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**14. ABSTRACT**
Rate coefficients have been measured for electron attachment to oxalyl chloride [ClC(O)C(O)Cl] and oxalyl bromide [BrC(O)C(O)Br] in He gas at 133 Pa pressure over the temperature range of 300-550K. With oxalyl chloride, the major ion product of attachment is $Cl_2^-$ at all temperatures (66% at 300 K); its import- ance increases slightly as temperature increases. Two other product ions formed are $Cl^-$ (18% at 300 K) and the phosgene anion $CCl_2^-$ (16% at 300 K) and appear to arise from a common mechanism. With oxalyl bromide, the $Br_2^-$ channel represents almost half of the ion product of attachment, independent of temperature. $Br^-$ accounts for the remainder. For oxalyl chloride, the attachment rate coefficient is small $[(1.8\pm0.5) \times 10^{-8}$ $cm^3$ $s^{-1}$ at 300 K] and increases with temperature. The attachment rate coefficient for oxalyl bromide $[(1.3\pm0.4) \times 10^{-7}$ cm3 $s^{-1}$ at 300 K] is nearly collisional and increases only slightly with temperature. Stable parent anions $C_2Cl_2O_2^-$ and $C_2Br_2O_2^-$ and adduct anions $Cl^-(C_2Cl_2O_2)$ and $Br^-(C_2Br_3O_2)$ were observed but are not primary attachment products. G2 and G3 theories were applied to determine geometries of products and energetics of the electron attachment and ion-molecule reactions studied. Electron attachment to both oxalyl halide molecules leads to a shorter C-C bond and longer C-Cl bond in the anions formed. *Trans* and *gauche* conformers of the neutral and anionic oxalyl halide species have similar energies are more stable than the *cis* conformer, which lies 200-300 meV higher in energy. For $C_2Cl_2O_2$, $C_2Cl_2O_2^-$, and $C_2Br_2O_2^-$, the *trans* conformer is the most stable conformation. The calculations are ambiguous as to the oxalyl bromide geometry (*trans* or *gauche*), the result depending on the theoretical method and basis set. The *cis* conformers for $C_2Cl_2O_2$ and $C_2Br_2O_2$ are transition states. In contrast, the *cis* conformers of the anionic oxalyl halide molecules are stable, lying 131 meV above *trans*-$C_2Cl_2O_2^-$ and 179 meV above *trans*-$C_2Br_2O_2$. Chien *et al.* [J. Phys. Chem. A 103, 7918 (1999)] and Kim *et al.* [J. Chem. Phys. 122, 234313 (2005)] found that the potential energy surface for rotation about the C-C bond in $C_2Cl_2O_2$ is "extremely flat." Our computational data indicate that the analogous torsional surfaces for $C_2Br_2O_2$, $C_2Cl_2O_2^-$, and $C_2Br_2O_2^-$ are similarly flat. The electron affinity of oxalyl chloride, oxalyl bromide, and phosgene were calculated to be 1.91 eV (G3) and 2.00 eV (G2), and 1.17 eV (G3), respectively.

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# Observation of dihalide elimination upon electron attachment to oxalyl chloride and oxalyl bromide, 300–550 K

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Rate coefficients have been measured for electron attachment to oxalyl chloride [ClC(O)C(O)Cl] and oxalyl bromide [BrC(O)C(O)Br] in He gas at 133 Pa pressure over the temperature range of 300–550 K. With oxalyl chloride, the major ion product of attachment is $Cl_2^-$ at all temperatures (66% at 300 K); its importance increases slightly as temperature increases. Two other product ions formed are $Cl^-$ (18% at 300 K) and the phosgene anion $CCl_2O^-$ (16% at 300 K) and appear to arise from a common mechanism. With oxalyl bromide, the $Br_2^-$ channel represents almost half of the ion product of attachment, independent of temperature. $Br^-$ accounts for the remainder. For oxalyl chloride, the attachment rate coefficient is small [$(1.8\pm0.5)\times10^{-8}$ cm$^3$ s$^{-1}$ at 300 K], and increases with temperature. The attachment rate coefficient for oxalyl bromide [$(1.3\pm0.4)\times10^{-7}$ cm$^3$ s$^{-1}$ at 300 K] is nearly collisional and increases only slightly with temperature. Stable parent anions $C_2Cl_2O_2^-$ and $C_2Br_2O_2^-$ and adduct anions $Cl^-(C_2Cl_2O_2)$ and $Br^-(C_2Br_3O_2)$ were observed but are not primary attachment products. G2 and G3 theories were applied to determine geometries of products and energetics of the electron attachment and ion-molecule reactions studied. Electron attachment to both oxalyl halide molecules leads to a shorter C–C bond and longer C–Cl bond in the anions formed. *Trans* and *gauche* conformers of the neutral and anionic oxalyl halide species have similar energies and are more stable than the *cis* conformer, which lies 100–200 meV higher in energy. For $C_2Cl_2O_2$, $C_2Cl_2O_2^-$, and $C_2Br_2O_2^-$, the *trans* conformer is the most stable conformation. The calculations are ambiguous as to the oxalyl bromide geometry (*trans* or *gauche*), the result depending on the theoretical method and basis set. The *cis* conformers for $C_2Cl_2O_2$ and $C_2Br_2O_2$ are transition states. In contrast, the *cis* conformers of the anionic oxalyl halide molecules are stable, lying 131 meV above *trans*-$C_2Cl_2O_2^-$ and 179 meV above *trans*-$C_2Br_2O_2^-$. Chien *et al.* [J. Phys. Chem. A **103**, 7918 (1999)] and Kim *et al.* [J. Chem. Phys. **122**, 234313 (2005)] found that the potential energy surface for rotation about the C–C bond in $C_2Cl_2O_2$ is "extremely flat." Our computational data indicate that the analogous torsional surfaces for $C_2Br_2O_2$, $C_2Cl_2O_2^-$, and $C_2Br_2O_2^-$ are similarly flat. The electron affinity of oxalyl chloride, oxalyl bromide, and phosgene were calculated to be 1.91 eV (G3), and 2.00 eV (G2), and 1.17 eV (G3), respectively. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2196409]
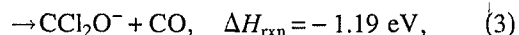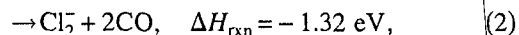
## I. INTRODUCTION

Oxalyl chloride has been the subject of a range of studies because it is an analog of the well-studied glyoxal and exists in two stable conformations at room temperature.[1,2] When energy is added to the molecule in the form of UV photons, multiple bonds break, forming $CCl_2O$(phosgene)+CO, Cl +CO+ClCO, or 2Cl+2CO, depending on the energy.[3–6] The rearrangement required by formation of phosgene is particularly intriguing.

