.94 | 1.00 | 0.20 | | |
| | $\text{CYXO}^{\bullet-}$ | | 0.06 | | | | |
| | $\text{C}_2\text{X}_2\text{O}_2^{\bullet-}$ | | | | 0.80 | | |
| | Loss of e^- | + | | | | | |
| O_2 | X^- | | 0.60 | 0.90 | 0.30 | 0.58 | Cl^- |
| | $\text{X}_2^{\bullet-}$ | | | | 0.02 | 0.24 | $\text{BrCl}^{\bullet-}$ |
| | $\text{O}^{\bullet-}$ | + | 0.32 | 0.07 | 0.40 | 0.12 | + |
| | OH^- | | 0.05 | 0.03 | | | |
| | $\text{O}_2^{\bullet-}$ | | | | 0.28 | | |
| | OX^- | | 0.03 | | | 0.04 | ClO^- |
| | $\text{CX}_2\text{O}^{\bullet-}$ | | | | | 0.02 | |

+ Indicates that the ion was formed. For the $\text{CH}_2^{\bullet-}$ ion, X and Y = H; for the $\text{CHCl}^{\bullet-}$ and $\text{CHBr}^{\bullet-}$ anions, X = halogen and Y = H; for the $\text{CF}_2^{\bullet-}$, $\text{CCl}_2^{\bullet-}$, and $\text{CBrCl}^{\bullet-}$ anion both X and Y = halogen.

^a The enthalpy of protonation in kcal mol^{-1} and the electron binding energy in eV are given in parentheses; see Refs. [2,3,50,51].

^b The product ions formed from the reactions of $\text{CH}_2^{\bullet-}$ with CS_2 , COS , CO_2 , and O_2 are taken from Ref. [65].

^c Product branching ratios are not determined because the $\text{CHBrCl}^{\bullet-}$ ion was also present in the reaction flow tube.

anions are similar to one another but differ from those of the $\text{CHCl}^{\bullet-}$ and $\text{CHBr}^{\bullet-}$ anions. The $\text{CF}_2^{\bullet-}$ anion displays unique reactivity. This difference in reactivity is, in part, not surprising since the $\text{CF}_2^{\bullet-}$ anion has a significantly lower electron binding energy than the other ions studied here and, in general, other fluoro-anions typically display distinct reactivity [74].

As demonstrated in Fig. 1 and by the formation of multiple product ions (Table 2), the reactivity of these carbene anions is complex. To be able to address these reactivity trends, we must first discuss the likely reaction mechanisms. In the following sections the reac-

tivity of the $\text{CHCl}^{\bullet-}$, $\text{CHBr}^{\bullet-}$, $\text{CCl}_2^{\bullet-}$, and $\text{CBrCl}^{\bullet-}$ anions will be discussed together while the reactivity of the $\text{CF}_2^{\bullet-}$ anion will be discussed separately. Since our experimental set-up does not allow for neutral product detection, the neutral products are inferred from the ionic products and the structures of the neutral and ionic products are based on molecular stability and on the occurrence of reasonable reaction mechanisms. Electronic structure calculations are used as a guide in determining these structures and mechanisms. The G3 calculated exothermicities for the observed fluorinated and chlorinated reactions are provided throughout the text and in Table 3; a more complete list of calculated exothermicities is provided in the Supplementary Information. The calculated results are compared to experimental values when possible.

3.1. Reactions of $\text{CHX}^{\bullet-}$ and $\text{CClX}^{\bullet-}$ (X = Cl and Br)

The reactions of $\text{CHX}^{\bullet-}$ (X = Cl and Br) with CS_2 produce X^- , $\text{C}_2\text{S}_2^{\bullet-}$, $\text{CHXS}^{\bullet-}$, and CXS^- , as shown below for $\text{CHCl}^{\bullet-}$ with CS_2 .



