

Reaction dynamics of Na_n^+ in collision with molecular oxygen

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Received: 4 July 1996 / Final version: 12 September 1996

Abstract. Reaction dynamics of sodium cluster ions, Na_n^+ ($n = 2 - 9$), in collision with molecular oxygen, O_2 was investigated by measuring the absolute dissociation cross sections and the branching fractions by using a tandem mass spectrometer equipped with several octapole ion guides. The mass spectrum of the product ions show that the dominant reaction channels are production of oxide ions, Na_kO_i^+ ($i = 1, 2$), and intact ions, Na_p^+ ($p < n$). With increase in the collision energy, the cross section for the production of the oxide ions decreased, while that for the production of the intact ions increased. The collision-energy dependences of the cross section for the oxide formation reveals that electron harpooning from the molecule to Na_n^+ preludes the oxide-ion formation. On the other hand, the collision-energy dependences of the cross sections for the intact ion formation is explained by a hard-sphere-collision model similar to the collisional dissociation of Na_n^+ by rare-gas impact.

PACS: 36.40

1 Introduction

Collective vibration of alkali metal cluster ions play an important role in their collisional dissociation because the excitation of the collective vibration causes the electronic structures to be modified through strong electron-vibration interaction [1–11]. This effect is actually manifested in the collisional dissociation of a spherical sodium cluster ion, such as Na_9^+ [6]. Another important feature in the collision of alkali metal clusters is electron transfer process which preludes the collisional reaction as the ionization potential of the alkali metal cluster ions is very small. Actually, electron transfer/electron harpooning occurs in the reaction of alkali metal cluster with molecules having large electron affinities, such as halogen molecules [12–14].

In this regard, we studied the collisional reaction of sodium cluster ions, Na_n^+ , with molecular oxygen, O_2 . The

results showed that the electron harpooning preludes the oxidation of Na_n^+ . Direct collisional dissociation by these molecules was also found to proceed without electron harpooning between Na_n^+ and target molecules.

2 Experiment

The apparatus consists of a smoke-ion chamber, a quadrupole mass spectrometer, a collision chamber and a magnetic sector-type mass spectrometer. The details have been reported elsewhere [5, 6]. Briefly, sodium vapor effusing from the oven was aggregated in the argon atmosphere in a liq. N_2 -cooled chamber. Clusters effused from the chamber were ionized by electron beams. The cluster ions thus generated were size-selected in the quadrupole mass spectrometer. A size-selected ion, Na_n^+ , transported through the octapole ion guides (OPIG) from the quadrupole mass spectrometer was allowed to collide with target molecules such as O_2 or N_2O in the collision chamber, which surrounded a portion of the OPIG. The pressure of the molecules was in the range of $10^{-5} - 10^{-4}$ Torr; the single collision condition was fulfilled in this pressure range because the intensities of the product ions were proportional to the sample pressure. The product ions from the collision chamber were mass-analyzed by the magnetic sector type mass spectrometer, and detected by a secondary electron multiplier. The output signal from the detector was amplified, discriminated and registered in a multichannel analyzer based on a personal computer.

3 Results

The mass spectra of ions produced by the reaction of Na_n^+ ($n=2-9$) with O_2 show that the dominant product ions observed are oxide ions, Na_kO^+ ($k = 2, 3$), Na_jO_2^+ ($j = 2, 3$), and intact ions, Na_p^+ ($p = 3, 5, 7$). In the reaction with N_2O , the dominant product ions observed are oxide ions, Na_kO^+ ($k = 2 - 5$), and intact ions, Na_p^+ ($p = 3, 5, 7$). The total reaction cross section, σ_r , was determined from the equation,

$$\sigma_r = \frac{k_B T}{P \ell} \ln \frac{I_{\text{off}}}{I_{\text{on}}}, \quad (1)$$

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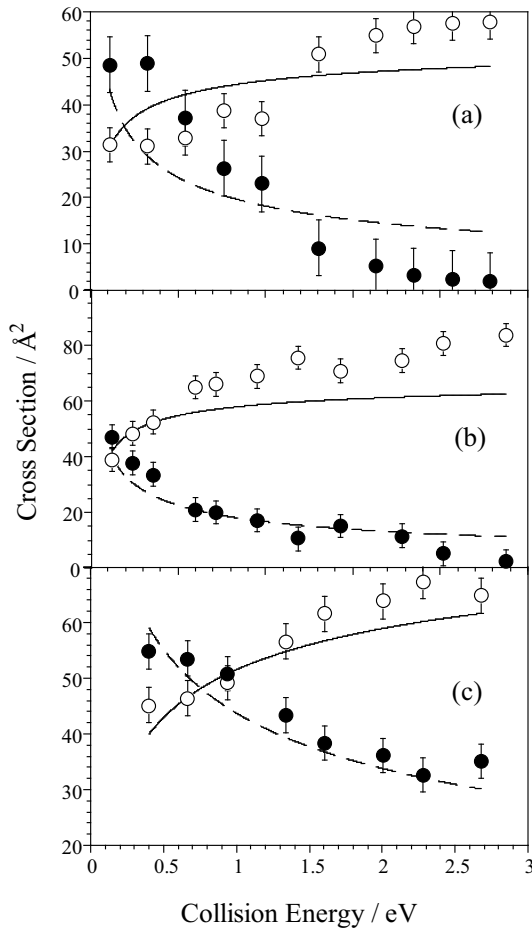


