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THE IONIZATION PROCESSES OF IODINE INTERPRETED BY THE MASS-SPECTROGRAPH

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Abstract

Positive ions produced in iodine by electron impact.—With an apparatus previously described in which positive ions, formed by electrons of definite energy are accelerated and then deflected magnetically around a semicircle into a Faraday cylinder, the relative numbers of the ions I^+, I_2^+, and I_3^+ were measured as a *function of pressure* from 2×10^{-5} to 4×10^{-3} mm. In the primary process of electron collision, I^+ and I_2^+ were both formed. I_2^+ was also formed in secondary collision from I^+ by the process $I^+ + I_2 = I_2^+ + I$ and I_3^+ was formed from I_2^+ by the process $I_2^+ + I_2 = I_3^+ + I$. Evidence and argument against other possibilities are given. The disappearing potentials of I^+ and I_2^+ were found to be identical, 9.3 volts.

Negative ions formed from iodine gas and free electrons.—Three negative ions I^-, I_2^-, and I_3^- were found to exist in quantities comparable with those of positive ions. Pressure-intensity relationships of these ions were also determined. I^- is formed both near the filament and in the ionization chamber according to the equation $I_2 + E^- = I^- + I$. I_2^- and I_3^- are not formed by collision with free electrons but as a result of secondary collisions of I^- and I_2^-, respectively, with I_2 molecules: $I^- + I_2 = I_2^- + I$; $I_2^- + I_2 = I_3^- + I$.

THE amount of spectroscopic and critical potential information concerning the halogens, acquired during the last few years, has made a study of the ionization processes occuring in these gases very desirable, but because of the relatively great reactivity of these elements such a study has thus far been postponed. Studies of all these elements may be impossible but knowledge of the ionization processes occurring with any one of them can, perhaps, be applied generally to the others. Iodine was selected for this investigation, offering perhaps less experimental difficulty than will the other members of this group and being that element about which we have the most information.

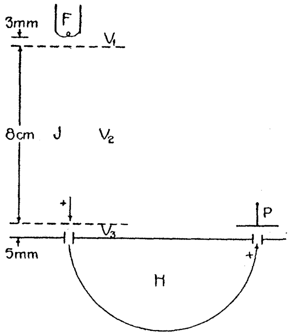

Fig. 1. Schematic arrangement of the fields.

A new apparatus was constructed for this work. In principle, it was the same as that employed by Hogness and Lunn, Smyth and others[1] differing in detail from that of Hogness and Lunn in that larger pole pieces and greater field strengths were used, thereby giving greater resolution for ions of greater mass. The radius of curvature of the ion path was 7 cm instead of 5 cm formerly used, and a field strength of 20,000 gauss was possible; 16,000 gauss, the maxmum used in this investi-

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[1] For references, see Smyth, Phys. Rev. **25,** 452 (1925), Hogness and Lunn, Phys. Rev. **30,** 26 (1927). Barton and Bartlett, Phys. Rev. **31,** 822 (1928). Kallman and Bredig, Zeits. f. Physik **34,** 736 (1925).

gation, made it possible to determine a mass of 381 with about 1 percent accuracy.

In discussing the present work, it will be occasionally necessary to refer to the various electrical fields employed. To facilitate the discussions, a schematic arrangement of the fields is given in the accompanying figure. The diagram indicates the distances between the various gauzes and the path of the positive ions. When negative ions were studied, V_2, V_3 and the polarity of the magnetic field were reversed. Electrons from the filament F enter the ionization chamber J and here produce ions of the gas. The various ions formed here follow the path indicated in the diagram. The magnetic field in the region H is kept constant and the e/m value for each ion is determined by the value of the voltage in the field through which the ion falls, according to the relationship

$$e/m = 2V/H^2r^2$$

where V is the applied voltage, H the magnetic field strength and r the radius of the circle which the ion follows in the magnetic field