Chien *et al.* carried out electronic structure calculations revealing that oxalyl chloride [ClC(O)C(O)Cl] has a "very flat" torsional potential energy surface (i.e., along the torsional angle between two ClCO groups).[7] Recently, Kim *et* *al.* reported more extensive computations also revealing an "extremely flat torsional potential energy surface" for oxalyl chloride.[8] The *trans* conformer was found to be the lowest energy structure, and the *cis* conformer was shown to be a global maximum on the torsional surface, 97 meV above the *trans* minimum. The *gauche* conformer was found to lie about 30 meV above the *trans* global minimum.

The question of thermal-energy electron attachment to $C_2Cl_2O_2$ is appealing because there are five exothermic attachment channels,[9] several of which are analogous to those active upon photolysis.

$$e^- + C_2Cl_2O_2 \rightarrow C_2Cl_2O_2^-, \quad \Delta H_{rxn} = -1.95 \text{ eV}, \tag{1}$$

$$\rightarrow Cl_2^- + 2CO, \quad \Delta H_{rxn} = -1.32 \text{ eV}, \tag{2}$$

$$\rightarrow CCl_2O^- + CO, \quad \Delta H_{rxn} = -1.19 \text{ eV}, \tag{3}$$
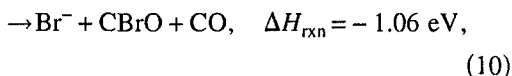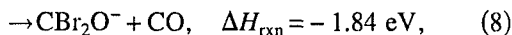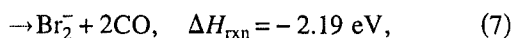
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$$\rightarrow CClO^- + CClO, \quad \Delta H_{rxn} = -0.50 \text{ eV}, \quad (4)$$

$$\rightarrow Cl^- + CClO + CO, \quad \Delta H_{rxn} = -0.34 \text{ eV}. \quad (5)$$

The exothermicities ($\Delta H_{rxn}$ at 298 K) given in the scheme above are from G3 calculations[10] to be described below, using the *trans*-$C_2Cl_2O_2$ conformer as the reactant. Neutral products are not observed in the present experiment; those shown in Eqs. (1)–(10) give the most exothermic reaction enthalpy.

Electron attachment to oxalyl bromide [BrC(O)C(O)Br] is equally interesting,[9]

$$e^- + C_2Br_2O_2 \rightarrow C_2Br_2O_2^-, \quad \Delta H_{rxn} = -2.05 \text{ eV}, \quad (6)$$

$$\rightarrow Br_2^- + 2CO, \quad \Delta H_{rxn} = -2.19 \text{ eV}, \quad (7)$$

$$\rightarrow CBr_2O^- + CO, \quad \Delta H_{rxn} = -1.84 \text{ eV}, \quad (8)$$

$$\rightarrow CBrO^- + CBrO, \quad \Delta H_{rxn} = -1.17 \text{ eV}, \quad (9)$$

$$\rightarrow Br^- + CBrO + CO, \quad \Delta H_{rxn} = -1.06 \text{ eV}, \quad (10)$$

where the exothermicities are from G2 calculations[11] to be described below, using the *trans*-$C_2Br_2O_2$ conformer as the reactant.

## II. EXPERIMENT

The present measurements were made in a flowing-afterglow Langmuir-probe (FALP) apparatus. The method[12] and the Air Force Research Laboratory apparatus[13] have been well described previously. The attachment reactions take place in a fast-flowing electron-He$^+$, Ar$^+$ plasma ($>95\%$ Ar$^+$ at 300 K) at 133 Pa of He gas. The oxalyl halides were used as obtained aside from freeze-pump-thaw degassing cycles.[14] Mixtures were prepared at room temperature in He gas of 0.75% $C_2Cl_2O_2$ and 0.25% $C_2Br_2O_2$ for accurate measurement of the flow rate of reactant into the FALP. Three different flow rates (giving three different concentrations) of reactant were used at each temperature to ensure that the apparent rate coefficient was independent of reactant flow rate. The electron density along the axis of the flow tube was measured with a movable Langmuir probe. The measurement of the ambipolar diffusion frequency $\nu_D$ was made in absence of reactant gas. An example of the electron density data obtained with and without $C_2Cl_2O_2$ present is shown in Fig. 1. The attachment rate coefficient $k_a$ was determined from a fit to the data of the solution to the rate equations describing diffusion and electron attachment.[12,13] The $k_a$ are estimated accurate to ±25%.

A mass spectrometer at the downstream end of the flow tube allowed determination of ionic products of the attachment reactions. Ionic product branching fractions may be measured at He buffer pressures higher than allowed for Langmuir probe operation. However, care must be taken to limit ion-ion recombination (more properly, mutual neutralization) that can be enhanced if reaction times are increased. When this is the case, product branching fractions can be
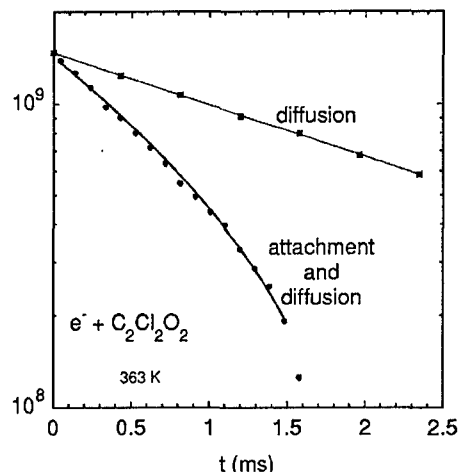


FIG. 1. FALP data for electron attachment to $C_2Cl_2O_2$ at 363 K. The He and $C_2Cl_2O_2$ concentrations were $2.67 \times 10^{16}$ and $2.33 \times 10^{10}$ cm$^{-3}$, respectively. The diffusion rate was measured in absence of reactant. The lines represent solutions to the rate equations governing diffusion and electron attachment plus diffusion.

distorted because the rate of recombination may differ significantly for the different product ions, particularly when one of the ion products is atomic. In our experiments, the various product ions recombine with differing rates with the dominant positive ion, Ar$^+$ ($>95\%$). Polyatomic ions tend to recombine with a rate coefficient around $5 \times 10^{-8}$ cm$^3$ s$^{-1}$ at 300 K.[15] Recombination between atomic ions, such as Ar$^+$ and Cl$^-$, is about two decades slower.[9] Little information is available about atomic-ion–diatomic-ion recombination, but modeling of the present tests indicates that Cl$_2^-$ recombines with Ar$^+$ slower than does CCl$_2$O$^-$. To avoid ion-ion recombination losses, branching fractions were determined at low plasma densities.

