Here δz and $\delta \tau$ are small space and time increments (chosen to be 0.05 and 0.0008, respectively). The inner boundary lattice point *l* depends upon the value of δz chosen. With $\delta z = 0.05$, r = R corresponds to z = 1 and l = 20.

$$P(j,i+1) - P(j,i) = a_j P(j,i) + b_j P(j+1,i) + c_j P(j-1,i); \quad j = l, ..., N$$
(B.2)

where $a_j = \alpha[(j - 1/2)^{-1} - (j + 1/2)^{-1} - 2]$, $b_j = \alpha[1 - (j + 1/2)^{-1}]$, $c_j = \alpha[1 + (j - 1/2)^{-1}]$, and $\alpha = \delta \tau \delta z^{-2}$. This is supplemented with an inner boundary condition

$$P(l-1,i) = P(l,i)\{-[a_l + c_{l-1}]/c_l - \gamma_i \alpha \delta z/c_l\}$$
(B.3)

and an equilibrium outer boundary condition $P(N,i) = 4\pi(N\delta Z)^2$. The inner boundary condition contains the time-varying intrinsic reactivity γ_i (= γ when h = 1; = 0 otherwise). The first term in brackets {} in eq B.3 enforces the reflecting wall condition when $\gamma_i = 0$. The initial condition in all gated reaction solutions is the equilibrium condition $P(j,0) = 4\pi(j\delta z)^2$. A more complete detailed discussion of this method is given elsewhere.^{30,31}

Gas-Phase Reactions of O⁻ and O₂⁻ with a Variety of Halogenated Compounds

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The flowing afterglow technique has been applied to a comparative study, for a series of halogenated compounds, of dissociative attachment and reaction with O^- and O_2^- . The ion product spectrum produced by reaction with O^- and O_2^- overlaps but is more diverse than that obtained by dissociative attachment. Absolute rate constants for the O^- and O_2^- reactions are reported. A few reactions, for which exothermic mechanisms can be written, were found to be quite inefficient.

Introduction

Gas-phase negative-ion chemistry is of interest in such diverse fields as aeronomy,^{1a} laser discharges, gas-phase acidities^{1b} and electron affinities,^{1c,2} negative chemical ionization analysis,^{1d} thermochemistry, and solvation effects.³ The reactions of the O⁻ and O₂⁻ anions are of particular interest in ionospheric ion chemistry and atmospheric-pressure chemical ionization and for making comparisons between gas-phase and solution chemistry. In negative chemical ionization analysis it is very likely that O⁻ and O₂⁻, if not the reactant ions of choice, either will be intermediates in forming the reactant ion⁴ or will be contaminant negative ions causing complications in the mass spectrum.^{1d}

Halogenated compounds have similarly received substantial recent attention as possible modifiers of atmospheric chemistry and as trace contaminants in the environment. Thus, ion-molecule reactions involving halogenated compounds are of interest in the overall mechanism of atmospheric chemistry and for developing analytic procedures for trace analysis.

To date there have been a very limited number of studies of the reactions of O_x^- (x = 1, 2, 3) with halogenated compounds. Tanaka et al.³ studied the reactions of a number of negative ions including O⁻ with singly halo-

genated methanes. Their interest was in the comparison of the rates of nucleophilic displacement reactions in the gas phase to the rates in solution. Fehsenfeld et al.⁵ have examined the reactions of O_2^- with CFCl₃ and with CF₂Cl₂ in order to assess the magnitude of a tropospheric or stratospheric sink for those halocarbons. Dotan et al.⁶ have examined the reactions of O^- with CCl₄ and of O^- and $O_2^$ with HCl with regard to the role of chlorinated compounds in atmospheric negative-ion chemistry. Siegel and Fite⁷ looked at the negative ions produced by atmosphericpressure ionization of several of the common fluorochlorocarbons and saw Cl⁻ as the only negative ion. However, the carrier gas used was not specified, so they may have observed only the dissociative attachment process rather than a charge-transfer or reactive process.