Reactions 1a and 1b presumably proceed by anion attack on the carbon atom of CS_2 , as shown in Scheme 1. These two reactions proceed through a $[\text{HC}(\text{Cl})-\text{CS}_2]^{\bullet-}$ intermediate followed by an intramolecular $\text{S}_\text{N}2$ reaction, where the sulfur atom attacks the β carbon atom to displace Cl^- . A trace amount of $\text{C}_2\text{S}_2^{\bullet-}$ is detected, which is the result of proton transfer before the initial products

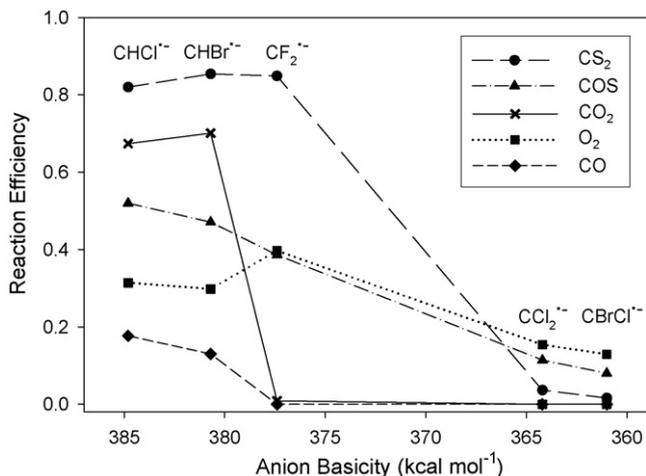


Fig. 1. Reaction efficiency versus anion basicity (lines are only intended to guide eye).

Table 3

Calculated and experimental reaction exothermicities (kcal mol⁻¹) for the reactions of CHCl^{•-}, CCl₂^{•-}, and CF₂^{•-}

| Reaction | Calc ^a | Exp ^b | BR ^c |
|---|-------------------|------------------|-----------------|
| CHCl ^{•-} + CS ₂ → Cl ⁻ + C ₂ HS ₂ [•] | 0 | | 0.07 |
| → C ₂ S ₂ ^{•-} + HCl | -64 | | 0.02 |
| → CHClS ^{•-} + CS | -11 | | 0.73 |
| → CClS ^{•-} + HCS [•] | -6 | | 0.18 |
| CHCl ^{•-} + COS → Cl ⁻ + C ₂ HOS [•] | -48 | | 0.90 |
| → C ₂ OS ^{•-} + HCl | -41 | | 0.03 |
| → CHClS ^{•-} + CO | -42 | | 0.07 |
| CHCl ^{•-} + CO ₂ → Cl ⁻ + C ₂ HO ₂ [•] | -25 | | 0.94 |
| → CHClO ^{•-} + CO | -37 | | 0.06 |
| CHCl ^{•-} + O ₂ → O ^{•-} + CHClO | -66 | | 0.32 |
| → OH ⁻ + COCl [•] | -88 | -91 | 0.05 |
| → Cl ⁻ + CHO ₂ [•] | -134 | -137 | 0.60 |
| → ClO ⁻ + CHO [•] | -68 | -70 | 0.03 |
| CHCl ^{•-} + CO → Cl ⁻ + C ₂ HO | -33 | -11 | 1.00 |
| → C ₂ O ^{•-} + HCl | -7 | -10 | Trace |
| CCl ₂ ^{•-} + CS ₂ → Cl ⁻ + C ₂ ClS ₂ [•] | -26 | | 1.00 |
| CCl ₂ ^{•-} + COS → Cl ⁻ + C ₂ ClOS [•] | -21 | | 0.94 |
| → CCl ₂ S ^{•-} + CO | -27 | | 0.06 |
| CCl ₂ ^{•-} + O ₂ → O ^{•-} + CCl ₂ O | -44 | | 0.12 |
| → Cl ⁻ + CClO ₂ [•] | -116 | -140 | 0.58 |
| → ClO ⁻ + CClO [•] | -52 | -63 | 0.04 |
| → CCl ₂ O ^{•-} + O | -39 | | 0.02 |
| → Cl ₂ ^{•-} + CO ₂ | -171 | -170 | 0.24 |
| CF ₂ ^{•-} + CS ₂ → CS ₂ ^{•-} + CF ₂ | -5 | -10 | 1.00 |
| CF ₂ ^{•-} + COS → CF ₂ S ^{•-} + CO | -34 | | 1.00 |
| CF ₂ ^{•-} + CO ₂ → C ₂ F ₂ O ₂ ^{•-} | -36 | | 1.00 |
| CF ₂ ^{•-} + O ₂ → O ^{•-} + CF ₂ O | -68 | | 0.40 |
| → F ⁻ + •CFO ₂ | -97 | | 0.30 |
| → O ₂ ^{•-} + CF ₂ | -5 | -7 | 0.28 |
| → F ₂ ^{•-} + CO ₂ | -114 | -116 | 0.02 |
| CF ₂ ^{•-} + N ₂ O → CF ₂ N ⁻ + NO [•] | -43 | <-4 | 0.90 |
| → F ⁻ + FCN + NO [•] | -7 | -10 | 0.10 |

