

Gasphase reactions of oxide and superoxide anions with CF4, CF3CI, CF3Br, CF3I, and C2F4 at 298 and 500 K

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Citation: The Journal of Chemical Physics **97**, 2372 (1992); doi: 10.1063/1.463941 View online: http://dx.doi.org/10.1063/1.463941 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/97/4?ver=pdfcov Published by the AIP Publishing

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Gas-phase reactions of oxide and superoxide anions with CF₄, CF₃Cl, CF₃Br, CF₃I, and C₂F₄ at 298 and 500 K

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(Received 6 April 1992; accepted 1 May 1992)

Rate constants and product branching fractions have been measured for the gas-phase reactions of oxide (O^-) and superoxide (O_2^-) anions with the halocarbons CF₄, CF₃Cl, CF_3Br , CF_3I , and C_2F_4 using a variable temperature-selected ion flow tube (VT-SIFT) instrument operated at 298 and 500 K. The reactions of O⁻ with CF_3X (X=Cl, Br, I) are fast and produce F^- , XF^- , and XO^- for all X. For CF_3Cl and CF_3Br , X^- is also formed. For CF₃I, CF₃ and IOF⁻ are minor products. O⁻ reacts rapidly with C_2F_4 producing F⁻ as the major ionic product, along with contributions from reactive detachment and minor formation of FCO⁻, CF₃⁻, and C₂F₃O⁻. The reaction of O₂⁻ with CF₃Cl is slow, and both clustering and X⁻ formation were observed. For CF₃Br and CF₃I, the reactions with O_2^- are fast, and nondissociative charge transfer was observed in addition to X^- formation. O_2^- reacts rapidly with C_2F_4 by reactive detachment, in addition to producing F^- as the major ionic product with smaller amounts of F_2^- , FCO⁻, FCO⁻, CF₃O⁻, and C₂F₄O⁻. O⁻ and O_2^- were both found to be unreactive with CF₄ at 298 and 500 K. The efficiencies of the reactions of both O^- and O_2^- with CF_3X are greater for the heavier halides at both 298 and 500 K. The rate constants for the reactions of O_2^- with CF₃X appear to correlate both with the rates of thermal electron attachment to CF_3X and with the electron affinities of CF_3X , indicating that the $O_2^- + CF_3X$ reaction mechanism may involve initial electron transfer followed by dissociation. Thus the negative electron affinity of CF₃Cl may explain the very slow rate for reaction with O_2^- despite the available exothermic pathways.

I. INTRODUCTION

Gas-phase reactions of negative ions with halocarbons are of basic interest for several reasons. They can be important in determinations of gas-phase acidities, electron affinities, and general thermochemistry. Gas-phase studies of reactions known to be important in solution provide insight into solvation effects and intrinsic reactivity. The effects of entering group and leaving group in displacement reactions are known to be important both in solution and in the gas phase. Halocarbons often exhibit chemistry which is very different from that of the corresponding hydrocarbons. It is also of interest to examine the extent to which the halocarbon negative-ion chemistry resembles other processes in halocarbons such as electron attachment, electron transfer from Rydberg atoms, and collisional ionization reactions.

Reactions of the oxide (O_-^-) and superoxide (O_2^-) anions have received attention because of their importance in fields such as ionospheric and stratospheric ion chemistry, chemical ionization mass spectrometry, microcircuit fabrication, and the chemistry of plasmas generated during hypersonic flight. Reactions of O_2^- with halocarbons are of interest with regard to detection sensitivity in atmospheric pressure ionization mass spectrometry¹ and in electron capture (EC) detectors for gas chromatographs.^{2,3} Fehsenfeld *et al.*⁴ studied the reactions of O_2^- with CF₂Cl₂ and

CFCl₃ as possible atmospheric removal processes for these halocarbons.

By studying the reactivity of O_2^- toward several halocarbons, McDonald and Chowdhury⁵ found that O_2^- is an excellent intrinsic gas-phase nucleophile. Tanaka *et al.*⁶ investigated reactions of a variety of negative ions, including O^- and F^- , with halomethanes as a means of determining the intrinsic nucleophilic reactivity of the anions. Streit⁷ used a flowing afterglow apparatus to study the reactions of O^- and O_2^- with a number of halogenated compounds, but the technique did not allow the ionic products to be assigned to a particular reactant ion, i.e., O^- or O_2^- .

In the present work, a variable temperature-selected ion flow tube instrument has been used to determine the rate constants and product branching fractions of the individual reactions of O^- and O_2^- with the halocarbons CF₄, CF₃Cl, CF₃Br, CF₃I, and C₂F₄ at two temperatures, 298 and 500 K. These are the first measurements of the branching fractions and temperature dependences of these reactions. The rate constants for the reactions with CF₃Cl and C_2F_4 have not been reported previously. The temperature-dependent measurements are applicable to the EC detector doping technique^{2,3} since EC detectors operate at temperatures from 473 to 673 K. Many of the secondary reactions occurring between the ionic products and the $CF_{3}X$ (X=Cl, Br, I) reactant neutrals were investigated separately at 298 K. The rate constants for these secondary reactions also have not been published previously.

The homologous series of CF_3X (X=F, Cl, Br, I) compounds in this study provides an opportunity for ex-

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amining periodic trends in reactivity. Comparisons with electron attachment, Rydberg atom electron transfer, and collisional ionization reactions provide additional information to aid in understanding the ion-molecule chemistry. Comparisons with the analogous reactions of the hydrocarbons CH_3X and C_2H_4 give an indication of the differences in the chemistry of hydrocarbons vs halocarbons.

II. EXPERIMENT

The measurements were made by using a variable temperature-selected ion flow tube apparatus⁸ operated at 298 and 500 K. Instruments of this type have been the subject of review,⁹ and only those aspects peculiar to the present study will be discussed in detail. O⁻ ions were produced by dissociative electron attachment to N₂O in a moderate pressure (~ 0.1 torr) electron-impact ion source. O_2^- was produced from a mixture of N_2O and O_2 in the source. The O⁻ produced from electron attachment to N₂O reacts with N₂O, forming NO⁻ which transfers its electron to O2. The ions were then mass selected in a quadrupole mass spectrometer and injected into the flow tube through a Venturi inlet. The reactant neutral was introduced downstream through one of two ring inlets and allowed to react with the ions for a known reaction time in a fast flow ($\sim 10^4$ cm s⁻¹) of He buffer gas maintained at \sim 0.4 Torr. The reactant and product ions were mass analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier. Rate constants were extracted from least-squares fits of the logarithm of the reactant ion signal plotted vs the concentration of added reactant neutral. The reaction time was determined from ion time-of-flight measurements. For the experiments conducted at 500 K, the temperature of the flow tube was raised using electrical resistance heaters. As an experimental check for a reaction product observed at 500 K but not at 298 K (ClO⁻ from the reaction of O⁻ with CF₃Cl), the kinetic energy of the O⁻ ions was increased at 298 K by applying a voltage to the rings of a drift tube located inside the flow tube. The drift tube has been described in detail previously.8

