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# Endoergic ion-molecule-collision processes of negative ions. I. Collision of $I^-$ on $SO_2$

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A new method has been developed for the investigation of endoergic ion-molecule-collision processes of negative ions. This method is, in effect, an extension of an earlier one developed by Refaey and Chupka used in connection with positive ions. An ion source with separate ionization and collision chambers was constructed and mounted on a Bendix time-of-flight mass spectrometer. I<sup>-</sup> ions produced in the ionization chamber by electron resonance capture of HI are pulsed to the desired energy where they enter a collision chamber containing a different gas. Cross sections for various endoergic ion-molecule-collision processes are measured as a function of the incident ion (I<sup>-</sup>) energy. Collision of I<sup>-</sup> on SO<sub>2</sub> gives the secondary ions SO<sub>2</sub><sup>-</sup>, IO<sup>-</sup>, O<sup>-</sup>, SO<sup>-</sup>, and S<sup>-</sup> and/or O<sub>2</sub><sup>-</sup> in the energy range 2-25 eV (cm). Experimental thresholds were used to determine heats of formation as well as the electron affinities of various species. The electron affinities of SO<sub>2</sub>, IO, SO, and S were determined as 1.05, 2.3, 1.2, and 2.0 eV. The onset for the formation of O<sup>-</sup> indicates that it is accompanied by the neutral ISO. This onset leads to  $\Delta H_f(ISO) = -16$  kcalmole<sup>-1</sup>. IS has been suspected as a product in two separate cases. A fairly good estimate of  $\Delta H_f(IS)$  can be set as 74 kcalmole<sup>-1</sup>.

# I. INTRODUCTION

In recent years considerable attention has been devoted to the determination of electron affinities and the heats of formation of negative ions. Several techniques have been employed, including dissociative resonance capture, <sup>1,2</sup> electron photodetachment, <sup>3,4</sup> the magnetron,<sup>5</sup> negative ion-molecule reactions, <sup>6</sup> calculations of crystal lattice energies, <sup>7</sup> and several others. <sup>4,7,8</sup> Because of the fact that electron affinities cannot be determined by direct electron attachment or by exoergic electron transfer, studies have recently been directed toward the measurement of the threshold energy of charge transfer reactions as a means of determining electron affinities. <sup>9-14</sup> The present study falls into this category.

Endoergic ion-molecule reactions of positive ions have been investigated by several authors who employed various techniques.<sup>15-19</sup> One of the most effective techniques is the tandem mass spectrometer developed by Lindholm<sup>19</sup> and extended to negative ions in several laboratories.<sup>9-12</sup> Tandem mass spectrometers are, however, very expensive, and attempts have been made to measure the threshold of charge transfer reactions by less elaborate means. Thus, Chupka and his associates<sup>20-23</sup> employed a dual mass spectrometer source with separate ionization and collision chambers to study positive ions and subsequently extended the technique to negative ions.<sup>13,14</sup>

The present study employed a modification of the Chupka dual source applied to a time-of-flight mass spectrometer. In addition to charge transfer, this study included ion-molecule reactions and dissociative charge transfer reactions.

#### **II. EXPERIMENTAL**

The primary ion used in this study has been I<sup>•</sup> formed from HI by dissociative reasonance capture. This choice was made for the following reasons. First, I<sup>•</sup> is a heavy ion (m/e = 127), and in colliding with light gases its energy in the laboratory will be greatly reduced to give the corresponding value in the center of mass system. Second, HI has a high cross section for dissociative resonance capture to produce I<sup>-</sup> at low electron energy ( $\approx 0.0 \text{ eV}$ ). Third, the spectrum produced at this electron energy will be that of I<sup>-</sup> ion only and many of the target gases of interest, such as SO<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>2</sub>, NO, and O<sub>2</sub>, can be used, since most of these gases do not produce negative ions at this low electron energy. Fourth, the initial translational energy of I<sup>-</sup> from HI is essentially thermal and is not sensitive to electron energy, since the greatest part of the translational energy released will be carried away by the hydrogen atom.

