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## CHEMI-IONIZATION REACTIONS OF Ca, Sr, Ba, AND Yb ATOMS WITH THE HALOGEN AND INTERHALOGEN MOLECULES

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Large variations are observed in the chemi-ionization cross sections for the thermal reactions of Ca, Sr, Ba, and Yb atoms with various halogen and interhalogen molecules, as well as chlorine dioxide. While the alkaline earth metal atom reactions generally produce ion products, this is only true for  $\text{Yb} + \text{F}_2$ . The absence of ions for the other Yb reactions is explained on energetic grounds. For the reaction of a metal atom (M) with a halogen ( $\text{X}_2$ ), the positive and negative ions are determined mass spectrometrically to be  $\text{MX}^+$  and  $\text{X}^-$ . For the interhalogens, both ion channels,  $\text{MX}^+ + \text{Y}^-$  and  $\text{MY}^+ + \text{X}^-$ , are observed, the dominant channel being the one more exoergic. Absolute chemi-ionization cross sections are estimated to range from 0.001 to  $1.6 \text{ \AA}^2$ , with an uncertainty of  $\pm 100\%$ . These cross sections decrease in the order  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Yb}$  for all oxidizer gases other than  $\text{F}_2$ . For a given alkaline earth metal, the cross sections decrease in the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ , the only exception being  $\text{Ba} + \text{F}_2$ . These large cross sections indicate that for all the reactions discussed here, the chemi-ionization channel is much more important than the chemiluminescence pathway.

### 1. Introduction

Chemi-ionization is well known in flames and other highly exoergic gas-phase reactions [1]; but this process has only recently been studied in thermal beams, in particular,  $\text{U} + \text{O}$  and  $\text{O}_2$  [2];  $\text{Th} + \text{O}$  and  $\text{O}_2$  [3]; the alkali dimers with the halogens [4-6]; Ba with  $\text{O}_2$  [7]; Ba, Sr, and Ca with  $\text{OH}$  [8];  $\text{Cl}_2$  [9],  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  [10]. To extend the latter studies, we have compared the measured chemi-ionization cross sections for the reactions of Ca, Sr, Ba, and Yb with  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{ClF}$ ,  $\text{ICl}$ , and  $\text{ClO}_2$ . Ytterbium, with the electronic configuration  $[\text{Xe}]4f^{14}6s^2$ , makes the comparison more interesting because its ground state,  $^1\text{S}_0$ , is identical with those of the alkaline earth atoms but the bond energies of its monohalides, except  $\text{YbF}$ , are much weaker [15].

Recent studies have determined the various open pathways for the reactions of alkaline earth metal atoms with various halogen and interhalogen molecules [9-16]. The dominant channel leads to product molecules in high vibrational levels of the ground state. Several low-lying electronic states of the products  $\text{MX}$  and  $\text{MX}_2$  can also be populated if sufficient exoergicity is released in the reactions. Furthermore, a chemi-ionization channel has been observed. It is this last channel that is the subject of this study.

### 2. Experimental

The reactions are carried out in a beam apparatus described previously [17]. A collimated beam of the metal, vaporized from a resistively-heated graphite oven, traverses a scattering chamber where it intersects a tenuous oxidizing gas. For measurements of relative chemi-ionization cross sections, the ovens are operated at temperatures corresponding to metal vapor pressures of about 0.01 torr, while the oxidizing gas is maintained at  $\sim 9 \times 10^{-5}$  torr, as measured by an ionization gauge and a Barocel capacitance

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manometer (Model 1173) located 30 and 10 cm, respectively, from the reaction region.

Ion products are detected by aluminum condenser plates (87 × 57 mm) centered in the path of the metal beam. For the determination of absolute cross sections, the dimensions of the plates are increased to 180 × 57 mm. One plate is connected to a high voltage power supply, the other to ground through a Keithley 417 fast picoammeter. The background current reading is typically  $10^{-12}$  A or less and remains at this level when only the metal beam or the oxidizing gas is turned on. When both are on, ion products are formed, and the picoammeter registers a positive reading when a positive voltage (usually 100 V) is applied to one of the plates. An identical reading of opposite sign is obtained when the voltage polarity is reversed.