The buffer and reactant gases were obtained commercially and used without further purification. The purities were as follows: He buffer (99.997%), CF₄ (99.99%), CF₃Cl (99.85%), CF₃Br (99.7%), CF₃I (>99%), C₂F₄ (>99.5%). The C₂F₄ contained approximately 0.01% limonene as a polymerization inhibitor; no ions attributable to this compound were observed in the product spectra. The accuracy of the measured overall rate constants is $\pm 25\%$ and the relative accuracy is $\pm 15\%$.⁸

To account for the effects of secondary reactions, the product branching fractions were plotted vs reactant neutral flow rate. These plots were then extrapolated to zero reactant flow rate to arrive at the branching fractions in the absence of secondary reactions. The reported branching data are the extrapolated values. In the determinations of product branching fractions, mass discrimination was minimized by operating the mass spectrometer at very low resolution. For several reactions, certain product masses were sufficiently similar that higher resolution was required to separate the peaks. In these cases, branching measurements were made under both low- and highresolution settings. The high-resolution data were used to determine the branching ratio between the species of similar mass, and this ratio was then applied to the lowresolution data wherein the species of similar mass appeared as a single broad peak. This method was needed for the reactions of O^- with CF_3X (X=Cl, Br, I) because of the mass resolution necessary for resolving XF⁻ vs XO⁻. For X=Cl, this was only necessary at 500 K because no ClO⁻ was formed at 298 K. This method was also used for the reaction of O_2^- with CF₃Cl at 298 K in order to resolve O_2^- vs Cl⁻. Using this method adds some uncertainty to the branching determinations for the applicable reactions. The maximum absolute uncertainty in the branching data is 50% for the above reactions and 40% for the other systems studied. In all cases, the sum of the product ion signals balanced the attenuation of the reactant ion signal to within 40%. Since much of the uncertainty is the result of residual mass discrimination, the uncertainty in the branching fraction depends upon the masses being compared. For similar masses, the uncertainty is much less than that quoted above but is difficult to estimate. The branching fractions are reported to be precise to within 5 percentage points. In many cases the precision is much better than this.

For the reactions of O^- and O_2^- with C_2F_4 , electron detachment (associative or reactive) was observed in addition to the formation of ionic reaction products. The branching fraction into the detachment channel was determined for these reactions by the standard technique¹⁰ of recording the ion current collected at the sampling nose cone as a function of C_2F_4 reactant neutral flow rate. The electrons formed in the reaction of interest diffuse rapidly to the flow-tube wall and are lost before reaching the nose cone. Thus the current at the nose cone decreases with increasing extent of reaction until leveling off at the point of complete reaction. The fraction of the reaction that proceeds by electron detachment is given by $(I_0 - I_c)/I_0$ where I_0 is the initial nose-cone current with no C_2F_4 added and I_c is the current when the reaction has gone to completion. The detachment fraction so derived is combined with the branching fractions of the ionic products to yield the reported branching fractions into all reaction channels. Electron detachment was confirmed for the O⁻ $+C_2F_4$ reaction by adding SF₆ upstream of the reaction region.¹¹ The anion SF_6^- was detected and is the result of attachment of the free electrons to SF₆.^{12,13} Charge transfer from O⁻ to SF_6 would be endothermic by ~0.4 eV. This test could not be performed for the O_2^- reaction because O_2^- reacts with SF₆ by charge transfer.¹⁴ However, the decrease of nose-cone current with added C_2F_4 was more pronounced for O_2^- than for O^- , supporting the conclusion that electron detachment occurs for O_2^- .

Many of the secondary reactions occurring in these systems were studied directly in separate experiments. The reactions of F^- with CF_3Br and CF_3I each formed two ionic products, and less-accurate branching measurements were made compared with those for the primary reactions.

TABLE I. Branching percentages, total rate constants, and efficiencies for reactions of O^- with selected halocarbons measured at 298 and 500 K. The detected ionic products and the assumed neutral products are also listed.

		Branching percentage		Total rate constant $(10^{-9} \text{ cm}^3 \text{ s}^{-1})$		Total efficiency (%)	
Reaction		298 K	500 K.	298 K	500 K	298 K	500 K.
0 ⁻ +CF ₄	→no reaction	•••		< 0.002	< 0.002	< 0.2	< 0.2
(1) $O^- + CF_3Cl$	\rightarrow F ⁻ +CF ₂ O+Cl	64	54	0.86	0.64	51	40
•	$\rightarrow Cl^- + CF_2O + F$	19	21				
	$\rightarrow ClO^- + CF_3$	0	2				
	$\rightarrow ClF^- + CF_2O$	17	23				
(2) $O^- + CF_3Br$	$\rightarrow F^- + CF_2O + Br$	45	34	1.4	1.3	75	71
	$\rightarrow Br^- + CF_2O + F$	8	11				
	\rightarrow BrO ⁻ + CF ₃	34 -	48			-	
	\rightarrow BrF ⁻ +CF ₂ O	13	8				
(3) O ⁻ +CF ₃ I	$\rightarrow F^- + CF_2O + I$	25	16	1.9	2.0	89	99
	$\rightarrow CF_3^- + IO$	3	5				
	$\rightarrow 10^{-} + CF_3$	62	68				
	\rightarrow IF ⁻ +CF ₂ O	6					
	$\rightarrow IOF^{-} + CF_{2}$	4	7		÷	- · · · ·	
$(7) O^- + C_2 F_4$	$\rightarrow F^- + C_2 F_3 O$	77	67	1.3	1.2	100	92
	\rightarrow FCO ⁻ + CF ₃	1	o				
	$\rightarrow CF_{1} + FCO$	2	4				
	$\rightarrow C_2 F_3 O^- + F$	2	3				
	$\rightarrow e^{-} + C_2 F_4 O$	17	26		_		

Approximate branching fractions for these two reactions are reported in Table III. Some mass discrimination may have occurred in these measurements, and no corrections for mass discrimination have been applied.

III. RESULTS AND DISCUSSION

Product branching fractions, rate constants, and reaction efficiencies measured at 298 and 500 K for the studied reactions of O⁻ and O₂⁻ are presented in Tables I and II, respectively. The collisional rate constants used in determining the efficiencies were calculated from the parametrized trajectory theory method^{15,16} employing the following values for molecular polarizabilities (Å³): CF₄, 3.838; CF₃Cl, 5.72; CF₃Br, 6.78; CF₃I, 8.32; C₂F₄, 4.22. Some of the ionic products subsequently reacted with the reactant neutral present in the flow tube. Selected secondary reactions were investigated at 298 K in separate experiments, and the results of these measurements are given in Table III.

