Negative Ion Mass Spectrometry

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Contents

I. Introduction

The subject of gaseous negative ions has received considerable attention in the last decade. An understanding of the formation processes for negative ions and the role negative ions play in various chemical processes is of fundamental importance in describing the nature of radiation phenomena, the formation of ions and electrons in the ionosphere, the production of ions in flames, and the use of negative ions in qualitative and quantitative analyses of materials using mass spectrometric techniques. In this review, covering the literature since the last comprehensive review by Melton[1] in 1960, an examination of current research areas involving gaseous negative ions and a discussion of the usefulness of the data in chemical analysis will be presented. In general the discussion will consider polyatomic negative ions in mass spectrometry. Recently, comprehensive reviews of atomic negative ions have appeared,[2-4] and discussions of the measurements of electron affinities including photodetachment studies[5-7] have been presented. Papers describing extensive results on a single class of compounds[8,9] have been published, and there may be some duplication in this review. Recently, Christophorou[10] published an excellent book which describes in detail the nature of radiation processes including negative ions.

It is important to evaluate the present understanding regarding the formation and properties of gaseous negative ions, to compare the results using different methods of investigation, and to delineate possible directions of future studies. To accomplish this the following topics will be considered.

1. The investigations which aid in providing a detailed description of the formation of negative ions in ground and excited states.
2. The application of appearance potential measurements in evaluating electron affinities.
3. The use of negative ion mass spectra in elucidating molecular structure.
4. The information on negative ion formation and destruction processes *via* ion–molecule reactions.
5. The advances made in the role of negative ions in the chemistry of the ionosphere.

This review will not discuss attempts to calculate electron affinities using various adaptations of SCF–MO or other approximations nor will any discussion be presented regarding the reactions of high energy negative ions (several keV and higher) with gaseous or solid targets. These discussions fall outside the scope or intent of the present review. The literature survey extends to January 1972.

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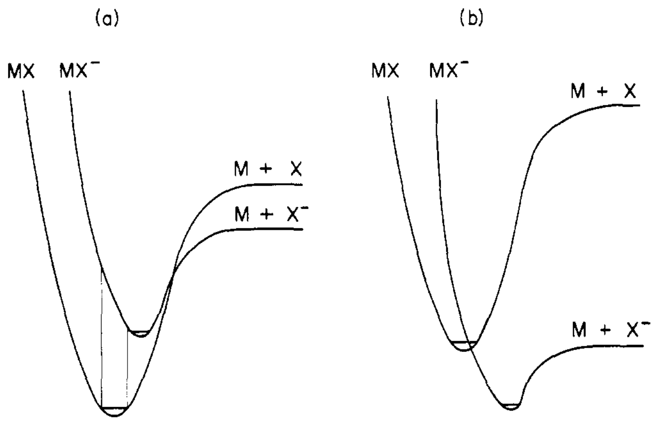

Figure 1. Potential energy curves for MX and MX^- where the electron affinity of MX is less than (a) and greater than (b) zero.

II. Negative Ions at Low Pressure, 10^{-7}–10^{-5} Torr

A. General Discussion

1. Instrumentation

Negative ions can be studied in most mass spectrometers provided the appropriate electric potentials and electric and magnetic fields can be reversed. In some instances special ion sources have been developed for producing intense heavy negative ion beams[11] and for ions at low energies.[12] A Penning ion source[13] has been used to produce polyatomic negative ions of the IV–VIa subgroups of the periodic table. Polymeric ions of Si_n^- with $n = 11$ and for S_n^- ions with $n = 10$ have been detected. Svec and Flesch[14,15] have described a mass spectrometer which simultaneously collects positive and negative ions. The instrument[14,15] has been used to study negative ions in chromyl chloride and fluoride.

2. Ion Formation and Energetics

Negative ions may be produced in conventional mass spectrometers at pressures of 10^{-7}–10^{-5} Torr by interaction of an energetic electron with a molecule. Depending on the electron energy and the nature of the molecule, three generalized processes have been observed as illustrated for a diatomic molecule MX

(a) Resonance capture

$$MX + e^- \rightarrow MX^- \tag{1}$$

(b) Dissociative resonance capture

$$MX + e^- \rightarrow M + X^- \tag{2}$$
$$MX + e^- \rightarrow M^- + X \tag{3}$$

(c) Ion-pair process

$$MX + e^- \rightarrow M^+ + X^- + e^- \tag{4}$$
$$MX + e^- \rightarrow M^- + X^+ + e^- \tag{5}$$

Process a produces a parent negative ion and occurs at near 0 eV, process b may be detected in the energy range 0–~15 eV, while ion-pair reactions, process c, are observed above about 10 eV.

A better understanding of these processes and the distribution of energy in the products may be obtained by examining potential energy diagrams for diatomic molecules and the negative ion. For these discussions, electron affinity is defined as the difference in energy between the ground-state neutral and an electron at infinity and the ground state of the negative ion.

Appropriate potential energy curves for MX and MX^- are shown in Figures 1a and 1b. Two situations arise; the electron affinity of MX is less than zero (case I) or greater than zero (case II). These are illustrated in Figure 1a and 1b, respectively. In case I, transitions from the ground state of the molecule occur according to the Franck–Condon principle, where electron motions are considered to be much more rapid than nuclear motions. Thus the transitions are vertical, and, depending on the difference in the internuclear equilibrium separation of the atoms in the ion and the neutral, a ground-state ion or an excited-state ion may be formed. Since the nuclear separation in MX^- is usually greater than in MX, the MX^- ion is formed in a vibrationally excited state and possibly in the dissociation continuum and is represented as MX^{-*}. The MX^{-*} ion is unstable and may decompose by autodetachment

$$MX^{-*} \rightarrow MX^* + e^- \tag{6}$$

or if excited above the dissociation asymptote may dissociate producing M^- and X or M and X^-. Stabilization of MX^{-*} may occur by collision with a neutral molecule (although this is unlikely at 10^{-7}–10^{-6} Torr) or by radiation emission. Collisional stabilization is not unique because competing collisional reactions may occur. Diatomic negative ions formed by resonance capture have not been detected in mass spectrometric studies because the lifetime is too short, $\ll 10^{-6}$ sec.