An interesting application of O_2^- chemistry has been made by Grimsrud and Miller^{8a} in demonstrating that oxygen doping of the carrier gas in gas chromatography significantly enhances the electron capture (EC) detector sensitivity to monohalogenated methanes. This has been extended by Phillips et al.,^{8b} who utilize the chemistry of O⁻ following dissociative attachment to N₂O to enhance the electron capture detector response to compounds which do not directly attach electrons.

In this study the reactions of O^- and O_2^- with a large number of halogenated compounds have been examined

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to obtain product distributions and absolute rate constants. For comparison the products of electron attachment, or dissociative attachment, to the same set of compounds were determined. A simple comparison may be made between dissociative attachment (eq 1) and reaction with

$$e + RX \rightarrow R + X^{-}$$
 $\Delta H_r = D_0(RX) - EA(X)$ (1)

 O^- or O_2^- if the reaction proceeds by dissociative charge transfer (eq 2). In the latter case the energy available to

$$O_2^- + RX \rightarrow O_2 + R + X^-$$

$$\Delta H_r = D_0(RX) + EA(O_2) - EA(X)$$
(2)

the reaction is decreased by the electron affinity of the reactant ion, 0.44 eV for O_2^{1c} and 1.46 eV for O_2^9 However, other mechanisms such as nucleophilic displacement or those that lead to some other bond formation on the product side of eq 2 are likely for the reactions of O^- and O_2^- . In these lie the differences that are seen between products and product distributions due to dissociative attachment or to reaction with O^- and O_2^- . In fact, for the halogenated compounds used in this study, known energetics demand that O^- react by some mechanism other than dissociative charge transfer. This is true only for a small number of the O_2^- reactions.

In a few instances F^- and O_3^- were present as reactant ions, and for those cases reaction rate constants for those ions are presented. Lastly, an attempt was made to produce O^- , free from O_2^- , by the reaction of NH_2^- with O_2 . The rate of this reaction and the actual mechanism are discussed.

Experimental Section

The present measurements were made in a room-temperature flowing afterglow apparatus which has been described previously.^{10,11} The carrier gas used in these studies was helium, purified by passage through a molecular-sieve trap held at 77 K. Volume flow rates of helium were typically 180 STP atm cm³ s⁻¹. The O⁻ and O_2^{-} reactant ions were formed by dissociative and three-body attachment processes, respectively, in a flow of oxygen of between 6 and 50 STP atm cm³ s⁻¹ that was allowed to pass the electron gun. These quantities of oxygen were sufficient to ensure that no free electrons remained in the reaction zone. Signal ratios of O^- and O_2^- were dependent upon O_2 flow and total pressure but were always comparable within a factor of 10. The flow tube was operated in the range 0.3–0.6 torr with linear flow velocities around 8000 cm s^{-1} .

Dissociative attachment was studied in a pure helium buffer so that the reactant negative charge was carried solely by electrons. The attaching neutral compounds were introduced into the flow tube at a point 58 cm downstream from the electron gun (\sim 7-ms flow time) so it was assured that the electron thermal distribution was representative of room temperature.

Reaction rate coefficients were derived as described.¹⁰ Gas flows, except for ICl and IBr, were measured by calibrated linear mass flowmeters. Flowmeter calibrations were determined for each gas by measuring the time rate of pressure change in standard volumes. Pressures were measured by electronic capacitance manometers. The nature of the reactant gas, which was frequently highly reactive, determined the accuracy of flow calibration, which

