AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **89**, 273 (1988); doi: 10.1063/1.455522 View online: http://dx.doi.org/10.1063/1.455522 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v89/i1 Published by the American Institute of Physics.

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Reaction of aluminum cluster ions with oxygen and nitrous oxide: Energetics and dynamics of cluster oxidation

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(Received 10 February 1988; accepted 25 March 1988)

We report a study of the absolute cross sections, reaction threshold energies, and product branching ratios for interactions of aluminum cluster ions $(Al_n^+, n = 1-9)$ with O_2 and N_2O . Most of the reactions are observed to have collision energy thresholds which are attributed to activation barriers or bottlenecks. At collision energies above threshold, excergic oxidation of the cluster ions occurs, and the resulting energy release causes extensive fragmentation to yield a variety of product ions. Comparison of threshold behavior for different product channels suggests that in addition to the dominant oxidation reactions, the clusters undergo Al abstraction, O_2 -Al⁺ exchange, and collision induced dissociation.

I. INTRODUCTION

We have undertaken a series of studies examining the fragmentation and reactive scattering of small metal cluster ions. The objectives are to obtain measurements of sufficient detail to allow elucidation of cluster properties and direct determination of cluster reaction dynamics. Aluminum, boron, and aluminum-lithium alloys have been chosen as initial systems for study from considerations of technological relevance, experimental tractability, and because they are relatively tractable for ab initio theory. The availability of theoretical work has proven invaluable in understanding experimental results for species such as metal clusters for which direct experimental data on geometric and electronic structures is unavailable. On the other hand, high quality, detailed experimental data is needed for simple cluster systems to provide benchmarks for evaluating theoretical techniques.

In this paper we report a study of aluminum cluster ion oxidation by O_2 and N_2O , in which cross sections for all product channels were measured as a function of collision energy from 0.25 to 10.0 eV for cluster ions containing up to nine atoms. By examining the threshold behavior of the various reactions and considering the properties of the clusters and the neutral collision partners, a surprising wealth of mechanistic insight can be obtained. The results are compared with other experimental work on aluminum cluster ions, with experimental and theoretical studies of neutral aluminum clusters, and with oxidation chemistry of aluminum surfaces.

Several previous papers have provided information on the properties aluminum cluster ions which has been essential in the analysis of the present results. Hanley, Ruatta, and Anderson¹ and Jarrold, Bower, and Kraus² have used collision induced dissociation (CID) to probe stability and bonding in the cluster ions. Hanley, Ruatta, and Anderson measured the cross sections and branching ratios as a function of collision energy for clusters containing up to seven atoms. This allowed direct determination of the dissociation thresholds for all fragmentation processes. Relevant results are: Aluminum cluster ions are quite weakly bound-lowest dissociation thresholds range from 0.90 to 2.25 eV for clusters up to Al_7^+ . Stability generally increases with size as expected for compact geometries. Al₇⁺ appears to be particularly stable, which probably reflects the closing of an electronic shell at 20 electrons.³ Ionization potentials for small clusters appear to be higher than that of the aluminum atom. Jarrold et al. examined total CID cross sections and branching ratios at a single collision energy for cluster ions containing up to 26 atoms. They derived the relative stabilities of the cluster ions and a set of ionization potentials using a statistical-thermal model for the dissociation process. Their conclusions are consistent with ours, including the observation that Al_7^+ is anomalously stable. Jarrold and Bower⁴ also studied CID of $Al_n O^+$ and $Al_n O_2^+$. They observed that the dominant fragmentation process involves loss of Al₂O molecules, but did not determine the fragmentation threshold energies.

Both groups have also reported work on reactions of aluminum cluster ions with O_2 . Hanley, Ruatta, and Anderson⁵ reported preliminary results on the collision energy dependence of Al_{1-5}^+ reactions with several species including with O_2 , and more recently Ruatta, Hanley, and Anderson⁶ reported a study of reactions of Al_{1-8}^+ with O_2 . We found that all size cluster ions react with O_2 in a very excergic process. The energy release is sufficient to cause extensive fragmentation of the oxidized cluster ion, generating a variety of product ions. Surprisingly, these excergic ion-molecule reactions were observed to have activation barriers which depend strongly on cluster size. The barriers were attributed to the energy required to dissociate O_2 . At high collision energies CID of the weakly bound Al_n^+ reagent clusters is important and accounts for ~50% of the product signal.

Jarrold and Bower^{7,8} measured cross sections and product branching ratios for reactions of Al_{3-26}^+ with O₂ at 1.2 and 4.2 eV. They found that for reagent cluster ions larger than 12 atoms, there is a propensity to lose 4 aluminum atoms (presumably as $2 Al_2O$), while cluster ions in the range from 7 to 12 atoms tend to lose 5 aluminum atoms ($Al_2O + Al_3O$ or $2Al_2O + Al$). These product distributions tie in well with their CID results on $Al_n O_{1-2}^+$. Smaller cluster ions reacted to form a variety of product ions, with branching ratios in reasonable agreement with our measurements at the same energies. Their conclusions about the reaction mechanism are similar to ours: Oxidation of aluminum cluster ions by O_2 vields a highly excited $Al_{1}O_{2}^{+}$ complex, which then fragments to stable products. They did not observe the activation barriers for oxidation since the collision energies examined are too high for the cross sections to be strongly affected by the barriers. RRKM theory was used to estimate the dissociation lifetimes of the oxidized cluster ion complex, and they concluded that the statistical lifetimes are consistent with the time scale of their experiment. On the other hand, from consideration of the energetics and branching ratios, they conclude that partitioning of the reaction exoergicity to the dissociation products is not statistical. Instead the Al₂O products appear to carry away a large fraction of the energy. They also concluded that the oxidation chemistry of ionic aluminum clusters is different from that observed for the equivalent neutral clusters.

For the present paper we have attempted to unravel the oxidation dynamics of small aluminum cluster ions in more detail by extending our cluster size range, and analyzing the threshold behavior of each product channel. As an additional probe of the oxidation mechanism, we have carried out the first study of N_2O reactions with aluminum clusters. The results suggest that the reaction mechanism deduced by both groups is oversimplified, and that several reactions occur in addition to oxidation and CID. These conclusions are dictated by the threshold studies, and point out the importance of careful measurement of the collision energy dependence of reactions.

Reactions of neutral aluminum clusters with O_2 have been studied by Cox *et al.*,⁹ using a flow tube reactor and a laser vaporization source. Their results are given as relative rate constants for different size clusters under thermal conditions (~350-500 K) and high pressure. They report high reactivity for the atom and dimer, roughly an order of magnitude less reactivity for Al₃-Al₇, then reactivity increasing with size from Al₈ through Al₃₀. The chemistry observed is addition of O₂ to the intact cluster to yield Al_nO₂, except that Al and Al₂ are proposed to react with O₂ by aggregation to form Al₃O₂. The trend in neutral cluster rate constants is about what would be expected if the reactions have activation barriers which vary with cluster size similarly to those we observed⁶ for the ion reactions.