In case II where the electron affinity of MX is greater than zero, the potential energy curve for the parent negative ion may or may not cross the Franck–Condon region. If it does cross the Franck–Condon region, reaction and/or dissociation processes similar to those for curve I may occur. If the MX^- curve does not intersect the vertical transition region as shown in Figure 1b, a different form of attachment is imagined. Here it is proposed[10] that attachment occurs in such a manner that vibrational excitation of the neutral molecule leads to subsequent capture of the incident electron. In another way of imagining the capture it is recognized that because of the low energy of the electron, long interaction times between the molecule and the electron may occur. Under such conditions the Born–Oppenheimer approximation may break down so that the nuclei relax and change from their normal configuration to a position on the negative ion curve.

A number of polyatomic molecules attach electrons for times long enough to be detected in conventional mass spectrometers. Such species are generally symmetric so that excess energy of the attached electron is shared with the many degrees of freedom. In these instances molecular ion lifetimes of 10^{-6} sec or greater have been reported.

The energy associated with the resonance capture process can be expressed for the reaction

$$MX + e^- \rightarrow MX^{-*} \tag{7}$$

$$\Delta H_{\text{react}} = AP(MX^-) = -EA(MX) + EE \tag{8}$$

where AP = appearance potential of MX^-, EA = electron affinity of MX, and EE = total excess energy (electronic, vibrational, rotational). Because of the difficulties of measuring EE experimentally, it is unlikely that appearance potential measurements for parent negative ions will yield meaningful electron affinities.

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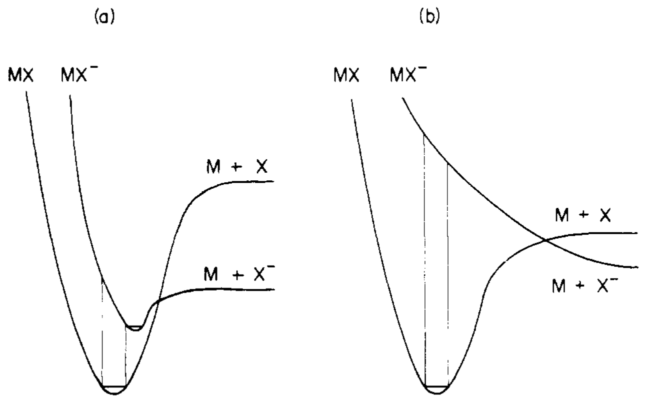

Figure 2. Potential curve for MX and MX^- showing attractive (a) and repulsive (b) states for MX^-.

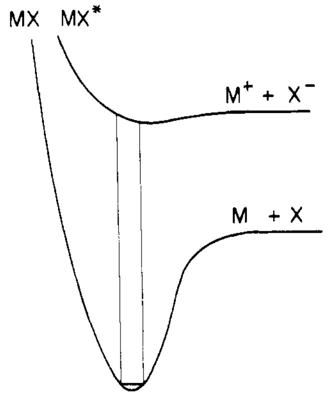

Figure 3. Potential energy curve for MX and MX* for an ion-pair process.

The second important process, dissociative resonance capture, may be explained by examining Figure 2a and 2b. The potential energy curve for MX^- is shown as an attractive state in Figure 2a and as a repulsive state in Figure 2b. Franck-Condon transitions to the attractive state will lead to dissociative capture if levels above the dissociation limit of MX^- are populated. Two possibilities exist, reactions 2 and 3, depending on the relative values of the electron affinities of M and X. In Figure 2a, the $EA(X) > EA(M)$; thus reaction 2 is expected. In addition to forming M and X^-, the molecular ion MX^{-*} is also formed.

In Figure 2b a repulsive state of MX^- is shown which dissociates to produce M and X^-. A vertical transition from MX produces MX^- in an unstable repulsive state which dissociates producing M and X^-. For dissociative resonance processes where the products are produced from levels above the dissociation limit, M and X^- will contain excess translational and excitation energy. The translational energy is partitioned between M and X^- according to the conservation of momentum.

The dissociative resonance process is conveniently used to measure the electron affinity of the negative ion product or the bond dissociation energy of MX. This evaluation proceeds from the appearance potential measurement for X^- and knowledge or a determination of the excess energy contributions. Either the electron affinity or bond energy may be evaluated if the other parameters are known according to the equation

$$\Delta H_{\text{react}} = \text{AP}(X^-) = D(\text{M-X}) - \text{EA}(X) + \text{KE} + \text{EE} \tag{9}$$

where D(M-X) is the bond dissociation energy of MX, EA the electron affinity of X, KE the total translational energy for M and X^-, and EE the internal excitation energy for M and X^-. The internal energy for polyatomic neutrals and ions includes electronic, vibrational, and rotational energies. Specific instances of evaluation of KE and EE will be discussed later.

The ion-pair process, illustrated in reactions 4 and 5 and represented in Figure 3, results in the formation of a negative ion X^- and a positive ion M^+. The electron in this reaction is imagined as supplying the energy for excitation. The ion-pair process occurs by dissociation or predissociation of an excited state of the neutral molecule MX to yield M^+ and X^-. If the vertical transition to MX occurs to levels above the dissociation limit, then M^+ and X^- may be formed with excess energy in a manner similar to that noted for dissociative resonance capture.

