

Electron Capture Processes in the Hydrogen Halides

D. C. Frost and C. A. McDowell

Citation: *The Journal of Chemical Physics* **29**, 503 (1958); doi: 10.1063/1.1744531

View online: <http://dx.doi.org/10.1063/1.1744531>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/29/3?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Radiative proton-capture nuclear processes in metallic hydrogen](#)

Phys. Plasmas **8**, 4284 (2001); 10.1063/1.1398281

[Dynamic plasma screening effects on electron capture process in hydrogenic ion–fully stripped ion collisions in dense plasmas](#)

Phys. Plasmas **4**, 2756 (1997); 10.1063/1.872144

[Electron spectroscopy of Rydberg states produced in capture processes](#)

AIP Conf. Proc. **360**, 537 (1996); 10.1063/1.49772

[Dissociative Electron Attachment to Hydrogen Halides and their Deuterated Analogs](#)

J. Chem. Phys. **48**, 1949 (1968); 10.1063/1.1668996

[Electron Capture by Protons Passing through Molecular Hydrogen](#)

J. Chem. Phys. **42**, 729 (1965); 10.1063/1.1695998



ments. The two results differ by 1.8×10^{-3} and yield an interpolated value of 0.7104.

Note added in proof.—Since this paper was completed, Carpenter and Krigbaum [J. Chem. Phys. **28**, 513 (1958)] have observed that the second virial coefficient given by Flory's uniform density sphere model⁴ is scarcely different from the results of the

more elaborate F-K and I-K theories. They conclude, as we have, that the assumed form of the averaged radical segment distribution about the molecular center of mass is of little importance compared with the neglect, implicit in the averaging process used in all three theories, of the connected nature of the polymer chain.

Electron Capture Processes in the Hydrogen Halides

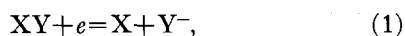
D. C. FROST AND C. A. McDOWELL

Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

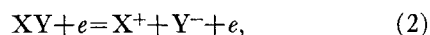
(Received May 2, 1958)

The formation of negative ions by resonance capture processes of the type $XY + e = X + Y^-$, has been studied for the hydrogen halides. A monoenergetic electron source has been used and it has been possible to determine the true shape of the resonance capture peaks in these cases. It has been found that the negative ions appear at energies which are in agreement with recent values for the dissociation energies of the H—X bonds, and the electron affinities of the halogen atoms.

EARLIER work¹ has shown that when molecules containing atoms with high electron affinities are subjected to electronic bombardment, negative ions are formed by two main processes,



where X represents a free radical or atom, and Y^- a stable negative ion, and process (2),



an ion pair dissociation in which a positive and a negative ion are produced. The former process is called a resonance capture process and it is the occurrence of this, when the hydrogen halides are bombarded with electrons, with which we are here concerned.

Most previous work in this field has been unsatisfactory, for the experimental methods were those which used bombarding electrons which had an approximately Maxwellian energy distribution. These earlier techniques thus did not permit the true shapes of the resonance capture peaks to be observed, and though there were good theoretical reasons² for suspecting that the true resonance capture peaks were much narrower than those observed,¹ these theoretical expectations could not be assessed because of the lack of satisfactory experimental methods for obtaining

electron beams with a very narrow energy spread. The recent development of a satisfactory experimental method³ of obtaining essentially monoenergetic electrons and the successful application of it to study the nature of the resonance capture processes in sulphur hexafluoride (SF_6) and hydrogen chloride⁴ has opened up new possibilities of obtaining accurate data on the true shapes of negative ion peaks formed by electron capture processes. These studies promise also to yield information concerning the nature of the potential energy curves and surfaces of molecules of the type XY^- .