The experiments were carried out on a Bendix timeof-flight (TOF) mass spectrometer model 12 series provided with model 1077 Bendix pumping system below the ion source region. The mass spectrometer is also equipped with model 3015 Bendix output scanner. A Leeds and Northrup dual channel speedomax XL flatbed 620 series recorder is used in these measurements.

Gases used were HI of 98.0% purity and  $SO_2$  of 99.9% purity provided by Matheson Gas Products. The gases were used without further purification. The pressure in the collision chamber was maintained constant throughout the measurements. The incident ion energy was varied from  $\approx 0$  to 100 eV in the laboratory system.

Thermochemical values employed in evaluating the results of this investigation are collected in Table I.

#### A. The ion source

The ion source shown in Fig. 1 was specially constructed for the purpose of this investigation. It consists of a high pressure ionization chamber having a narrow electron entrance slit and a small (1.25 mm diameter) exit port. Since it is unimportant in these

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TABLE I. Thermochemical values employed in evaluating the results of this investigation.

Species	$\Delta H_f (\text{kcal/mole})^a$	E. A. (eV) <sup>b</sup>	$\Delta H_f$ ion	
0	59.55	1.47	25.6	
s	66.64	2.077	18.6	
$1^{2}P_{3/2}$	25.535	3.07	-45.5	
$I^{2}P_{1/2}$	47.27	•••	•••	
SO	1.496	1.1	- 24	
$SO_2$	-70.944	1.0	94	
ю	41.8	•••	•••	
O <sub>2</sub>	0	0.45, 1.1	-10.5, -25.4	
<sup>a</sup> Taken from Ref. 38.		<sup>b</sup> Taken from Ref. 40.		

measurements to know the pressure in the ionization chamber, no provision has been made to monitor its value. The body of the ionization chamber is insulated from the repeller and drawout plates by thin sheets of Teflon that cover only places of possible contact. Although provisions have been made to apply a repeller potential, it was found that better focusing and ion intensity are obtained when the repeller plate is grounded. Gas enters the ionization chamber through a 0.5 mm diameter hole in the center of the repeller plate. Although no provision has been made to monitor the pressure in the ionization chamber, a good indication is obtained by an ion gauge connected to the ion source region. The flow of gas to the ionization chamber is controlled by a needle valve. Primary ions leave the ionization chamber through a 1.25 mm diameter hole in the draw-out plate.

The collision chamber consists of a metal box connected to the gas inlet system through a needle valve and to a variable capacitance (mks type 77 Baratron) pressure gauge. The collision chamber is separated from the ionization chamber and from the plate following it by buffer zones approximately 1 mm thick to facilitate pumping and minimize gas cross contamination. The inlet and exit ports of the collision chamber and the port in the final plate are aligned concentrically and have



FIG. 1. The ion source of the Refaey and Chupka type with separate ionization and collision chambers.



FIG. 2. The control grid pulse (C. G. P.) and the draw-out as shown on a dual channel oscilloscope. The rise of the C. G. P. marks the beginning of the cycle.

diameters 1.5, 2.0, and 2.0 mm, respectively. The length of the collision chamber is 12 mm, but calculations of the cross sections are based on an effective path length of 13 mm to include possible contributions from the buffer zones.

The draw-out pulse is applied to the entire collision region (draw-out plate, collision chamber, and the plate following the collision chamber). After leaving the collision region, the ions are further accelerated to a final potential of 3500 V. The ions leave the ion source region through a 2.5 mm diameter hole where they enter the flight tube. This last hole separates the ion source region from the flight tube region which permits the separate pumping of both regions. To minimize electric field penetration between various regions of the ion source, all holes are covered with an etched molybdenum mesh of 100 lines/in. and more than 80% transmission.