Similarly, for polyatomic ion products, the products may contain excess internal and translational energy. For the ion-pair process there is a certain threshold energy; below the critical energy the ion-pair process will not be observed. The probability of ion-pair formation increases approximately linearly above threshold up to an energy roughly three times the threshold. Beyond this energy the probability declines steadily about as the inverse of energy. The ion-pair process may be expected when other forms of excitation are involved, *e.g.*, photon beam or discharge sources.

For the ion-pair process the minimum energy, the appearance potential, can be represented as

$$\Delta H_{\text{react}} = \text{AP}(X^- \text{ and } M^+) = D(\text{MX}) + \text{IP}(M) - \text{EA}(X) + \text{KE} + \text{EE} \tag{10}$$

where IP(M) is the ionization potential of M and the other variables have been defined previously. A study of ion-pair processes can thus provide information on electron affinities, bond energies, or ionization potentials. Since ionization potentials are evaluated with more accuracy and precision by other measurements, the emphasis in ion-pair processes has centered on evaluating electron affinities and bond energies. Negative ions may be produced by other processes at higher ion source pressures, and these will be discussed later in this review.

B. Experimental Measurements

Studies of negative ions are usually classified according to the method of investigation. Unimolecular decomposition reactions at low pressures using conventional electron impact mass spectrometry are considered first. Investigations have included qualitative identification of compounds and functional group analysis, appearance potential measurements of negative ions, determination of lifetimes of temporary negative ions, and isotopic abundance measurements. A significant amount of work has been expended in evaluating the energetics of negative ion formation. Because the available data are important in providing an understanding of the probable processes for negative ion formation and give a basis for theoretical explanations of the experimental observation, a discussion of the energetic processes expressed in eq 8, 9, and 10 is presented now.

The problems associated with the measurement of negative ion mass spectra and appearance potentials have been detailed elsewhere.[1,8] A brief summary of the experimental problems is presented here. Since molecules with electronegative groups, halogens, nitro, etc., have been studied most frequently, the behavior of these materials in the ion source is important. The lifetime of the electron-emitting filament is often very short because of reactions of the compounds with the wire, oftentimes tungsten. Use of rhenium or thoria coated tungsten filaments extends the lifetime. Reactions on the filament often change the emission characteristics so that the energy distribution may become distorted or ill shaped. In addition deposits on the walls of the source may lead to alteration of the electrostatic field in the source and thus distort the electron energy distribution and shift the electron energy.

Because the electrons are produced from a filament at about 2000°K, pyrolysis of the sample on the filament may result, and the formation of noncharacteristic negative ions may occur. These latter ions will necessarily be of reduced intensity, and their abundance will also depend on the filament temperature. Thus careful consideration of pyrolysis and pyrolysis negative ion formation must be considered in accounting for the formation of low-intensity negative ions at any electron energy.

For appearance potential studies involving ion-pair or resonance capture processes, it is important that the thermal energy distribution be well defined and as narrow as possible. If distorted energy distributions are present, spurious and unreal resonance capture peaks result. Such erroneous peaks may make the interpretation of the energetic result difficult. Broadening of the distribution may also occur by improper alignment of the source collimating magnet. A measure of the electron energy distribution may be made by determining the resonance electron capture curve for SF_6^- from SF_6 at near-zero electron energies. Since the thermal energy distribution is often 0.5 eV wide at half-height, other methods of controlling the electron energy distribution have been used so that fine structure in the ionization efficiency curves[16] may be detected. The approaches taken include the RPD method designed and perfected by Fox[17] and the electron velocity selector of Brion.[18]

The RPD and the velocity selector techniques lead to reductions in electron beam intensity and therefore in ion current. However, both methods have been used with success. In view of this possible difficulty, other techniques have been reported where the full distribution was used and a detailed analytical examination of the ionization efficiency curves employed to extract more precise appearance potential values.

The analytical methods employed include the deconvolution process, introduced by Morrison[19] for studies of positive ions and used by Thynne[20,21] in negative ion studies. The deconvolution process extracts the ionization probability behavior from the ionization efficiency curve by using an experimentally measured or estimated electron energy distribution. The energy, E, of the bombarding electron is the sum of its thermal energy, U, and the potential difference in the electron gun, V, *i.e.*, $E = (U + V)$. The thermal energy distribution, mU, is given for the fraction of electrons having an energy in the interval U to $U + \Delta U$. The ion current, $i(V)$, for electrons of nominal energy V, measured as a function of E, is then the product of the probability of ionization, $I(E)$, and the electron energy distribution function mU, integrated over all values of U for individual values of V. The resulting integral,[19] the convolution integral, is

$$i(V) \propto \int_{U=0}^{\infty} I(U + V)mU\mathrm{d}U \qquad (11)$$

and it is the function $I(E)$ which is desired. Morrison[19] successfully determined $I(E)$ for positive ions using an iterative unfolding procedure[22] and Fourier transforms for evaluation. Morrison[19] indicated that the deconvolution results were little affected by large variations in the electron energy spread mU. In applications of deconvolution to negative ions,[20] selection of an incorrect electron energy distribution may shift the relative onset values unequally, yield unresolvable onset values, or alter the width of single resonance peaks. It is emphasized[20] that reliable values of appearance potentials, peak maxima, and peak widths can be obtained if an accurate value of the electron energy distribution is known. As mentioned earlier, this distribution may be evaluated using the ionization efficiency curve for SF_6^- (SF_6)[23] or other ions formed by capture of thermal electrons.