TABLE I: Negative-Ion Products Resulting from Electron Attachment or Reaction with O⁻ and O₂

neutral	of electron attachment ^a	products of reaction with O ⁻ and O_2^{-b}
HCl	none	Cl ⁻ (0.95), OH ⁻ (0.05)
HBr	none	$Br^{-}(0.95), OH^{-}(0.05)$
Cl ₂	Cl-	Cl_2^- (0.6), Cl^- (0.3), ClO^- (0.1)
ICĪ	Cl-, I-	$Cl_2^- (\geq 0.95)$, $ICl^- (< 0.05)$,
TD	D - I-	101_2
IBr	Br, I	$Br^{-}(0.8), 1^{-}(\leq 0.1), 1Br^{-}$
NOR	D	$(\leq 0.1), 1Br_2 = c$
NOF	F F	$F^{-}(0.55), NO_{2}^{-}(0.45)$
NO ₂ F	F^2 , NO_2^2 , NO_3^2C	$F^{-}(0.7), NO_{2}^{-}(0.2), NO_{3}^{-}$
NF	г -	(U.I) $\mathbf{F}^{-}(0.95)$ $\mathbf{F}^{-}(0.15)$
	ד- רוד - רוד -	CIE = (>0.05)
	$\mathbf{P}_{u^{-}}$	$\nabla \Gamma_2 (= 0.50)$ $\nabla (0.8) P_{2} (0.1) P_{2} O(0.1)$
OF 3 DI	Di	BrF^{-c}
CHBr,	Br⁻	$Br^{-}(0.85), BrO^{-}(0.15)$
CF ₂ ClBr	Br ⁻ , Cl ⁻	$Br^{-}(0.5), Cl^{-}(0.4), F^{-}$
-		$(\leq 0.05), BrO^{-} (\leq 0.05)$
CF ₃ I	I-	$I^{-}(0.4), OI^{-}(0.4), F^{-}(0.2)$
CCl₄	Cl-	$Cl^{-}(0.8), ClO^{-}(0.1), CCl_{3}^{-}$
		(≤0.1)
$C_2 F_5 Br$	Br ⁻ , F ⁻	$F^{-}(0.55), Br^{-}(0.35), BrO^{-}$
		$(0.1), BrF^{-c}$
SOCl ₂	Cl-	$Cl^{-} (\geq 0.95), Cl_{2}^{-}, ^{c} SOCl_{3}^{-c}$
SO ₂ Cl ₂	Cl^{-} , $SO_{2}Cl^{-}$	SO_2Cl^- (0.8), $SO_2Cl_2^-$ (0.2),
	-	Cī - c

^a Where multiple products are listed, they are listed in descending order of abundance. ^b Approximate fracttional abundances are listed. No correction has been made for mass discrimination. ^c Due to secondary reaction.

in turn is the major contributor to uncertainty in the rate constants. Conservative error limits (no better than $\pm 30\%$) are specified with the rate constants in the following section. It was necessary to connect the sample tubes containing ICl and IBr directly to the flow tube so only a qualitative observation of reaction rates could be made.

Reagents were obtained from commecial sources and were used without further purification with the exception that ammonia, used as a source for the NH_2^- ion, had to be dried in order to eliminate the very rapid secondary reaction of NH_2^- with H_2O which produces OH^- .

Results and Discussion

In Table I is presented, for a series of halogenated compounds, a comparison of the products and product distributions arising from thermal electron dissociative attachment to those resulting from reaction with O⁻ and O_2^{-} . In work of this type dealing with many halogenated species, it was usual to have persistent background ion signals, most commonly Cl⁻, but never with an intensity greater than a few percent of the O^- or O_2^- signals. However, for this reason and because no attempt was made to correct for mass discrimination, the product ratios listed in Table I are meant only to be semiquantitative. It was not possible to specify the products or assign product distributions resulting specifically from reaction with O⁻ or with O_2^{-} . In most cases the observed products can be explained by any one or some combination of dissociative, displacement, or reactive charge-transfer reactions of O_2^- . The reaction mechanisms for O⁻ are limited to displacement or reactive charge transfer because the electron affinity of the oxygen atom is too high to allow dissociative charge transfer.