The ion source is operated in the same fashion as those of conventional Bendix time-of-flight sources. Electrons are held back from entering the ionization chamber by the so-called control grid bias (C.G.B.) applied to the control grid (first electron grid). This bias is negative with respect to the filament. At the beginning of each cycle (100  $\mu$ sec), a pulse (C.G.P.), Fig. 2, applied to the control grid makes it positive with respect to the filament and allows the electrons to pass through to the ionization chamber. A pair of collimating slits each 0.38 mm wide and 2 mm long are used to insure that the electron beam crosses the ionization chamber in the median plane between the repeller and the draw-out plates. Immediately after the C.G.P. drops to zero, the draw-out pulse, Fig. 2, is applied to the collision region. The draw-out pulse is variable to control the collision energy and of much larger duration to assure removal of primary ions from the ionization chamber. The pulse used in these experiments has a sharp rise time (~ 10<sup>-7</sup> sec) and a duration of 30  $\mu sec.$ It is essentially square at the top except for some small ripple at the start. After leaving the collision region, both primary and secondary ions are further accelerated to a final potential of 3500 V where they enter the flight tube.

The input potential to the circuit used to provide the



FIG. 3. Ionization efficiency curves of  $I^-(HI)$  at various values of the control grid bias.

draw-out pulse is monitored by a Fluke Model 8100 A digital multimeter. It was found that the meter reading coincides fairly well with the pulse height as checked by a calibrated oscilloscope. For this reason the meter reading is taken directly as a measure of the pulse height.

The production of the primary ions is greatly affected by the relative magnitudes of the control grid bias to the control grid pulse. The pulse used in this investigation, Fig. 2, is about 19 V at its highest point. The ionization efficiency curves of I<sup>-</sup> from HI at various values of the control grid bias are shown in Fig. 3. It is clear that the ion intensity increases as the control grid bias becomes less negative, allowing more electrons to pass through to the ionization chamber. There is also an apparent increase in the appearance potential which indicates a change in the electron energy distribution caused by the change in the control grid bias. It is obvious that the best operating conditions would be that in which the control grid pulse and the control grid bias are comparable in values as shown by the bottom curve in Fig. 3. However, at these conditions the primary ion intensity would be too low to produce sufficient amounts of secondary ions. The value of the control grid bias has been held as close (0.5-3.0 eV apart) to the pulse height as measurements permit and kept constant throughout each measurement.

#### B. The cross section

Owing to the fact that secondary ion peaks are broader than normal peaks and because of the changes in the focusing properties of the ions due to changes in the draw-out pulse, the area under the peak rather than its height is considered a better measure of the ion intensity. The cross sections are evaluated using the relation

$$\sigma = (I_s/I_p)(1/nL) , \qquad (1)$$

where  $I_s$  and  $I_p$  are the integrated secondary and primary

ion intensities, respectively, *n* is the concentration of the neutral molecules, and *L* is the effective length of the collision region. In these experiments  $I_s/I_p < 0.05$ .

Because product ions may be lost, the cross sections reported here are only lower limits,

# C. The mass or time-of-flight shift

It was observed that secondary ions (produced by collision) do not appear in the mass spectrum at the positions estimated for the corresponding primary ions (produced in the ionization chamber), but appear delayed in time. For example, O<sup>-</sup> ions produced by collision of I<sup>-</sup> on  $SO_2$  at a draw-out pulse of 100 V and a final potential of 3500 V appear about 1.6  $\mu$ sec later than O<sup>-</sup> ions produced in the ionization chamber under the same conditions. This shift is about 1.1  $\mu$ sec in the case of SO<sup>-</sup>. Of course, O<sup>-</sup> and SO<sup>-</sup> formed by dissociative resonance capture of  $SO_2$  do not appear at the same electron energy as I<sup>-</sup> from HI. However, if the electron energy is increased until O<sup>-</sup> and SO<sup>-</sup> are formed from the SO<sub>2</sub> gas leaked to the ionization chamber, their positions on the oscilloscope screen, Fig. 4(b), can then be determined relative to those produced by collision, Fig. 4(a).

The mass (or time-of-flight) shift is related to the flight time of an ion of the same mass formed in the ionization chamber which is then accelerated at the same draw-out energy, and after passing through the collision chamber, is accelerated to a final energy of 3500 V. The comparable time for the secondary ion is



0 S+02 SO SO2 I 10



FIG. 4. (a) The spectrum produced by collision of  $\Gamma$  on SO<sub>2</sub> at  $\Gamma$  energy of about 15 eV (c. m.) and electron energy of 1.5 eV. (b) The spectrum produced when the electron energy is raised to 4.5 eV. O<sup>-</sup> and SO<sup>-</sup> are produced in the ionization chamber.  $\Gamma$  intensity is still high but very low compared with  $\Gamma$  intensity in Fig. 4(a).