Another method of determining the onset energy from the ionization efficiency curve, the EDD method, has been introduced by Winters, *et al.*[24] The energy distribution difference method, EDD, is an analytical procedure which reduces the effective energy distribution. The measurement is carried out using a conventional electron bombardment source, without retarding grids, or pulsed electron gun operation. As with the RPD method, values of Δi are plotted *vs.* V to obtain the appearance potential. In Winters' method Δi is evaluated according to the expression

$$\Delta i = i(V) - b \cdot i(V + 0.1) \qquad (12)$$

where $i(V)$ is the measured ion current at electron energy V, and at $(V + 0.1)$ eV, and b is an empirical constant determined for the filament and mass spectrometer used. The results yield appearance potential data comparable to that using RPD techniques, including the detection of electronic excitation.

Thus by use of deconvolution techniques[19-21] or other interpretative methods,[24,25] reliable appearance potentials may be obtained. For complete knowledge of the distribution of energy in the resonance processes, reactions 2 and 3 and the ion-pair reaction (reactions 4 and 5), KE and EE must be evaluated.

Excess translational energy (KE) in most negative ion appearance potential studies has been assumed zero or negligible. A number of authors[25-28] have shown that this neglect is not justified. In studies by Franklin and coworkers,[25,29,30] translational energies have been determined using a Bendix TOF mass spectrometer. The evaluation of the average translational energy[29] involves a measurement of the peak width at half-height for the m/e in question. The translational energy is measured *vs.* the electron energy for the low-energy resonance process. Translational energy at the appearance potential is obtained by extrapolation of translational energy *vs.* electron energy curve. Since translational energy is measured only for the ion, the total excess translational energy (ion and neutral) is obtained from the principle of conservation of momentum according to the expression given by Haney and Franklin.[31] The power of the work of Haney

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and Franklin[31] has been demonstrated for negative ions by DeCorpo, Bafus, and Franklin.[25] By assuming that (1) the fragment negative ions are produced by decomposition of the parent negative ion, (2) the energy transfer among N harmonic oscillators is rapid, (3) a statistically determined fraction of the average excess energy will appear as translational energy in the product ion and neutral, and (4) rotational energy is negligible and electronic excitation can be deduced, the total excess energy may be evaluated according to the relationship

$$\mathrm{KE(translational)} = E^*/\alpha N \qquad (13)$$

where E^* = total excess energy (translational and vibrational; electronic not included in E^* but accounted for), α = correction factor to account for the fact that one-third to one-half of the oscillators are active in the decomposition process, $\alpha \cong 0.42$, and N = number of harmonic oscillators. Following the procedure outlined, values of the heats of formation of halogen molecular ions, X_2^-, have been reported.[30] Because of the simplicity of the TOF translational energy measurement and the apparent ease of correlating translational energy with total excess energy, it would seem that greater use of the procedure will appear in the future to better describe the energetics of negative ion formation.

In investigations by Curran[32] translational energies were measured for fragment halide ions from simple halocarbon molecules. Since the analyzer operates at high potential and the ion source and collector operate at ground potential, Curran[32] measures translational energy by varying the potential of the ion source *vs.* ground. Translation energy data and appearance potentials were used by Curran[32] to evaluate bond energies in halocarbons.

Additional methods[33-36] for measuring ion translational energies have been reported, and in some instances[35-37] negative ions have been studied.

III. Mass Spectra

The measurement and tabulation of negative ion mass spectra have not received the attention devoted to positive ions. This situation exists for several reasons; first, cross sections for negative ion formation are smaller by at least an order of magnitude, and, secondly, the negative ions observed are severely dependent on the electron energy. In general at high electron energies, greater than 10–15 eV, only ion-pair processes will be detected. At lower energies only resonance processes occur. To conquer the first problem high pressures may be used, but under such conditions other complexities are encountered. When high electron energies (70 eV) are used at high pressures, secondary electrons are produced and a broad distribution of energies (0–70 eV) results so ion formation may occur by ion-pair or resonance processes. The ion abundances may not be directly related to the first power of the pressure due to ion–molecule reactions and secondary electron capture reactions. In spite of these problems, investigations of negative ion mass spectra at selected electron energies and at fixed energies (70–80 eV) have been reported. Appearance potential studies have provided information on bond energies and electron affinities and in other instances have been used as an aid in structure elucidation.

A. Appearance Potential Determinations: Resonance Capture Processes

1. Hydrogen

Dissociative capture processes result in the formation of the hydride ion, H^-,[38-41] with maxima at electron energies of 3.75 eV (sharp resonance),[38] 8–13 eV (broad resonance),[39,40] and 14 eV (sharp resonance).[39,40] The 3.73-eV onset[38] is in good agreement with the calculated value using the H_2 dissociation energy and the electron affinity of H. A comparison of D^- formation at 3.73[38] and at 14 eV[42] suggests that at low energies the H_2^- potential energy curve is broad and is the unstable ($^2\Sigma_u^+$) ground state of H_2^-.[42] At other energies the transition is to a repulsive state of the H_2^- curve. The dissociative process produces the H^- ion and H atom with kinetic energy at 8–13 eV and an excited H* (n = 2) at 14 eV,[38,39] with low translational energy for the products. In the 11–12.5-eV region the formation of H^- occurs from the H_2^- ($^2\Sigma g^+$) state with translational energy.[40]

Locht and Momigny[41] have studied H^- dissociative attachment peak shapes to evaluate thresholds, kinetic energy distributions, and relative positions of potential energy curves for H_2^{-*}, which decay to H^- and H. The cross section is approximated as the initial vibrational wave function, $\Psi(E)$, written in terms of the electron energy, E. Convolution of portions of the reflected effective wave function, $(\Psi(E))^2$, with a selected electron energy distribution yields model functions which are used to fit experimental data. Upon selection of the appropriate model, the range of kinetic energy for H^- in the dissociative process is established. Linear extrapolation of the rising portion of the *IE* curve is used to evaluate the threshold. The threshold values around 4 and 14 eV are consistently lower than those measured using RPD techniques.