An example of a reaction of O_2^- which must proceed by a mechanism other than dissociative charge transfer is that

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TABLE II: Rate Constants for the Reactions of O⁻ and O₂⁻ with Halogen-Containing Molecules

	rate constant ^a fe	or reaction with
neutral	0-	0 ₂ -
HCl	$(1.3 \pm 0.4) \times 10^{-9} c$	$(1.2 \pm 0.4) \times 10^{-9} c$
	$(2.0 \pm 0.6) \times 10^{-9}e$	$(1.6 \pm 0.5) \times 10^{-9} d$
HBr	$(1.0 \pm 0.3) \times 10^{-9}$	$(5.2 \pm 1.6) \times 10^{-10}$
Cl,	$(1.0 \pm 0.3) \times 10^{-9}$	$(8.1 \pm 2.4) \times 10^{-10}$
ICİ	fast ^b	fast ^b
IBr	fast ^b	fast ^b
NOF	$(9 \pm 4) \times 10^{-10}$	$(6 \pm 3) \times 10^{-10}$
$NO_{2}F$	$(1.7 \pm 0.8) \times 10^{-9}$	$(1.4 \pm 0.7) \times 10^{-9}$
NF ₃	$(3.7 \pm 1.1) \times 10^{-10}$	$(2.4 \pm 0.7) \times 10^{-10}$
CIF,	$(1.1 \pm 0.4) \times 10^{-9}$	$(9.6 \pm 3.8) \times 10^{-10}$
CF Br	$(1.3 \pm 0.4) \times 10^{-9}$	$(1.1 \pm 0.3) \times 10^{-9}$
CH Br,	$(1.4 \pm 0.4) \times 10^{-9}$	$(1.1 \pm 0.3) \times 10^{-9}$
CF_2CIBr	$(7.2 \pm 2.2) \times 10^{-10}$	$(5.2 \pm 1.6) \times 10^{-10}$
CF I	$(1.1 \pm 0.3) \times 10^{-9}$	$(8.6 \pm 2.6) \times 10^{-10}$
CClઁ₄	$(1.0 \pm 0.3) \times 10^{-9} c$	$(7.9 \pm 2.4) \times 10^{-10}$
,	$(1.4 \pm 0.4) \times 10^{-9} e$	
$C_{2}F_{3}Br$	$(7.2 \pm 2.2) \times 10^{-10}$	$(5.5 \pm 1.7) imes 10^{-10}$
SŎĊĺ,	$(1.8 \pm 0.9) \times 10^{-9}$	$(1.4 \pm 0.7) \times 10^{-9}$
SO ₂ Cl ₂	$(1.8 \pm 0.9) \times 10^{-9}$	$(1.4 \pm 0.7) \times 10^{-9}$

^a Units: cm^3 molecule⁻¹ s⁻¹. ^b Qualitative observation because flow calibration could not be made. ^c This work. ^d Reference 12. ^e Reference 6.

of O_2^- with CF₃Br. The dissociative charge-transfer mechanism (eq 3) is endothermic by 0.13 eV. However,

$$O_2^- + CF_3Br \rightarrow O_2 + CF_3 + Br^-$$

$$\Delta H_* = +0.13 \text{ eV}$$
(3)

the major product observed, F^- , may be accounted for by the following reaction pathway, which is exothermic by 0.67 eV:

$$O_2^- + CF_3Br \rightarrow CF_2O + BrO + F^-$$

$$\Delta H_* = -0.67 \text{ eV}$$
(4)

An examination of Table I indicates that the major product of dissociative attachment usually appeared as the major product of reaction with O^- and O_2^- . However, the product spectrum arising from reaction with O⁻ and O₂⁻ was much richer and could serve to differentiate between such molecules as CF₃Br and CHBr₃. In only a few instances did the major product of dissociative attachment not appear as the major product of reaction with O⁻ and O_2^{-} . This was usually just a matter of different order of product distribution, but for two molecules-ClF3 and SO₂Cl₂—the major product of dissociative attachment did not appear at all in the product list for O^- and O_2^- reactions. Presumably the energy available from the formation of F-O and Cl-O bonds in the neutral products of these reactions drives the reaction to form molecular ion fragments rather than the atomic ions which are produced by dissociative attachment.