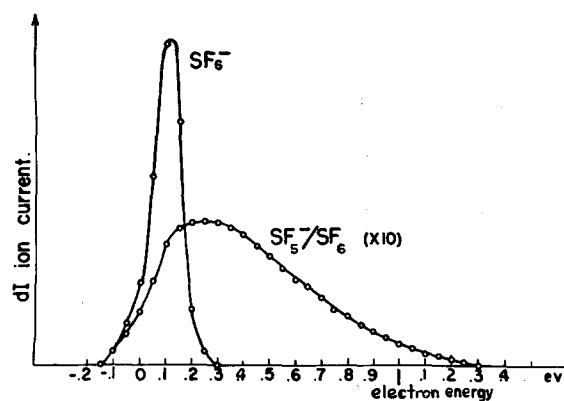


FIG. 1. The ionization efficiency curves for the formation of the SF_6^- and SF_5^-/SF_6^- ions from sulphur hexafluoride.

¹ H. D. Hagstrum, *Revs. Modern Phys.* **23**, 185 (1951); Craggs, McDowell, and Warren, *Trans. Faraday Soc.* **48**, 1093 (1952); J. D. Craggs and C. A. McDowell, *Repts Progr. in Phys.* **38**, 375 (1955).

² H. S. W. Massey, *Negative Ions* (Cambridge University Press, London and New York, 1950).

³ Fox, Hickam, Kjeldaa, and Grove, *Phys. Rev.* **84**, 859 (1951); Fox, Hickam, and Kjeldaa, *ibid.*, **89**, 555 (1953).

⁴ R. E. Fox, *J. Chem. Phys.* **25**, 642 (1956).

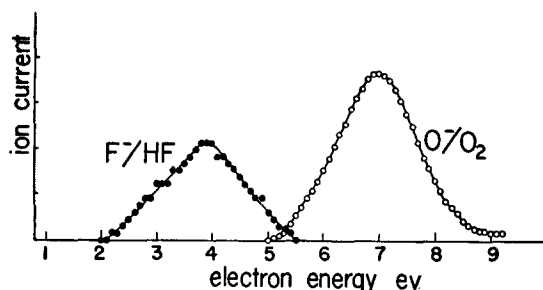


FIG. 2. The ionization efficiency curve for the formation of the F^- ion from hydrogen fluoride by a resonance capture process.

EXPERIMENTAL

The Metropolitan-Vickers MS1 mass spectrometer, modified as previously described,⁵ was used to determine the shapes of the negative ion peaks formed as the result of electron capture processes. Sulphur hexafluoride (SF_6) supplied by the Matheson Chemical Company was used to fix the zero of the electron energy scale. It was not possible to use the Fox method for F^- from hydrogen fluoride for the negative ion current was too small. The appearance potential was determined using the O^-/O_2 resonance capture peak at 4.53 ± 0.03 eV as a standard.⁶

Pure commercial specimens of hydrogen chloride and hydrogen bromide were used. The hydrogen iodide was synthesized by passing hydrogen and iodine over heated platinized asbestos and condensing the product in liquid nitrogen. The hydrogen fluoride was prepared by heating potassium hydrogen fluoride in a copper block furnace.

EXPERIMENTAL RESULTS

The resonance capture peak for the SF_6^- ion has been shown by Fox⁴ to reflect the energy distribution of the bombarding electrons. Normally,¹ the electron

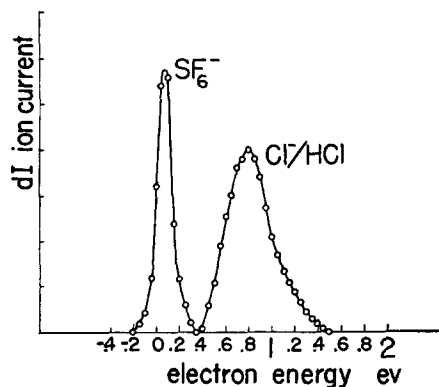


FIG. 3. The ionization efficiency curve for the formation of the Cl^- ion from hydrogen chloride by a resonance capture process.