Dowell and Sharp[42] have detected breaks in the 11–12.5-eV range dissociative process which were attributed to vibrational resonance in the dissociative process. Recently Spence and Schulz[43] have shown that rotational excitation does not affect the cross section at 3.75 eV. This result is in contrast to the theoretical prediction.[44]

2. Halogens: X_2, HX, MX_n Compounds

The formation of F^- from F_2 by dissociative capture and ion-pair reactions has been investigated to evaluate $D(F_2)$.[45] At near zero eV, F^- is formed with 1.78 eV total excess energy. The resonance maximum is about 1.6 eV. The appearance potential for the ion-pair process is 15.8 eV and the total excess energy 0.26 eV. In molecular chlorine,[46,47] bromine,[46] and iodine,[46,48,49] dissociative

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resonance and ion-pair processes are noted and appearance potentials measured using the RPD method. Fragments were assumed to be produced in their ground states. Halide ions have been detected[50] from the hydrogen halides. From a comparison of the calculated onset values, using D(HX) and EA(X), and the measured appearance potentials of X^-, it appears that the X^- ions must be formed with excess kinetic energy.

Detection of halide ions from a variety of compounds has been reported,[51-54] and appearance potentials and excess energies have been measured. The results are summarized in Table I.

3. *Oxygen*

Oxygen has been studied using mass spectrometric and total ionization techniques.[36,47,54-63,70] The O^- ion is formed with kinetic energy by dissociative attachment (DA) onsetting at about 3.5 eV and the maximum at around 6.5 eV. Ion-pair production occurs at about 17.4 eV.

An interesting result[36] of these studies is that the thermal energy of the target molecule, in this case O_2, is important in evaluating the kinetic energy in the fragment ions. In early studies[59] where retarding curves had been used to measure kinetic energy, the effect of thermal energy of the parent molecule, and thus of the ions, had been ignored.[36,59] This fact resulted in significant disagreement between electron affinities determined by photodetachment and electron beam methods. Chantry and Schulz[36] have rectified the differences.

The excess energy, in the center-of-mass system, for dissociative attachment reactions is given by the expression

$$E_R = V_e - (D - A) \tag{14}$$

where V_e is the energy available and D and A are the dissociation energy and electron affinity, respectively, for a reaction of the type

$$O_2 + e^- \rightarrow O_2^{-*} \rightarrow O^- + O \tag{15}$$

The kinetic energy of the ion, E_0, is

$$E_0 = \left(1 - \frac{m}{M}\right)[V_e - (D - A)] \tag{16}$$

where m = mass of O^- and M = mass of O_2^-.

The ion energy measured in the laboratory system[36] is the vector sum of the initial thermal velocity of O_2 and the center of mass velocity of O^-, E_0. The result is that orientation and magnitude of the initial thermal velocity produce a rather large spread in the kinetic energy of the fragment ions measured in the laboratory frame of reference.

Chantry and Schulz[36] have measured kinetic energy distributions, using a Wien filter as a function of electron energy, V_e. The distribution is broadened as the electron energy is increased and as the temperature of the target molecule, O_2, is increased. The peak in the ion energy distribution curve is taken as the most probable ion energy and from a plot of E_0 *vs.* V_e, extrapolation of E_0 to 0 yields $V_e = (D - A)$ and permits an evaluation of A of O^- = 1.5 eV. This value is in agreement with the photodetachment measurement.[2]

Studies of the variation of the cross section and onset energy with temperature for O^- formation from O_2 have been reported[37,56] using electron beam techniques. Henderson, *et al.*,[56] observe that the maximum in the cross section in the 5-eV region increases from 1.25×10^{-18} at 300°K to 1.93×10^{-18} cm^2 at 1930°K. In addition, the onset energy is lowered by about 2.5 eV upon heating O_2 from 300 to 1930°K. From knowledge of $D(O_2)$ and EA(O) the total excess energy is at least 2.1 eV. It is argued that the excess energy is in the form of vibrational excitation of O_2. Electronic excitation is ruled out because measured activation energies at different electron energies are less than the energy of the excited state of oxygen ($a^1\Delta_g$). Rotational excitation is deemed not responsible by comparing the cross-section behavior using O_2 produced from a furnace with large aperture and low pressure where effusive flow occurs and O_2 produced in a furnace at high pressure and small orifice diameter. For the first case the vibrational and rotational temperature would be equal, while in the second the vibrational temperature nearly equals that of the furnace and the rotational temperature would be diminished significantly with significant rotational cooling of at least 1000°K. No shift of the O^- curve was noted, and it is concluded that vibrational excitation only is responsible for the shift.[56]

O'Malley[292] has, *via* a theoretical calculation, reproduced the experimental data of Henderson, *et al.*[56] O'Malley assumes that the initial distribution of rotational states is negligible. He suggests that the temperature dependence arises from the effect on the initial distribution of excited vibrational states on the rapidly varying survival probability.

The data of Spence and Schulz[37] confirm the temperature-dependent cross-section behavior. It is suggested[37] that slight differences between measured cross sections[37,56] are the result of different electron energy distributions.

The angular distribution of O^- from O_2 has been studied[58] at 330°K where the cross section maximizes at 6.7 eV. Maxima in the angular distribution occur at about 40° and 130°. Analysis of the angular distribution as a function of energy suggests that O^- dissociative attachment occurs from a $^2\Pi_u$ resonance repulsive state.

Recently, Chantry[57] has studied the 15-eV O^- formation from O_2. It is demonstrated that the high-energy O^- peaks in O_2 and others like it in CO, N_2O, and NO result from so-called "partner" peaks arising from capture of inelastically scattered electrons. These scattered electrons occur from energy loss collisions with O_2 producing lower energy electrons which can be subsequently captured and promote dissociative attachment. The expected quadratic pressure dependence for the "partner" peak ion current is observed supporting the general reaction scheme

$$e^-(E^* + E_1) + O_2 \rightarrow O_2^* + e^-(E_1) \tag{17}$$

$$e^-(E_1) + O_2 \rightarrow O^- + O \tag{18}$$

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Similar processes were noted[57] for O^- formation in N_2O, CO, and NO.