^a G3 calculated reaction enthalpies.

^b Enthalpies of formation are determined from the thermo chemical data on the NIST webbook [78] or from the JANAF thermo chemical tables [79].

^c This work.

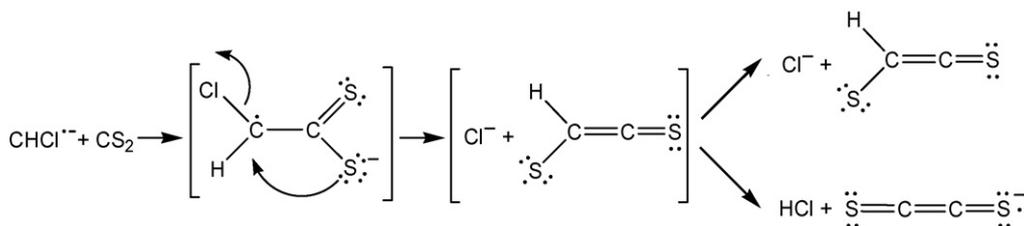
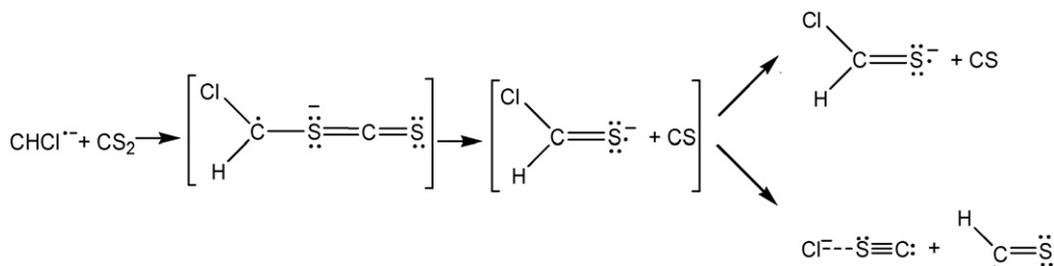
from 1a separate. While proton transfer to form C₂S₂^{•-} is thermodynamically favored, it is a minor product whose formation is likely influenced by kinetic or dynamic factors within the product ion–molecule complex. Reactions 1c and 1d most likely proceed by carbanion attack on the sulfur atom of CS₂, as shown in Scheme 2. Reaction 1c is the result of the displacement of neutral CS. The CClS^{•-}

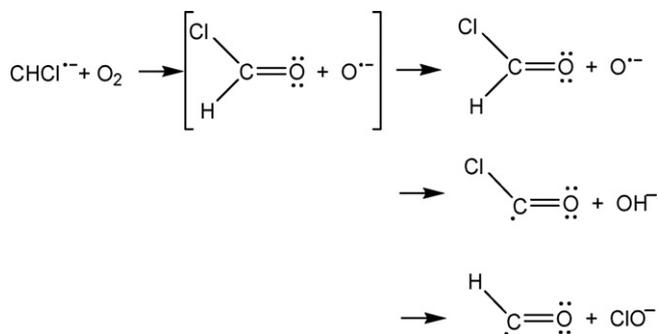
ion (1d) is formed from hydrogen atom transfer before the initial products of 1c separate; G3 calculations predict that this ion is a [Cl⁻•S≡C] ion–dipole bound complex.