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the sum of the times for I<sup>-</sup> to be accelerated into the collision chamber plus the time for the secondary ion to travel from its point of formation to the collector. If we assume collision to occur at the center of the collision chamber and allow the secondary ion its proportional share of the energy in the center of mass, reasonable agreement between calculated and observed mass shifts is obtained; thus, calculated shifts for O<sup>-</sup> and SO<sup>-</sup> are 1.8  $\mu$ sec and 1.2  $\mu$ sec, respectively, as compared to measured shifts of 1.6  $\mu$ sec and 1.1  $\mu$ sec.

The mass shift observed in this investigation is one of the great advantages of the TOF operation. In these studies it has eliminated concern over possible interference between secondary ions and ions of the same mass formed in the ionization chamber.

### **D.** Experimental difficulties

As will be seen subsequently, unusually intense backgrounds were observed with O<sup>-</sup> and SO<sup>-</sup>. This fact made determination of the thresholds difficult and consequently the measurements on these ions were repeated several times starting at the lowest possible energies to assure the true thresholds being included. O<sup>-</sup> and SO<sup>-</sup> are both formed from SO<sub>2</sub> at relatively low energies by dissociative resonance capture, and the background of these ions results from this reaction with stray electrons in the collision chamber. The electrons must be formed by collisional detachment from I<sup>-</sup>, since electrons from the electron beam are excluded from the ionization chamber. In a few experiments effects due to stray electrons from the filament were detected and results of these experiments were discarded.

There is some variation in measured cross section between determinations for the same process, but the structure of the curves and the various onsets are quite reproducible. Uncertainties in the measurement of reactant and product ion intensities, resulting from multiplier fatigue, are the main cause of variations in cross section. Although cross contamination between gases in the ionization and collision chambers was not expected to cause serious difficulties, there is some indication that cross contamination may have contributed to the variation in cross section discussed above. The best results were obtained when this contamination was kept to a minimum. This was done by first introducing HI gas into the ionization chamber and then controlling the flow to give high I<sup>-</sup> intensity. The pressure of HI gas leaked to the collision chamber is then measured. The target gas is then introduced into the collision chamber to a pressure (usually about 10 times the previous value) that does not cause an appreciable drop in I<sup>-</sup> intensity and give rise to measurable product intensities. The flows of both gases are then finally adiusted around the previous settings to optimize both  $\Gamma$  and product ions intensities. Repeated measurements under different conditions indicate that in most cases the cross sections are reproducible within 25% of their average value.

# E. Determination of thresholds

It will be observed that the experimental cross section curves, calculated from Eq. (1) as a function of the

incident ion  $(I^{\sim})$  energy, show in some cases a significant amount of curvature at the threshold. This curvature can primarily be attributed to the thermal energy spread of the target gas molecules and the kinetic energy distribution of the incident ion.

The incident ion energy is taken to be one-half the draw-out pulse voltage, but actually the primary ion beam will have an energy distribution related to the width of the electron beam. The experimental results suggest that in this work, this energy distribution does not significantly affect the results.

The Doppler broadening<sup>14,24</sup> resulting from the thermal energy spread of the neutral target molecules probably accounts for most of the observed curvature at the threshold. To account for the effect of Doppler broadening on the thresholds, prior knowledge of the threshold law is required. Phase space theory of J. C. Light,<sup>25</sup> P. Pechukas and J. C. Light,<sup>26</sup> and D. G. Truhlar<sup>27</sup> predicts an abrupt threshold and a linear increase in the cross section within an energy range of  $\simeq 0.1$  eV. Calculations<sup>27</sup> extended over a larger energy range indicate a gradual departure from linearity with a negative curvature, reaching a maximum and then decreasing with energy. The present measurements are qualitatively consistent with such threshold behavior.