In subsidiary experiments to identify the positive and negative ions and to determine branching ratios for competing ionization channels, a crossed molecular beam apparatus with mass spectrometric detection is employed. A thermal metal beam is crossed by a halogen beam produced from either a low-pressure nozzle source or from a room-temperature effusive source. The resulting ions are extracted from the scattering zone into a separate UHV detection chamber where they are mass analyzed by a quadrupole mass filter (Extranuclear Laboratories, Inc.) and detected by an electron multiplier with a positive-negative preamplifier (Extranuclear Laboratories, Inc. Model 032-4) and a fast electrometer (Keithley Model 600A).

The reagents, except  $\text{ClO}_2$ , are obtained commercially. Chlorine dioxide is prepared from the reaction of  $\text{KClO}_3$  with  $\text{H}_2\text{C}_2\text{O}_4$  (Bray's method) [18] and trapped at dry ice temperatures. Immediately prior to a run, this trap is briefly opened to the pumps to remove excess  $\text{Cl}_2$  and  $\text{CO}_2$ .

### 3. Results

To obtain a rough idea about the absolute cross sections, we choose the  $\text{Yb} + \text{F}_2$  reaction as a standard. The number of ions collected per second,  $I_{\text{ion}}$  is related to the following parameters:

$$I_{\text{ion}} \approx n_{\text{M}} n_{\text{O}} v_{\text{rel}} (\Delta V) \sigma_{\text{ion}}, \quad (1)$$

when  $n_{\text{M}}$  and  $n_{\text{O}}$  are the densities of the metal beam and oxidizing gas, respectively;  $v_{\text{rel}}$  is taken as the relative velocity of the reactants in the center-of-mass frame;  $\sigma_{\text{ion}}$  is the chemi-ionization cross section; and  $\Delta V$  is the volume of the reaction zone.

To insure that essentially all ions are collected in the absolute cross section measurements, we use condenser plates that covered the length of the metal beam (see experimental section). The metal flux is determined by collecting for a period of three hours the atoms either impinging on a thin Pyrex disc or entering a 250 ml flask in the path of the beam, located about 18 cm from the entrance of the scattering chamber. An iron-constantan thermocouple attached to the flask indicated negligible temperature rise in the course of the run, suggesting that the sticking coefficient (assumed to be unity) does not change over this period of time. The Yb film has a metallic luster and its weight does not appreciably change on exposure to the air.

The average weight of ytterbium film collected in three runs is  $5.8 \pm 1.8$  mg on the Pyrex disc and  $6.0 \pm 1.5$  mg inside the flask. The cross section of the metal beam is  $1.5 \text{ cm}^2$  and the mean velocity of Yb at 850 K is  $\sim 3.5 \times 10^4 \text{ cm/s}$ . Thus, the metal density,  $n_{\text{M}}$ , is estimated to be  $\approx (6.0 \pm 1.6) \times 10^{10} \text{ atoms/cm}^3$ . The relative velocity,  $v_{\text{rel}}$ , is taken to be  $4.6 \times 10^4 \text{ cm/s}$  for  $\text{Yb} + \text{F}_2$  and the reaction zone,  $\Delta V$ , corresponding to the volume occupied by the conical metal beam, is  $\approx 35 \pm 5 \text{ cm}^3$ .