POSITIVE IONS

The following processes represent the mechanism of the principal reactions producing the positive ions, I^+, I_2^+ and I_3^+:

Primary processes:
(1) $I_2 = I_2^+ + E^-$
(2) $I_2 = I^+ + I + E^-$

Secondary processes:
(3) $I^+ + I_2 = I_2^+ + I$
(4) $I_2^+ + I_2 = I_3^+ + I$

The method of distinguishing between primary and secondary processes was the usual one of determining the dependence of the relative intensities of the various ions upon pressure. Four different pressures were employed, 4×10^{-3}, 7×10^{-4}, 1×10^{-4} and 2×10^{-5}, a pressure variation of 200 fold. These pressures are the equilibrium pressures of the vapor over solid iodine at −18.5°, −33°, −45°, and −55°C, respectively. The iodine was contained in a large tube immediately adjoining the ionization chamber. The variations of the relative intensities of the four ions I^+, I_2^+, I_3^+, and I^{++} are shown in Table 1. Each determination is the mean of several.

TABLE I. *Variation of the relative intensities of the ions* I^+, I_2^+, I_3^+, *and* I^{++}.

Pressure in mm	2×10^{-5}	1×10^{-4}	7×10^{-4}	4×10^{-3}
$\frac{\text{Intensity of } I_2^+}{\text{Intensity of } I^+}$	0.6	1.3	16	32
$\frac{\text{Intensity of } I_3^+}{\text{Intensity of } I^+}$	—	Very small	0.26	2.5
$\frac{\text{Intensity of } I^{++}}{\text{Intensity of } I^+}$	—	0.07	0.05	0.15

The first intensity ratio against pressure given in the table indicates that the formation of I_2^+ is a secondary process involving the comsumption of

I^+, formed by a primary act, but if I_2^+ were formed only by a secondary process, then the intensity ratio of I_2^+ to I^+ should fall practically to zero at the lowest pressure. The fact that at this very low pressure the intensities of I_2^+ and I^+ are of the same order of magnitude indicates that I_2^+ is also formed by a primary process (Eq. 1). The mean free path of the ions at this lowest pressure is so large as to preclude the possibility of such a large proportion of necessary secondary collisions. This view is, to some extent, substantiated by the very small absolute intensities of both ions at this pressure; long free paths for the electrons and ions going hand in hand.

The simplest primary process is then represented by $I_2 = I_2^+ + E^-$. The primary process involving the formation of I^+ may be either the spontaneous dissociation of the iodine molecule, simultaneous with its ionization, or it may be the ionization of the iodine atom formed by thermal dissociation at the filament. The former of these processes is, we believe, the principal one. While it is true that there would be a large percentage of atomic iodine present if the gas came to thermal equilibrium with the filament, it is, on the other hand, evident that on account of the clean-up of atomic iodine by the metallic walls[2] and the possibility of recombination on the different surfaces the amount of atomic iodine present in the ionization chamber could not be appreciably large. This is substantiated by a study of the disappearing potentials of the ions I^+ and I_2^+. Smyth and Compton and more recently Fruth[3] have found that the ionization potential for the atom is 8 volts while that for the molecule is 9.5 volts, a difference of 1.5 volts. In our work, there was no appreciable difference found between the disappearing potentials of I^+ and I_2^+. The I^+ cannot then be formed from the iodine atom in appreciable quantities. The only possibility left is the process $I_2 = I^+ + I + E^-$.

The formation of I_3^+ must be a secondary process. The second ratio in the above table clearly proves this. Here again there are two possible processes accounting for its formation, $I_2^+ + I_2 = I_3^+ + I$ and $I^+ + I_2 = I_3^+$. The former of these is undoubtedly the process occurring. The latter is ruled out by the necessity that the relative kinetic energy of the colliding I^+ ion and the I_2 molecule plus their internal energies be equal to one of the discrete quantum levels of the resulting I_3^+ ion.[4] Without energy dissipation through light emission or collision with a third body, such a process is impossible or at least extremely improbable. Only when the relative kinetic energies of the colliding particles are *exactly* equal to the energy of some quantum state of the resulting molecule can this process take place. While it is possible that infra-red light is given out we do not believe it to be the case, since no such spectrum due to recombination between atoms or molecules has, as yet, been observed. The process we are urging is principally a tertiary one

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[2] Professor Franck has informed us of some unpublished work by Bonhoeffer on such a clean-up of atomic iodine.