## III. ELECTRON ATTACHMENT RESULTS

### A. Rate coefficients and ion products

The measured $k_a$ for $C_2Cl_2O_2$ are given in Table I for the temperature range of 300–550 K (in 133 Pa He gas). At 300 K, $k_a = (1.8 \pm 0.5) \times 10^{-8}$ cm$^3$ s$^{-1}$. In order to determine the efficiency of electron attachment, the polarizability of $C_2Cl_2O_2$ was determined from density functional calculations with a large basis set [B3LYP/6-311+G(3$df$)], yielding a value of 8.9 Å$^3$. Using this value and the Klots electron capture theory,[16] the maximum electron capture rate coefficient for $C_2Cl_2O_2$ is estimated to be $3.2 \times 10^{-7}$ cm$^3$ s$^{-1}$, indicating electron attachment occurs once in every 18 colli-

TABLE I. Rate coefficients and ion product branching fractions for electron attachment to $C_2Cl_2O_2$. The experimental uncertainty is ±25% for $k_a$. The branching fraction uncertainty is ±0.05.

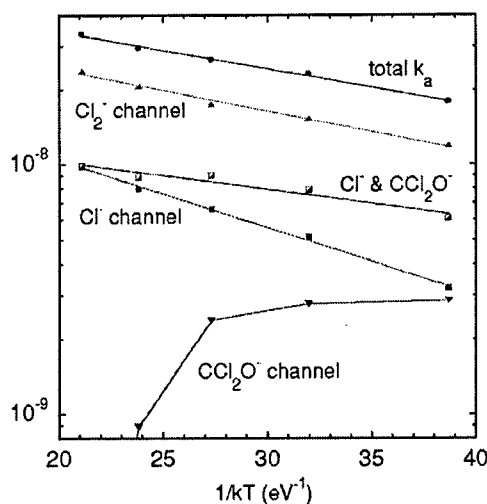| $T$ (K) | $k_a$ (cm$^3$ s$^{-1}$) | Cl$_2^-$ | Cl$^-$ | CCl$_2$O$^-$ |
|---------|------------------------|----------|--------|--------------|
| 300 | $1.8 \times 10^{-8}$ | 0.66 | 0.18 | 0.16 |
| 363 | $2.3 \times 10^{-8}$ | 0.66 | 0.22 | 0.12 |
| 425 | $2.6 \times 10^{-8}$ | 0.66 | 0.25 | 0.09 |
| 487 | $3.0 \times 10^{-8}$ | 0.70 | 0.27 | 0.03 |
| 550 | $3.4 \times 10^{-8}$ | 0.71 | 0.29 | 0.002 |

FIG. 2. Arrhenius plot of total and partial rate coefficients for electron attachment to oxalyl chloride.

sions. The $k_a$ value increases as the temperature increases, in a way that may be described by an activation energy of 35 meV. The ion products of attachment to $C_2Cl_2O_2$ are also listed in Table I. The major ion product at all temperatures studied is $Cl_2^-$ (66% at 300 K). The minor ion products are $Cl^-$ (18% at 300 K) and the phosgene anion $CCl_2O^-$ (16% at 300 K). As the temperature increases, the partial $k_a$ (total $k_a$ times branching fraction) for both the $Cl_2^-$ and $Cl^-$ channels increase, while that for the $CCl_2O^-$ channel decreases, as shown in Fig. 2. Looking more closely at the data in Table I, it appears that loss of phosgene anion is primarily replaced by formation of $Cl^-$, so we have also plotted the partial $k_a$ for both of these reaction channels together (sum) in Fig. 2.

One measurement of the ion product branching fraction was carried out at an electron temperature of $T_e \approx 5000$ K, with a gas temperature of 372 K, using a pure Ar buffer gas, as described in Refs. 12, 17, and 18. The high electron temperature did not affect the $Cl_2^-$ branching fraction, but the $CCl_2O^-$ product channel decreased while the $Cl^-$ formation increased. The branching fractions at high $T_e$ were 66% ($Cl_2^-$), 28% ($Cl^-$), and 6% ($CCl_2O^-$). Though not measured at high $T_e$, $k_a$ is expected to be much smaller than for the truly thermal case.[12]

The measured $k_a$ for $C_2Br_2O_2$ are given in Table II along with ion product branching fractions. The 300 K value for $k_a$ is $(1.3 \pm 0.4) \times 10^{-7}$ cm$^3$ s$^{-1}$. Br$^-$ accounts for 55% of the ion product of attachment, and Br$_2^-$ the remainder. No bromine analogy to the phosgene anion product formed in the

TABLE II. Rate coefficients and ion product branching fractions for electron attachment to $C_2Br_2O_2$. The experimental uncertainty is $\pm 25\%$ for $k_a$. The branching fraction uncertainty is $\pm 0.05$.

| $T$ (K) | $k_a$ (cm$^3$ s$^{-1}$) | Br$^-$ | Br$_2^-$ |
|---|---|---|---|
| 300 | $1.3 \times 10^{-7}$ | 0.55 | 0.45 |
| 363 | $1.4 \times 10^{-7}$ | 0.56 | 0.44 |
| 425 | $1.5 \times 10^{-7}$ | 0.55 | 0.45 |
| 487 | $1.6 \times 10^{-7}$ | 0.54 | 0.46 |
| 550 | $1.5 \times 10^{-7}$ | 0.53 | 0.47 |

$C_2Cl_2O_2$ reaction was observed, though calculations described below indicate that electron affinity (EA) (CBr$_2$O) = 1.76 eV, and the reaction is exothermic [Eq. (8)]. The fact that $k_a$ and the Br$^-$/Br$_2^-$ branching fraction change little with temperature indicates that attachment occurs on nearly every collision. According to the Klots electron capture theory,[16] using our calculated polarizability of 11.4 Å$^3$ for $C_2Br_2O_2$ [B3LYP/6-311+G(3$df$)], the collision rate coefficient is estimated as $3.4 \times 10^{-7}$ cm$^3$ s$^{-1}$, implying attachment to $C_2Br_2O_2$ upon every three collisions at 300 K.