The rate constants measured for O⁻ and O₂⁻ reactions are given in Table II. Rate constants involving F⁻, O₃⁻, and NH₂⁻ are given in Table III. An inspection of Table II shows that, with one exception, the reactions are fast and, where comparison to previous measurements is available, agreement is good. The rates of reaction of O⁻ and O₂⁻ with NF₃ are noticeably slower than the other listed rates and are also substantially slower than is predicted theoretically. The Langevin formulation¹³ rate constant for O⁻ + NF₃, using a calculated polarizability of

TABLE III: Reaction Rate Constants

reaction	rate constant, cm ³ molecule ⁻¹ s ⁻¹
$F^- + C_2 F_5 Br$	$(4.1 \pm 1.2) \times 10^{-10}$
F⁻ + SÔCl,	$(1.4 \pm 0.7) \times 10^{-9}$
$F^- + SO_2CI_2$	$(1.6 \pm 0.8) \times 10^{-9}$
$O_3^- + SOCl_2$	$(1.4 \pm 0.7) \times 10^{-9}$
$O_3^{-} + SO_2Cl_2$	$(1.3 \pm 0.7) \times 10^{-9}$
$NH_2 + O_2 \rightarrow HNO + OH^-$	$(4.6 \pm 1.4) \times 10^{-11}$

 NF_3 by the method of Miller and Savchik,¹⁴ is 1.0×10^{-9} cm³ molecule⁻¹ s⁻¹. This calculation is made intentionally ignoring the dipole moment of NF_3 which, if accounted for, would make the theoretical prediction even larger. Mechanisms can be written for the reactions of O⁻ and O₂⁻ with NF₃ (eq 5) which are both thermodynamically and

$$O_2^{-(2\pi)} + NF_3^{(1A)} \rightarrow NO_2^{(2A)} + F_2^{(1\Sigma)} + F^{-(1S)}$$
$$\Delta H_r = -0.51 \text{ eV}$$
$$O^{-(2P)} + NF_3^{(1A)} \rightarrow NO^{(2\pi)} + F_2^{(1\Sigma)} + F^{(1S)}$$
$$\Delta H_r = -1.44 \text{ eV}$$
(5)

spin allowed, so without knowledge of the reaction surface there is no obvious explanation for the low reaction rate. Slow exothermic ion-molecule reactions have been explained by Pellerite and Brauman¹⁵ in terms of a double-welled reaction surface with an inhibiting internal barrier.

The reaction of NH_2^- with O_2 (Table III) presents another case of a low rate constant for a thermodynamically favored reaction. The hydroxyl anion was the sole ionic product of this reaction. The low rate suggests that the reaction is spin disallowed, which is, in fact, the case for production of ground-state HNO.

$$NH_2^{-(1A)} + O_2(^3\Sigma) \rightarrow HNO(^{1}A) + OH^{-(1\Sigma)}$$
$$\Delta H_r = -1.43 \text{ eV}$$
(6)

However, the first excited state of HNO lies approximately 0.8 eV above the ground state¹⁶ so the reaction

$$NH_2^{-(1A)} + O_2(^{3}\Sigma) \rightarrow HNO(^{3}A) + OH^{-(1\Sigma)}$$

$$\Delta H_r \sim -0.6 \text{ eV}$$
(7)

is allowed by spin and energetics. Unlike the observations of Tanaka et al.,¹⁷ though, the existence of this allowed channel seems to have little effect on the reaction rate constant.

These results bear upon the electron capture doping technique only to the extent that reaction of O^- or O_2^- with these halogenated molecules is faster than electron attachment. The diversity of the product spectrum should not affect the EC technique. Because electron attachment rates were not determined in this work nor are the anion reaction rates known at 200–400 °C (typical EC operating temperature), these results merely indicate the potential of oxygen anion reactions in an EC detector.