The average ion current for the  $\text{Yb} + \text{F}_2$  reaction is  $(7.0 \pm 0.2) \times 10^{-8} \text{ A}$ , corresponding to  $(4.4 \pm 1.2) \times 10^{11} \text{ ion/s}$ , at an  $\text{F}_2$  pressure of  $\approx 9 \times 10^{-5} \text{ torr}$  ( $n_{\text{O}} \approx 3 \times 10^{12} \text{ molecules/cm}^3$ ). From eq. (1), we find  $\sigma_{\text{ion}} \approx 0.016 \text{ Å}^2$ . Simple propagation of error theory suggests that this value is only accurate to within a factor of 2. Using this result, the relative measured ion currents for the other reactions (corrected for variations in the  $v_{\text{rel}}$  values) are converted to absolute cross sections. The results are listed in table 1. These relative ion currents are accurate to within 30%. For the particular reactions  $\text{Ba} + \text{Cl}_2$  and  $\text{Ba} + \text{I}_2$ , we find the ratio  $\sigma_{\text{ion}}(\text{Ba} + \text{Cl}_2)/\sigma_{\text{ion}}(\text{Ba} + \text{I}_2)$  to be  $280 \pm 80$ . Recently, Beck and Hahn [9] estimated this cross section ratio to be  $260 \pm 50$ , giving us additional confidence in our relative cross section measurements.

We notice that the cross sections decrease in the

Table 1

Comparison of chemi-ionization cross sections with  $\Delta E$ , the total energy released in the ion products

| Reaction  | IP(MX)  | EA(X) <sup>a)</sup> | $\sigma_{\text{ion}}$ ( $\text{\AA}^2$ ) | $\Delta E$ (eV) |
|---|---------|---------------------|--|-----------------|
| $\text{Ba} + \text{F}_2 \rightarrow \text{BaF}^+ + \text{F}^-$      | 4.9 b)  | 3.45                | 0.5                                      | 2.5             |
| $\text{Ba} + \text{Cl}_2 \rightarrow \text{BaCl}^+ + \text{Cl}^-$   | 4.6 c)  | 3.61                | 1.4                                      | 1.31            |
| $\text{Ba} + \text{Br}_2 \rightarrow \text{BaBr}^+ + \text{Br}^-$   | 4.3 c)  | 3.36                | 0.6                                      | 1.21            |
| $\text{Ba} + \text{I}_2 \rightarrow \text{BaI}^+ + \text{I}^-$      | 4.0 c)  | 3.06                | 0.005                                    | 1.20            |
| $\text{Ba} + \text{ClF} \rightarrow \text{BaF}^+ + \text{Cl}^-$     | 4.9 b)  | 3.61                | 0.5                                      | 1.64            |
| $\quad \quad \quad \rightarrow \text{BaCl}^+ + \text{F}^-$          | 4.6 c)  | 3.45                | 0.5                                      | 1.08            |
| $\text{Ba} + \text{ICl} \rightarrow \text{BaCl}^+ + \text{I}^-$     | 4.6 c)  | 3.06                | 0.04                                     | 1.08            |
| $\quad \quad \quad \rightarrow \text{BaI}^+ + \text{Cl}^-$          | 4.0 c)  | 3.61                | 0.02                                     | 1.06            |
| $\text{Ba} + \text{ClO}_2 \rightarrow \text{BaCl}^+ + \text{O}_2^-$ | 4.6 c)  | 0.44                | 0.1                                      | 0.52            |
| $\text{Sr} + \text{F}_2 \rightarrow \text{SrF}^+ + \text{F}^-$      | 5.1 e)  | 3.45                | 1.5                                      | 1.66            |
| $\text{Sr} + \text{Cl}_2 \rightarrow \text{SrCl}^+ + \text{Cl}^-$   | 4.8 c)  | 3.61                | 0.04                                     | 0.36            |
| $\text{Sr} + \text{Br}_2 \rightarrow \text{SrBr}^+ + \text{Br}^-$   | 4.6 c)  | 3.36                | 0.002                                    | 0.31            |
| $\text{Sr} + \text{ClF} \rightarrow \text{SrF}^+ + \text{Cl}^-$     | 5.1 e)  | 3.61                | 0.019                                    | 1.30            |
| $\quad \quad \quad \rightarrow \text{SrCl}^+ + \text{F}^-$          | 4.8 c)  | 3.45                | 0.001                                    | 0.16            |
| $\text{Sr} + \text{ICl} \rightarrow \text{SrCl}^+ + \text{I}^-$     | 4.8 c)  | 3.06                | < 0.001                                  | 0.15            |
| $\quad \quad \quad \rightarrow \text{SrI}^+ + \text{Cl}^-$          | 4.5 c)  | 3.61                |  | 0.25            |
| $\text{Sr} + \text{ClO}_2 \rightarrow \text{SrCl}^+ + \text{O}_2^-$ | 4.8 d)  | 0.44                | 0.005                                    | -0.55           |
| $\text{Ca} + \text{F}_2 \rightarrow \text{CaF}^+ + \text{F}^-$      | 5.5 f)  | 3.45                | 2.0                                      | 1.54            |
| $\text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}^+ + \text{Cl}^-$   | 5.2 c)  | 3.61                | 0.01                                     | 0.27            |
| $\text{Ca} + \text{Br}_2 \rightarrow \text{CaBr}^+ + \text{Br}^-$   | 5.0 c)  | 3.36                | 0.002                                    | 0.16            |
| $\text{Ca} + \text{ClF} \rightarrow \text{CaF}^+ + \text{Cl}^-$     | 5.5 f)  | 3.61                | 0.004                                    | 0.73            |
| $\quad \quad \quad \rightarrow \text{CaCl}^+ + \text{F}^-$          | 5.2 c)  | 3.45                | -  | 0.04            |
| $\text{Ca} + \text{ICl} \rightarrow \text{CaCl}^+ + \text{I}^-$     | 5.2 c)  | 3.06                | < 0.001                                  | 0.04            |
| $\quad \quad \quad \rightarrow \text{CaI}^+ + \text{Cl}^-$          | 4.8 c)  | 3.61                | < 0.001                                  | 0.42            |
| $\text{Ca} + \text{ClO}_2 \rightarrow \text{CaCl}^+ + \text{O}_2^-$ | 5.2 d)  | 0.44                | 0.002                                    | -0.53           |
| $\text{Yb} + \text{F}_2 \rightarrow \text{YbF}^+ + \text{F}^-$      | ~6.0 g) | 3.45                | 0.015                                    |                 |