The most intriguing, and surprising, feature of these results is the dominance of the dihalide ion product, because its formation requires cleavage of two carbon-halide bonds and the ground electronic states of the oxalic halides do not have the *cis* conformation (Refs. 7 and 8 and computational results below). Formation of dihalide anions from electron attachment to molecules is rare but has been observed before in thermal electron attachment for some brominated compounds.[19-22] An 8% Br$_2^-$ ion product was observed in attachment to CF$_2$Br$_2$ under single-collision conditions[19] and 15% in 133 Pa of He gas.[20] A few percent dihalide ion products (including Cl$_2^-$, Br$_2^-$, and ClBr$^-$) were observed in work with CHCl$_2$Br, CCl$_2$Br$_2$, and CHClBr$_2$ in another FALP experiment.[21] In a recent electron beam experiment on CHCl$_2$Br, Ipolyi et al.[23] did not observe Cl$_2^-$ ion product, contrary to the small Cl$_2^-$ product (2%) noted by Smith and Španěl[21] in 133 Pa of He buffer gas. In none of these cases was the dihalide the major ion product, as observed here with $C_2Cl_2O_2$.

Zook et al. studied ten dibromated hydrocarbons and fluorocarbons and discovered that the fraction of Br$_2^-$ ion product of attachment increased with buffer gas pressure to as high as 60% for CF$_3$CFBrCF$_2$Br in 1 atm N$_2$ buffer.[22] In the pressure range of 130–530 Pa, seven different buffer gases were used by Zook et al.. The least effective buffer gases in promoting Br$_2^-$ formation were H$_2$ and He, and the most effective was isobutane.[22] Increasing the N$_2$ gas temperature (373–473 K) caused a slight increase in Br$_2^-$ formation for CH$_3$CHBrCH$_2$Br, CH$_2$BrCH$_2$Br, and CH$_2$BrCF$_2$Br, and a decrease in Br$_2^-$ formation for CF$_2$Br$_2$, CF$_2$BrCF$_2$Br, CHFBrCF$_2$Br, and CF$_3$CFBrCF$_2$Br.[22] Based on their data and the fact that the parent anions were not observed even at high pressures, Zook et al. proposed that the vibrationally excited anions formed upon electron attachment could be divided into three categories: (a) those with little internal excitation would preferentially form Br$_2^-$, (b) those with moderate excitation would form Br$^-$ unless excitation was removed by the buffer gas during the lifetime of the nascent anion, and (c) those with high internal energy would have a very short lifetime for decay into Br$^-$.

We measured the ion product branching fractions from 50–400 Pa at room temperature to see if the present systems have a pressure dependence analogous to those found in the experiments of Zook et al.[22] We did not observe a change in the branching fractions in either of the $C_2Cl_2O_2$ and $C_2Br_2O_2$ cases, within our uncertainty of $\pm 5\%$ points. For reasons given earlier, these measurements were made with low initial electron density ($10^9$ cm$^{-3}$).

Electron attachment reactions of both oxalyl halides are

dominated by production of dihalide and halide product anions, even though there are three other exothermic channels. Whether the dihalide ions are formed in a concerted or sequential fashion (within the complex) is an important question. So, too, is the question of how phosgene anion is formed in the oxalyl chloride reaction. Our data do not directly probe reaction intermediates but our kinetic data provide insights into the reaction mechanism(s).

The absence of the parent ion in both reactions indicates that the decomposition to products occurs on a time scale short compared to collisions with helium (<60 ns). This conclusion is reinforced by the lack of pressure dependences in the branching fractions (over our pressure range of 50–400 Pa). In the $C_2Br_2O_2$ case, neither the rate nor the branching fractions change with temperature, even though the $Br^-$ and $Br_2^-$ channels differ in exothermicity by approximately 1 eV. These data suggest that the reaction is proceeding at its maximum rate and that the energy is not randomized before dissociation, i.e., dissociation is prompt.

In the electron attachment reaction of oxalyl chloride, both rate coefficient and branching fractions change with temperature and electron kinetic energy. More specifically, the channel forming phosgene anion is reduced when temperature or electron kinetic energy is increased while the channel forming chloride ion is enhanced. This correlation suggests that the two channels are mechanistically linked. A reasonable hypothesis is that chloride ion is formed first in the reaction mechanism and then reacts with the neutral fragment to form the phosgene anion. As the temperature or electron kinetic energy is increased, the lifetime of complex decreases and limits the efficiency of this second step in the mechanism. As a result, more chloride ion is observed at the expense of phosgene anion. In the oxalyl bromide reaction, more energy is provided by the larger exothermicity of the $Br^-$ channel and no phosgene anion analog is observed. An alternative hypothesis is that phosgene anion is formed first and some (or all) of the chloride ion is formed from subsequent decomposition of this molecular anion (within the complex). As energy of the complex is increased, more chloride ion is formed. The absence of the phosgene anion analogue in the oxalyl bromide reaction, in this view, occurs because so much energy is present in the complex that none of the phosgene anion analogue can survive. Unfortunately, our data cannot distinguish between these two mechanisms.

The fact that the dihalide ion product branching fraction does not decrease with increasing temperature in either reaction suggests that it is not formed from the halide ion, that is, in a stepwise mechanism. The lack of correlation between the temperature dependence of the phosgene anion branching fraction and that of dichloride ion argues against decomposition of the phosgene anion as the source of $Cl_2^-$ as well. It seems reasonable, then, that the dihalide anion in both reactions is formed from a concerted mechanism that is distinct from the mechanism(s) forming the other product ions. One important question remaining is, why is dihalide ion formation so efficient and the dominant product channel in electron attachment to oxalyl chloride? Our computational work described below, taken together with that in the literature, provides a partial answer to this question.
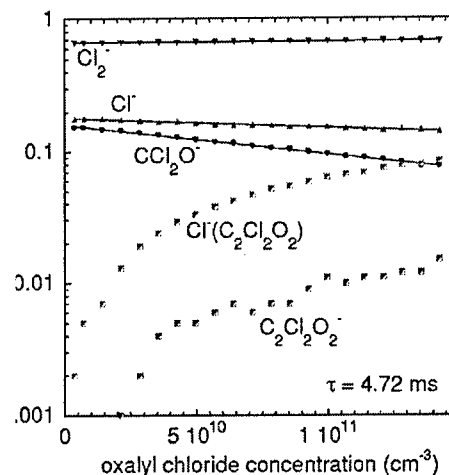


FIG. 3. Secondary ion-molecule reactions following electron attachment, at 300 K, with a reaction time of 4.72 ms. $Cl_2^-$ does not appear to react with $C_2Cl_2O_2$. The $Cl^-$ intensity shows decay at a rate of $3.5 \times 10^{-10}$ cm$^3$ s$^{-1}$, and the $CCl_2O^-$ intensity decays at a rate of $1.1 \times 10^{-9}$ cm$^3$ s$^{-1}$.