The reactions of CHX^{•-} (X = Cl or Br) with COS and CO₂ proceed similarly to the corresponding reactions with CS₂; such parallels in reactivity of anions with these three neutral reactants have previously been reported in the literature [59,60]. The product ions formed are consistent with either attack on the neutral reagent carbon atom, analogous to the mechanism shown in Scheme 1, or attack on neutral reagent sulfur (or oxygen) atom, analogous to the mechanism shown in Scheme 2. As the neutral reagent is changed from CS₂ to COS and CO₂, sulfur/oxygen atom attack becomes the minor pathway for the CHCl^{•-} anion and is not observed for the CBr^{•-} anion.

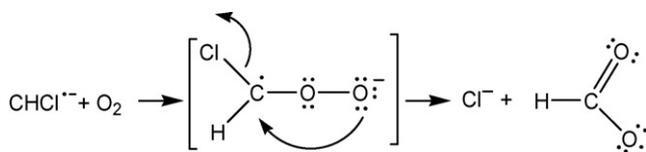
The product ions formed in the reactions of CCl₂^{•-} and CBrCl^{•-} with CS₂ are consistent with a mechanism that is analogous to Scheme 1 only. For the reactions of CBrCl^{•-} with CS₂, either Cl⁻ or Br⁻ can be displaced by an intramolecular S_N2 reaction. The formation of BrCl^{•-} is due to halogen atom abstraction, in contrast to proton transfer, before the initial products separate; in some encounters, the electron remains with C₂S₂. Both of these dihalo anions react with COS but do not react with CO₂ within our detection limits. The reaction of CCl₂^{•-} with COS primarily proceeds by anion attack on the carbon atom of COS; additionally, a minor channel of anion attack on the sulfur atom of COS is also observed. The CBrCl^{•-} anion reacts with COS exclusively by attack on carbon.

An interesting observation is that the reaction efficiencies (Fig. 1) for the mono- and dihalocarbene do not mirror each other. For the CHCl^{•-} and CBr^{•-} anions, the reaction with CS₂ is most efficient, followed by CO₂, then by COS. In contrast for these three neutral reactants, the efficiency is greatest for the reactions of CCl₂^{•-} and CBrCl^{•-} with COS, followed by CS₂, while CO₂ is below our detection limits. As established above, these carbene anions primarily react with this neutral series by nucleophilic attack on the neutral reagent carbon atom; with the exception of CHX^{•-} with CS₂, anion attack on the neutral reagent sulfur/oxygen atom is at most a minor pathway. This mechanism (shown in Scheme 1) is complex and multiple factors influence the observed reaction efficiency. If we consider the first step of the reaction mechanism, we would expect the reactivity to increase as the number of oxygen atoms in the neutral reagent increases, since in CO₂ there is a greater partial positive charge on the carbon atom as compared to CS₂. However,

**Scheme 1.****Scheme 2.**



Scheme 3.



Scheme 4.

while oxygen is more electronegative, sulfur can expand its valence and therefore more readily accept the negative charge. Following the anion attack on the carbon atom of the neutral reagent, halide displacement occurs as a result of an intramolecular S_N2 reaction. Here we must consider two further factors, the nature of the leaving group (Cl or Br) and of the nucleophile (S or O). It is known that Br^- is a better leaving group than Cl^- and that sulfur anions are comparable nucleophiles to oxygen anions. Since multiple factors must be considered, predicting the reaction efficiency trend is not straightforward. Furthermore, it is likely that the individual factors may have a different overall net effect for different anions, and hence the observed trends for the mono- and dihalocarbenes differ from one another.