A. O^-+CF_3X

The reactions of O⁻ with CF₃X (X=Cl, Br, I) are fast, and include production of F⁻, XO⁻, and XF⁻ for all X (ClO⁻ from CF₃Cl was observed only at 500 K):

TABLE II. Branching percentages, total rate constants, and efficiencies for reactions of O_2^- with selected halocarbons measured at 298 and 500 K. The detected ionic products and the assumed neutral products are also listed.

		Branching percentage		Total rate constant $(10^{-9} \text{ cm}^3 \text{ s}^{-1})$		Efficiency (%)	
Reaction		298 K	500 K	298 K	500 K.	298 K	500 K
$O_2^-+CF_4$	→no reaction			< 0.002	< 0.002	< 0.2	< 0.2
(4) $O_2^2 + CF_3Cl$	\rightarrow Cl ⁻ + CF ₃ O ₂	66	100	< 0.004	<0.002	< 0.3	< 0.2
	$\rightarrow O_2^- \cdot CF_3Cl$	34	0				
(5) $O_2^- + CF_3Br$	$\rightarrow Br^- + CF_3O_2$	45	97	1.0	0,70	77	56
	\rightarrow CF ₃ Br ⁻ +O ₂	55	. 3				
(6) $O_2^- + CF_3I$	$\rightarrow I^- + CF_3O_2$	88	100	1.5	1.4	97	97
	$\rightarrow CF_3I^- + O_2$	12	0				
(8) $O_2^- + C_2 F_4$	\rightarrow F ⁻ +FCO+CF ₂ O	48	38	0.83	0.54	85	55
	\rightarrow F ₂ ⁻ +F ₂ C ₂ O ₂	10	8				
	\rightarrow FCO ⁻ + CF ₂ O + F	4	0				
	$\rightarrow FCO_2^- + CF_3$	1	2				
	$\rightarrow CF_3O^- + FCO$. 1	3				
	$\rightarrow C_2F_4O^-+O$	7	-0				
	$\rightarrow e^- + C_2 F_4 O_2$	29	50			-	

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TABLE III. Total rate constants and efficiencies for reactions of selected halocarbons measured at 298 K.

Reaction		Total rate constant $(10^{-10} \text{ cm}^3 \text{ s}^{-1})$	Efficiency (%)
F ⁻ +CF ₃ Cl	→F ⁻ ·CF ₃ Cl	< 0.03	< 0.2
F^-+CF_3Br	$\rightarrow Br^{-} + CF_4 (\sim 25\%)$	0.84	5.0
F ⁻ +CF ₃ I	$\rightarrow I^{-} + CF_{4} (\sim 10\%)$ $\rightarrow I^{-} + CF_{4} (\sim 10\%)$ $\rightarrow F^{-} \cdot CF_{3}I (\sim 90\%)$	7.2	36
Cl ⁻ +CF ₃ Cl	→Cl ⁻ ·CF ₃ Cl	< 0.03	< 0.3
$Br^- + CF_3Br$	\rightarrow Br ⁻ ·CF ₃ Br	< 0.03	< 0.4
I ⁻⁺ CF ₃ I	→I ⁻ ·CF ₃ I	< 0.05	< 0.6
$ClO^- + CF_3Cl$	→no reaction	< 0.05	< 0.5
BrO^-+CF_3Br	→BrO ⁻ ·CF ₃ Br	0.099	1
IO^-+CF_3I	→products	1.3	15
ClF^-+CF_3Cl	\rightarrow no reaction	< 0.05	< 0.5
BrF ⁻ +CF ₃ Br	→BrF ⁻ ·CF ₃ Br	< 0.03	< 0.4
IF ⁻ +CF ₃ I	$\rightarrow F^- \cdot CF_3I + I$	9.4	104

$$O^{-}+CF_{3}Cl \rightarrow F^{-}+CF_{2}O+Cl \quad \Delta H = -166 \text{ kJ mol}^{-1},$$
(1a)

$$\rightarrow$$
 Cl⁻+CF₂O+F

$$\Delta H = -208 \text{ kJ mol}^{-1}$$
, (1b)

$$\rightarrow \text{ClO}^- + \text{CF}_3 \quad \Delta H = +24.1 \text{ kJ mol}^{-1}, \tag{1c}$$

$$\rightarrow$$
 ClF⁻+CF₂O, $\Delta H = -233$ kJ mol⁻¹, (1d)

 $O^- + CF_3Br \rightarrow F^- + CF_2O + Br \quad \Delta H = -235 \text{ kJ mol}^{-1},$ (2a)

$$\rightarrow Br^- + CF_2O + F$$

$$\rightarrow$$
 BrO⁻+CF₃ ΔH =-19.5 kJ mol⁻¹, (2c)

$$\rightarrow$$
 BrF⁻+CF₂O,

$$\Delta H = (-402) \text{ kJ mol}^{-1}, (2d)$$

(2b)

$$O^{-}+CF_{3}I \rightarrow F^{-}+CF_{2}O+I \quad \Delta H = -300 \text{ kJ mol}^{-1},$$
(3a)

$$\rightarrow$$
 CF₃⁻+IO ΔH =+10 kJ mol⁻¹, (3b)

$$\rightarrow$$
 IO⁻+CF₃ ΔH =-31.7 kJ mol⁻¹, (3c)

$$\rightarrow IF^{-} + CF_2O \quad \Delta H = (-499) \text{ kJ mol}^{-1}, \tag{3d}$$

$$\rightarrow IOF^- + CF_2, \quad \Delta H = ?.$$
 (3e)

Reported thermochemistry is taken from Lias *et al.*¹⁷ unless otherwise noted. The heats of formation for ClO⁻, BrO⁻, and IO⁻ are based on the heats of formation of the XO neutrals and recently published electron affinity values for XO determined by laser photoelectron spectros-copy.^{18,19} The heats of formation used for BrF⁻ and IF⁻

result from estimated electron affinities based on electron affinities of similar halogen and interhalogen diatomics. When possible, neutral products are inferred from the known thermochemistry and conservation of mass. However, the large exothermicities associated with many of the reactions reported in this paper allow for several possible sets of neutral products for some reaction channels.