As cluster size increases, the chemistry should eventually approach that seen for aluminum surfaces. O_2 chemistry with clean aluminum has an extensive literature which has recently been reviewed by Batra and Kleinmann.¹⁰ O_2 chemisorbs strongly on aluminum, and though there have been some suggestions that a stable molecular precursor can be formed,¹¹ most evidence suggests that adsorbed O_2 is unstable with respect to dissociation. For example, Crowell, Chen, and Yates¹² observed dissociative chemisorption down to 122 K, and work by Hoffman *et al.*¹³ demonstrated that oxygen dissociatively adsorbs on aluminum (111) even at 30 K ($kT \cong 3$ meV). Clearly if there are barriers to the dissociation, they are very small. Once oxygen is dissociated,

migration to subsurface sites and formation of an oxide phase occur.

The interaction of nitrous oxide with clean aluminum surfaces has not received the attention given to the Al-O₂ system. Elev and Wilkinson¹⁴ and Hunt and Ritchie¹⁵ have studied adsorption of N₂O on evaporated aluminum films at mTorr pressures and temperatures between 195 and 683 K. Rapid chemisorption of N₂O and oxidation of the films were observed. Because both these studies were carried out under conditions where thick oxide films formed and at high background pressures, they give little insight into the interactions of N₂O with clean, unoxidized aluminum surfaces. The important observations were that oxidation is spontaneous, and that no nitrosyl or nitride products were observed. Recently Pitts et al.^{16,17} reported a study of N₂O interaction with clean aluminum films and polycrystalline surfaces in UHV. They found that N_2O adsorbs but does not react at room temperatures, contrary to the finding of the earlier work. They did observe that oxide formation can be stimulated by bombardment of the surface with an electron beam.

Compared to transition metals, aluminum is a tractable system for quantum chemistry computations. Upton has reported a study^{18,19} of aluminum clusters containing up to six atoms. More recently, Bauschlicher and co-workers^{20,21} reported similar work on Al₂-Al₆ and Al₁₃. The two sets of calculations are in reasonable agreement with each other, and are largely consistent with experiment, however, lack of detailed experiments on neutral clusters limits the comparisons which can be made. Both studies found that the clusters have compact, high coordinate geometries, although there is some disagreement regarding the most stable structures. For the larger clusters there are many low energy structures. This suggests that in experiments, several isomers may be present for each reagent cluster, but that they are likely to have similar properties. As expected, the clusters have many low energy electronic states. Binding energies are calculated to be on the order of 1 eV/atom, which is consistent with the dissociation thresholds we observe for the cation clusters.¹ Ionization potentials were observed to generally increase with cluster size, ¹⁸ also consistent with the rather crude experimental meaurements.^{1,2,9}

II. EXPERIMENTAL

A detailed description of our metal cluster ion beam apparatus has recently been published¹ and the experimental method will only be summarized here. Positively charged aluminum cluster ions are formed by sputtering of a high purity foil (Puratronics) with a 12 keV beam of argon atoms and ions. The sputtering process produces a size distribution of aluminum cluster ions that is largest for Al⁺ and decreases roughly monotonically with increasing cluster size. In order to quench excited states of the clusters which may have been formed in the sputtering process, the cluster ions are injected into the maze-like channel of a specially designed radiofrequency ion trap where they undergo about 5000 collisions with a helium buffer gas. The cooled cluster ions are injected into a homemade Wien-type mass filter where the size of interest is selected. The cluster beam is then decelerated and injected into the first of a pair of rf octapole ion guides. In the second guide the collision energy is set and the cluster ions are passed through a gas cell which surrounds the guide, into which 1.0×10^{-4} Torr of oxygen or nitrous oxide reactant gas flows. This pressure was found to be low enough to insure that reactions take place under single collision conditions. The temperature of the gas in the reaction cell is estimated to be ~350 K. Product ions and unreacted cluster ions are collected by the ion guide, accelerated into a quadrupole mass analyzer, mass analyzed, and counted.

Reaction cross sections are calculated²² from measurements of product signal when the scattering cell is filled with the reagent gas and when the identical gas flow is diverted into the background of the vacuum chamber. To check the calibration of our absolute cross section scale we have studied the reactions $Al^+(O_2,O)AlO^+$ and $Ar^+(D_2,D)ArD^+$ and compared with previous measurements (Refs. 23 and 24, respectively).

The major source of error in the cross sections is the uncertainty in the collection/detection efficiency for the reagent and product ions. Quadrupole transmission is the worst problem, and is particularly serious for systems like these in which the reagent and product ions have dissimilar masses, and where light product ions may be produced with substantial recoil energy. The use of ion guides helps in collection of the scattered product ions, but we still cannot ensure uniform quadrupole transmission. We therefore estimate that our cross sections could be in error by as much as a factor of 2, particularly for channels where the product and reagent masses are dissimilar. This does not affect comparison of equivalent product cross sections for different size reagent clusters. We are currently constructing a new cluster instrument using large sector mass analyzers which should ameliorate this problem.



FIG. 1. Cross sections for reaction of A1 $^+$ with O2 and N2O. The only product in both cases is AlO $^+.$

III. RESULTS

The cross sections for reaction of Al⁺ with O₂ and N₂O to form AlO⁺ are plotted as a function of collision energy in Fig. 1. Energetics calculated from published thermochemical data²⁵⁻²⁷ show the reaction with O₂ to be ~3.4 eV endoergic, while the reaction with N₂O is nearly thermoneutral. The experimental threshold observed for the O₂ reaction is quite close to the thermochemical value, and our results for both reactions are in good agreement with previous measurements.^{23,28} The fact that the threshold for the N₂O reaction is significantly higher than the thermodynamic limit could be due to spin conservation either forcing reaction to form excited AlO^{+ 1}\Pi ($T_e \approx 0.25 \text{ eV}$),²⁹ or simply causing a barrier to formation of ground state products. Since the Al⁺ reactions have been discussed in detail previously, we will not consider them further.

The integral cross sections for products observed in reaction of Al_n^+ (n = 2-9) with oxygen at collision energies from 0.25 to 10 eV are plotted in Figs. 2-4. The analogous cross sections for reactions with N_2O are plotted in Figs. 5 and 6. For the sake of clarity only the major product channels are plotted; in each case these account for > 95% of the total reaction cross section. For the reactions with oxygen, the data shown are the average of four different runs done over a five month period. The consistency of the individual runs was good. The nitrous oxide plots are the average of two data sets. Data quality for Al_8^+ and Al_9^+ is lower because there is a sharp drop in reagent cluster ion intensity above the heptamer. In particular there is a problem with background in the Al_{n-1}^+ signal for the larger reagent clusters. The cross sections for these channels have been estimated by background subtraction and are shown in the figures as dashed curves. To aid comparison, all cross sections are plotted on a 5 $Å^2$ scale, however, this puts the cross section for $Al_8^+ + O_2 \rightarrow Al^+$ off scale. This channel is anomalous and continues to increase almost linearly with collision energy up to 13.5 $Å^2$ at 10 eV.

There are several obvious features of the data. The cross sections for reaction with oxygen are generally larger than those with N₂O. Reactions with both O₂ and N₂O result in extensive fragmentation of the cluster framework. O₂ reactions tend to produce a greater variety of product ions, and a much greater fraction of oxide product ions. Branching ratios for the different types of products observed at 1.0 and 4.0 eV are given in Tables I and II.