The distribution in center-of-mass (c.m.) energy caused by the thermal motion of the target gas molecules has been derived by Chantry<sup>24</sup> for the case of a monoenergetic particle beam interacting with target molecules having an isotropic Maxwellian velocity distribution corresponding to a temperature T. If the nominal c.m. energy  $E_0$  exceeds a few kT, then the distribution has a full-width at half-maximum (FWHM) of

$$W_{1/2} = (11. \, 1\gamma k T E_0)^{1/2} , \qquad (2)$$

where T is in °K,  $\gamma = m/(m+M)$ , and m and M are the projectile and target masses. The distribution given by Chantry gives rise to a tail in the experimental cross section curve. Linear extrapolation yields a threshold which is shifted to lower energies by an amount  $\Delta E_T$ given by

$$3\gamma kT < \Delta E_T < 0.6 W_{1/2}(E_T)$$
, (3)

where  $W_{1/2}(E_T)$  is the Doppler width evaluated at c.m. beam energy of  $E_0 = E_T$ . The lower limit in (3) represents the shift in the case of a linearly rising cross section while the upper limit is the shift corresponding to a step-function cross section. Here the shift will be calculated in an approximate manner as

$$\Delta E_T = 0.2 W_{1/2}(E_T) . (4)$$

For the thresholds obtained in these measurements,  $\Delta E_T$  ranges from 0.12 to 0.23 eV.

# III. RESULTS AND DISCUSSIONS

The experimental results are shown in Figs. 5-11. Figure 5 shows the variation of the cross sections for various ions resulting from the collision of  $I^{-}$  on  $SO_2$  as a function of the incident ion ( $I^{-}$ ) energy. The observed secondary ions in the energy range 2-25 eV (unless otherwise specified, the center-of-mass energy will be



FIG. 5. Cross sections for production of various ions resulting from collision of  $I^{-}$  on SO<sub>2</sub>. The upper curve  $(\Sigma \sigma_i)$ represents the sum of all cross sections.

given) are SO<sub>2</sub>, IO<sup>-</sup>, O<sup>-</sup>, SO<sup>-</sup>, and (S<sup>-</sup> and/or O<sub>2</sub><sup>-</sup>). Figure 4(a) shows the spectrum taken at an I<sup>-</sup> energy of about 15 eV. Those ions were identified as secondary ions by several methods. One of these methods is the ionization efficiency curves shown in Fig. 6. It is obvious that the secondary ion currents follow closely the current of the primary ion I<sup>-</sup>. The observed ions must constitute at least 85%-90% of the total current of product ions in this energy range.

The curves in Fig. 5 resemble the breakdown curves<sup>28-32</sup> obtained for the fragmentation of positive molecular ions. Such breakdown curves result from the decomposition of normally stable ions as the energy is increased. Reese *et al.*<sup>33</sup> observed  $FSO_2^-$  formed from  $F_2SO_2$  and determined its appearance potential from which an approximate electron affinity of 2 eV for  $FSO_2$ can be deduced. Similarly,  $ISO_2$  would also be expected to have a positive electron affinity. Since, also, the sum of the cross sections of the various processes is approximately constant between 7.5 and 15 eV, it is possible that the present results may be interpretable in terms of the breakup of an intermediate  $ISO_2^-$  complex. At sufficiently high energies, direct reactions are to be expected and may dominate.

In the following paragraphs each of the secondary ions will be examined separately.

### A. $SO_2^-$

In Fig. 7 two sets of data obtained 6 months apart are plotted. Almost identical values of the threshold are obtained from both curves. Although the cross sections are slightly different, the two curves also show fairly close agreement of the probable onset of a second process at 2.9 eV. The measurements shown in the filled circles were discontinued at about 3.8 eV so comparison at higher energies cannot be made.

The threshold for SO<sub>2</sub> formation occurs at 1.9 eV.



FIG. 6. Ionization efficiency curves  $e + HI \rightarrow I^- + H$  and of the secondary ions.

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FIG. 7. Energy dependence of the cross section for the production of  $SO_2^-$  as a result of collision of  $\Gamma^-$  on  $SO_2$ . Full and open circles represent different measurements.