⁵ D. C. Frost and C. A. McDowell, Proc. Roy. Soc. (London) A232, 227 (1955); D. C. Frost and C. A. McDowell, Can. J. Chem. 36, 39 (1958).

⁶ D. C. Frost and C. A. McDowell, "The ionization and dissociation of oxygen by electron impact" (to be published).

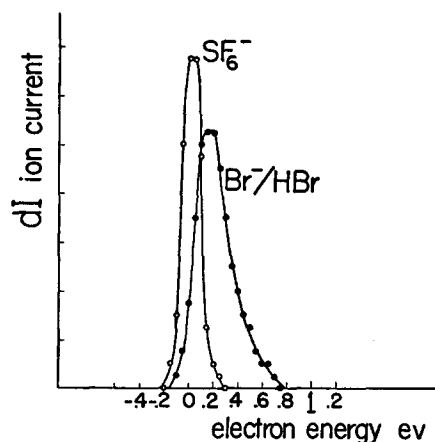


FIG. 4. The ionization efficiency curve for the formation of the Br^- ion from hydrogen bromide by a resonance capture process.

energy distribution is about 2 eV wide, but it is found that in the retarding-potential-difference method of Fox³ most of the energy distribution is contained within 0.2 eV. Figure 1 shows the ionization efficiency curves for the SF_6^- and SF_5^- ions from SF_6 obtained under the same conditions. It was necessary to know the shape of the SF_5^- peak since it appears at mass 127, and would therefore interfere with the measurements of the I^- ion current from hydrogen iodide. The true shape of the I^- resonance capture peak was obtained by subtracting the contribution of the SF_5^- ion from the total negative ion current for mass 127. The F^- ion current from SF_6 did not interfere with the F^- peak for hydrogen fluoride, as the F^- ion peaks for the two compounds appear at different energies. Typical resonance capture peaks for the F^- ion from hydrogen fluoride, the Br^- ion from hydrogen bromide, the Cl^- ion from hydrogen chloride, and the I^- ion from hydrogen iodide, are shown in Figs. 2-5, respectively.

The appearance potentials of the various negative ions formed by the resonance capture processes and the

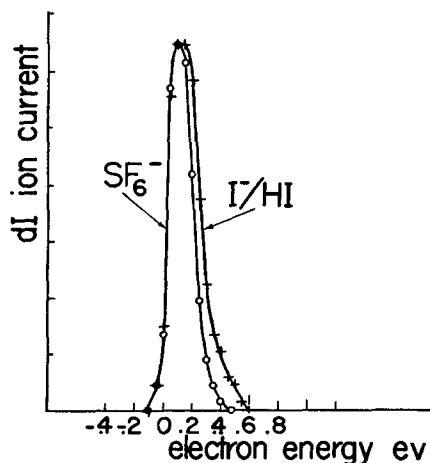


FIG. 5. The ionization efficiency curve for the formation of the I^- ion from hydrogen iodide by a resonance capture process.

TABLE I. Electron impact data on X⁻/HX resonance capture peaks.

Ion	Appearance potential (ev)	Peak maximum (ev)	Over-all width (ev)
F ⁻	1.88±0.06
Cl ⁻	0.62±0.04	0.77±0.10	0.92±0.06
Br ⁻	0.10±0.03	0.21±0.05	0.72±0.04
I ⁻	0.03±0.04	0.05±0.04	0.53±0.05

true over-all widths of the resonance capture peaks are given in Table I. The appearance potentials were determined by measuring the energy difference between the SF₆⁻ ion and X⁻ ion intercepts with the electron energy axis. The maximum of the SF₆⁻ ion peak has been found by Fox⁴ to correspond to an average electron energy of 0.03 ev, and so the energies at which the X⁻ peak maxima occurred were determined by measuring the energy difference between the SF₆⁻ and X⁻ peak maxima in each case, and adding 0.03 ev.