Figures 2-6 show that with the exception of Al_2^+ reacting with O_2 , all cluster ion reaction cross sections decrease at low collision energies to varying degrees. This suggests the existence of energy thresholds for the reactions, the nature and magnitudes of which are discussed in detail below. Note that while quantitative estimates of the threshold energies can only be obtained by modeling the data, our discussion and conclusions are based primarily on trends in threshold behavior of the raw data.

One very important point which is not obvious from the raw data is that for each reagent cluster ion, there is a set of product channels which have nearly identical threshold behavior, and in most cases, at least one channel which is quite





distinct. To illustrate, in Fig. 7 we have replotted the product cross sections for Al₆⁺ reacting with O₂ and N₂O, and scaled the cross sections so that they coincide at a single collision energy just above threshold (0.75 eV of O₂ and 1.5 eV for N_2O). Note that in the O_2 reactions the threshold behavior for the Al⁺, Al₂⁺, Al₃⁺, Al₂O⁺, and possibly Al₄⁺ products is identical. In contrast the threshold for Al_{n-1}^+ (Al_5^+) production is higher, and since its cross section is zero at the scaling energy it was left unscaled. For reaction with N_2O_1 again there is a set of channels with nearly identical behavior, while the Al_{n-1}^+ channel appears to have substantially different threshold behavior (and was not scaled). This pattern appears to hold for all reagent cluster ions larger than Al_3^+ , although for the larger clusters the background in the Al_{n-1}^+ signal causes some uncertainty in its threshold behavior.

IV. DISCUSSION

Based on these results together with related CID work on pure^{1,2} and oxidized⁴ aluminum cluster ions, and electronic structure calculations on the neutral clusters, $^{18-21}$ we have developed a "working model" for the mechanisms and energetics involved in aluminum cluster ion oxidation. While the accuracy of this model is by no means proven, it provides a useful framework for thinking about the problem. We first outline the model for reaction with O₂, followed by a detailed discussion of the data and its relation to the proposed mechanisms. The analogous discussion is then presented for oxidation by N₂O. The final section of the paper discusses the magnitude and nature of the thresholds observed for the various cluster ion reactions, and deals with cluster size dependent trends observed in the chemistry and their relation to cluster physical properties.

A. Reaction with O₂

Our data suggest that there are four principle processes which occur in collisions between Al_n^+ (n > 2) and O_2 .





1. "Oxidative fragmentation"

As detailed below, for all size reagent cluster ions there are at least several exoergic oxidation reactions, and these appear to be the dominant processes at low collision energies. The collision energy dependence of the cross sections for oxidation products suggests the existence of cluster size dependent bottlenecks to reaction. The energy required to drive oxidation increases with increasing reagent cluster size from the dimer (no threshold) up to Al_7^+ , then decreases with size. Since the O_2 bond is by far the strongest in the cluster- O_2 system, and since O_2 dissociation is obviously necessary in the oxidation process, it seems reasonable to attribute the observed bottlenecks, at least in a formal sense, to activation barriers for breaking the O_2 bond. This issue is discussed in detail below.

The process of separating the oxygen atoms and binding them to multiple aluminum atoms is energetically very favorable (> 10 eV). Since aluminum cluster ions are quite weakly bound (average stability $\sim 1.5 \text{ eV}^1$), extensive fragmentation of the oxidized intermediate complex occurs and produces a variety of products. As detailed below, the thermochemistry of different product channels resulting from oxidative fragmentation varies widely, and it might be expected that different products would have different collision energy dependence due to competition between channels. While this is true at high energies, one of the more important findings in this study is that all the oxidation channels have nearly identical threshold behavior (Fig. 7). This is consistent with an oxidation mechanism in which a bottleneck hinders formation of the $Al_n O_2^+$ oxidized intermediate which subsequently fragments to the observed product channels. The bottleneck is thus the same for all reactions which involve the oxidized intermediate, and they all have very similar collision energy dependence. Competition between different product channels does appear to be important in controlling the product branching ratios at energies above threshold.



FIG. 4. Cross sections for reaction of Al_9^+ with O_2 . Key to products is $1 = Al^+$, $2 = Al_2^+$, $3 = Al_3^+$, ..., crossed circle = Al_2O^+ , diamond = Al_3O^+ , and triangle = Al_7O .

FIG. 5. Cross sections for reaction of Al_2^+ through Al_5^+ with N_2O . Key to products is $1 = Al^+$, $2 = Al_2^+$, $3 = Al_3^+$, ..., star = AlO^+ , and crossed circle = Al_2O^+ .

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FIG. 6. Cross sections for reaction of Al_6^+ through Al_9^+ with N₂O. Key to products is $1 = Al^+$, $2 = Al_2^+$, $3 = Al_3^+$, Dashed curve is estimated cross section for Al_{n-1}^+ .

TABLE I. Branching ratios (in %) for $Al_n^+ + O_2 \rightarrow$ selected products.

TABLE II. Branching ratios (in %) for $Al_n^+ + N_2O \rightarrow$ selected products.

Parent cluster		Total oxides	Al+	Al_{n-1}^{+}	Total other	Parent cluster	Parent Total cluster oxides		Al_{n-1}^{+}	Total other
Al ₂ ⁺						Al,+			, <u></u> ,	
	1 eV	43.5	56.5	56.5		1 eV	24.4	75.6	75.6	•••
	4 eV	11.4	88.6	88.6	•••	4 eV	5.9	94.1	94.1	
Al_3^+						Al ₁ ⁺				
	l eV	24.9	47.5	27.6	•••	1 eV	47.3	19.3	33.4	
	4 eV	19.8	30.3	49.8	•••	4 eV	15.2	24.5	60.3	
Al ₄ +						AL ⁺		2110	00.5	
	l eV	39.0	33.4	10.0	17.6	1 eV	17.2	52.4	2.0	28.4
	4 eV	10.5	35.6	33.1	20.8	4 eV	10.6	40.2	2.0	19.9
Al ₅ +						Al.+	10.0	10.2	27.2	17.7
	1 eV	21.5	47.6	3.0	27.9	1 eV	~1	29.6	~1	70.4
	4 eV	14.1	33.7	22.1	30.0	4 eV	<1	44.8	05	45.6
Al ₆ ⁺						AL ⁺		44.0).5	43.0
-	1 eV	35.9	31.6	0.8	31.7	1 eV	~1	27.6	3.4	69.0
	4 eV	13.6	33.0	17.8	35.5	4 eV	<1	31.0	10.0	59.0
Al_7^+						A1.+		51.0	10.0	59.0
,	1 eV	8.1	30.6	0.0	61.2	1 eV	~1	0.1	-1	00.0
	4 eV	11.9	34.8	8.5	44.8	4 eV		20.0	< 1 0 8	90.9 70.2
Al_8^+						A1.+	<.	20.0	2.0	70.2
•	1 eV	2.0	8.8	56.0	33.2	1 eV	~1	15.2	0.0	94.9
	4 eV	7.2	24.2	43.6	25.0	4 eV		24.2	10.7	56 1
Al,+						A1.+		27.2	19.7	50.1
	1 eV	26.9	16.6	•••	56.5	1 øV	<i>.</i> 1	12.4		96.6
	4 eV	23.3	23.5		53.2	1 EV 4 eV	<1	18.9		81 1

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FIG. 7. Cross sections for reactions of Al_6^+ with O_2 and N_2O , scaled so that all cross sections have identical magnitude at a single energy just above the lowest observed threshold. The Al_5^+ cross sections which have very different threshold behavior have been left unscaled. Key to products is $1 = Al^+$, $2 = Al_2^+$, $3 = Al_3^+$, ..., and crossed circle = Al_2O^+ .