The present 298 K rate constant for reaction (2) is in excellent agreement with the value measured by Streit⁷ using a room-temperature flowing afterglow (FA) apparatus. For reaction (3), however, the present rate constant at 298 K is 73% larger than the FA value. The reason for the discrepancy is not apparent. However, the FA results show a lower reaction efficiency for CF₃I than for CF₃Br, while the present data show increasing efficiencies in the series from CF₃Cl to CF₃Br to CF₃I. This same efficiency trend in the CF₃X series is seen for the reactions of O₂⁻ and F⁻ with CF₃X, results for which are reported later in this paper.

Production of X⁻ was observed for CF₃Cl and CF₃Br but not for CF_3I , despite the fact that I^- formation would be exothermic by $267 \pm 4 \text{ kJ mol}^{-1}$. The relative amount of X^- product decreases from ~20% for CF₃Cl to ~10% for CF_3Br , a trend consistent with the lack of I^- from CF₃I. In addition to forming the ionic products mentioned above, the reaction of O^- with CF_3I produced minor amounts of CF_3^- and IOF^- . CF_3^- and the XOF^- analogs of IOF⁻ were not observed for CF₃Cl or CF₃Br. The CF₃⁻ channel would be endothermic for CF₃Cl and CF₃Br by 56 ± 11 and 20 ± 11 kJ mol⁻¹, respectively. The heats of formation of XOF⁻ (X=Cl, Br, I) are not known. The small rate constants for the CF_3^- channel (equal to the product of the CF_3^- branching fraction and the overall rate constant) in the $O^{-}/CF_{3}I$ system [reaction (3b)] are consistent with the 10 ± 11 kJ mol⁻¹ endothermicity of this channel, i.e., the ratio of the CF_3^- rate constant to the collisional rate constant may be set equal to a Boltzmann factor $\exp(-\Delta H/kT)$ to derive an upper limit to the endothermicity. The limits so derived, 9.0 and 12 kJ mol⁻¹ at 298 and 500 K, respectively, are approximately equal to the 10 kJ mol⁻¹ endothermicity calculated from published thermochemistry.

The observed periodic trends in the CF₃X series are as follows. As the molecular weight of CF₃X increases, i.e., proceeding down group VII, the relative abundances of F^- , X^- , and XF^- decrease, while that of XO^- increases. All four of these channels become more exothermic with increasing molecular weight of CF₃X. Regarding the XO⁻ channel, which increases with increasing weight of X, published thermochemistry indicates that formation of ClOis endothermic by $24.1 \pm 6 \text{ kJ mol}^{-1}$ while the BrO⁻ and IO⁻ channels are exothermic. The greater amount of IO⁻ compared with BrO⁻ could result from a lowering of an energy barrier in the reaction coordinate with increasing exothermicity. Alternatively, if formation of BrO⁻ were slightly endothermic (a possibility allowed by the error limits for ΔH) then the greater amount of IO⁻ could be explained simply by the enthalpies for production of XO⁻. Endothermic production of BrO⁻ would be consistent with the positive temperature dependence of this channel. Also, the rate constant for the endothermic channel forming ClO⁻ (only observed at 500 K) is consistent with the 24.1 kJ mol⁻¹ endothermicity of this channel. The derived upper limit to the endothermicity, 20 kJ mol⁻¹, is close to the 24.1±6 kJ mol⁻¹ endothermicity from the published thermochemistry. While the ClO⁻ product was not observed at 298 K, the maximum rate constant expected for this channel at 298 K based on the endothermicity is 1.0 $\times 10^{-13}$ cm³ s⁻¹ which is below our detection limit. The ClO⁻ product was also observed with an electric potential applied to the drift tube portion of the flow tube at 298 K. The threshold for detection of the ClO⁻ reaction product under these conditions occurred at an average ion-neutral center-of-mass kinetic energy below 0.05 eV.

The overall rate constants k increase in the series $k(CF_3CI) < k(CF_3Br) < k(CF_3I)$ at both temperatures. The same trend is seen in the reaction efficiencies: the reaction of CF_3CI is less efficient than the reaction of CF_3Br , which is below collisional efficiency, while the reaction of CF_3I proceeds at the collision rate. As noted above, the exothermicities of the major reaction paths increase with heavier CF_3X , as do the reaction efficiencies. Again, this may be a result of a lowering of energy barriers as reaction exothermicity is increased. Stated differently, the barrier may play less of a role in governing reactivity with increasing exothermicity.

For CF₃I and CF₃Br, the rate constants measured at the two temperatures 298 and 500 K are the same within experimental precision. However, for the less-efficient CF₃Cl reaction, a negative temperature dependence of $T^{-0.6}$ was measured. Inefficient ion-molecule reactions often exhibit negative temperature dependences, while more efficient reactions usually show less steep or flat dependences on temperature.²⁰ In each reaction [reactions (1)– (3)] the F⁻ channel decreases with increasing temperature. As mentioned above, XO⁻ production is favored at the higher temperature.

The variety of reaction products suggests that initial attack of O⁻ on CF₃X occurs both at carbon and at X. Attack at carbon would lead to the products F⁻ and X⁻. Attack of O⁻ at X would yield XO⁻ and, in the case of CF₃I, CF₃⁻. The product ion IOF⁻ observed from CF₃I could arise either from a complex in which oxygen is attached to carbon (following O⁻ attack at carbon), or from a two-step process in which OI⁻ is formed from O⁻ attack at I followed by reaction of OI⁻ with CF₃ within the complex before separation into products.

A similarity between these reactions and gas-phase neutral reactions of CF_3X is apparent in the X-atom abstraction channel leading to XO^- . The trend of increasing rate for X abstraction with increasing weight of CF_3X measured for O^- in the present study has also been observed for reactions of CF_3X with H (Refs. 21–25) and Na (Ref. 26) atoms. Furthermore, the measured activation energies for $H+CF_3X$ decrease with increasing CF_3X mass.^{21,24,25}

The present results can be compared qualitatively with those for collisional ionization reactions of energetic alkali atoms with $CF_{3}X$ (X=Cl, Br, I).²⁷⁻³⁰ In the alkali-atom

experiments, X⁻ was the major negative ion observed for all X, along with smaller amounts of F^{-.28-30} Other anions observed included CF₃⁻ and XF⁻; CF₃X⁻ was observed at low energies for CF₃Br and CF₃I but not for CF₃Cl (discussed in the next section). In their collisional ionization study, Compton, Reinhardt, and Cooper³⁰ observed greater relative abundances of CF₃⁻ from CF₃I than from CF₃Br. In the present study of O⁻ + CF₃X, CF₃⁻ was observed as a product only from CF₃I and not from CF₃Cl or CF₃Br.