With a Doppler correction of 0. 12 eV, this becomes 2. 02 eV. Since E.A. $(I)^{34}$  is 3. 07 eV, then E.A. $(SO_2)$  is 1. 05 eV. The apparent second onset of 2. 9 eV (3. 05 eV including Doppler correction) may be due to the process

$$\mathbf{I}^{-} + \mathrm{SO}_2 \rightarrow \mathrm{SO}_2^{-} + \mathrm{I}_{2p_{1/2}} , \qquad (5)$$

which corresponds to E.A. $(SO_2) = 1.05$  eV. This value is in good agreement with earlier reported ones.<sup>35,36</sup>

# B. 10<sup>-</sup>

The energy dependence of the cross section near threshold for the formation of IO<sup>-</sup> by collision of I<sup>-</sup> on  $SO_2$  is shown in Fig. 8. At low I<sup>-</sup> energies, the I<sup>-</sup> peak exhibits a long tail which precludes possible detection of low IO<sup>-</sup> intensities. For this reason the cross section curve is extrapolated to give a threshold of 4.5 eV. With a Doppler correction of 0.2 eV, this becomes 4.7 eV. The formation of IO<sup>-</sup> at onset takes place via the mechanism

$$I'' + SO_2 \rightarrow IO'' + SO , \qquad (6)$$



FIG. 8. Energy dependence of the cross section for the production of IO<sup>-</sup> as a result of collision of I<sup>-</sup> on SO<sub>2</sub>.

which gives  $\Delta H_f(\text{IO}^{-}) = -11.5 \text{ kcal mole}^{-1}$ . This value is in good agreement with the value  $-19 \text{ kcal mole}^{-1}$ (-14 kcal mole<sup>-1</sup> Doppler corrected) obtained from collision of I<sup>-</sup> on O<sub>2</sub><sup>37</sup> and, in combination with<sup>38</sup>  $\Delta H_f(\text{IO})$ = 41.8 kcal mole<sup>-1</sup>, gives E. A. (IO) = 2.3 eV.

# **C.** O<sup>-</sup>

O<sup>-</sup> produced by collision of I<sup>-</sup> on SO<sub>2</sub> has been reported.<sup>39</sup> The results are shown in Fig. 9, and give a threshold of 5.3 eV. With a Doppler correction of 0.2 eV, the threshold becomes 5.5 eV.

The early formation of  $O^-$  by collision of  $I^-$  on  $SO_2$  as indicated by the onset at 5.5 eV does not correspond to the process

$$I^- + SO_2 \rightarrow O^- + I + SO , \qquad (7)$$

since this process requires an energy of at least 7.1 eV, when E.A.(O) is taken as 1.47 eV.<sup>40</sup> The 5.5 eV onset must be attributed to



FIG. 9. Energy dependence of the cross section for the production of O<sup>-</sup> as a result of collision of I<sup>-</sup> on SO<sub>2</sub>. Full and open circles represent different measurements.

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FIG. 10. Energy dependence of the cross section for the production of SO<sup>-</sup> as a result of collision of  $\Gamma$  on SO<sub>2</sub>. Full circle points represent repeated measurements on an expanded scale by a factor of 2.

$$I^{-} + SO_2 \rightarrow ISO_2^{-} \rightarrow O^{-} + ISO , \qquad (8)$$

which gives  $\Delta H_f(\text{ISO}) = -16$  kcal mole<sup>-1</sup>. This corresponds to a bond dissociation energy, D(I-SO), of about 43 kcal mole<sup>-1</sup>, which is not unreasonable.

The high background cross section indicated by the scattered points below 5.3 eV comes primarily from the dissociative resonance capture by  $SO_2$  of electrons collisionally detached from I<sup>-</sup>.

A rise in the cross section curve, Fig. 9, at about 10.8 eV may be associated with the process

$$I^- + SO_2 \rightarrow O^- + IO + S , \qquad (9)$$

which has a calculated threshold of 10.9 eV. A third rise at about 12.1 eV may be due to the process

$$I^{+} + SO_{2} \rightarrow O^{-} + IS + O , \qquad (10)$$

which gives  $\Delta H_f(IS) = 74$  kcal mole<sup>-1</sup>, in reasonable agreement with other deductions (see below), or to the complete breakup process



FIG. 11. Energy dependence of the cross section for the production of S<sup>-</sup> and/or  $O_2^-$  as a result of collision of I<sup>-</sup> on  $SO_2$ . The dashed line represents the level of the background signal.

$$I^{-} + SO_2 \rightarrow O^{-} + I + S + O , \qquad (11)$$

which has a calculated threshold of 12.8 eV.