Ozone has been studied by Curran,[64] and O_2^- and O^- were formed *via* dissociative attachment processes at $E_e < 2.0$ eV at low pressure. A weak O_3^- ion signal was detected at high (unmeasured) source pressures. Presumably O_3^- is produced by an ion-molecule reaction although no measurement of O_3^- ion current *vs.* pressure or electron energy was carried out.[64] From translational energy measurements and the appearance potentials for O_2^-, a lower limit of $EA(O_2) > 0.58$ eV was calculated. No account of vibrational excitation in O_2^- could be made. Berry[2] selects a value of $EA(O_2) = 0.15$ from photodetachment experiments. More recent results[488] using laser photodetachment techniques have established that $EA(O_2) = 0.44$ eV.

4. Water

Several studies of the negative ions produced from water have been carried out using mass spectrometric[62,65-68] and electron trap techniques[69] to contribute information useful in a complete description of the interaction of water with ionizing radiation. The possible reactions in water have been summarized,[67] and the ions detected are H^-, O^-, and OH^-.[62,65,67,68] It is likely that OH^- is formed *via* an ion-molecule reaction (see the discussion later in the review). In the mass spectrometric studies the ion abundances measured at the maxima for dissociative capture are not in exact agreement. Melton and Neece[65] report the relative cross sections are $H^- > O^-$ while Cottin[68] reports the opposite variation in ion intensity $O^- > H^-$. This discrepancy may be due to discrimination in the mass spectrometer for high-energy ions. At 100 eV, the cross sections vary, $H^- > O^- > OH^-$.[67] There are slight disagreements in the reported appearance potential data among the various investigators.[65,66,68] Three maxima are noted for O^-[65,66] and two for H^-.

5. Nitrogen Oxides

a. NO

The oxides which have been studied are NO, N_2O, and NO_2. In NO at low source pressures only O^- is observed.[70-76] Using appearance potential data [71] ≈ 7.0 eV and information on translational energy,[72] a value for *D*(NO) was determined.[71] Excellent agreement between the mass spectrometric and spectroscopic *D*(NO) values supported the contention that N and O^- were formed in their ground states.[71] There is a report[76] of the formation of O^- and N in their ground states, although the onset for O^- is lower, $AP(O^-) = 5.0$ eV, than that reported by any others.[62,70-75] Recent studies[74,75] have shown, however, that O^- is formed without translational energy at onset and that N is produced in an excited state, $N(^2D)$. At high electron energy resolution[75] fine structure in the O^- IE curve is interpreted as O^- formation from the ground state and excited states of NO^-.

Parent negative ion formation, NO^-, at low pressure has not been noted. Since the autodetachment lifetime is about 10^{-14} sec,[73] this is expected.

b. N_2O

Early studies of O^- formation from N_2O using total ionization[63,77,78] indicated two low-energy capture processes at less than 3 eV, although the measured cross sections do not agree in magnitude exactly. Mass spectrometric investigations[79] have shown that the negative ion observed is, in fact, O^-. Since the values of $D(N_2O)$ and EA(O) indicate that O^- onset should be less than 0 eV, Chantry[80] has examined the formation of $O^-(N_2O)$ as a function of temperature to examine the role internally excited N_2O molecules play in O^- production. Chantry observes a decrease in the appearance potential with increasing temperature and a 0.15-eV onset at room temperature, ~295°K. Striking variations in the low-energy maxima are observed while the high-energy 2.25-eV maximum is relatively insensitive to temperature. At low temperatures it is postulated[80] that a single resonance peak would be observed. Since the electron energy is too small to excite N_2 to an excited state, N_2 and O^- are assumed to be formed in their ground states.

The important conclusions[80] are that (a) the discrepancies in reported cross sections result from differences in target gas temperature, (b) electron attachment occurs with "hot N_2O molecules," and (c) dissociative attachment occurs from two distinct states of N_2O^-.

The states suggested[80] correspond to the ground state and $^2\Sigma$ state, of N_2O^-, for the 0.15- and 2.25-eV peaks, respectively. The temperature dependence at 0.15 eV is explained as arising from exciting a bending mode of ground state (N_2O) and is related to the energy separation of the ground states of N_2O and N_2O^- and their dependence on bond angle. The temperature-insensitive peak (2.25 eV) is associated with population of the highest energy states ($^2\Sigma$) of N_2O^-, and the decomposition to N_2 and O^-.

c. NO_2

Low-pressure investigations[81,82] of NO_2 have shown that primary ions O^-, O_2^-, and NO^- and the secondary NO_2^- ion are formed. Fox noted that[81] the NO_2^- ion current varied approximately as the second power of NO_2 pressure, indicative of an ion-molecule reaction or collisional stabilization of excited NO_2^-. Fox noted only O^- occurring *via* a dissociative process given in Table I. In recent studies[82] with greater detection sensitivity, primary ions NO^- and O_2^- were detected. The appearance potentials were used to set lower limits of $EA(O_2) \geq 1.1$ eV and $EA(NO) \geq 0.65$ eV. Recent measurements[488,489] indicate that $EA(O_2) = 0.44$ eV and $EA(NO) = 0.024$ eV. Charge-transfer reactions involving ion-molecule collision processes have produced NO^- and O_2^- and will be discussed later.