The $CHCl^{\bullet-}$ and $CHBr^{\bullet-}$ ions react with O_2 with the same efficiency to produce analogous products. The reaction of $CHCl^{\bullet-}$ with O_2 produces $O^{\bullet-}$, OH^- , Cl^- and ClO^- .

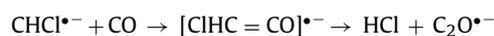


Reaction 2a proceeds by an S_N2 reaction with anion attack at the oxygen to displace $O^{\bullet-}$. Before the product ion–molecule complex dissociates, $O^{\bullet-}$ can abstract either a hydrogen or chlorine atom to form OH^- (2b) or ClO^- (2d), respectively (Scheme 3). The formation of Cl^- in 2c is the major product. Analogous to the above reactions with CS_2 , COS and CO_2 , where the displaced halide is also observed, this reaction most likely proceeds through an $[CHClC-O-O]^{\bullet-}$ intermediate followed by an intramolecular S_N2 reaction where, in a concerted step, the terminal O atom attacks the carbon to displace Cl^- .

The dihalocarbanions, $CCl_2^{\bullet-}$ and $CBrCl^{\bullet-}$, react with O_2 to form similar product ions as the corresponding reactions of $CHX^{\bullet-}$ ($X=Cl$ and Br) with O_2 , the majority of which can be explained by the above mechanisms. The reaction of $CCl_2^{\bullet-}$ with O_2 additionally produces minor amounts of $CCl_2O^{\bullet-}$, which is due to electron transfer from $O^{\bullet-}$ within the product ion–molecule complex. The reactions of $CCl_2^{\bullet-}$ and $CBrCl^{\bullet-}$ with O_2 also produce the dihalide anions. These dihalide anions could be formed from a mechanism similar to Scheme 4, where X atom abstraction occurs within the prod-

uct ion–molecule complex before the initial products separate to form $XY^{\bullet-}$ and CO_2 . Interestingly, the product ions formed in the reactions of $CCl_2^{\bullet-}$ and $CBrCl^{\bullet-}$ with O_2 are comparable to the carbene cation reaction of $CBr_2^{\bullet+}$ with O_2 , which has previously been studied by Cooks and co-workers [75]. In that work, the authors speculate that this reaction proceeds through a $Br_2CO_2^{\bullet+}$ intermediate, which can eliminate CO_2 to form $Br_2^{\bullet+}$. Additionally, this intermediate can rearrange to form $BrCO^+$ and BrO^+ and, in a competitive process, $BrCO^{\bullet}$ and BrO^{\bullet} .

Both $CHCl^{\bullet-}$ and $CHBr^{\bullet-}$ react with CO to primarily produce the displaced halide (3a). For the reaction of $CHCl^{\bullet-}$, a trace amount of $C_2O^{\bullet-}$ is also formed (3b), while for the reaction of $CHBr^{\bullet-}$ a trace amount of C_2HO^- is detected.