Fig. 1a–c. Collision-energy dependences of the cross sections for the production of oxide ions, Na_nO^+ and Na_nO_2^+ (●), and intact cluster ions, Na_n^+ (○), from Na_5^+ (panel a), Na_7^+ (panel b) and Na_9^+ (panel c) in collision with O_2 . The solid and broken curves are the calculated cross sections as given in the text

where I_{on} and I_{off} represent the intensities of the relevant parent cluster ion with and without the target molecule, respectively, P and T are the pressure and the temperature of the target molecule in the collision chamber, respectively, ℓ is the effective path length of the collision region, and k_B is Boltzmann's constant. The cross section, σ_p , for a given product ion was obtained as,

$$\sigma_p = \sigma_r \frac{I_p}{\sum I_p}, \quad (2)$$

where I_p is the intensity of the product ion and the summation is made all the product ions detected. Figure 1 shows the cross sections for the production of the oxide and the intact ions, in the collision of Na_n^+ ($n=5, 7$ and 9) with O_2 as a function of the collision energy in the center-of-mass frame; the collision energy is hitherto given in the center-of-mass frame, unless otherwise noted. The cross section for the production of the oxide ions decreases, while that for the intact ions increases, as the collision energy increases. Figure 2 shows the cross sections for the production of Na_kO^+ , and Na_jO_2^+ , in the collision of Na_n^+ ($n=5, 7$ and 9) with O_2 as a function of the collision energy. The cross section for

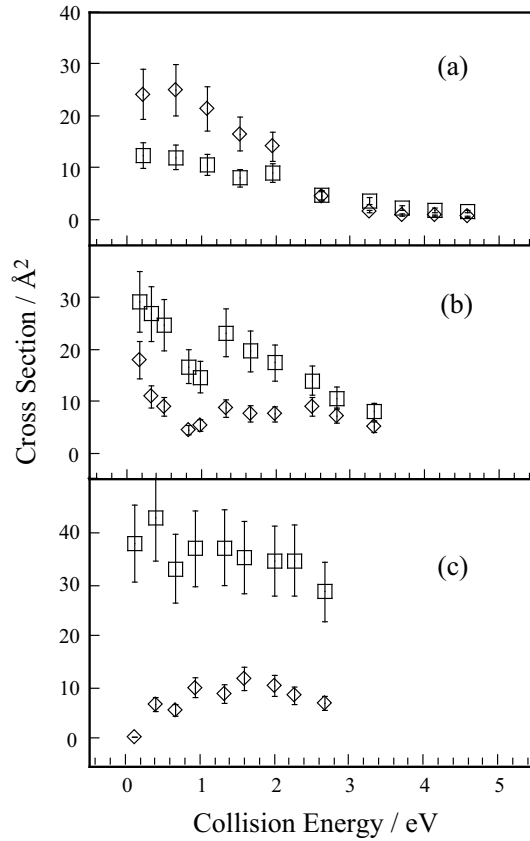


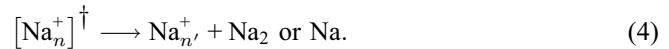
Fig. 2a–c. Collision-energy dependences of the cross sections for the production of Na_kO^+ (□), and Na_jO_2^+ (◇), from Na_5^+ (panel a), Na_7^+ (panel b) and Na_9^+ (panel c) in collision with O_2

the production of oxide ions ($\text{Na}_k\text{O}^+ + \text{Na}_j\text{O}_2^+$) is weakly dependent on the collision energy. The cross section for the Na_jO_2^+ production does not change significantly with the size of the product ion, n , while the cross section for the Na_kO^+ production increases with n .