[3] H. D. Smyth and K. T. Compton, Phys. Rev. **16**, 501 (1920); H. F. Fruth, Phys. Rev. **31**, 614 (1928).

[4] See Born and Franck, Zeits. f. Physik **31**, 410 (1925).

since most of the I_2^+ ions are themselves due to a secondary process. There should then be a larger rate of increase of the ratio I_3^+/I^+ with pressure. With a five or six-fold increase in pressure, there is about a ten-fold increase in the ratio I_3^+/I^+ while there is only a two-fold increase in the I_2^+/I^+ due to a secondary process for this same pressure change. The evidence favors the process $I_2^+ + I_2 = I_3^+ + I$.

The secondary formation of I_2^+ can only be $I^+ + I_2 = I_2^+ + I$, a collision in which the I^+ ion robs the I_2 molecule of an electron. That this process can take place it is necessary that either the I^+ ion is in an excited state or that the ionization potential for the formation of I^+ from atomic iodine is greater than that for the formation of I_2^+ from the molecule. It is rather improbable that sufficiently large numbers of the I^+ ion would remain in the excited state, so we must conclude that the iodine atom has a greater ionization potential than the iodine molecule has, to form unexcited I_2^+; a conclusion which, at first sight, appears contradictory to previous experimental work. Smyth and Compton, and Fruth[3] have shown that the formation of I^+ from atomic iodine requires 8 volts energy and that of I_2^+ from I_2, 9.5 volts. However, as Condon[5] has pointed out in the case of H_2, the I_2^+ formed by this process may very well retain a considerable amount of energy in vibrational form, an amount sufficient to make the ionization potential of I_2 to form *unexcited* I_2^+ actually smaller than that of the iodine atom. As we shall show later, the most probable transition is, we believe, one from the normal molecule I_2 to an I_2^+ ion with vibrational energy near the convergence limit of the vibrational states. That the normal level of I_2^+ is at least 1.5 volts below the convergence limit of the vibrational states, we can prove by thermodynamic argument. The process represented by Eq. (3) may be looked upon as the robbing of either an electron or an atom from the I_2 molecule by the I^+ ion. Both processes are thermodynamically equivalent. The heat of dissociation of the I_2^+ formed must be greater than 1.5 volts or this process of atom exchange could not occur. This value also represents the difference in the observed ionization potentials of Fruth. While the normal level of I_2^+ is not attainable by electron ionization, yet in a collision such as that above, this transition may be entirely possible; so that the ionization of the I_2 to the normal state of I_2^+ would then be lower than that of the iodine atom to form I^+.

It is difficult to draw conclusions regarding the formation of I^{++}. This ion was found only in small amounts. As the table shows, there is no systemic variation of I^{++}/I^+. It is probably the result of a primary process, with the I^{++} ions disappearing by secondary collisions, as does the I^+. The concentration of I^+ is so small in the ionization chamber as to preclude I^{++} formation by secondary electron ionization of this ion.