#### D. SO<sup>-</sup>

Open circle points in Fig. 10 represent the variation of the cross section for the formation of SO<sup>-</sup> as a function of I<sup>-</sup> energy. Full circle points represent a second set of measurements of the cross section on a scale expanded by a factor of 2. The cross section falls to zero near 5.6 eV. With a Doppler correction of 0.2 eV, the onset energy is 5.8 eV and corresponds to the process

$$I^{-} + SO_{2} - SO^{-} + IO , \qquad (12)$$

which gives  $\Delta H_f(SO^-) = -26.5$  kcal mole<sup>-1</sup>. This value in combination with  $\Delta H_f(SO) = 1.5$  kcal mole<sup>-1</sup> gives E.A. (SO) = 1.2 eV, in good agreement with earlier determinations. <sup>36,41,42</sup>

	A. P. (eV)			E. A. (eV)	
Reaction products	Observed	Corrected	∆H <sub>f</sub> (ion) (kcal mole <sup>-1</sup> )	Calculated	Best estimate
$\overline{\mathrm{SO}_2^2 + \mathrm{I}_{2p_3/2}}$	1.90	2.02		1.05	$1.05 \pm 0.10$
$SO_2^- + I_{2p1/2}$	2.90	3.05		1.05	
$IO^{-} + SO(^{3}\Sigma_{g}^{-})$	4.5	4.7	-11.5	2.30	
0 <sup>-</sup> +1 <b>S</b> O	5.3	5.5	-16 <sup>a</sup>		
O' + IO + S	$\sim 10.8$		23		1.6
O' + IS + O	$\sim 12.1$		74 <sup>a,b</sup>		
SO <sup>-</sup> + IO	5.6	5.8	-26.5	1.20	1.1
$S^{-} + I + O_2$	6.9	7.13	21.5	2.0	2.1
O <sub>2</sub> +IS	6.9	7.13	74 <sup>a,c</sup>		

<sup>a</sup> $\Delta H_f$  of neutral. <sup>b</sup>Tentative.

<sup>c</sup>Based upon  $\Delta H_f(O_2) = -25$  kcal mole<sup>-1</sup>.

# E. S<sup>-</sup> and/or O<sub>2</sub><sup>-</sup>

The onset energy for the production of ions of mass 32 is near 6.9 eV. With a Doppler correction of 0.23 eV the threshold energy becomes 7.13 eV, which is consistent with the process

$$I^{+} SO_{2} - S^{+} + O_{2} + I(2P_{3/2})$$
 (13)

This gives  $\Delta H_f(S^-) = 21.5$  kcal· mole and E.A.(S) = 2.0 eV, in good agreement with previously reported values.<sup>43,44</sup>

If  $O_2^{-}$  is the principal secondary ion of mass 32, the reaction at 7.13 eV is probably

$$I^{-} + SO_2 \rightarrow O_2^{-} + IS \quad (14)$$

This yields  $\Delta H_f(IS) = 58$  or 75 kcal  $\cdot$  mole when  $\Delta H_f(O_2^-)$  is taken, respectively, as -10.5 or -25 kcal mole<sup>-1</sup>. The higher value is in good agreement with the  $\Delta H_f(IS) = 74$  kcal mole<sup>-1</sup> given by Eq. (10) above.

# **IV. CONCLUSIONS**

The method of Refaey and Chupka<sup>20-22</sup> has been adapted to a pulsed operation with a TOF mass spectrometer. The instrument has been used to determine the threshold energies of several product ions formed by the collision of I<sup>-</sup> with  $SO_2$ . The results obtained give reproducible values, and these agree reasonably well with results obtained by other methods. The principal reactions and the corresponding measured results are summarized in Table II.

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