The increasing efficiency of the oxalyl chloride reaction with temperature indicates that a barrier to reaction is present in the reaction coordinate. Unfortunately, the source of this apparent "activation energy" cannot be identified because of the similarity of the total and partial rate coefficient temperature dependences (Fig. 2) and the limited precision of these data. Either a barrier to formation of the nascent parent anion $C_2Cl_2O_2^-$ exists or the barriers associated with each product channel combine to give an "average" activation energy of 35 meV. All barriers are relatively small in the present study.

## B. Secondary ion reactions

Secondary ion reactions were observed in the attachment mass spectra, as shown in Fig. 3. Notable is the production of the stable parent anion, $C_2Cl_2O_2^-$. $Cl_2^-$ does not appear to react with $C_2Cl_2O_2$. The $C_2Cl_2O_2^-$ secondary ion is created by charge transfer from phosgene anion, a process that is 0.74 eV exothermic according to G3 calculations discussed below. The $CCl_2O^-$ intensity decays at a rate of 1.1 $\times 10^{-9}$ cm$^3$ s$^{-1}$. It is not energetically possible for $Cl^-$ to charge transfer to $C_2Cl_2O_2$, but $Cl^-$ was seen to form an adduct with $C_2Cl_2O_2$ at a rate of $3.5 \times 10^{-10}$ cm$^3$ s$^{-1}$ in 133 Pa of He gas. Ion intensity balance implies that much of the $Cl^-(C_2Cl_2O_2)$ ion intensity also comes from phosgene anion donation of chloride, a process which is exothermic by 0.23 eV according to the G3 calculations. The structure of the $Cl^-(C_2Cl_2O_2)$ anion is described in the computational section: it consists of a $Cl^-$ anion lying above the average plane of the $C_2Cl_2O_2$ molecule, equidistant (2.550 Å) from the two C atoms, with a bond enthalpy of 1.09 eV.

The major secondary product ion observed in the reaction with oxalyl bromide was the adduct, $Br^-(C_2Br_2O_2)$. Very small signals of parent anion $C_2Br_2O_2^-$ were also detected, indicating that the anion is stable. However, the chemistry that forms this anion could not be determined.

## C. Positive ion reactions

The positive ion chemistry of oxalyl chloride has been studied by Fridgen and Parnis,[24] who noted that $Ar^+$ reacting with oxalyl chloride produces primarily $CClO^+$, a process which was apparent in our positive-ion mass spectra as well. We found that $Ar^+$ reacting with oxalyl bromide produced 70% $CBrO^+$ and 30% $Br_2^+$.

## IV. COMPUTATIONAL METHOD AND RESULTS

Calculations were performed in this work using the GAUSSIAN 03W set of programs.[25] Calculations of EAs and bond strengths for $C_2Cl_2O_2$ and fragments and secondary ions were carried out using the G3 compound method, primarily in order to obtain electron attachment reaction enthalpies.[10] The G3 method has been shown accurate *on average* to 91 meV for ionization potentials and electron affinities of non-hydrogen-containing molecules.[10] The G3 method in the GAUSSIAN 03W program set is only implemented for atoms through Ar, so we applied the somewhat less accurate G2 method to the bromine-containing compounds.[11] Of course, any nonrelativistic method will suffer at the bromine row of the periodic table. We applied the G2 method to the chlorine compounds as well, for comparison. Results of the calculations are given in Table III. "G3" calculations for neutral $C_2Cl_2O_2$ have already been reported by Chien *et al.*,[7] but new values are given here (in Table III) because Chien *et al.*[7] deviated from the formal G3 prescription[10] by using higher-level zero-point corrections [from MP2(full)/6-31G(*d*) calculations instead of Hartree-Fock (HF)/6-31G(*d*)]. Since we applied the G3 method to anions and fragment neutrals to determine EAs, bond enthalpies, and reaction enthalpies, it was important to consistently hold to the G3 formulation.[10]

The structure of the neutral $C_2Cl_2O_2$ molecule has been thoroughly covered by Chien *et al.*[7] and Kim *et al.*,[8] who found that the *trans* structure was the lowest energy conformer, and that the *cis* structure was simply a transition state on a very flat surface. In the present work, geometry optimization using second-order Møller-Plesset perturbation theory (MP2) with the 6-31G(*d*) basis set on all electrons yielded the *trans* structure as the lowest energy conformer, in agreement with Chien *et al.*[7] and Kim *et al.*[8] The *cis* structure was found to be 98 meV higher in energy than the *trans* one, and was seen to be a transition state with a negative force constant for torsional motion about the C–C bond. (Kim *et al.* obtained 97 meV from a much more thorough study.[8])

The $C_2Cl_2O_2^-$ anion was found to be similar in appearance to the neutral, but the C–C bond is shorter (1.432 versus 1.547 Å), the C–Cl bond is longer (1.865 versus 1.744 Å), and the C=O bond is relatively unchanged (1.224 versus 1.202 Å). Interestingly, though the *cis*-$C_2Cl_2O_2^-$ anion lies higher in energy than the *trans*-$C_2Cl_2O_2^-$ anion (by 131 meV), as is the case for the neutral molecule, it has all positive force constants in the anion. The *cis* anion is *not* a transition state. While we do not have calculations of the complete torsional potential energy surface as was provided for the neutral molecule by Kim *et al.*,[8] the similarity of anion and neutral structures, torsional frequencies, and *trans*-

TABLE III. Results of Møller-Plesset and density functional calculations for neutral and anionic $C_2Cl_2O_2$ and the phosgene fragment $CCl_2O$ and bromine analog $CBr_2O$. Total energies, enthalpies, and zero-point energy (ZPE) are in hartrees. Other species studied in this work are listed in supplementary material obtained through EPAPS.