2. "Collision induced dissociation (CID)"

At high collision energies it is clear that many collisions are nonreactive but transfer sufficient energy to the reagent cluster ion to cause fragmentation to Al_{n-x}^{+} . We have studied CID of aluminum cluster ions with xenon, ¹ argon, ⁵ and nitrogen³⁰ target gases, and the thresholds and branching ratios are well characterized under conditions identical to those used in the present study. The lowest energy CID thresholds range from 0.9 eV for small cluster ions, to 2.25 eV for Al_7^{+} . Nearly all the product channels observed in the present study turn on at energies well below the equivalent CID thresholds. From comparison with CID cross sections (Ref. 1, Fig. 2), it is clear that chemical processes dominate in the low collision energy regime. The comparison also suggests that about half of the product signal at collision energies above 5 eV is due to CID.

3. "Aluminum atom abstraction"

An important reaction channel is production of Al_{n-1}^+ . At high collision energies Al_{n-1}^+ can be produced by simple CID, however, the thresholds observed in collisions with O_2 are 1 to 1.5 eV below the corresponding CID thresholds.^{1,5,30} The only energetically possible reaction is

$$\mathrm{Al}_n^+ + \mathrm{O}_2 \rightarrow \mathrm{Al}_{n-1}^+ + \mathrm{AlO}_2,$$

which is ~ 3 eV exoergic depending on reagent cluster size. Previous studies categorized this reaction as one of those resulting from the oxidative fragmentation mechanism, and indeed the calculated thermochemistry is in the same range as typical oxidation reactions. Figure 7 shows, however, that the threshold behavior of this channel is clearly different from that of the oxidation channels, suggesting that Al_{n-1}^{+} production does not involve the same intermediate that appears to be common to all the oxidative fragmentation products.

We suggest a mechanism in which an O_2 molecule collides with the cluster ion with sufficient energy to drive oxidation. For some reason (incorrect collision geometry?) the O_2 does not dissociate, and instead recoils from the cluster ion, abstracting an aluminum atom in the process. It is not surprising that AI_{n-1}^+ is not produced by oxidative fragmentation. In oxidation, the O₂ molecule dissociates and the O atoms become strongly bound to multiple Al atoms. It is then energetically unfavorable to recombine the O atoms on a single center for elimination of AlO₂.

4. "Molecular adsorption/exchange"

Since O_2 is a triplet molecule and the cluster ions have low-lying unfilled or partially filled orbitals, the binding of O_2 to the cluster ion should be quite strong. On bulk aluminum, this molecular adsorbed state is unstable with respect to O_2 dissociation followed by surface oxidation. For aluminum cluster ions larger than the dimer, there are bottlenecks which inhibit the oxidation reaction at low collision energies. In the case of the Al_3^+ reagent cluster there appears to be an exchange reaction driven by the molecular binding, and Al^+ displacement is observed with no activation energy. For the larger (and more strongly bound) reagent cluster ions this process is not observed, nor do we see it in collisions with closed shell reagents.

To show how the experimental data has lead to the proposed mechanisms, it is necessary to examine the individual reactions in some detail. Using our CID threshold data¹ and thermochemical data from the literature^{25,26,31} we can estimate the energetics for some of the cluster ion reactions. Especially for the larger reagent cluster ions, much of the thermochemistry is unknown or uncertain. The important point is that for all the Al_n^+ (n > 1) reagent cluster ions, there are exoergic oxidation channels.

The dimer and to some extent the trimer react differently from the larger cluster ions. This is not surprising since their stabilities, electronic structures, and density of internal states are very different from large clusters. For the dimer ion reaction, the Al⁺ and Al₂O⁺ production channels have cross sections which peak at low collision energy and fall off rapidly as the energy is increased. The Al₂O⁺ cross section continues to fall off as is typical for exoergic ion-molecule reactions, while the Al⁺ channel increases above $\sim 1 \text{ eV}$ and is nearly energy independent above 3 eV. The most likely reactions resulting in these products and their energetics are summarized below (energies given in eV—exoergic reactions shown as negative numbers):

$$Al_2^+ + O_2 \rightarrow Al_2O^+ + O \quad (-3.18),$$
 (1a)

$$Al_2^+ + O_2 \rightarrow Al^+ + AlO_2 \quad (\sim -4),$$
 (1b)

$$Al_2^+ + O_2 \rightarrow Al^+ + AlO + O \quad (+0.79),$$
 (1c)

$$Al_2^+ + O_2 \rightarrow Al^+ + Al + O_2 \quad (+0.90).$$
 (1d)

At low collision energies Al^+ must be due to formation of AlO_2 via exoergic process (1b) with a cross section that decreases rapidly with increasing collision energy, while at higher energies the endoergic processes (1c) and (1d) (CID) dominate.

AlO⁺ is observed as a minor channel with a small energy threshold. The energetics for this product channel are

$$Al_{2}^{+} + O_{2} \rightarrow AlO^{+} + AlO \quad (-0.97),$$
 (2a)

$$Al_2^+ + O_2 \rightarrow AlO^+ + Al + O \quad (+4.3).$$
 (2b)

The apparent threshold for reaction (2a) at low collision energies may be due to competition with the major, more exoergic product channels, or perhaps to a barrier for this reaction. The onset of reaction (2b) results in a small increase in the AlO⁺ cross section at high collision energy. Reactions (2b) and (1c) can be thought of as involving formation of Al_2O^+ [reaction (1a)] with internal energy high enough to cause further fragmentation.

For reaction of aluminum trimer cation with oxygen there are three main ionic products:

$$Al_{3}^{+} + O_{2} \rightarrow Al_{2}O^{+} + AlO \quad (-6.9),$$
 (3a)

$$Al_3^+ + O_2 \rightarrow Al_2O^+ + Al + O \quad (-1.7),$$
 (3b)

$$Al_3^+ + O_2 \rightarrow Al_2^+ + AlO_2 \quad (\sim -4),$$
 (4a)

$$Al_{3}^{+} + O_{2} \rightarrow Al_{2}^{+} + Al + O_{2} \quad (+1.12), \qquad (46)$$

$$Al_3^+ + O_2 \rightarrow Al_2^+ + AlO + O (+1.01),$$
 (4c)

$$Al_3^+ + O_2 \rightarrow Al^+ + Al_2O_2 \quad (\sim -9.2),$$
 (5a)

$$Al_3^+ + O_2 \rightarrow Al^+ + Al_2O + O \quad (-3.4),$$
 (5b)

$$Al_3^+ + O_2 \rightarrow Al^+ + 2AlO \quad (-3.4),$$
 (5c)

$$Al_3^+ + O_2 \rightarrow Al^+ + Al_2 + O_2 \quad (+0.9).$$
 (5d)