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TABLE I. Appearance Potentials for Negative Ions: Resonance Capture Processes

Ion	Molecule	Products	AP	KE	Max	Method	Ref
		Nonmetals					
H^-	H_2	$H^- + H$	3.73	No	3.75	MS	38
	H_2	$H^- + H(?)$	3.43	Yes	3.73	MS	41
	H_2	$H^- + H(?)$	8.0	Yes	11.0	TI	39, 40
	H_2	$H^- + H^*$	14.0	Yes	14.4	TI	39, 40
	D_2	$D^- + D$	14.0	No	14.4	TI, MS	38, 40
	HD	$D^- + H$	14.0	No	14.4	TI	40
	H_2O	$H^- + OH$	5.5	No	6.4	MS	65
	H_2O	$H^- + OH$	4.8	No	6.0	MS	68
	H_2O	$H^- + OH?$		Yes	6.5	TI	69
	H_2O	$H^- + OH$		No	8.0	MS	68
	H_2O	$H^- + O + H$		Yes	8.8	TI	69
	H_2O	$H^- + O + H$		No	8.6	MS	65
	CH_4	$H^- + CH_3$		No	~9	TI	102
	CH_4	$H^- + CH_3$	8.5			MS	99
	CH_4	$H^- + CH_3$	8.3			MS	100
	CH_4	$H^- + CH_3$	9.5			MS	100
	CH_4	$H^- + CH_3$	9.9			MS	99
	CH_4	$H^- + CH_3$	~10.2			MS	62
	CD_4	$D^- + CD_3$		No	~9.5	TI	102
	C_2H_2	$H^- + C_2H$	7.6			MS	100
	C_2H_4	$H^- + ?$	7.6			MS	100
	C_2H_4	$H^- + ?$	9.7			MS	100
	C_2H_6	$H^- + C_2H_5$	~9.5			MS	62
	C_2H_6	$H^- + ?$	8.3			MS	100
	C_3H_6	$H^- + ?$	7.7			MS	100
	C_3H_8	$H^- + ?$	7.8			MS	100
	C_3H_8	$H^- + C_3H_7$	~9.0			MS	62
	$CH_2{=}C(CH_3)_2$	$H^- + ?$	7.8			MS	100
	$n\text{-}C_4H_{10}$	$H^- + C_4H_9$	~8.7			MS	62
	$n\text{-}C_4H_{10}$	$H^- + C_4H_9(?)$	4.0		5.7	MS	98
	$n\text{-}C_4H_{10}$	$H^- + ?$	7.8			MS	100
	$i\text{-}C_4H_{10}$	$H^- + ?$	7.4			MS	100
	C_6H_6	$H^- + C_6H_5$	7.9			MS	100
	C_6H_6	$H^- + ?$	~10			MS	100
	CH_3NH_2	$H^- + CH_3NH$		No	4.85	MS	139
	CH_3NH_2	$H^- + CH_3NH$		No	5.52	MS	138
	CH_3ND_2	$D^- + CH_3ND$		No	5.82	MS	138
	CH_3NH_2	$H^- + CH_2 + NH_2$		No	9.50	MS	138
	CH_3ND_2	$H^- + CH_2 + ND_2$		No	9.71	MS	138
	CH_3NH_2	$H^- + CH_2NH + H$		No	8.27	MS	139
	CH_3ND_2	$D^- + CH_2ND + H$		No	9.53	MS	138
	CH_3NH_2	$H^- + CHNH_2 + H$		No	6.83	MS	138
	CH_3ND_2	$H^- + CHND_2 + H$		No	6.3	MS	138
	CH_3ND_2	$D^- + CH_3 + ND$		No	7.30	MS	138
	$(CH_3)_2NH$	$H^- + ?$		No	4.66	MS	139
	$(CH_3)_2NH$	$H^- + ?$		No	7.98	MS	139
	$(CH_3)_3N$	$H^- + ?$		No	8.16	MS	139
	CH_3OH	$H^- + CH_3O$	7.4	No	8.2	MS	100
	CH_3OH	$H^- + ?$	9.3	No	10.8	MS	100
	$C_2H_2O^a$	$H^- + COCH$	5.41	No	6.1	MS	130
	$C_2H_2O^a$	$H^- + CO + CH?$	8.5	No	9.7	MS	130
	C_2H_5OH	$H^- + ?$	4.5	No	6.0	MS	62
	C_2H_5OH	$H^- + ?$		No	7.7	MS	62
	C_2H_5OH	$H^- + ?$		No	9.5	MS	62
	C_2H_5OH	$H^- + C_2H_5O?$	7.0	No		MS	100
	C_2H_5OH	$H^- + ?$	7.8	No		MS	100
	CH_3CHO	$H^- + ?$	4.8	No	6.1	MS	62
	CH_3CHO	$H^- + ?$		No	8.2	MS	62
	$(CH_3)_2CO$	$H^- + ?$	6.5	No	8.5	MS	62
	$(C_2H_5)_2CO$	$H^- + ?$	5.1	No	6.5	MS	62
	$(C_2H_5)_2CO$	$H^- + ?$		No	8.4	MS	62
	CF_2CH_2	$H^- + ?$	5.0		7.2	MS	105
	CF_2CH_2	$H^- + ?$	8.5		10.7	MS	105
	CH_3COCH_2Cl	$H^- + ?$	4.8	No	6.2	MS	62
	CH_3COCH_2Cl	$H^- + ?$		No	8.1	MS	62
	NH_3	$H^- + NH_2$	3.9	No		MS	135
	NH_3	$H^- + NH_2$	~4.5	Yes	5.65	MS	137