Conclusions

The product distributions and rate constants have been reported for the reactions of O^- and O_2^- with a series of halogenated compounds. In general, the product spectrum is more diverse but overlaps with that obtained from electron dissociative attachment processes. These data

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should be useful for analytical purposes in the application of negative chemical ionization analysis and should further add to our understanding of atmospheric ion-molecule reactions resulting from inadvertent or intentional modification of the stratosphere or ionosphere. Several reactions, those of O and O_2^- with NF₃ and that of NH₂⁻ with O_2 , were found to be substantially slower than expected and are added to the interesting list of exothermic, yet slow, ion-molecule reactions. The apparent universal reactivity of O^- and O_2^- with halogenated molecules suggests that the technique of enhancing the response of electron capture detectors by oxygen doping should be widely applicable.

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Determination of Acyl Chain Conformation at the Lipid Interface Region: Raman Spectroscopic Study of the Carbonyl Stretching Mode Region of Dipalmitovi Phosphatidylcholine and Structurally Related Molecules

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The two carbonyl stretching modes of 1,2-dipalmitoyl phosphatidylcholine (DPPC) at approximately 1721 and 1739 cm^{-1} reflect the structural inequivalence of the two acyl chains at the lipid interface region. A comparison of the Raman spectra of DPPC to a series of related lipid systems whose carbonyl groups exist in various lipid environments confirms the assignment of the higher and lower frequency components to the sn-1 and sn-2 chain carbonyl groups, respectively. In particular, frequencies for carbonyl groups from about 1727 to 1744 cm⁻¹ reflect a nearly straight chain or trans conformation about the C_2 - C_1 bond of the $C_3C_2C_1$ (=0)0 structural unit for the ester group of the sn-1 acyl chain. Frequencies from about 1716 to 1728 cm⁻¹ are characteristic of the carbonyl group for the sn-2 chain, which assumes an approximately gauche conformation about the C_2-C_1 bond (see Figure 1 for bond definitions). The samples used in addition to DPPC for spectral comparisons are (a) γ -palmitoyl-L- α -lysophosphatidylcholine (lysolecithin), whose single acyl chain exists in a nearly trans conformation about the C₂-C₁ bond, (b) 1,2,3-propanetriol trihexadecanoate (tripalmitin) whose 1- and 2-chains form a single, nearly straight chain unit, while the 3-chain bends analogously to the sn-2 chain of DPPC, and (c) 1,3-dipalmitoylglycerol (1,3-dipalmitin) whose $C_3C_2C_1(=0)O$ structural elements probably assume a nearly trans conformation about the C_2 - C_1 bond with one of the carbonyl groups being hydrogen bonded to the hydroxyl group of a neighboring glycerol unit.

Introduction

Among the vast array of physical techniques used to probe biological membrane processes, vibrational spectroscopy offers a potentially powerful method for assessing the contributions of bilayer lipids to the structural and dynamical properties of membrane assemblies. In particular, frequency, intensity, and linewidth changes of selected vibrational spectroscopic transitions are extremely sensitive to conformational alterations and packing rearrangements involving either the polar headgroups or the hydrocarbon chain segments of bilayer lipids.^{1,2} The advantages of using vibrational techniques to relate the effects of bilayer reorganizations to the dominant lipid-lipid and lipid-protein interactions which define membrane functions stem from several sources. First, the experimental accessibility of numerous spectroscopic transitions originating from various functional groups of the lipid provides information pertinent to localized regions of the bilayer. Second, the spectroscopic data are obtained in a noninvasive manner; that is, inferences regarding bilayer behavior are derived from molecular probes which do not intrinsically perturb the lipid environment.

Although correlations exist between the behavior of the vibrational spectra and the properties of the headgroups and acyl chains comprising the bilayer, spectroscopic probes of the lipid interface region are not as well characterized. The interface region, defined by the $-C_2C_1$ (= O)OC_{glycerol} structural unit in Figure 1, acts as a link between the polar and hydrophobic region of the molecule.³ Since the conformational inequivalence of the acyl chains of like-chain phosphatidylcholine and phosphatidylethanolamine crystals has been demonstrated by X-ray diffraction techniques,⁴⁻⁶ an understanding of the spectra reflecting the interface region is important for monitoring the behavior of the individual chains as a function, for example, of either temperature or intermolecular interactions. For the systems exhibiting this conformational inequivalence at the interface region, the sn-2 chain ini-

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