Since the three major products can all be produced at low collision energy by exoergic reactions, it is interesting to compare the threshold behavior of the cross sections. Al_2^+ and Al_2O^+ cross sections both decrease at low collision energies—evidence for a barrier or bottleneck for these oxidation reactions. The Al^+ production cross section is clearly quite different, showing little evidence of a bottleneck. We suggest that the source of Al^+ at very low collision energies is exchanged with O_2 driven by the strong interaction of molecular oxygen with aluminum cluster ions:

$$Al_{3}^{+} + O_{2} \rightarrow [Al_{3} - O_{2}]^{+} \rightarrow Al^{+} + Al_{2} - O_{2}.$$
 (5e)

Since Al_3^+ is quite weakly bound (0.90 eV¹), it seems reasonable that triplet O₂ can displace Al⁺, particularly if Al₂ is left in its triplet ground state.³² Examination of Figs. 2-4 shows that this production of Al⁺ with no bottleneck does not occur with the larger, more strongly bound reagent clus-

ter ions. As the collision energy increases, presumably the oxidation reactions (5a), (5b), and (5c) turn on as sources for Al^+ .

At collision energies above $\sim 1 \text{ eV}$ simple collision induced dissociation [reactions (4b) and (5d)] is possible. In addition, excergic oxidation products such as Al_2O^+ tend to be unstable at high collision energies and can dissociate, causing the drop in the oxide product ion cross sections and contributing to a rise in the cross sections for Al^+ , Al_2^+ , and AlO⁺. It is interesting to note that in CID of Al_3^+ with nitrogen,³⁰ argon,⁵ and xenon¹ we observe Al_2^+ and Al^+ at energies above $\sim 2 \text{ eV}$ in a roughly 4:1 ratio, while for larger reagent cluster ions the Al⁺ channel always dominates. This branching ratio inversion is believed to result because spin conservation forbids production of the ground state Al^+ + triplet Al_2 channel. In collisions with O_2 and N_2O_2 , the trimer ion is again unique in having an inverted $Al^+:Al_{n-1}^+$ ratio, suggesting that CID is a major mechanism at high energies.

For the tetramer and larger cluster ions, it becomes increasingly difficult to determine the detailed energetics of the reactions responsible for the observed product ions. This is partly because little is known about the thermochemistry of polyatomic aluminum oxide molecules, and partly because a large number of different reactions can generate a given ionic product. For the tetramer then, we list only the most obvious reactions for each observed product ion.

The major reactions in order of decreasing importance at low energies are

$$Al_4^+ + O_2 \rightarrow Al_2O^+ + Al_2O^- (\sim -10),$$
 (6a)

$$Al_4^+ + O_2 \rightarrow Al_2O^+ + AlO + Al \quad (\sim -6.5), \quad (6b)$$

$$Al_4^+ + O_2 \rightarrow Al_2O^+ + Al_2 + O \quad (\sim -2.5),$$
 (6c)

$$AI_4^+ + O_2 \rightarrow AI^+ + AI_2O + AIO \quad (\sim -7),$$
 (7a)

$$Al_4^+ + O_2 \rightarrow Al^+ + 2AlO + Al \quad (\sim -2),$$
 (7b)

$$AI_4^+ + O_2 \rightarrow AI^+ + AI_3 + O_2 \quad (+0.85),$$
 (7c)

$$AI_{4}^{+} + O_{2} \rightarrow AI_{2}^{+} + AI_{2}O + O \quad (\sim -2.5), \quad (8a)$$

$$AI_4^+ + O_2 \rightarrow AI_2^+ + 2AIO \quad (\sim -2.5),$$
 (8b)

$$Al_4^+ + O_2 \rightarrow Al_2^+ + Al_2 + O_2 \quad (+2.55),$$
 (8c)

$$Al_4^+ + O_2 \rightarrow Al_3^+ + AlO_2 \quad (\sim -3),$$
 (9a)

$$Al_4^+ + O_2 \rightarrow Al_3^+ + Al + O_2 \quad (+2.03).$$
 (9b)

Reaction (6) is the dominant channel at low collision energies, which is consistent with the observation in this study and those of Jarrold and co-workers^{4,8} that Al_2O is a particularly abundant product of aluminum cluster ion oxidation and in CID of aluminum oxide cluster ions. Al_2O^+ also appears to be favored, partly because it is a stable product, but also because for an oxide, it has a low IP (7.7 eV compared to 9.5 eV for AlO^+).²⁶ Reactions (6b) and (6c) [(7a) and (8a)] can be thought of as reaction (6a) in which the Al_2O (Al_2O^+) product fragments are due to excess internal energy.

Al⁺ production is also a major channel at low collision energies. The fact that its threshold behavior is similar to that of the Al₂O⁺ channel suggests that the primary source of Al⁺ at low energies is oxidative fragmentation (7a) and (7b). Unlike Al_2O^+ , the Al^+ cross section remains high as collision energy is increased, partly because of fragmentation of larger oxidation product ions such as Al_2O^+ , and partly from nonreactive CID (7c). Al^+ is the dominant product in CID of the tetramer ion with inert targets as well.¹

 Al_2^+ can form via exoergic oxidative processes and also via CID at collision energies above 2.55 eV. The threshold behavior for this channel is similar to that of Al^+ and Al_2O^+ , suggesting that at low energies all three products result from the oxidative fragmentation mechanism. As with Al^+ , the Al_2^+ cross section remains large at high collision energies due to CID and to fragmentation of Al_2O^+ products.

The only product channel with significantly different threshold behavior is Al_3^+ . This product can form via CID (9b) only at collision energies above 2 eV, thus the low energy component must be due to reaction (9a) which is our proposed aluminum atom abstraction mechanism.

For the larger reagent cluster ions the basic trends continue. In each case there are a number of product channels which have similar threshold behavior, suggesting that a common mechanism is involved. These we classify as oxidative fragmentation. Cross sections for oxide products such as Al_2O^+ fall off at high collision energies, while cross sections for products such as Al^+ , Al_2^+ , etc., remain high because additional channels such as CID and fragmentation of larger oxidation products turn on at high energies.

In each case the aluminum atom abstraction reaction

$$Al_n^+ + O_2 \rightarrow Al_{n-1}^+ + AlO_2$$

is observed with a threshold significantly higher than seen for the oxidative fragmentation channels, but well below the threshold for CID. At high collision energies CID appears to account for $\sim 50\%$ of the product signal.

For reagent cluster ions larger than Al_6^+ there are product channels which are not clearly assigned to one of the mechanisms proposed above. For example, in the case of Al_7^+ , the Al^+ , Al_2^+ , and Al_3^+ channels are dominant and clearly have identical threshold behavior ("oxidative fragmentation"), while the Al_6^+ channel has a higher threshold ("abstraction"). Al_2O^+ , Al_4^+ , and Al_5^+ are minor channels which have much broader, ill defined thresholds which appear to lie between the two extremes. The origin of these products is unclear, but probably involves a combination of oxidation at low collision energies and CID at high energies. That our oversimplified model fails to explain details at this level is not surprising.