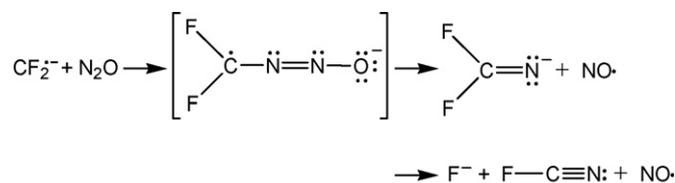


The formation of these products is consistent with a mechanism where the anion attacks the carbon atom of CO . In an analogous manner to the other reactions discussed thus far, Cl^- could be displaced by an intramolecular S_N2 mechanism where the O atom attacks the carbon atom in the β position. However, if this were indeed the case, the resulting neutral species is probably not stable. Instead, if the addition of $CHCl^{\bullet-}$ to CO is sufficiently exothermic, the $C-Cl$ bond could break to produce very stable products, Cl^- and $H-C\equiv C-O^{\bullet}$. Alternatively, the initially formed intermediate, may undergo a retro-carbene reaction to make HCl and $:C=C=O^{\bullet-}$ directly; proton transfer within the product ion–molecule complex then would form Cl^- and $HCCO^{\bullet}$. In this case, both mechanisms are feasible; however, neither one likely occurs for the other reactions discussed above that also produce the displaced halide. Less energy is required to form a $C=O$ bond from a $C\equiv O$ bond, than to form a $C-O$ from $C=O$ bond. Neither $CCl_2^{\bullet-}$ nor $CBrCl^{\bullet-}$ react with CO . This is consistent with calculations, which predict the reaction of $CCl_2^{\bullet-}$ with CO to be endothermic.

3.2. Reactions of $CF_2^{\bullet-}$

The reactivity of the $CF_2^{\bullet-}$ anion is different than that of other carbene anions, due in part, to its lower electron binding energy. As a result, this anion can react by electron transfer. This is the case for the reaction of $CF_2^{\bullet-}$ with CS_2 , where electron transfer is the only pathway observed, consistent with calculations, which predict that electron transfer is the only exothermic pathway. The reactions of $CF_2^{\bullet-}$ with COS , CO_2 , and O_2 show some similarities and some differences to the other anions discussed above. For example, $CF_2^{\bullet-}$ reacts with COS via anion attack on the sulfur atom of COS to exclusively produce CF_2S^- , analogous to Scheme 2. A mechanism analogous to Scheme 1 to form F^- is predicted to be endothermic. The reaction of $CF_2^{\bullet-}$ with CO_2 exclusively forms $C_2F_2O_2^{\bullet-}$. This is most likely the result of anion addition to the carbon atom of CO_2 , similar to the addition reaction of OH^- with CO_2 [76], rather than from a clustering process. For the reaction of $CF_2^{\bullet-}$ with O_2 , electron transfer is exothermic and this pathway is viable as evident by the formation of $O_2^{\bullet-}$. Additionally this reaction produces $O^{\bullet-}$, F^- , and $F_2^{\bullet-}$, which are analogous to the products formed from $CClX^{\bullet-}$ ($X=Cl$ and Br) with O_2 .

It has previously been demonstrated that neither $CHCl^{\bullet-}$ nor $CHBr^{\bullet-}$ react with N_2O [50], even though the reaction of $CHCl^{\bullet-}$ with N_2O is predicted to be exothermic. As would be expected, $CCl_2^{\bullet-}$ and $CBrCl^{\bullet-}$ also do not react with N_2O . $CF_2^{\bullet-}$, however,



Scheme 5.

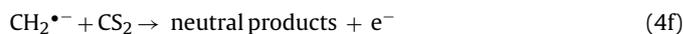
does react with N_2O to produce CF_2N^- and F^- in a 0.90 to 0.10 branching fraction, respectively. This reaction most likely proceeds by attack of the anion on the terminal nitrogen atom of N_2O , as shown in Scheme 5. The addition of $\text{CF}_2^{\bullet-}$ is sufficiently exothermic ($\Delta H \sim -43 \text{ kcal mol}^{-1}$) such that F^- can be displaced. In this case, addition–dissociation is similar to the reaction of $\text{CHX}^{\bullet-}$ with CO , where X^- is displaced. The $\text{CF}_2^{\bullet-}$ anion, however, does not react with CO ; this reaction is predicted to be endothermic. Similar nitrogen atom transfer reactions have previously been observed for reactions of radical anions and N_2O [62,77].

