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Associative detachment reactions of negative ions with O_3

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Associative detachment reactions of the type $A^- + B \rightarrow AB + e$ have been studied recently[1] using flow-drift techniques. These experiments yield rate coefficients based on observations of the disappearance of the negative ion reagent as the concentration of B is increased. Neither electrons nor neutral products are directly monitored in such experiments. It is difficult to determine branching ratios for other negative-ion reaction channels from measurements of this type. An alternative method which has been utilized to study associative detachment processes employs an ion beam-collision chamber apparatus[2] in which electrons produced in the detachment reaction are directly observed. Other channels producing negative ions are not monitored, however. A third method, recently developed in our laboratory[3] is also based on ion beam-collision chamber experiments, but both negative ion products and electrons from the negative ion–neutral collision can be readily monitored. Cross sections for negative ion products are obtained as previously described,[4] while detached slow electrons are monitored by using SF_6 as a scavenger in the collision chamber, and measuring the resultant SF_6^- currents. The wide translational energy range accessible to the tandem mass spectrometer used for these experiments (0.3–180 eV in the laboratory system) facilitates studies of the energy dependences of the reactions. At the lowest energies employed (~0.3 eV), cross sections for associative detachment reactions determined by this method are quite reliable, since the direct reaction of most simple negative ions (for example, O^- or S^-) with SF_6 is endoergic, and the observed SF_6^- can be formed only by capture of the electrons released in the detachment reaction. At higher translational energies, contributions to the SF_6^- signal from the direct reaction become more important and must be subtracted from the total SF_6^- current to obtain a measure of the associative detachment channel.

In the present experiments, we have employed the SF_6 scavenger technique to observe associative detachment reactions of several negative ions with O_3 which have not previously been reported. Table I summarizes the reaction rate coefficients determined for these reactions. These rate coefficients k are related to the experimentally determined cross sections σ via the relation, $k = \sigma \bar{v}$, where $\bar{v}$ is the average incident ion velocity at the corresponding laboratory energy employed.

Of particular interest is the associative detachment reaction

$$S^- + O_3 \rightarrow SO_3 + e \quad , \qquad (1)$$

for which the rate approaches the gas kinetic collision rate. This reaction is highly exoergic, and apparently the reactants approach each other along attractive potential surfaces which lead into the autodetaching region. A fairly long-lived collision complex must be formed in order to permit the extensive rearrangement which is necessary for the sulfur atom insertion to occur. It is also interesting to note that one of the fastest associative detachment reactions previously observed,[1b,3] $O^- + SO_2 \rightarrow SO_3 + e$ yields the same final products as Reaction

TABLE I. Rate coefficients for various negative ion reactions with O_3.[a]

Reaction	10^{-10} cm^3/molecule · sec
$O^- + O_3 \rightarrow 2O_2 + e + 2.65$ eV[b]	3 ± 1[c]
$\rightarrow O + O_3^- + 0.7$ eV	2 ± 0.4[d]
$\rightarrow O_2^- + O_2 + 3.1$ eV	0.1 ± 0.05
$OH^- + O_3 \rightarrow O_2 + HO_2 + e - 0.16$ eV	< 0.01 (not observed)
$\rightarrow OH + O_3^- + 0.3$ eV	5 ± 0.2
$\rightarrow HO_2^- + O_2$	0.3 ± 0.1
$\rightarrow O_2^- + HO_2 + 0.28$ eV	0.1 ± 0.05
$S^- + O_3 \rightarrow SO_3 + e + 6.4$ eV	11 ± 2
$\rightarrow S + O_3^- + 0.1$ eV	0.9 ± 0.3
$\rightarrow SO^- + O_2 + 3.5$ eV	0.3 ± 0.1
$\rightarrow O_2^- + SO + 2.8$ eV	0.08
$\rightarrow SO_2 + O^- + 4.3$ eV	0.01
$\rightarrow SO_2^- + O + 3.9$ eV	0.02
$SH^- + O_3 \rightarrow (OH + SO_2) + e + 3.3$ eV	5.5 ± 1
$\rightarrow SH + O_3^- - 0.15$ eV	0.6 ± 0.3
$\rightarrow HSO^- + O_2$	1.0 ± 0.4
$\rightarrow SO^- + HO_2 + 1.5$ eV	0.2 ± 0.1
$\rightarrow SO + HO_2^-$	0.06
$\rightarrow SO_2^- + OH + 4.4$ eV	0.02
$\rightarrow SO_2 + OH^- + 5.1$ eV	0.01
$\rightarrow S^- + ?$	0.09
$\rightarrow O^- + ?$	0.01

[a] Measured with reactant ions of ~0.3 eV laboratory energy.