B. Reaction with N₂O

There are several properties of N_2O which might be expected to result in different chemistry with aluminum cluster ions as compared with O_2 . There is obviously the possibility of reactions to form nitrides or nitrosyl products. No nitrogen containing product ions were observed in these experiments, and in a separate study³⁰ we found that small aluminum cluster ions do not react appreciably with N_2 except by simple CID. It appears that in reaction with aluminum cluster ions, N_2O is essentially a carrier for an oxygen

atom. For oxidation reactions, the single O atom in N_2O results in lower exothermicity; 3–7 eV compared to 5–10 eV for O_2 . This is still large compared to the bond energies in the cluster ions.

The electronic ground state of N₂O is closed shell $({}^{1}\Sigma^{+})^{27(a)}$ while O₂ is a biradical $({}^{3}\Sigma_{g}^{-})^{.25}$ The dissociation energies of N₂O to ground state products $[D(N_2-O) \cong 1.7 \text{ eV}; D(N-NO) \cong 4.93 \text{ eV}]^{27}$ are both smaller than that of O₂ $(5.115 \text{ eV})^{.25}$ however, the lowest dissociation channel (to O ${}^{3}P$) is spin forbidden. The energy for dissociation to N₂ and O ${}^{1}D$ (~3.66 eV) is still less than the O₂ bond energy. It seems likely that in reactions with the aluminum cluster ions, spin restrictions will be relaxed, allowing formation of products correlating to O ${}^{3}P$. Even if this is not the case, most oxidation reactions are still exoergic.

Our data is consistent with a reaction mechanism for N_2O in which the same four basic processes are important that were proposed to explain the O_2 results.

1. Oxidative fragmentation

As for O_2 , the main chemistry appears to be oxidation followed by fragmentation of the oxidized cluster ion to yield a distribution of product ions. The oxidation reactions have collision energy thresholds for all size reagent cluster ions (including the dimer). For a given reagent cluster size, the threshold behavior of the different oxidation product channels is similar. It seems likely that the origin of the thresholds is again (at least formally) the energy required to dissociate the oxidizer (N₂O). The product distributions are dominated by bare aluminum fragments (Al_x⁺). That these are not entirely due to CID is clear from comparison of the thresholds and branching ratios with those found for CID with Xe,¹ Ar,⁵ or N₂.³⁰

2. Collision induced dissociation

At high collision energies, nonreactive fragmentation of the weakly bound reagent cluster ions is important. From comparison of product distributions as a function of collision energy with those obtained using inert targets^{1,5} we estimate that CID accounts for ~50% of the observed fragments. CID of the N₂O without fragmentation of the cluster ion is also likely, however, we are not sensitive to processes where the ion mass is invariant.

3. Aluminum atom abstraction

Reaction to produce Al_{n-1}^+ proceeds by a mechanism with different threshold behavior than that of the oxidation channels (Fig. 7). As in the case of O₂ we propose that this reaction may be thought of as a process in which N₂O collides with the cluster, and abstracts a single atom. For N₂O, unlike O₂, it is also possible for oxidative fragmentation to produce the n - 1 fragment ion; this produces a low energy tail extending down to the oxidative fragmentation threshold (see Al₅⁺ channel in Fig. 7).

4. Molecular adsorption

Since N_2O is a singlet, the interaction energy of the intact molecule with aluminum cluster ions is expected to be smaller than in the case of O_2 . Thus although there is probably a reasonably large $Al_n - N_2O$ binding energy, exchange reactions such as reaction (5e) are not observed for N_2O .

To show how the experimental data has lead to the proposed model, we again examine the individual reactions in some detail. Energies are given in eV, and negative values denote excoergic channels. Where the thermochemistry^{25-27,31} is known, we give the reaction energy first assuming spin exchange allows formation of products correlating to O (³P), followed by the energy assuming only O (¹D) is involved.

For the reaction of the dimer ion with N_2O , the three observed channels are

$$Al_2^+ + N_2O \rightarrow Al_2O^+ + N_2 \quad (-6.6),$$
 (10)

$$Al_2^+ + N_2O \rightarrow Al^+ + AlO + N_2$$
 (-2.7; +0.2),
(11a)

$$Al_2^+ + N_2O \rightarrow Al^+ + Al + N_2O$$
 (+0.9), (11b)

$$Al_2^+ + N_2O \rightarrow AlO^+ + Al + N_2 \quad (+0.8).$$
 (12)

The first two reactions are observed to have similar threshold behavior, suggesting that both result from excergic oxidation at low energies. The observation that Al_2O^+ is a minor oxidation product despite the fact that it is energetically most favorable, suggests that little of the reaction excergicity is partitioned to the N₂ product, making it unlikely that Al_2O^+ can be formed which is stable with respect to dissociation to $Al^+ + AlO$ [reaction (11a)] or $AlO^+ + Al$ [reaction (12)]. At high collision energies the branching ratios suggest that Al^+ production via CID (11b) is a major channel.

All three products observed in reaction of Al_3^+ with N₂O can be produced by exoergic reactions:

$$Al_{3}^{+} + N_{2}O \rightarrow Al^{+} + N_{2} + Al_{2}O \quad (-7.2), \quad (13a)$$

$$Al_{3}^{+} + N_{2}O \rightarrow Al^{+} + N_{2} + AlO + Al \quad (-1.5),$$

(13b)
$$Al_{2}^{+} + N_{2}O \rightarrow Al_{2}^{+} + N_{2} + AlO$$
 (-2.4/-0.3),

$$H_3 + H_2 O \rightarrow A I_2 + H_2 + A O (-2.4/-0.3),$$
 (14)

$$Al_3^+ + N_2O \rightarrow Al_2O^+ + N_2 + Al$$
 (-5.5). (15)

Within experimental error, all three channels have identical threshold behavior, indicating that a common oxidative fragmentation mechanism is responsible. Unlike the larger clusters, there does not appear to be anything special about the threshold for the Al_{n-1}^+ (dimer) channel to suggest an abstraction mechanism, however, this may simply reflect a dominant contribution to the Al_2^+ signal from the oxidation reaction. The large branching ratio for Al_2O^+ at low energies (unlike the situation for reaction of Al_2^+) presumably results from there being three products to absorb the reaction exoergicity. Above 2 eV the Al_2O^+ channel drops off as decomposition to smaller fragments becomes more likely. At energies above 1 eV, CID to produce both Al^+ and Al_2^+ is possible, and the branching ratios suggest that ~60% of the signal at 10 eV is CID.

Reactions of all the larger cluster ions are quite similar. The ionic products consist of broad distributions of pure aluminum cluster fragments, with no oxide ion products. All observed products can be formed via exoergic reactions, yet all channels have collision energy thresholds. For each reagent cluster ion there is a set of product channels having identical threshold behavior suggesting they all result from a common mechanism (oxidative fragmentation). In most cases the Al_{n-1}^+ channel has a distinctly higher threshold which we attribute to an abstraction reaction although there may be a low energy tail due to oxidative fragmentation. Collision induced dissociation of the reagent cluster ion contributes to all the product channels at high collision energies.