DISCUSSION

Negative ions arising from a resonance capture process such as indicated by Eq. (1) will have appearance potentials, $V(Y^-)$, given by the equation,

$$V(Y^-) = D(XY) - E(Y) + K.E. + E.E., \quad (3)$$

where $D(XY)$ is the dissociation energy of the XY bond, $E(Y)$ is the electron affinity of the Y atom, E.E. represents any excitation energy if any of the products are formed in excited states, and K.E. represents any kinetic energy with which the products are endowed. The dissociation energies of the hydrogen halides and the electron affinities of the halogen atoms are known. It is therefore possible to estimate the minimum appearance potentials to be expected for each of the halogen negative ions. These data have been collected in Table II. The observed appearance potentials and the energies at which the maxima of the ion peaks occur are in the order to be expected, as

shown by the data in Table II. It is obvious that the Br⁻, Cl⁻, and F⁻ ions are required, by the corresponding values of the dissociation energies of the hydrogen halides and the electron affinities of the halogen atoms, to be formed initially with kinetic energy. An inspection of Figs. 2-4 shows that the resonance capture peaks for these ions are not quite symmetrical. This is seen by contrasting the shapes of these peaks with that for the SF₆⁻ ion, which is shown in each of Figs. 2-4. The asymmetry to the high energy side of the maxima of these halogen negative ion peaks is caused by ions being formed with kinetic energy when the parent molecules capture electrons with energies in excess of that at which the peak maxima occur. In the case of hydrogen iodide, the electron affinity of the iodine atom ($E=3.24$ ev) is greater than the dissociation energy of the H-I bond ($D_0=3.06$ ev). Thus if the hydrogen iodide molecule captures electrons with only thermal energies, I⁻ ions will result. This, of course, means that the appearance potential of the I⁻ ion from hydrogen iodide should be approximately zero. Figure 5 shows that the I⁻ resonance capture peak from hydrogen iodide overlaps the SF₆⁻ resonance capture peak very closely, in agreement with these expectations.

The data in Table II make it possible to sketch roughly the potential energy curves for the HX molecule and the hypothetical HX⁻ molecular ions formed by electron capture. Figures 6 and 7 indicate the required potential energy curves for the cases of hydrogen bromide and hydrogen iodide. The dissociation limits of the upper (HX⁻) potential energy curves (to which transitions from the HX ground state take place to produce X⁻ ions) must in each case be at an energy of $D(HX) - E(X)$ with respect to the HX ground state. The shape of the true resonance capture peak for the X⁻ ion should be a reflection of the HX ground state vibrational eigenfunction in the upper (HX⁻) potential energy curve. The approximate shape of the upper (HX⁻) potential energy curve can be sketched if the appearance potential of the X⁻ ion, the energy at which the resonance capture peak occurs, and the width of the resonance capture peak are known. The data in Tables I and II have been used to enable

TABLE II. Spectroscopic and electron impact data for hydrogen halides. (Note: The "errors" quoted are standard deviations.)

X	D(HX) ev	E(X) ev ^a	V _{calc.} (X) ev	r _e (HX) Å ^b	Observed electron energy at (ev):	
					X ⁻ onset	Peak maximum
F	5.83 ^a	3.63	2.20	0.9171	1.88±0.06 ^d	4.0 ±0.2 ^d
Cl	4.43 ^b	3.78	0.65	1.2746	0.62±0.05	0.77±0.05
Br	3.75 ^b	3.54	0.21	0.4138	0.10±0.05	0.21±0.05
I	3.06 ^b	3.24	-0.18	1.6041	0.03±0.03	0.05±0.05

^a Hurley, Proc. Phys. Soc. (London) A69, 301 (1956).^b Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd edition.^c Pritchard, Chem. Revs. 52, 529 (1953).^d Using O⁻/O₂ as a standard.