[b] Exoergicities were calculated using known heats of formation (Ref. 5) and electron affinities, [EA(O) = 1.462 eV; EA(OH) = 1.825 eV; EA(S) = 2.077 eV; EA(SH) = 2.319 eV, EA(O_2) = 0.44 eV; EA(SO) = 1.1 eV; EA(SO_2) = 1.097 eV, Refs. 6–12], and from the recently obtained electron affinity of ozone EA(O_3) = 2.15 ± 0.15 eV (Ref. 13).

[c] All associative detachment rate coefficients were determined relative to the rate, $k = 1.4 \times 10^{-10}$ cm^3/molecule · sec for the reaction $O^- + NO \rightarrow NO_2 + e$.

[d] All charge transfer and particle transfer rate coefficients were determined relative to the rate $k = 1.2 \times 10^{-9}$ cm^3/molecule · sec for the reaction $O^- + NO_2 \rightarrow NO_2^- + O$.

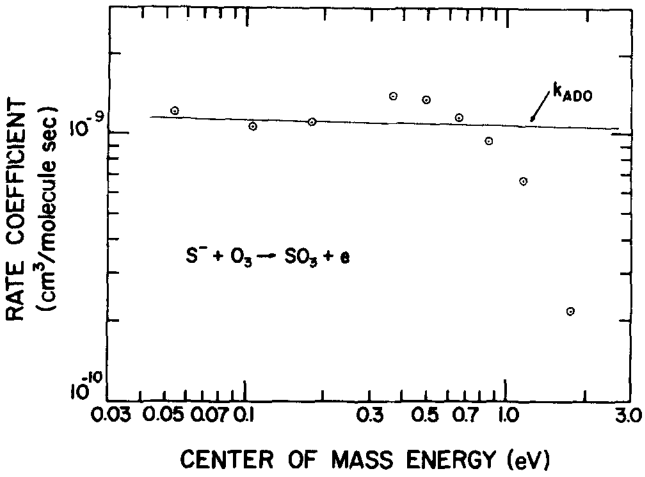

FIG. 1. Rate coefficients for $S^- + O_3 \rightarrow SO_3 + e$ as a function of relative kinetic energy. The predictions of the average dipole orientation (ADO) theory[15] are given. (A polarizability, $\alpha = 4 \times 10^{-24}$ cm³, was employed for ozone.[16])

(1). Apparently, both of these associative detachment reactions are quite rapid, in spite of the fact that more than three atoms are involved, because none of the alternative charge transfer or particle transfer channels is more exoergic.[14] The final products of Reaction (1) may however be SO_2 and O, since SO_3 carries away most of the reaction exoergicity as internal energy and is therefore likely to dissociate.

The rate coefficient for Reaction (1) as a function of relative kinetic energy has also been determined in the present study, as shown in Fig. 1. The decreasing rate with increasing energy is typical of that previously observed for other associative detachment reactions.[1]

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Dissociative electron attachment in nitrogen trifluoride

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The chemical physics of the gas nitrogen trifluoride is currently of interest owing to its applicability in the development of HF/DF chemical lasers and its use in the rare gas–halide laser systems.[1–8] Since these lasers are electron-beam or discharge initiated, the reaction of electrons with NF_3 is of particular interest.[9]

The rate constant for the dissociative attachment of thermal energy electrons (300–350 °K) to nitrogen trifluoride has been measured using a flowing afterglow technique described in a previous publication.[10] The rate constant obtained for the reaction

$$e^- + NF_3 \rightarrow F^- + \text{products} \qquad (1)$$

is $2.1 \pm 0.8 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹. This rate constant was obtained using a filament electron source, and with an argon buffer gas pressure of 0.8 torr.

The rate constant for thermal energy electron attachment in nitrogen trifluoride has previously been measured by Mothes *et al.*[11] using an electron cyclotron resonance technique. The current measurement agrees well with the value, 2.4×10^{-11} cm³ molecule^{-1} sec^{-1} at 300 °K, obtained by Mothes *et al.* In addition, the current research establishes the identity of the ionic attachment products.

The only product ion observed in the present study is