A noticeable trend in the reactions is the progressively larger branching ratio for production of Al_{n-2}^+ (+ Al_2O) as cluster size increases. This is consistent with the observation by Jarrold *et al.*⁸ that loss of two Al_2O molecules is the preferred channel for reaction of large aluminum cluster ions with O₂, and again points to the similarity in oxidation mechanisms for O₂ and N₂O. The reason there is not a strong propensity for Al_{n-4}^+ production in reactions of small Al_n^+ with O₂, is simply that the small clusters cannot dissipate the reaction exoergicity and undergo more extensive fragmentation.

C. Oxidation thresholds

In a beam-gas experiment like ours, both the ion beam energy distribution and thermal motion of the target gas cause a spread about the nominal collision energy, and this distorts the experimental threshold behavior. In our experiments the ion beam energy spread is 0.25 eV FWHM, and the neutral gas temperature is ~ 350 K. In the threshold region, the collision energy broadening (which depends on reagent cluster size) is mainly due to ion beam spread and has FWHM of ~ 0.35 eV. We can correct the data for this broadening and estimate "true" threshold energies using a conventional deconvolution procedure discussed in detail previously.^{1,33} Essentially we guess the energy dependence of the true cross section, convolute with the known broadening functions, compare to experiment, and iterate until we get good agreement. This procedure is straightforward for reactions with experimental thresholds within the accessible collision energy range (i.e., ≥ 0.15 eV). We have not attempted to extract the threshold dependence for reactions where experimental cross sections are still substantial at our lowest energy, since the procedure would require an extrapolation which is quite dependent on choice of the model threshold law. The best fit deconvoluted thresholds are given in Tables III and IV. The error limits quoted for the threshold energies have been derived from the range of trial cross section functions which yield acceptable fits to the data. These absolute error limits are quite large, thus the numerical values quoted serve mainly to show the magnitude of the reaction barriers. In drawing conclusions regarding relative barrier heights or reaction mechanisms, we have relied solely on the trends in threshold behavior of the raw data, not on the results of deconvolution.

An artifact that can affect collision energy thresholds is the kinetic shift. The idea is that product signal will not be observed unless the excess energy (and thus the fragmentation rate of the oxidized intermediate complex) is high enough to result in fragmentation within the observation

TABLE III. Threshold energies (in eV) for $Al_n^+ + O_2 \rightarrow Al_m O_p^+$.

Parent cluster	Product channel											
	Al ⁺	AlO+	Al ₂ ⁺	Al ₂ O ⁺	Al ₃ ⁺	Al ₃ O ⁺	A14+	Al ₅ ⁺	Al_6^+	Al ₇ ⁺	Al ₇ O ⁺	Al ₈ ⁺
Al+		3.65 ± 0.14		<u></u>						<u> </u>		
Al_2^+	N.T. ^b	<0.25	••	N.T.								
Al_3^+	<0.25	U.M.°	≼0.25	<0.25	•••	N.O.						
Al_4^+	<0.25	N.O.ª	≼0.25	≤0.25	<0.25	N.O.	•••					
Al ₅ ⁺	<0.25	N.O .	<0.25	<0.25	<0.25	N.O.	0.52 ± 0.07	•••				
Al ₆ +	≤0.25	N.O.	≼0.25	<0.25	<0.25	N.O.	0.45 ± 0.05	1.35 ± 0.13	•••			
Al_7^+	0.25 ± 0.07	N.O .	0.25 ± 0.07	0.65 ± 0.13	0.25 ± 0.07	N.O.	0.65 ± 0.13	1.45 ± 0.13	2.4 ± 0.15	•••	N.O.	
Al_8^+	≼0.25	N.O .	≤0.25	0.45 ± 0.25	<0.25	U.M.	<0.25	0.50 ± 0.25	0.80 ± 0.10	U.M .	U.M.	•••
Al,+	<0.25	N.O.	≼0.25	0.36 ± 0.10	<0.25	<0.25	<0.25	<0.25	0.55 ± 0.07	<0.25	<0.25	U.M.

^a N.O. = Product channel not observed.

^b N.T. = No threshold.

 $^{\circ}$ U.M. = Unable to measure.

time scale ($\sim 100 \,\mu$ s). Since we never observe signal at the Al_nO₂⁺ complex mass, we can conclude that fragmentation is much faster than 100 μ s, which is not surprising in light of the high excergicity of the reactions and the small size of the clusters. For very large clusters. Jarrold and Bower⁸ have shown that kinetic shifts may be important.

For reaction with oxygen, the thresholds for the channels we call oxidative fragmentation are all 0.25 eV or smaller; really too small to be extracted accurately from our data. Al_7^+ has the highest oxidation thresholds $(Al^+, Al_2^+,$ and Al_3^+ channels), which are estimated to be right at 0.25 eV. From comparison of the raw cross sections, it is clear that oxidation of Al_2^+ proceeds with no threshold, then increasing thresholds appear with increasing reagent cluster ion size up to Al_7^+ . As size increases further to eight and nine atoms, the thresholds decrease. The trends in O₂ oxidation thresholds thus appear similar to the observed trends in stability (CID thresholds) for the reagent cluster ions.^{1,2} For N₂O reactions the oxidation thresholds range from 0.15 to 0.45 eV, but in this case do not follow any obvious pattern.

The observation of thresholds for aluminum cluster ion oxidation reactions is somewhat surprising. Exoergic ionmolecule reactions generally have no activation barriers and display a characteristic functional form which peaks at low collision energies and decreases as the energy is raised. The most straightforward explanation for the existence of thresholds is that there are activation barriers which prevent reaction at low energies. A related possibility which may explain why some of the channels have reduced but nonzero cross sections at low energies, is that the potential surfaces for the reactions may be restricted at low energies (i.e., only collisions which attain a narrow range of critical geometries can react with no barrier) but then the surfaces open up as the available energy increases. For reactions of N₂O and for O₂ reactions with the larger cluster ions, our data suggests real barriers must exist. For the reactions of small clusters with O₂, where experimental thresholds are not observed, either the barriers must be small (tens of meV) or we are simply observing potential surface bottlenecks.

The physical origin of the thresholds for these exoergic reactions is unclear. For reactions with either O_2 or N_2O , it is necessary to break a relatively strong molecular bond before oxidation can go to completion. This is obviously a concerted process driven by formation of strong Al–O bonds; still the molecular dissociation is the most likely source of a bottleneck for oxidation. Breaking the N_2 –O bond (1.7 or 3.66 eV)²⁷ requires less energy than for O_2 (5.116 eV²⁵), yet thresholds for oxidation by N_2O are higher than the analo-

Parent cluster	Product channel											
	Al ⁺	AlO ⁺	Al ₂ ⁺	Al ₂ O ⁺	Al ₃ ⁺	Al ₄ +	Al ₅ +	Al ₆ ⁺	A l ₇ ⁺	Al ₈ ⁺		
A 1 ⁺		0.75 ± 0.15						<u> </u>		• ••••		
Al_2^+	0.15 ± 0.22	U.M. ^b	•••	0.15 ± 0.21								
Al_3^+	0.45 ± 0.19	N.O.ª	0.45 ± 0.14	0.45 ± 0.14	• • •							
Al₄ ⁺	0.25 ± 0.21	N.O .	0.25 ± 0.21	0.25 ± 0.21	0.8 ± 0.2	•••						
Al,+	0.40 ± 0.15	N.O.	0.40 ± 0.15	N.O.	0.5 ± 0.2	1.2 ± 0.55	•••					
Al ₆ +	0.20 ± 0.29	N.O.	0.35 ± 0.14	N.O.	0.20 ± 0.09	0.20 ± 0.18	0.80 ± 0.44					
Al_7^+	0.40 ± 0.07	N.O .	U.M .	N.O.	1.0 ± 0.4	0.40 ± 0.29	<0.25	U.M.				
Al_8^+	0.35 ± 0.13	N.O.	N.O.	N.O.	N.O .	0.70 ± 0.20	0.35 ± 0.28	0.35 ± 0.08	U.M.	•••		
Al ₉ ⁺	≼0.25	N.O .	N.O.	N.O.	N.O.	N.O.	1.40 ± 0.20	0.7 <u>±</u> 0.2	≤0.25	U.M .		