| System | G3[a] | G2[b] |
|---|---|---|
| *trans*-$C_2Cl_2O_2(C_{2h}, {}^1A_g)$ | | |
| ZPE | 0.019 93 | 0.019 93 |
| Total energy (0 K) | −1146.646 63 | −1145.837 94 |
| Enthalpy (298 K) | −1146.639 76 | −1145.831 08 |
| EA (eV) | 1.91 | 1.82 |
| *trans*-$C_2Cl_2O_2^-(C_{2h}, {}^2A_u)$ | | |
| ZPE | 0.017 08 | 0.017 08 |
| Total energy (0 K) | −1146.717 00 | −1145.904 66 |
| Enthalpy (298 K) | −1146.709 01 | −1145.896 72 |
| *cis*-$C_2Cl_2O_2(C_{2v}, {}^1A_1)$ | | |
| ZPE | 0.019 78[c] | 0.019 78[c] |
| Total energy (0 K) | −1146.643 03 | −1145.834 22 |
| Enthalpy (298 K) | −1146.637 04 | −1145.828 23 |
| *cis*-$C_2Cl_2O_2^-(C_{2v}, {}^2B_1)$ | | |
| ZPE | 0.017 57 | 0.017 57 |
| Total energy (0 K) | −1146.712 15 | −1145.899 71 |
| Enthalpy (298 K) | −1146.705 07 | −1145.892 63 |
| *trans*-$C_2Br_2O_2(C_{2h}, {}^1A_g)$ | | |
| ZPE | ⋯ | 0.018 66 |
| Total energy (0 K) | ⋯ | −5371.505 59 |
| Enthalpy (298 K) | ⋯ | −5371.498 26 |
| EA (eV) | ⋯ | 2.00 |
| *trans*-$C_2Br_2O_2^-(C_{2h}, {}^2A_u)$ | | |
| ZPE | ⋯ | 0.016 71 |
| Total energy (0 K) | ⋯ | −5371.578 96 |
| Enthalpy (298 K) | ⋯ | −5371.571 37 |
| *gauche*-$C_2Br_2O_2(C_2, {}^1A)$ | | |
| ZPE | ⋯ | 0.018 49 |
| Total energy (0 K) | ⋯ | −5371.505 18 |
| Enthalpy (298 K) | ⋯ | −5371.497 73 |
| *cis*-$C_2Br_2O_2(C_{2v}, {}^1A_1)$ | | |
| ZPE | ⋯ | 0.018 48[c] |
| Total energy (0 K) | ⋯ | −5371.500 73 |
| Enthalpy (298 K) | ⋯ | −5371.494 27 |
| *cis*-$C_2Br_2O_2^-(C_{2v}, {}^2B_1)$ | | |
| ZPE | ⋯ | 0.016 434 |
| Total energy (0 K) | ⋯ | −5371.572 398 |
| enthalpy (298 K) | ⋯ | −5371.564 780 |
| $CCl_2O(C_{2v}, {}^1A_1)$ | | |
| ZPE | 0.010 52 | 0.010 52 |
| Total energy (0 K) | −1033.380 93 | −1032.663 10 |
| Enthalpy (298 K) | −1033.376 05 | −1032.658 22 |
| EA (eV) | 1.17 | 1.06 |
| $CCl_2O^-(C_{2v}, {}^2A_1)$ | | |
| ZPE | 0.006 79 | 0.006 79 |
| Total energy (0 K) | −1033.424 05 | −1032.702 19 |
| Enthalpy (298 K) | −1033.417 37 | −1032.695 51 |
| $CBr_2O(C_{2v}, {}^1A_1)$ | | |
| ZPE | ⋯ | 0.009 25 |
| Total energy (0 K) | ⋯ | −5258.331 60 |

TABLE III.  (*Continued.*)

| System | G3[a] | G2[b] |
|---|---|---|
| Enthalpy (298 K) | ⋯ | −5258.326 25 |
| EA (eV) | ⋯ | 1.76 |
| $CBr_2O^-(C_{2v}, {}^2A_1)$ | | |
| ZPE | ⋯ | 0.006 38 |
| Total energy (0 K) | ⋯ | −5258.396 18 |
| Enthalpy (298 K) | ⋯ | −5258.389 21 |

[a]G3 compound method detailed in Ref. 10 for main-group atoms up through Ar. ZPE determined using the Hartree-Fock method [with the 6-31G(*d*) basis set], with frequencies scaled by 0.8929.
[b]G2 compound method detailed in Ref. 11, applicable for atoms through Kr. ZPE as in footnote a.
[c]Transition state; this ZPE does not include one imaginary frequency for torsional motion about the C–C axis.



FIG. 4. The *gauche* structure of $C_2Br_2O_2$ (top), and the secondary anion $Cl^-(C_2Cl_2O_2)$ (bottom), from MP2(full)/6-31G(*d*) optimization. Bond lengths are in Å. For *gauche*-$C_2Br_2O_2$, the Br–Br dihedral angle viewed along the C–C backbone is 69.5°, but increases to 89.4° if a large basis set [6-311+G(3*df*)] is used.

*cis* isomerization energies suggest that the anion torsional potential energy surface will also be relatively flat. EA($C_2Cl_2O_2$) was found to be 1.91 eV from G3 theory, which includes zero-point energies. Interestingly, it is close to thermoneutral for $C_2Cl_2O_2$ to fall apart into phosgene and CO, based on the G3 results. Heats of formation from the NIST WebBook[26] yield a similar result, but the uncertainties in either of these approaches are such that the dissociation could be either slightly endothermic or exothermic.

Geometry optimization for $C_2Br_2O_2$ points to either the *trans* or *gauche* conformer as the lowest energy state. Strict G2 yielded *trans*, indicating that the nonplanar *gauche* structure lies 11 meV above the *trans* structure but is also a true minimum. Applying the G2 prescription to the $C_2Br_2O_2$ geometry optimized using a larger basis set [MP2(full)/6-311 +G(3*df*)] resulted in the opposite conclusion: the *gauche* conformer lying 10 meV below that of the *trans* conformer. Both methods indicate that the *cis* conformer is a transition state lying about 135 meV above the *trans* conformer (139 meV for strict G2 and 132 meV for modified G2). Application of density functional theory (DFT), using the B3LYP functional[27,28] and 6-311+G(3*df*) basis set, gave a different result that only the *gauche* structure is a true minimum, lying 21 meV below a *trans* transition state and 157 meV below a *cis* transition state. Van Mourik *et al.* examined DFT vs MP2 geometries in a recent article, concluding that DFT is poor at handling intramolecular dispersion forces, and that the MP2 structure is correct (despite basis set superposition errors), especially if a large basis set is utilized.[29] Neither G2 theory nor density functional theory is accurate enough to make a definite statement about *trans* versus *gauche* for the lowest energy conformer of $C_2Br_2O_2$. We can conclude, however, that the potential energy surface for rotation about the C–C bond (torsion) in oxalyl bromide is relatively flat, requiring relatively little energy to rotate between conformers.