a) Refs. [19–21]. b) Ref. [22]. c) Ref. [23].

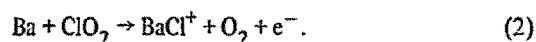
d) For  $\text{Ba} + \text{ClO}_2$ , the  $\text{O}_2^-$  ion was not detected; for Sr or Ca with  $\text{ClO}_2$ , no mass spectrometric identification was made.

e) Refs. [22–24]. f) Refs. [23,25,26]. g) See text.

order  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Yb}$  for the same oxidizer gas, with the exception of  $\text{F}_2$ . For a given alkaline earth atom, the cross sections decrease in the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ , the only exception being  $\text{Ba} + \text{F}_2$ . We see that these simple trends encounter difficulties in the case of  $\text{F}_2$ . This may be a manifestation, in part, of the anomalous electron affinity of  $\text{F}_2$ ,  $\text{EA}(\text{F}_2) = 3.45$  eV, which should be compared to  $\text{EA}(\text{Cl}_2) = 3.61$  eV,  $\text{EA}(\text{Br}_2) = 3.36$  eV, and  $\text{EA}(\text{I}_2) = 3.06$  eV [19–21].

For the reactions involving the interhalogens, there

are two competitive channels,  $\text{MX}^+ (\text{MY}^+)$  and  $\text{Y}^- (\text{X}^-)$ , the dominant channel being the one more exoergic (see table 1). In the reaction of Ba with  $\text{ClO}_2$ , however, a search failed to find the negative ion  $\text{O}_2^-$ , although the positive ion  $\text{BaCl}^+$  is seen. We assume that in this case the reaction proceeds as follows:



It is possible that the reactions of Ca and Sr atoms with  $\text{ClO}_2$  will follow the same mechanism, but we have not verified this mass-spectrometrically.