TABLE IV. Threshold energies (in eV) for $Al_n^+ + N_2O \rightarrow Al_mO_p^+$.

^a N.O. = Product channel not observed.

^b U.M. = Unable to measure.

gous O_2 thresholds. This is reasonable because the driving force for dissociating O_2 is stronger. O_2 with two unpaired electrons should bind strongly to aluminum clusters, and as the O atoms separate both atoms can form strong bonds to aluminum atoms. Singlet N_2O should bind weakly to the cluster ions, and since N_2 is nonreactive, only Al–O binding of one oxygen atom drives the dissociation.

There are a number of other possible sources for oxidation thresholds, including barriers for insertion of the oxidizer into the cluster, and energy required for electronic configuration changes. These seem less likely than dissociation barriers because the experimental thresholds do not correlate with trends in cluster stabilities and even/odd electronic structure as would be expected for these mechanisms. *Ab initio* investigation of the interaction of O₂ and N₂O with small aluminum cluster ions should be feasible, and would be of great interest in understanding the oxidation process.

D. Cluster ion size effects

To complete the discussion of the oxidation chemistry of aluminum cluster ions, it is interesting to examine how the various reaction parameters depend on cluster size. Total reactivity is an obvious property to examine, but it is not clear at which collision energies reactivities should be compared. The neutral cluster work of Cox *et al.*⁹ was done at thermal energies, while Jarrold and Bower's⁸ experiments with aluminum cluster ions were carried out at two collision energies, 1.2 and 4.2 eV. In Fig. 8 we plot total reactivities at several energies including 1.0 and 4 eV. For reaction with oxygen, the trends at 1, 4, and 10 eV are similar. The total cross sections increase from the dimer to tetramer, decrease gradually to a local minimum for Al_7^+ , then rise sharply for



FIG. 8. Total cross sections for Al_n^+ reacting with O_2 and N_2O at four translational energies.

 Al_8^+ and Al_9^+ . The data at 0.5 eV does not show the increase with size for the small clusters; this is a result of the increasing reaction thresholds. The fact that Al_7^+ is the least reactive cluster ion is consistent with the finding that it is the most stable cluster in this size range, ^{1,2} and presumably reflects its stable electronic structure. Further evidence of the special nature of Al_7^+ is the propensity of Al_9^+ to fragment in high energy collisions with O₂ to give Al_7^+ (apparently via CID), and the large branching ratio for the reaction $Al_9^+ + N_2O \rightarrow Al_7^+ + Al_2O$. The large total cross section for reaction of Al_8^+ with O₂ at high collision energies results from fragmentation to Al^+ and (presumably) Al_7 with an anomalously large cross section. This effect is seen to a much lesser degree for collisions with N₂O.

The agreement between our total cross sections at 1 eV and those of Jarrold and Bower is quite good both in magnitude and trends with cluster size. At 4.2 eV they observed the total cross section to increase sharply with cluster size. We see relatively little size dependence up to the stable heptamer, then a sharp increase for the eight and nine atom clusters. The source of the discrepancy is unclear. The experiments are similar in design, but differ in the cluster ion sources, lower gas cell pressures in our work, and our use of octapole ion guides to aid product collection. Generally our branching ratios are in agreement with those of Jarrold and Bower, thus the disagreement is really in the absolute scale. The same effect was observed in comparison of aluminum cluster ion CID studies from both groups. Fortunately, the conclusions drawn by both groups regarding the reaction dynamics are mainly derived from branching ratios, oscillations in properties with size, and in our case, the detailed collision energy dependence of the reactions. The conclusions drawn about the properties of the cluster ions, and the chemistry involved in oxidation are quite similar. Our measurements provide more direct and detailed information on the energetics and reaction dynamics for small clusters, while they are able to follow the chemistry up to larger cluster sizes.

It is not possible to make direct comparison between our data and the thermal kinetic work⁹ on neutral aluminum clusters. It is interesting, however, to note that the trends in reaction rates observed as a function of neutral cluster size are similar to what would be expected for reactions of the cluster ions at thermal collision energies: the dimer ion should be reactive, while the trimer through heptamer ions should react very slowly due to the observed bottlenecks. For the neutral clusters, the rate increases as size increases from Al₈, while for the ions we see the barriers begin to drop for Al₈⁺ and Al₉⁺.

As reagent cluster ion size increases we observe a sharp drop in the branching ratio to produce oxide ion products. We attribute this to the fact that the oxide fragments have higher ionization potentials than the pure aluminum fragments; thus the oxide fragments tend to be neutral. For the small clusters, the number of fragments produced must be small, thus for O_2 there is a high probability that ionic oxide products will be observed. As the cluster size increases, the probability of producing three or more fragments or large fragments containing both O atoms increases, leaving at least one pure aluminum fragment to carry the charge. Jarrold and Bower have observed that for large aluminum cluster ions, no oxides are produced, and the dominant reaction is

$$\mathrm{Al}_n^+ + \mathrm{O}_2 \rightarrow \mathrm{Al}_{n-4}^+ + 2\mathrm{Al}_2\mathrm{O}.$$

The fact that we observe very few oxide ion products in reaction with N_2O simply reflects that with a single O atom, there is always a pure aluminum fragment to carry the charge.

For the small clusters, the major ionic oxide product is Al_2O^+ . As cluster size increases we see Al_3O^+ , but if larger oxide cluster fragments are produced, they must be neutral. The only real exception to this trend is the large cross section for the reaction

$$Al_9^+ + O_2 \rightarrow Al_7O^+ + Al_2O.$$

Whether this reflects stability of Al_7O^+ , or of Al_2O , is unclear.

Examination of Figs. 2–4 shows that for all size reagent clusters the cross section for the reaction

 $Al_n^+ + O_2 \rightarrow Al_2O^+$

rises to a peak, then decreases as collision energy is increased. For even size reagent cluster ions the Al_2O cross section peaks sharply and is a dominant product at low energies. For odd size clusters Al_2O channel turns on more slowly, peaks at higher collision energies, and has a smaller peak cross section. The drop in Al_2O^+ formation at high energies is likely due to formation of internally excited Al_2O^+ products which are unstable with respect to dissociation. The reason that the internal excitation should oscillate with cluster size is unclear.

ACKNOWLEDGMENTS

We would like to thank Luke Hanley for helpful discussions about the experiments and data analysis. This work is supported by the U. S. Office of Naval Research under Contract No. N00014-85-K-0678.

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