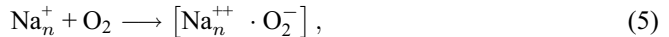
4 Discussion

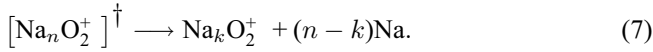
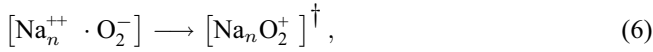
4.1 Reaction scheme

On the analogy of the collisional dissociation of Na_n^+ with rare gas atoms, the parent cluster ion, Na_n^+ , is considered to be vibrationally excited by collision, and then Na_2 or Na are released sequentially [6] as

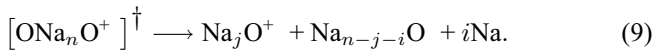
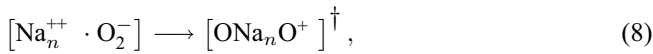


On the other hand, the oxide ions, Na_kO^+ and Na_jO_2^+ , are considered to be produced through formation of a collision complex, $[\text{Na}_n^{++} \cdot \text{O}_2^-]$ by electron harpooning from Na_n^+ to O_2 [7]. As the oxidation of Na_n^+ is exothermic, the heat of the oxidation must be released by dissociation of Na atom:





Two potential curves are relevant to the reaction, with respect to the distance, $R(\text{Na}_n^{++} \dots \text{O}_2)$. In the beginning, Na_n^+ approaches O_2 along the incoming potential curve (A) which is correlated to $\text{Na}_n^+ + \text{O}_2$, and the electron harpooning from Na_n^+ to O_2 takes place at the crossing, R_c , and the collision system is switched on the charge exchange potential curve (B) which is correlated to $\text{Na}_n^{++} + \text{O}_2^-$. As a result, a collision complex, $[\text{Na}_n^{++} \cdot \text{O}_2^-]$, is formed. If no electron harpooning takes place, Na_n^+ approaches much closer to O_2 pass through the crossing along the potential curve (A) as a diabatic process. It is conceivable that Na_kO_2^+ is produced from the complex, $[\text{Na}_n^{++} \cdot \text{O}_2^-]$ (processes (6) and (7)), with releasing several Na atoms. On the other hand, Na_kO^+ is produced through breaking of O-O bonding in $[\text{Na}_n\text{O}_2^+]^\dagger$:



As the electron affinity of O_2 is large and the ionization potential of Na_n^+ is sufficiently large, oxygen molecule in the cluster ion is likely to be in a form of O_2^- . Therefore, the bond breaking of O_2^- should be considered. The process of Na_kO^+ formation is likely to be the dissociation of O_2^- in strongly electron-donating medium.

The intact ion, Na_p^+ , is produced by the direct collision of O_2 with Na_n^+ without electron harpooning as argued above.

4.2 Reaction cross section

The diabatic transition probability, P , at R_c is approximated by the Landau-Zener relation,

$$P = \exp\left(-\frac{\pi^2 R_c^2 \Delta E^2}{4e^2} \sqrt{\frac{m}{2E_{\text{tr}}}}\right), \quad (10)$$

where ΔE and E_{tr} show an energy gap at R_c and a translational energy of the collision system, respectively, and m is the reduced mass of the collision system [12]. The interparticle distance, R_c , at the potential crossing is estimated by the ionization potential of Na_n^+ [15] and the electron affinity of O_2 . It is highly probable that the collision system passes the potential crossing twice; Then, the cross section, σ_{ex} , for the complex formation is calculated as,

$$\sigma_{\text{ex}} = \left(1 - \frac{P}{2 - P}\right) \pi R_c^2. \quad (11)$$

It is reasonable to consider that once the $[\text{Na}_n^{++} \cdot \text{O}_2^-]$ complex is formed, it reacts almost completely into the oxide ions, and the large heat of the oxidation can be dissipated rapidly by releasing the fragments (processes (7) and (9)). In this case, the cross section for the production of the oxide ions can be approximated by the cross section, σ_{ex} , for the formation of the charge-exchange complex. The broken

curve in Fig. 1 show the calculated cross section thus obtained. As shown in Fig. 1, the calculation reproduces well the measured cross sections.

Direct collision of Na_n^+ with O_2 is likely to proceed after diabatic transition at the potential crossing at an impact parameter less than a characteristic radius, R_g , within which the electron density is sufficiently large. If the intact ions are produced in this collision as is the case of rare-gas atom impact, the cross section, σ_{intact} , for the production of the intact ions is given by

$$\sigma_{\text{intact}} = P^2 \pi R_g^2. \quad (12)$$

The R_g value can be approximated by $n^{1/3} r_s + r_{\text{O}_2}$, where r_s is the Wigner-Seitz characteristic radius, and r_{O_2} is effective radius of O_2 . As shown in Fig. 1, the solid curve calculated from eq.(12) agrees with the experimental cross sections for the production of the intact ions. This finding indicates that almost the same mechanism for the rare gas impact operates in the Na and the Na_2 release from Na_n^+ by O_2 impact. The collision-energy dependences of the cross sections for the Na and the Na_2 release were also explained by the model proposed in the paper that collisional deformation play a central role for the dissociation mechanism [6].

The reaction of Na_n^+ with N_2O can be explained similarly as shown above.

The present work was supported by Grant-in-Aid for Scientific Research in Priority Areas by the Ministry of Education, Science and Culture of Japan.

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