Geometry optimization of oxalyl bromide anion yielded results similar to those found for oxalyl chloride anion. In particular, the *trans* conformer is the lowest energy but the *cis* conformer lies 178 meV above this state and is stable (not a transition state). Again, these data suggest that potential energy surface for rotation about the C–C bond in oxalyl
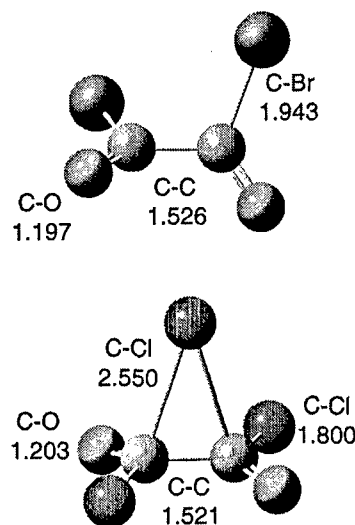
bromide anion is also relatively flat. Bond length changes were analogous to the $C_2Cl_2O_2$ case: the C–C bond is shorter in the anion (1.428 versus 1.551 Å), the C–Br bond is longer (2.081 versus 1.930 Å), and the C=O bond is relatively unchanged (1.198 versus 1.215 Å). EA($C_2Br_2O_2$) was found to be 2.00 eV from G2 theory.

The various structures and energies, including fragment and secondary species related to the present work, such as $C_2XO_2$ and $CXO$ neutrals and anions ($X$=Cl and Br), were deposited as supplementary material with the journal's Electronic Physics Auxilliary Publication Service (EPAPS).[30] EAs are included in Table III; it is interesting that EA($C_2Cl_2O_2$) and EA($C_2Br_2O_2$) are so similar. Among species required for the energetics calculations, the most interesting structures were found for the *gauche*-$C_2Br_2O_2$ conformer and the $Cl^-(C_2Cl_2O_2)$ adduct anion (with a similar structure for the bromine case), as shown in Fig. 4. The extra Cl atom in the adduct occupies a bridging position above the average plane of the $C_2Cl_2O_2$ substrate. The bond dissociation enthalpy $D^0_{298}(C_2Cl_2O_2-Cl^-)$ was calculated to be 1.09 eV at 298 K.

If the attachment reaction channel forming the dihalide anion [Eqs. (2) and (7)] is both concerted and prompt, as suggested by our kinetic data, then orbital overlap between the dissociating halide atoms is critical. Our computational results, taken together with those of Chien *et al.*[7] and Kim *et al.*,[8] demonstrate that rotation about the C–C bond, needed to change the ground state to the higher energy *cis* conformer, requires relatively little energy for neutral and anion species, when considering the nearly 2 eV of energy gained upon electron attachment. Even before attachment has taken place, both *trans* and *gauche* conformers are present in the room temperature gaseous sample.[1,2] Therefore, it is not surprising that a significant amount of dihalide anion is formed in these reactions. The extremely large percentage of dihalide product observed in these reactions, however, is surprising, espe-

cially in the oxalyl chloride reaction where the $Cl_2^-$ product channel is more abundant that the sum of the $Cl^-$ and $CCl_2O^-$ product channels, even though the *trans* conformer is more stable than the *gauche* and *cis*. We must conclude that dihalide anion elimination occurs on a short time scale that does not allow full energy randomization and that the initial state formed upon electron attachment has sufficient halogen orbital overlap to allow the elimination to occur.

## V. CONCLUSIONS

Thermal electron attachment rate coefficients and product branching fractions have been measured for oxalyl chloride and oxalyl bromide from 300 to 550 K, in a He buffer gas at 133 Pa. The major ion product of attachment to $C_2Cl_2O_2$ is $Cl_2^-$, despite the fact that neutral and anion ground state structures have a *trans* conformation. Branching fractions for the three product ions $Cl_2^-$, $Cl^-$, and $CCl_2O^-$ (the phosgene anion) were measured over the same temperature range, and over the He pressure range of 50–400 Pa at 300 K. No pressure dependence was observed but the temperature dependence of $Cl^-$ and $CCl_2O^-$ product channels indicates that these products are formed from a common mechanism. The temperature dependence of the $Cl_2^-$ branching fraction suggests that this anion is formed in a concerted, rather than stepwise, mechanism. The parent ion $C_2Cl_2O_2^-$ was seen to exist but is not a primary product of attachment; it is formed from secondary ion-molecule chemistry.

Electrons attached to $C_2Br_2O_2$ with an approximately collisional rate coefficient that is seven times greater than that for reaction of $C_2Cl_2O_2$ at 300 K. Rate coefficient and product branching fractions were temperature independent. Attachment yielded only $Br^-$ and $Br_2^-$ ion products, with the $Br^-$ slightly favored over $Br_2^-$. The phosgene anion analog was not observed in this reaction. The parent ion $C_2Br_2O_2^-$ was also observed but is not a primary product.

Electronic structure calculations were carried out using G2 and G3 theories. The geometry for $C_2Cl_2O_2$ agrees with the work of Chien *et al.*[7] and Kim *et al.*[8] The lowest energy conformer for $C_2Cl_2O_2$ and $C_2Cl_2O_2^-$ (using G3), and for $C_2Br_2O_2^-$ (using G2) is *trans*. The $C_2Br_2O_2$ ground state structure is either *trans* or *gauche*, still unresolved because of the small energy difference between the two conformers: density functional theory indicates that only the nonplanar *gauche* structure of $C_2Br_2O_2$ is a true minimum, and a G2-like prescription for a geometry obtained with a large basis set also gave the *gauche* structure as the lowest energy one. The potential energy surface for the anions were not studied in Refs. 7 and 8; we find that *cis*-$C_2Cl_2O_2^-$ and *cis*-$C_2Br_2O_2^-$ are *not* transition states, but are minima lying 132 and 178 meV higher in energy than the *trans* anions, respectively. The calculations yield $EA(C_2Cl_2O_2)=1.91$ eV, $EA(C_2Br_2O_2)=2.00$ eV, and $EA(\text{phosgene})=1.17$ eV. Geometries and other information not contained in Table III have been deposited with EPAPS for retrieval at no cost.[30]

Electronic structure calculations indicate that the torsional potential energy surface for rotation about the C–C bond in both neutral and anionic oxalyl halide molecules is

relatively flat. Kim *et al.* mapped out this surface for neutral oxalyl chloride in great detail; our results (using G2 and G3) extend theirs by determining *trans* and *cis* conformations for the oxalyl chloride anion and oxalyl bromide neutral and anion. The small energy required to align halogen atoms in these molecules may facilitate efficient formation of the dihalide ion product.