The reactions of O⁻ with two of the corresponding monohalomethanes CH₃Cl (Refs. 6 and 31) and CH₃Br (Ref. 6) have been studied previously. Like CF₃X, CH₃Cl and CH₃Br react rapidly with O⁻, but the chemistry is different from that for O⁻+CF₃X. The reactions of O⁻ with CH₃X (X=Cl, Br) produce OH⁻ and CHX⁻ in addition to forming the X⁻ product observed for the CF₃X reactions.

CF₄ was observed to be unreactive with O⁻ at 298 and 500 K in spite of the fact that production of $F_2^-+CF_2O$ would be exothermic by 110±10 kJ mol⁻¹. The lack of reactivity is presumably the result of a large barrier to breaking two strong C-F bonds. In contrast, the reaction of O⁻ with CCl₄ studied by Dotan *et al.*³² is fast and produces ClO⁻+CCl₃. The analogous pathway forming OF⁻+CF₃ in the case of CF₄ is highly endothermic. O⁻ is also quite reactive with methane, the analogous hydrocarbon, producing OH⁻+CH₃.³³⁻³⁵ Electron attachment to CF₄ is negligibly slow for thermal electrons,³⁶⁻⁴¹ but recently it has been shown that CF₄⁻ can be formed from electron attachment to CF₄ clusters.⁴²

B. $O_2^- + CF_3X$

The reactions of O_2^- with CF_3X (X=Cl, Br, I) are fast for X=Br and I, slow for CF_3Cl , and produce X⁻ in each case:

$$O_2^- + CF_3Cl \rightarrow Cl^- (+CF_3O_2) \quad \Delta H = -90 \text{ kJ mol}^{-1},$$
(4a)

$$\rightarrow O_2^- \cdot CF_3 Cl, \quad \Delta H = ?,$$
 (4b)

$$O_2^- + CF_3Br \to Br^- (+ CF_3O_2)$$
 $\Delta H = -136 \text{ kJ mol}^{-1},$ (5a)

$$\rightarrow$$
 CF₃Br⁻+O₂, $\Delta H = -48.0 \text{ kJ mol}^{-1}$, (5b)

$$O_2^- + CF_3 I \rightarrow I^- (+ CF_3 O_2)$$
 ΔH = −171 kJ mol⁻¹, (6a)
→ CF_3 I^- + O_2, ΔH = −108 kJ mol⁻¹. (6b)

In addition to X^- formation, charge transfer occurs for CF₃Br and CF₃I, but does not in the case of CF₃Cl, which clusters with O₂⁻ in addition to forming Cl⁻. The clustering channel was not observed for the bromide and iodide. It is likely that clustering was observed only for CF₃Cl because of the extreme inefficiency of the Cl⁻ channel. The efficient bimolecular reaction channels may preempt clustering for CF₃Br and CF₃I, an effect observed in other ion-molecule systems.⁴³ The absence of nondissociative

charge transfer to CF_3Cl is not surprising since the electron affinity (EA) of CF_3Cl is negative (discussed below). CF_3Br and CF_3I have positive EA's. O_2^- is unreactive with CF_4 , and there appear to be no exothermic bimolecular pathways available.

In the reaction channels producing X^- (X=Cl, Br, I), it is energetically possible to form either the neutral product shown parenthetically above, CF₃O₂, or the neutrals CF₂O+OF. In the CF₃I reaction [reaction (6a)], formation of CF₃+O₂ would also be exothermic, but would be endothermic for CF₃Cl and CF₃Br. The CF₃O₂ product appears to be more likely than CF₂O+OF because the latter case, while exothermic, would require breaking the C-X and C-F bonds in CF₃X and the O₂ bond. The heat of formation of CF₃O₂ used here is -615 kJ mol^{-1.44}

The present 298 K rate constant for reaction (5) is in excellent agreement with Streit's FA value,⁷ but the two experiments disagree for the reaction with CF₃I [reaction (6)]. As mentioned above for O^-+CF_3I , the present 298 K rate constant for CF₃I is substantially larger than the FA value. The rate constants for the reactions of O^- and O_2^- with CF₃I reported here are 73% and 74% larger than the FA values, respectively. The reason for the disagreement is not apparent, but the constant ratio of the results is suggestive of a systematic error.

Identifying periodic trends in the O_2^- data is complicated by the fact that the reaction with CF₃Cl features product channels different from those in the CF₃Br and CF₁I reactions. The rate constant for the X⁻ channel increases from Cl to Br to I, and the exothermicity of X⁻ formation also increases with heavier X. A similar trend in reactivity is seen in the reactions of F⁻ with CF₃X (discussed below) and in numerous anionic reactions of CH₃X.^{20,45,46} The rate constant for the channel producing X^{-} from $F^{-}+CF_{3}X$ (X=Cl, Br, I) increases with heavier CF₃X (and increasing reaction exothermicity). These trends for O_2^- and F^- are in the opposite direction of that for the reactions of O^- with CF_3X , for which both X^- and the sum of X^- and F^- decrease with heavier CF_3X while the exothermicities of these channels increase. The different trends in these systems reflect the differences in the competition among reaction channels for these systems; additional channels compete in the O⁻ reaction.

Both the branching fraction and the rate constant for the channel for charge transfer from O_2^- to CF₃X are greater for X=Br than for X=I. It should be pointed out again that for CF₃I, formation of I⁻+CF₃+O₂ is exothermic, while production of Br⁻+CF₃+O₂ from CF₃Br would be endothermic by 18.7±5.3 kJ mol⁻¹. It is possible that the smaller amount of CF₃X⁻ from CF₃I compared with CF₃Br is a result of decomposition of CF₃I⁻ into CF₃+I⁻. This is discussed further below.

The temperature dependences of the rate constants vary for these reactions. For CF₃I, the overall rate constant k is collisional^{15,16} and invariant with temperature within experimental precision. For CF₃Br, k is less than collisional and decreases with temperature as $T^{-0.7}$. As was mentioned for the O⁻ reactions, it is not uncommon for rate constants of exothermic ion-molecule reactions to ex-

hibit negative temperature dependences when the reactions are inefficient, i.e., slower than the collision rate. The negative dependences are generally explained by assuming that the reaction proceeds via a long-lived complex. Magnera and Kebarle⁴⁷ have pointed out that as collision energy increases, the higher internal energy of the complex is accompanied by an increase in the density of states of the loose transition state early in the reaction coordinate which is larger than that of the tight transition state leading to products. This facilitates back decomposition of the complex to reactants compared with the case of collisions at lower energy.

At 500 K, the channel leading to X⁻ represents all or nearly all of the reactivity for X=Cl, Br, and I. In the case of CF₃Cl, the clustering channel (4b) was not observed at 500 K, and this is not surprising since most ion-molecule clustering reactions exhibit very strong negative temperature dependences.²⁰ For CF₃Br and CF₃I, the percentages for X⁻ formation at 500 K increase to 97% and 100%, respectively. In these cases, the contribution by the nondissociative charge-transfer channel is reduced dramatically or eliminated with increasing temperature. The added energy (translational plus internal) at the higher temperature facilitates the decomposition of the parent negative ion CF₃X⁻.