#### 4. Discussion

For chemi-ionization reactions of the general type



it is useful to consider a thermodynamic cycle shown in fig. 1. From conservation of energy we can write

$$\Delta E = D_0^0(MX) - D_0^0(XY) + EA(Y) - IP(MX) + [E_{int}(M) + E_{int}(XY) + E_{trans}^i], \quad (4)$$

where  $\Delta E$  is the energy released into the products, i.e., in eq. (4)

$$\Delta E = E_{int}(MX^+) + E_{int}(Y^-) + E_{trans}^f. \quad (5)$$

The symbols  $D_0^0$ ,  $EA$ , and  $IP$  stand for the dissociation energy, electron affinity, and ionization potential, respectively;  $E_{int}$  is the internal energy (vibrational-rotational); and  $E_{trans}^i$  and  $E_{trans}^f$  are the initial and final relative translational energies, respectively. Chemi-ionization can only occur for reactions where  $\Delta E \geq 0$ , i.e.,

$$D_0^0(MX) - D_0^0(XY) + EA(Y) - IP(MX) + [E_{int}(M) + E_{int}(XY) + E_{trans}^i] \geq 0. \quad (6)$$

Although the values for  $D_0^0(X_2, XY)$  have been determined with a reasonable degree of accuracy, some of the best estimates for  $D_0^0(MX)$  in the literature are merely lower bounds to the true values. Furthermore, with the exceptions of BaF, SrF, and CaF, the values we have used for  $IP(MX)$  are based on Krasnov's calculations [23]. Estimates for  $E_{int}(M)$ ,  $E_{int}(XY)$  and  $E_{trans}^i$  are obtained in the usual manner [27,28]. Despite the lack of accurate thermodynamic data, table 1 shows that chemi-ionization occurs where  $\Delta E \geq 0$ , with two exceptions, Sr + ClO<sub>2</sub> and Ca + ClO<sub>2</sub>. We suggest that for these two cases either the values of  $D_0^0(MX)$  or  $IP(MX)$ , or both, are incorrect by a few tenths of an eV.

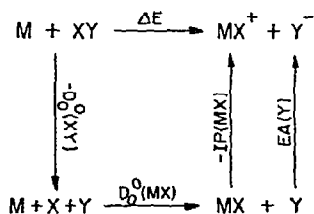


Fig. 1. A thermodynamic cycle for the chemi-ionization reaction  $M + XY \rightarrow MX^+ + Y^-$ .

Recently we have estimated a lower bound of 5.0 eV for  $D_0^0(YbF)$  and 3.2 eV for  $D_0^0(YbCl)$  [11]. Following this trend in dissociation energies,  $D_0^0(YbBr)$  and  $D_0^0(YbI)$  are expected to be  $\approx 3$  eV. The ionization potentials of the ytterbium monohalides, on the other hand, have not, to our knowledge, been measured or calculated. We may assume that their values are less than 6 eV, in analogy with the fact that  $IP(MX) < IP(M)$  for the alkaline earth monohalides [22–25].

Among the Yb reactions,  $\Delta E$  is greater than zero for only the Yb + F<sub>2</sub> reaction. It is this case for which  $D_0^0(YbF)$  is sufficiently large to offset  $IP(YbF)$ . Although  $\Delta E$  can predict when chemi-ionization is allowed, it does not, unfortunately, tell us about the magnitudes of the relative chemi-ionization cross sections.

Recent studies [15,29,30] have shown that, in reactions of Ba, Sr, and Ca with the halogens, as well as Yb + F<sub>2</sub>, the cross sections for chemiluminescence are normally less than 0.01 Å<sup>2</sup>. Thus the results in table 1 indicate that for these reactions, the chemi-ionization reaction rate is much larger than the chemiluminescence reaction rate, and that all chemiluminescent reactions are capable of producing ions. However, the present results suggest the speculation that when the chemi-ionization channel is open, it reduces the chemiluminescence produced.

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