Finally, $C_2Cl_2O_2$ and $C_2Br_2O_2$ should prove to be good sources of $Cl_2^-$, $CCl_2O^-$, and $Br_2^-$, in flow tube and ion beam experiments, if these source gases are used at low fractional pressure. These ions are not easily formed by other means. There are few reported ion-molecule reactions studied with $Cl_2^-$, and to the best of our knowledge, none with $CCl_2O^-$ or $Br_2^-$.[31]

## ACKNOWLEDGMENTS

[1] K. Hagen and K. Hedberg, J. Am. Chem. Soc. **95**, 1003 (1973).

[2] J. R. Durig, J. F. Davis, and A. Wang, J. Mol. Struct.: THEOCHEM **375**, 67 (1996).

[3] J. Pola, Collect. Czech. Chem. Commun. **47**, 3258 (1982).

[4] W. Schroeder, M. Monnier, G. Davidovics, A. Allouche, P. Verlaque, J. Pourcin, and H. Bodot, J. Mol. Struct. **197**, 227 (1989).

[5] M. Ahmed, D. Blunt, D. Shen, and A. G. Suits, J. Chem. Phys. **106**, 7617 (1997).

[6] C.-Y. Wu, Y.-P. Lee, and N. S. Wang, J. Chem. Phys. **120**, 6957 (2004).

[7] S.-H. Chien, K.-C. Lau, W.-K. Li, and C. Y. Ng, J. Phys. Chem. A **103**, 7918 (1999).

[8] S. Kim, S. E. Wheeler, N. J. DeYonker, and H. F. Schaefer III, J. Chem. Phys. **122**, 234313 (2005).

[9] A sixth (and unlikely) channel deserves mention, yielding $CCl_2^-+CO_2$ from attachment to $C_2Cl_2O_2$, and $CBr_2^-+CO_2$ from $C_2Br_2O_2$. This channel is endothermic by 67 meV for $C_2Cl_2O_2$ and exothermic by 157 meV for $C_2Br_2O_2$, at 298 K. In both cases, the calculated enthalpies are not accurate enough to say more than "nearly thermoneutral."

[10] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, J. Chem. Phys. **109**, 7754 (1998); the G3 method has been extended for main-group atoms through Kr by L. A. Curtiss, P. C. Redfern, V. Rassolov, G. Kedziora, and J. A. Pople, *ibid.* **114**, 9287 (2001); see also L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *ibid.* **123**, 124107 (2005).

[11] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991); L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, and R. Binning, *ibid.* **103**, 6104 (1995); J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, and L. Random, *ibid.* **107**, 5016 (1995).

[12] D. Smith and P. Španěl, Adv. At., Mol., Opt. Phys. **32**, 307 (1994).

[13] T. M. Miller, A. E. S. Miller, J. F. Paulson, and X. Liu, J. Chem. Phys. **100**, 8841 (1994).

[14] Two samples of $C_2Cl_2O_2$ were used, one from Sigma-Aldrich and the other from Fluka, both stated to be ≥99% pure. We measured a vapor pressure of 21 kPa at 300 K. The $C_2Br_2O_2$ was obtained from Sigma-Aldrich and stated to be 97% pure. We measured a vapor pressure of 3.5 kPa at 297 K. Neither compound presented any handling problems aside from requiring a glove box during transfers to prevent exposure to water vapor.

[15] D. Smith and N. G. Adams, in *Physics of Ion-Ion and Electron-Ion Col-*

*lisions*, edited by F. Brouillard and J. W. McGowan (Plenum, New York, 1983).

[16] C. E. Klots, Chem. Phys. Lett. **38**, 61 (1976).

[17] P. Španěl, Int. J. Mass Spectrom. Ion Process. **149/150**, 299 (1995).

[18] J. M. Van Doren, J. F. Friedman, T. M. Miller, A. A. Viggiano, S. Denifl, P. Scheier, T. D. Märk, and J. Troe, J. Chem. Phys. **124**, 124322 (2006).

[19] S. H. Alajajian, M. T. Bernius, and A. Chutjian, J. Phys. B **21**, 4021 (1988).

[20] D. Smith, C. R. Herd, N. G. Adams, and J. F. Paulson, Int. J. Mass Spectrom. Ion Process. **96**, 341 (1990).

[21] D. Smith and P. Španěl, Int. J. Mass. Spectrom. **205**, 243 (2001).

[22] D. R. Zook, W. B. Knighton, and E. P. Grimsrud, Int. J. Mass Spectrom. Ion Process. **104**, 63 (1991); these authors note an early report of dihalide ion product in an electron beam experiment with $CBr_4$ and $CHI_3$ by J. J. DeCorpo and J. L. Franklin, J. Chem. Phys. **54**, 1885 (1971).

[23] I. Ipolyi, S. Matejčik, and E. Illenberger, Eur. Phys. J. D **35**, 257 (2005).

[24] T. D. Fridgen and J. M. Parnis, J. Phys. Chem. A **101**, 5117 (1997).

[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN-03W, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

[26] P. J. Linstrom and W. G. Mallard, *NIST Chemistry WebBook, NIST Standard Reference Database No. 69* (National Institutes of Standards and Technology, Gaithersburg, MD, 2003).

[27] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[28] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1993); K. Burke, J. P. Perdew, and Y. Wang, in *Electron Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998).

[29] T. van Mourik, P. G. Karamertzanis, and S. L. Price, J. Phys. Chem. A **110**, 8 (2006).

[30] See EPAPS Document No. E-JCPSA6-124-010617 for MP2(full)/ 6-31G(*d*) geometries for the molecules listed in Table III and for geometries and energies of other molecules related to the present work $[X^-(C_2X_2O_2), C_2XO_2, CXO, \text{ and } CXO^-, \text{ with } X=Cl \text{ and } Br]$. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

[31] Y. Ikezoe, S. Matsuoka, M. Takebe, and A. A. Viggiano, *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986* (Maruzen, Tokyo, 1987).