The parent anion CF₃Cl⁻ has not been observed in studies of the reactions of CF₃Cl with ions (this work), electrons,⁴⁸⁻⁵¹ or energetic Cs atoms.²⁹ This is not surprising since the vertical and adiabatic EA's of CF₃Cl are negative,⁵²⁻⁵⁵ and, while there is a shallow well in the CF₃Cl⁻ potential curve, the crossing of the ionic and neutral potential curves occurs above the dissociation asymptote.⁵² CF₃Cl⁻ has been observed in a solid tetramethylsilane matrix at 101 K.⁵⁶ The matrix study⁵⁶ and electron-scattering experiments^{54,55} have indicated that the extra electron in CF₃Cl⁻ resides in the a_1 (σ^*) antibonding orbital associated with the C–Cl bond.

The negative EA of CF₃Cl may explain the low reactivity of CF_3Cl with O_2^- compared with the much faster reactions of O_2^- with CF₃Br and CF₃I reported here as well as with CF_2Cl_2 and $CFCl_3$ studied by Fehsenfeld et al.⁴ All of these halomethanes, which react rapidly with O_2^- , have positive EA's. The reactions with O_2^- may initially proceed by electron transfer within the ion-dipole complex, followed by dissociation. The negative EA of CF₃Cl precludes initial electron transfer and may thereby be responsible for the very slow reaction rate. In fact, the rate constants reported here and in the literature⁴ for reactions of O_2^- with fully halogenated methanes correlate with the halomethane EA's. Furthermore, the rate constants reported in the literature for attachment of thermal electrons to these halomethanes also correlate with the halomethane EA's. These correlations are shown graphically in Fig. 1, and the data are tabulated with their references in Table IV. Jones et al. ⁵⁷ showed a correlation between the reactivity of transitionmetal complex anions with haloalkanes and the haloalkane thermal electron attachment rate constants, but found that the haloalkane EA's did not correlate with anion reactivity in those cases. Those studies involved a much larger num-



FIG. 1. Correlation between the electron affinity of halomethanes and the rate constant for (a) reaction with O_2^- at 298 K, and (b) attachment of thermal electrons. The values are taken from the present work and from references given in Table IV. The rate constant denoted for the reaction of O_2^- with CF₃Cl is an upper limit, i.e., $k \leq 4 \times 10^{-12}$ cm³ s⁻¹.

ber of haloalkanes than have been studied for reactivity with O_2^- . Based on the correlation with attachment rate, Jones *et al.*⁵⁷ proposed an electron-transfer mechanism for the transition-metal complex anion reactions. Thus there appears to be a similarity between the processes of electron attachment and electron transfer in these systems. The correlations between the O_2^- reaction rate and both EA and electron attachment rate lend support to the proposed electron-transfer mechanism. In addition, there is a striking qualitative similarity between the efficiencies of electron attachment and O_2^- reaction.^{15,16} In both the electron attachment and O_2^- reactions, the reactions with CF₃I are approximately collisional; the reactions with CF₃Br are

TABLE IV. Halomethane electron affinities and rate constants for reactions of halomethanes with O_2^- and thermal electrons.

Neutral	EA (eV)	$k_{298 \text{ K}} (\text{O}_2^-)$ (10 ⁻⁹ cm ³ s ⁻¹)	$k (e^{-})$ (10 ⁻⁹ cm ³ s ⁻¹)	
CF ₃ Cl	-0.4 ^a	< 0.004 ^b	0.00017°	
J.			0.00019 ^d	
CF_2Cl_2	0.4 ^e	0.21 ^f	3.2 ^g	
			1.8 ^h	
CF₃Br	0.91 ⁱ	1.0 ^b	16 ^j	
			15 ^h	
CFCl ₃	1.3°	0.76 ^f	260 ^g	
			310 ^h	
CF ₃ I	1.57 ⁱ	1.5 ^b	310 ^k	
			240 ¹	
			170 ^m	
^a Reference 5	3.	hReference 8	37.	
^b Present results.		ⁱ Reference 30.		
°Reference 52.		^j Reference 64.		
^d Reference 85.		^k Reference 88.		
References 53 and 86.		¹ Reference 89.		
^f Reference 4.		^m Reference	90.	
^g Reference 1	3.			

fast but below collisional; and those with CF_3Cl are very slow (see Table IV).

Further support for the electron-transfer mechanism is found in two recent studies. Knighton and Grimsrud⁶⁰ examined reactions of selected molecular anions (A^-) with a number of halomethanes and found that, for a given halomethane, the reactivity decreases with increasing EA of the donor molecule (A). In a similar study, Pan and Ridge⁶¹ found a correlation between reactivity and electrophile EA for reactions of transition-metal complex anions with a series of electrophiles. These results, combined with the other information presented above, including the present O_2^- data, suggest that the efficiency of electron transfer in these systems may be related to the difference between the electron detachment energy of the reactant anion and the EA of the reactant neutral.

An important difference between the electron attachment and O_2^- reactions can be seen in the products. Attachment of low-energy electrons to CF3X results exclusively in X^- formation for X=Cl, Br, and I, with no production of the parent anion CF₃X^{-.48,50,51,62-67} Similarly, electron transfer from K (nd) Rydberg atoms to CF₃Br (Refs. 68 and 69) and CF₃I (Ref. 68) results in exclusive production of Br⁻ and I⁻, respectively, with no CF_3X^- formation. The fact that CF_3X^- is not produced by electron attachment but is formed in the reactions of O_2^- with CF₃Br and CF₃I may be a result of energetics. Unlike a free electron, the electron in O_2^- is only available at the cost of the O_2^- detachment energy, 43.5 kJ mol⁻¹. This leads to a lower exothermicity for electron transfer from O_2^- compared with attachment of free electrons. The lower exothermicity facilitates stabilization of the parent anion against unimolecular fragmentation. Indeed, the branching fraction of CF₃Br⁻ is much greater than that of $CF_{3}I^{-}$, which is consistent with the lower EA of $CF_{3}Br$. Less excess energy must be dissipated in the CF₃Br reaction compared with CF_3I , and therefore the excited CF₃Br⁻ complex should live longer and have a greater likelihood of being stabilized via third-body collisions. This is also consistent with the observations at 500 K of a small amount of CF₃Br⁻ but no CF₃I⁻. As mentioned in the preceding section, collisional ionization reactions of energetic alkali atoms with CF₃Br and CF₃I produce minor amounts of the parent anion CF₃X⁻ at low energies.²⁷⁻³⁰ However, in contrast to the present results for $O_2^- + CF_3X$, the findings of Compton, Reinhardt, and Cooper³⁰ for the collisional ionization reactions show a greater relative abundance of CF_3X^- formation for CF_3I than for CF_3Br .