So far we have discussed the differences in the reactivity of $\text{CF}_2^{\bullet-}$ in terms of its lower electron binding energy ($e\text{BE}(\text{CF}_2^{\bullet-}) = 0.180 \text{ eV}$ [2]). Several groups have attributed the stability of the neutral halocarbene singlet state (and destabilization of the triplet state) to two factors, the electronegativity of the substituents and the ability for the halogen to donate electron density to the carbon through π -backbonding [3,48]. These two effects are magnified in the case of neutral CF_2 , since fluorine is the most electronegative halogen and since the C–F bond is shorter than the C–Cl and C–Br bonds and, therefore, there is good overlap between the carbon and fluorine atom π -orbitals. As a result, the electron binding energy of $\text{CF}_2^{\bullet-}$ (and $\text{CHF}^{\bullet-}$) is significantly lower than that of the chloro and bromo carbene anions ($e\text{BE}(\text{CHCl}^{\bullet-}) = 1.210 \text{ eV}$; $e\text{BE}(\text{CHBr}^{\bullet-}) = 1.454 \text{ eV}$; $e\text{BE}(\text{CCl}_2^{\bullet-}) = 1.590 \text{ eV}$; $e\text{BE}(\text{CBr}_2^{\bullet-}) = 1.84 \text{ eV}$ [2,3,51]). While this explanation accounts for its propensity to undergo electron transfer, it clearly does not explain every difference between $\text{CF}_2^{\bullet-}$ and the other anions studied here.

In general, for these carbene anions, the reaction efficiency increases as the anion basicity increases. It is not surprising that $\text{CF}_2^{\bullet-}$ is considerably more basic than $\text{CCl}_2^{\bullet-}$ and $\text{CBr}_2^{\bullet-}$, since F^- is considerable more basic than Cl^- and Br^- . Thus, due to its basicity and its electron binding energy, we would expect $\text{CF}_2^{\bullet-}$ to be highly reactive; this expectation is experimentally observed in some instances. Additionally, $\text{CF}_2^{\bullet-}$ is a hard base due to its small size; typically hard bases are good nucleophiles. However, since fluorine is so electronegative, the fluorine substituents inductively withdraw electron density from the carbon σ -orbital, decreasing the nucleophilicity of the anion. As a result $\text{CF}_2^{\bullet-}$ reacts with COS fairly efficiently by sulfur atom transfer but does not react with CO .

3.3. Comparison to the isoelectronic $\text{CH}_2^{\bullet-}$ anion

The product ions formed in the reactions of $\text{CH}_2^{\bullet-}$ with CS_2 , COS , CO_2 , O_2 , CO , and N_2O have been previously documented [65]. The ionic products formed in the reaction with CS_2 , COS , CO_2 , and O_2 are included in Table 2. The reaction of $\text{CH}_2^{\bullet-}$ with CS_2 shows some similarities to the reactions of $\text{CXY}^{\bullet-}$ studied here.



Evidence of anion addition to the carbon atom of CS_2 is observed in 4a–c; however, instead of the sulfur atom attacking the β carbon atom in an intramolecular $\text{S}_{\text{N}}2$ reaction, $\text{S}^{\bullet-}$ is displaced. The product ions formed in 4b and 4c are a result of proton or hydrogen atom transfer within the product ion–molecule complex of 4a before the initial products separate. In contrast, sulfur anion displacement is not observed for the reactions of $\text{CHX}^{\bullet-}$ and $\text{CCIX}^{\bullet-}$ ($\text{X} = \text{Cl}$ and Br) with CS_2 since halides are better leaving groups. Reaction 4d is the result of carbanion attack on the sulfur atom of CS_2 followed by loss of CS , analogous to Scheme 2.

Reaction 4e proceeds by electron transfer, which parallels the reaction of $\text{CF}_2^{\bullet-}$ with CS_2 , again due to the low electron binding energy of $\text{CH}_2^{\bullet-}$. The $\text{CH}_2^{\bullet-}$ and $\text{CF}_2^{\bullet-}$ anions show additional parallels in reactivity. For example, both anions react with N_2O by attack on the terminal nitrogen. A notable difference in the reactivity of $\text{CH}_2^{\bullet-}$ is that this anion has a propensity to react via associative or reactive electron detachment. In fact, electron detachment is the major channel for the reaction of $\text{CH}_2^{\bullet-}$ with CS_2 (4f) and the sole channel for reactions with CO_2 and CO . While we cannot fully exclude the possibility of electron detachment in the present study, it is at most a minor process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.07.007.

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