The disappearing potentials were obtained in the usual manner from plots of the intensities of the peaks against V_1. Corrections were made by using argon as the comparison gas, 15.4 volts being taken as its ionization

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[5] Condon, Proc. Nat. Acad. **13,** 466 (1927).

potential. Seven determinations of the disappearing potentials of I_2^+ gave a mean of 9.3 volts with a maximum deviation of 0.3 volts. Taking into account the possible error introduced in the method of correcting for contact potentials, etc., the error may undoubtedly be somewhat larger than this. Three determinations of the disappearing potential of I^+ gave an identical value of 9.3 volts. While these absolute values may be somewhat in error, it is certain that they are identical within a few tenths of a volt. This we take as evidence that the most probable transition is from the normal molecule to an ionized one near the convergence limit of the vibrational states; those transitions beyond the convergence limit resulting in dissociation, and those below into the I_2^+ with vibrational energy almost equal to the convergence limit. This means that the I_2^+ ion has a larger moment of inertia than the normal I_2. We have already pointed out that the heat of dissociation of I_2^+ is greater than that of I_2. This combination is one which is seldom encountered in band spectra work.[6]

The disappearing potential of I^{++} obtained from a single determination was 35.0 volts. If we assume that it results from a primary process, then by subtracting the heat of dissociation (1.5 volts) and the ionizing potential of iodine atom (8 volts), we obtain 25.5 for the ionizing potential of I(II). This value is not as accurate as that for the other ions because of the smaller quantities present, and may be in error by a few volts.

NEGATIVE IONS

Three negative ions were found, I^-, I_2^-, and I_3^- with intensities of the same order of magnitude as those of the positive ions. The principal processes which result in the formation of these various ions we believe to be the following:

(5) $I_2+E^-=I^-+I$ Primary
(6) $I^-+I_2=I_2^-+I$ Secondary
(7) $I_2^-+I_2=I_3^-+I$ Tertiary

The pressure-intensity data upon which we base our conclusions are given in Table II.

TABLE II. *Variation of the relative intensities of the ions* I^-, I_2^-, *and* I_3^-.

Pressure in mm Hg	1×10^{-4}	7×10^{-4}	4×10^{-3}
$\frac{\text{Intensity } I_2^-}{\text{Intensity } I^-}$	0.005	0.1	0.5
$\frac{\text{Intensity } I_3^-}{\text{Intensity } I_2^-}$	0.4	1.0	2.0
$\frac{\text{Intensity of } I^- \text{ from filament}}{\text{Intensity of } I^- \text{ from ionization chamber}}$	5.3	2.9	0.35

These results show conclusively that the formation of I^- is the only primary process. To demonstrate that the I^- was formed, both near or at the

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[6] See Birge, Molecular Spectra, Int. Crit. Tables, in press.

filament and in the ionization chamber, V_1 was made large and two peaks were obtained, one for the I^- formed at the filament and one for those formed in the ionization chamber. With a constant magnetic field strength, the ratio e/m is proportional to V, the applied analyzing voltage, where V is the total field through which the ion falls. For those ions formed at the filament, V is the sum of V_1, V_2, and V_3; for those ions formed in the ionization chamber, it is equal to V_3 plus a portion of V_2, depending upon where in the chamber the ion is formed. The same total voltage must be applied to have ions of the same e/m value traverse the same path through the magnetic field. For those ions formed in the ionization chamber, V_3 must be larger than for those formed at the filament and two distinct peaks are thus obtained when V_1 is large, V_2 small and V_3 varied. By reversing the field V_2, that peak due to the ions formed in the ionization chamber, was obliterated, while that due to the ions formed at the filament was unaffected. The ions I_2^- and I_3^- were formed only in the ionization chamber.