It should be pointed out that, while there is evidence supporting an electron-transfer mechanism for the O_2^- reactions, the present data are also consistent with a nucleophilic displacement mechanism. The reactivity of O_2^- with CF_3X increases in the order expected based on $S_N 2$ leaving group ability, i.e., $I^- > Br^- > Cl^-$. McDonald and Chowdhury⁵ studied the reactions of two corresponding monohalomethanes CH_3X (X=Cl, Br) with O_2^- . These reactions proceed at rates close to the collisional values and produce only X⁻. CH₃Cl and CH₃Br have negative EA's, and the mechanism is believed to be bimolecular nucleophilic displacement $(S_N 2)$.⁵ McDonald and Chowdhury pointed out that O_2^- appears to be an excellent gas-phase $S_N 2$ nucleophile despite its low proton affinity.

$C. O^{-} + C_2 F_4$

The reaction of O^- with C_2F_4 proceeds at approximately the collision rate at 298 and 500 K and involves formation of four ionic products as well as electron detachment:

$$O^{-}+C_{2}F_{4} \rightarrow F^{-}(+C_{2}F_{3}O) \quad \Delta H = ?,$$
 (7a)

$$\rightarrow \text{FCO}^{-}(+\text{CF}_3) \quad \Delta H = -353 \text{ kJ mol}^{-1},$$
(7b)

$$\rightarrow$$
 CF₃⁻(+FCO) $\Delta H = -272 \text{ kJ mol}^{-1}$, (7c)

$$\rightarrow C_2 F_3 O^- + F \quad \Delta H > -77 \text{ kJ mol}^{-1}, \tag{7d}$$

$$\rightarrow e^{-}(+C_{2}F_{4}O), \quad \Delta H = ?.$$
 (7e)

Channel (7a) forming F^- accounts for over 90% of the ionic products at both temperatures. The neutral products for channels (7a), (7b), (7c), and (7e) are shown parenthetically because production of other species is energetically possible. Specifically, the neutrals in (7a) could be alternatively $CF + CF_2O$ (exothermicity = 82.8 ± 9 kJ mol^{-1}), CF₂+FCO (58±63 kJ mol⁻¹), CF₃+CO (269 ± 6 kJ mol⁻¹), or C₂F₂O+F (estimated to be exothermic). Reaction channel (7b) could involve either CF₃ as written or $CF_2 + F$ which would be endothermic by only 2 ± 12 kJ mol⁻¹. The channel (7c) could produce FCO (as written), or it could form F+CO with an exothermicity of 128 ± 11 kJ mol⁻¹. The products listed in the reaction equations above seem the most likely because they describe two pairs of product channels which differ only by the location of the charge, i.e., Eqs. (7a) and (7d) are related in this way as are Eqs. (7b) and (7c). The product distributions measured at 298 and 500 K are approximately the same. The minor product ion FCO⁻ was observed only at 298 K; this may be a result of lower detection sensitivity at 500 K. The product ion $C_2F_3O^-$ could reasonably have two possible structures: $O = C^{-} - CF_{3}$ or $O(F)C = CF_{2}$.

The gas-phase negative-ion chemistry of C_2F_4 has not been studied extensively. Su *et al.*⁷⁰ studied the reactions of C_2F_4 with F⁻ and with some perfluorocarbanions. Dawson and Nibbering⁷¹ examined the chemistry of C_2F_4 with various anions derived from nitriles. Attachment of thermal electrons to C_2F_4 is negligibly slow in the gas phase.^{38,72} Electron impact on C_2F_4 at low energies (1–10 eV) produces F⁻, CF₂⁻, CF₃⁻, and $C_2F_3^-$, with F⁻ being the major ion.^{73,74}

There are many exothermic reaction pathways available in the reaction of C_2F_4 with O⁻ (and with O₂⁻ as discussed below). This is, in general, a result of several factors including ionic reaction products of high electron detachment energy, the very weak C=C bond in C_2F_4 , and the strong C=O bonds which can form. The strength of

Because of the multiplicity of possible neutral products accompanying the ionic product F⁻, discussed above, it is difficult to propose a mechanism for this channel (7a). However, since the minor channel (7d), forming $C_2F_3O^-$ +F, was observed, it is possible that channels (7a) and (7d) share a common mechanism involving attack of O⁻ at carbon followed by dissociation of a C-F bond. In this mechanism, the electron could remain on either fragment, leading to either $F^++C_2F_3O$ or $C_2F_3O^-+F$ as products. A similar mechanism may obtain for reaction channels (7b) and (7c), producing $FCO^- + CF_3$ and $CF_3^- + FCO_3$, respectively, since they too differ only by the location of the negative charge. These channels both require migration of a fluorine atom and again involve attack of O⁻ at carbon. While associative detachment is almost certainly exothermic (the heat of formation of C_2F_4O is not known), there are other exothermic reactive detachment channels available. One likely set of products in the reactive detachment channel would be $e^- + CF_2O + CF_2$ which would be exothermic by 274 ± 7 kJ mol⁻¹. Formation of e^- +FCO +CF₃ would also be exothermic (by 84 ± 63 kJ mol⁻¹) but would necessarily involve migration of F.

The reaction of O^- with C_2H_4 , the hydrocarbon analog of C_2F_4 , has been extensively studied.^{11,34,35,75,76} Unlike the $O^- + C_2F_4$ reaction, the main channel of the C_2H_4 reaction is associative detachment, and only one of the ionic products, $C_2H_3O^-$, is analogous to an ion produced in the C_2F_4 reaction. The other minor ionic products from C_2H_4 are $C_2H_2^-$, OH^- , C_2OH^- , and C_2H^- . In the C_2F_4 reaction, production of $C_2F_2^-$ would be exothermic but was not observed. OF^- formation is endothermic, and the energetics are not known for C_2OF^- and C_2F^- (all of which were not observed). The much smaller extent of associative detachment in the case of C_2F_4 compared with C_2H_4 may be simply a result of the much higher EA's of the fluorinecontaining species compared with their hydrogencontaining analogs.