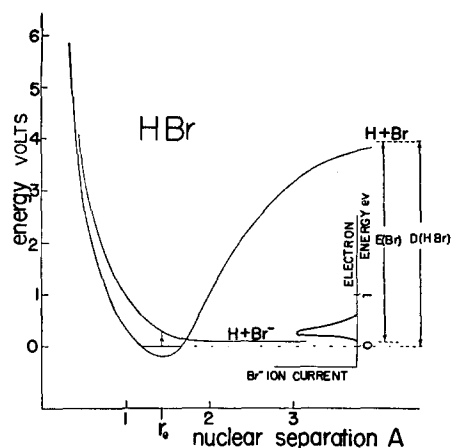


FIG. 6. Potential energy diagram for the transition $\text{HBr} + e = \text{H} + \text{Br}^-$.

Figs. 6 and 7 to be drawn and in these we have illustrated the mode of production of the I^- and Br^- ions from hydrogen iodide and bromide. It is clear that all our observations are in good agreement with what is to be expected from the theory of the origin of the

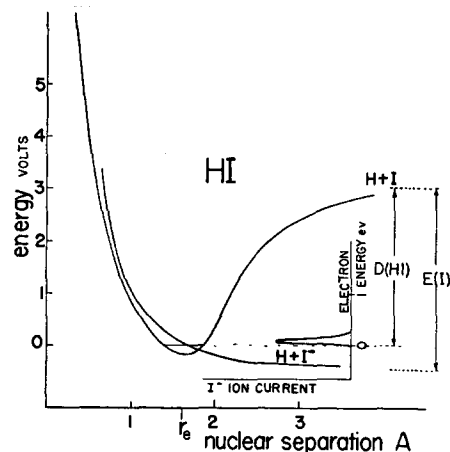


FIG. 7. Potential energy diagram for the transition $\text{HI} + e = \text{H} + \text{I}^-$.

X^- ions formed from the hydrogen halides by electron capture processes.

ACKNOWLEDGMENT

We should like to thank the National Research Council of Canada for generous support of this work.

Gaseous Detonations. XI. Double Waves

MARK CHER* AND G. B. KISTIAKOWSKY

Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts

(Received May 7, 1958)

Photographic studies of detonations of benzene-oxygen mixtures with the slit and rotating drum camera arrangement have shown under well defined conditions the occurrence of a sharp luminous front receding at a constant rate (*ca* 73m/sec) from the detonation wave front. The same phenomenon has been observed in several other hydrocarbon-oxygen mixtures but not in mixtures of hydrogen and oxygen. Measurements of gas densities by the method of x-ray absorption gave confirmatory evidence that the secondary fronts are shock waves in the domain of the rarefaction wave. A qualitative theory of the secondary wave is developed by analogy with the steady supersonic gas flow through convergent-divergent nozzles. It is concluded that the secondary wave is due to entropy increase in the rarefaction wave, caused by a spontaneous reaction. Detonation velocity measurements of benzene-oxygen mixtures and thermodynamic velocity calculations show indeed that thermodynamic equilibrium is not attained in the *C-J* state of the detonation wave, but the nature of the lagging chemical reaction cannot be established.

IT was shown in two earlier papers from this Laboratory^{1,2} that a luminous wave is formed some distance behind the detonation front in detonating mixtures of 71% acetylene and 29% oxygen. The secondary wave was observed to overtake the detonation front, the resulting single wave then propagating with a velocity

* Present address: Department of Chemistry, University of California at Los Angeles.

¹ G. B. Kistiakowsky and W. G. Zinman, *J. Chem. Phys.* **23**, 1889 (1955).

² G. B. Kistiakowsky and P. C. Mangelsdorf, Jr., *J. Chem. Phys.* **25**, 516 (1956).

intermediate between those of the initial waves. This phenomenon, occurring only in mixtures of a very narrow composition range, was attributed to the occurrence of a delayed exothermic reaction in which the residual unburned acetylene of the primary reaction zone was decomposed into carbon and hydrogen. The original purpose of the present investigation was to search for other gaseous detonations in which carbon precipitation or other nucleation reactions might occur. Rather unexpectedly a different phenomenon was observed; namely, a compressional