Since I^- is formed by a primary process and as we have seen from the results on positive ions that there is no appreciable amount of atomic iodine present, the mechanism for the formation of I^- must be either $I_2+E^-=I^-+I$ or $I_2=I^-+I^+$. If the latter of these processes were the only one occurring, I^- would not be obtained at voltages lower than that necessary to produce I^+. The I^- ion has been obtained with electron voltages as low as 3 volts. These ions are undoubtedly also formed with electrons of zero velocity but it was always necessary to maintain a small voltage in the field to draw the negative ions along the path necessary for analysis, so fields less than 3 volts were impracticable. This alone does not eliminate the possibility that at higher voltages the latter process accompanies the former. We calculate that, if this were true, I^+ should be produced with electrons of 6 volts, assuming the electron affinity of atomic iodine to be 3.5 volts[7] and taking 8 volts as the ionization potential of the atom[8] and 1.5 volts[9] as the heat of dissociation of I_2. This is far outside the limit of error of our minimum value of 9.3 volts. Furthermore, we should expect that with the transition of an electron from one atom to the other in the iodine molecule, simultaneous dissociation would be improbable. In general, dissociation, simulataneous with any electron transition in a molecule occurrs only when the moment of inertia in the excited state is greater than that in the normal or initial state.[10] On account of the polar nature of the molecule resulting from the transtition of an electron from one atom to the other, we should expect the attraction between the positive and negative components of the molecule to be greater and hence the moment of inertia smaller; a condition under which simultaneous or spontaneous dissociation could not occur. Therefore, we believe, the first process, $I_2+E^-=I^-+I$ is the only primary one that occurs in the gaseous phase. If, as we believe

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[7] Born, Verh. d. Deutch. Phys. Ges. **21**, 13 (1919); **21**, 679 (1919).

[8] Fruth, reference 3.

[9] Kuhn, Zeits. f. Physik **39**, 77 (1926).

[10] See Franck, Trans. Faraday Soc. **21**, 536 (1925).

this process occurs with electrons of zero velocity, then the electron affinity of atomic iodine must be greater than 1.5 volts, the heat of dissociation of the iodine molecule.

Since I_2^- is formed by secondary collision, the process can only be that represented by Eq. (6), $I^- + I_2 = I_2^- + I$. The rather surprising conclusion here is that the electron affinity of molecular iodine is greater than that of atomic iodine. It is important here to emphasize that the process $I_2 + E^- = I_2^-$ does *not* take place in spite of the tendency of this process to be greater energetically than that of the primary process (Eq. 5). As has been pointed out above, it would be necessary that radiation be emitted in this process. The evidence seems to be continually increasing that such double-collisional processes resulting in the formation of a single molecule never take place in chemical reactions. It might, however, seem reasonable to expect I_2^- ions to be formed in contact with the filament, contrary to experimental fact. We do not venture a guess as to the mechanism of the process occurring in contact with the filament. It is complicated on account of the filament's being at a relatively high temperature as well as being a source of electrons.

There are two possible processes for the formation of I_3^-: the one we have already given in Eq. (7), $I_2^- + I_2 = I_3^- + I$ and $I^- + I_2 = I_3^-$. Examination of the data given in the second line of Table II indicates that I_3^- is formed as a tertiary process, formed from I_2^- as represented in the former of the two possibilities given. The same triple-collision or light-emission argument used previously applies here against the latter process. It seems, perhaps, a bit surprising that the relative amount of I_3^- should be as great as it is, if it is formed by a tertiary process. However, this can easily be accounted for by assuming a mean free path of I_2^- slightly smaller than that of I^-, not an unreasonable assumption.

The possibility that any of the ions are formed on the surface of the gauzes is, we believe, ruled out by the reproducibility of the intensities of all of the ions.

Returning to the primary process (Eq. 5), it is interesting to speculate on the mechanism of the process occurring here. We have shown that this process occurs even when the electrons have considerable velocities, as high as 30 volts (no upper limit was determined). The very interesting question of the dissipation of the excess energy arises. If all of it is in the form of kinetic energy of the dissociating partners, it is difficult to picture such a mechanism in the way Franck[10] has done for the dissociation of molecules excited by light absorption or electron impact. If it is all emitted by radiation, why then is not I_2^- formed as a primary process? It may be a combination of these but none of these possibilities is reconcilable with any existing knowledge.[11]

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[11] It has been suggested that the negative ions could be formed from the secondary electrons of the positive ion process. It is difficult to account for a sufficient number of such secondary electrons to give the large intensities of I ions observed here.