$D. O_2^- + C_2 F_4$

The reaction of O_2^- with C_2F_4 proceeds by electron detachment and formation of six ionic products:

$$O_2^- + C_2 F_4$$

$$\rightarrow F^{-}(+FCO+CF_{2}O) \quad \Delta H = -363 \text{ kJ mol}^{-1},$$
(8a)

$$\rightarrow F_{2}^{-}(+C_{2}F_{2}O_{2}) \quad \Delta H = -324 \text{ kJ mol}^{-1},$$
(8b)

$$\rightarrow FCO^{-}(+CF_2O+F) \quad \Delta H = -304 \text{ kJ mol}^{-1},$$

$$\Delta FCO^{-}(\perp CE_{\star}) \quad \Delta H = -534 \text{ kI mol}^{-1}$$
 (8d)

$$\rightarrow$$
 CF₃O + (FCO) $\Delta H = -356$ kJ mol⁻, (8e)

$$C_2F_4O^- + O \quad \Delta H = ?, \tag{8f}$$

$$\rightarrow e^{-}(+C_2F_4O_2), \quad \Delta H = ?. \tag{8g}$$

 F^- represents the major ionic product at both temperatures. As was the case for the reaction of O⁻ with C₂F₄, the neutral products for several channels of reaction (8) cannot be assigned uniquely because of the high exothermicities. For example, in channel (8a) it is energetically allowed for the neutrals to be FCO+CF₂O (as written) or CO₂+CF₃ (exothermicity=402±6 kJ mol⁻¹).

In contrast to the reaction of O^- with C_2F_4 , which is approximately collisional at 298 and 500 K, the overall rate constant for reaction (8) is below collisional and decreases with increasing temperature as $T^{-0.8}$. As discussed for reaction (5), the negative temperature dependence is often interpreted as an indication of reaction occurring through a long-lived complex. The ionic products FCO⁻ and $C_2F_4O^-$ observed at 298 K were not detected at 500 K.

The electron-transfer mechanism for the reactions of O_2^- with CF_3X proposed earlier would appear to be invalid for reaction (8). Attachment of thermal electrons to C_2F_4 is negligibly slow in the gas phase,^{38,72} and electron-impact studies^{73,74,77} have not revealed any of the parent anion $C_2F_4^-$. The EA of C_2F_4 may in fact be negative.^{78,79} However, metastable $C_2F_4^-$ has been observed by collisional ionization of tetrafluorosuccinic anhydride by energetic Cs atoms,⁸⁰ and $C_2F_4^-$ has been prepared by electron attachment to C_2F_4 in solid solution.⁸¹

Two reasonable mechanistic possibilities for the initial step in reaction (8) involve either anionic or radical attack of O_2^- at carbon. If O_2^- acts as a nucleophile and attacks at carbon 1, this would lead to a $C_2F_4O_2^-$ intermediate with the negative charge on carbon 2. Radical attack by O_2^- at carbon 1 would produce the $C_2F_4O_2^-$ intermediate with the charge on oxygen and a radical electron on carbon 2. Both of these intermediates appear to be reasonable candidates, and the present data do not indicate a preference for one over the other. Determining the mechanism is made more difficult by the high exothermicities, which prevent the deduction of neutral product identities.

The electron detachment channel is the major pathway at 500 K. As was discussed for the reaction of O⁻ with C_2F_4 , detachment for $O_2^- + C_2F_4$ may involve either associative detachment or reactive detachment. A number of exothermic reactive detachment pathways are possible, such as formation of $e^- + 2CF_2O$ (exothermicity=579±4 kJ mol⁻¹). Associative detachment forming $C_2F_4O_2$ in a ring structure appears to be a reasonable possibility.

E. Secondary reactions

Table III lists the rate constants and products for selected secondary reactions measured at 298 K. These reactions were studied directly in order to better understand the nature of the ions appearing in the product mass spectra of the reactions of interest. The halide ions (F^- , Cl^- , Br^- , and I^-) all react by clustering to the CF_3X reactant neutral. F^- also reacts via nucleophilic displacement with CF_3Br and CF_3I (exothermicity=248±4 and 284±4 kJ mol⁻¹, respectively); however, clustering is the major reaction pathway in these reactions. Furthermore, the F^- + CF_4I clustering reaction is fast. Experiments are planned to examine in greater detail this competition between clustering and displacement. A displacement channel for the F^-+CF_3Cl reaction, while exothermic, was not observed. The clustering reactions of X⁻ with CF₃X (X=Cl, Br, I) are all very slow. No reaction was observed for ClO⁻ with CF₃Cl, while BrO⁻ was found to cluster to CF₃Br. IO⁻ reacted at a moderate rate with CF₃I forming product(s) of higher mass than detectable with the present mass spectrometer. This reaction did not form observable amounts of I⁻ or I₂⁻, which would be exothermic by 279±8 and 98±8 kJ mol⁻¹, respectively. By analogy with the BrO⁻ +CF₃Br reaction, the product of IO⁻+CF₃I is probably the cluster product, IO⁻·CF₃I. ClF⁻ did not react with CF₃Cl, while BrF⁻ clustered slowly to CF₃Br.

Perhaps the most noteworthy of the secondary reactions is the fast reaction of IF⁻ with CF₃I which produced an ionic product with a mass of 215 Daltons. A likely structure for this product is $F^- \cdot CF_3 I$, i.e., a cluster ion of F^- and CF_3I . This ion is formed, along with I^- , in the encounter of F^- with CF_3I , mentioned above. The ion $F^- \cdot CF_3I$ corresponds to the first intermediate complex in the nucleophilic displacement reaction of F^- with CF_3I . SIFT studies of nucleophilic displacement usually do not enable the detection of the complexes involved in the reaction, although these complexes have been examined re-cently by other techniques.⁸²⁻⁸⁴ The observation here of $F^- \cdot CF_3I$ would indicate that this complex is long lived, which is not surprising given the high polarizability of CF_3I . Another possible structure for the ion is $(F_3C-I F)^{-}$ with the iodine atom chemically bound to both C and F.

IV. SUMMARY

The reactions of O^- and O_2^- with the studied halocarbons exhibit a rich chemistry, forming many ionic products in some cases. The reactivity of CF_3X (X=Cl, Br, I) toward O^- , O_2^- , and F^- increases with increasing molecular weight of CF_3X . The reactivity of O_2^- with CF_3X correlates with both the EA and electron attachment rate of CF_3X , suggesting a mechanism involving initial electron transfer. The reactions of F^- with CF_3Br and CF_3I proceed by nucleophilic displacement (minor channel) and clustering (major channel); this competition is somewhat surprising for such simple systems which have exothermic channels available.

ACKNOWLEDGMENTS

I thank Al Viggiano and John Paulson for critical readings of the manuscript and for helpful discussions. I thank Amy Stevens Miller, Jane Van Doren, Tom Miller, Dave McFadden, David Smith, and Paul Burrow for helpful discussions. The technical assistance of Paul Mundis and John Williamson is also appreciated.

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