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
H^-	NH_3	$H^- + NH_2$	4.8	No	5.8	MS	62
	NH_3	$H^- + NH_2$	5.3	Yes	5.65	MS	136
	NH_3	$H^- + NH_2$?		No	5.78	MS	138
	NH_3	$H^- + NH_2$	8.6	No	10.00	MS	62
	NH_3	$H^- + NH_2$		No	10.46	MS	138
	ND_3	$D^- + ND_2$		Yes	10.5	MS	136
	ND_3	$D^- + ND_2$	5.3	Yes	5.65	MS	136
	ND_3	$D^- + ND_2$	~4.5	Yes	5.86	MS	137
	ND_3	$D^- + ND_2$		Yes	10.5	MS	136
	SiH_4	$H^- + SiH_3$	7.9	No		MS	152
	PH_3	$H^- + PH_2$	5.4	No	6.5	MS	152
	PH_3	$H^- + PH_2$	5.4	No		MS	160
	PH_3	$H^- + PH + H$	7.5	No	9.7	MS	152
	PH_3	$H^- + PH + H$?	7.5	No		MS	160
	AsH_3	$H^- + AsH_2$	5.3	No	6.7	MS	152
	AsH_3	$H^- + AsH + H$?	7.4	No	~9	MS	152
F^-	F_2	$F^- + F$	0	Yes	1.6	MS	45
	HF	$F^- + H$	1.88	No	4.0	MS	54
	CF_4	$F^- + CF_3$	4.6	Yes		MS	25
	CF_4	$F^- + CF_3$	4.7	No	6.8	MS	158
	C_2F_4	$F^- + C_2F_3$	1.9	No		MS	115
	C_2F_4	$F^- + C_2F_3$	1.8	No	3.6	MS	107
	C_2F_4	$F^- + CF + CF_2$?	5.6	No	5.4	MS	107
	C_2F_4	$F^- + C + CF_3$?	6.3	No	7.0	MS	107
	C_2F_4	$F^- + C + F + CF_2$	10.3	No	11.5	MS	107
	C_2F_6	$F^- + C_2F_5$	2.0	No		MS	115
	C_2F_6	$F^- + C_2F_5$	2.2		3.75	MS	109
	C_2F_6	$F^- + C_2F_5$	1.7	No	2.10	MS	106
	C_2F_6	$F^- + C_2F_5$(?)	2.25	No	3.80	MS	106
	C_2F_6	$F^- + CF_2 + CF_3$?		No	4.5	MS	106
	C_3F_8	$F^- + C_3F_7$	1.7	No		MS	115
	C_3F_8	$F^- + C_3F_7$?	1.8		3.0	MS	109
	C_3F_8	$F^- + C_3F_7$?	1.35			MS	114
	C_4F_8	F^- + ?	3.0		4.3	MS	109
	C_4F_8	F^- + ?			6.8	MS	109
	C_4F_8	F^- + ?			8.0	MS	109
	C_4F_8	F^- + ?			9.6	MS	109
	C_4F_8	F^- + ?			10.3	MS	109
	c-C_4F_8	$F^- + C_4F_7$	1.8	No		MS	115
	n-C_4F_{10}	$F^- + C_4F_9$	1.8	No		MS	115
	c-C_5F_8	$F^- + C_5F_7$	1.8	No		MS	115
	c-C_6F_6	$F^- + C_6F_5$	?			MS	115
	c-$C_6F_{11}CF_3$	$F^- + C_7F_{13}$	1.7	No		MS	115
	CF_3H	$F^- + CHF_2$?	2.9			MS	106
	CF_3H	F^- + ?	3.7			MS	106
	CF_3H	$F^- + 2F + CH$?	9.3			MS	106
	CF_2CH_2	$F^- + CH_2CF$	1.6		2.5	MS	105
	CF_2CH_2	F^- + ?	3.3		4.2	MS	105
	CF_2CH_2	F^- + ?	4.6		5.2	MS	105
	CF_2CH_2	F^- + ?	5.4		7.3	MS	105
	CF_2CH_2	F^- + ?	8.7		10.6	MS	105
	CF_2CH_2	F^- + ?	11.1		11.4	MS	105
	CF_3CH_3	$F^- + C_2H_3F_2$	1.5			MS	106
	CF_3CH_3	F^- + ?	2.4			MS	106
	CF_3CH_3	F^- + ?	2.9			MS	106
	CF_3CH_3	F^- + ?	3.6			MS	106
	CF_3CH_3	F^- + ?	5.2			MS	106
	CF_3CH_3	$F^- + CF + F + CH_3$	9.5	No		MS	106
	COF_2	$F^- + COF$	2.1	No	2.7	MS	20, 117
	CF_3OF	$F^- + CF_3O$?	0.0	No	0.6	MS	117
	CF_3OF	F^- + ?	3.5	No	6.3	MS	117
	CF_3OF	F^- + ?	~7.8	No		MS	117
	CF_3COCF_3	$F^- + CF_2 + CO + CF_3$?	3.1	No	4.3	MS	108
	CF_3COCF_3	F^- + ?	5.7	No	7.2	MS	108
	CF_3COCF_3	F^- + ?	9.0	No		MS	108
	CCl_3F	$F^- + CCl_3$	1.8	Yes		MS	32
	CCl_3F	$F^- + CCl_3$	2.6	Yes	3.2	MS	32
	C_2F_5Cl	$F^- + C_2F_4Cl$	2.0	No		MS	115

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
F^-	BF_3	$F^- + BF_2^*$	10.5	Yes		MS	25
	BF_3	$F^- + BF_2$	10.7	No	~11.5	MS	150
	NF_3	$F^- + NF + F$		No	1.7	MS	140
	NF_3	$F^- + N + 2F$		No	3.4	MS	140
	SiF_4	$F^- + SiF_3$	10.85	No	11	MS	158
	SF_4	$F^- + SF_3$	0.2	No	0.65	MS	167
	SF_6	$F^- + SF_5$	0	No	0	MS	181
	SO_2F_2	$F^- + SO_2F$		No	3.2	MS	165
	SF_5Cl	$F^- + SF_2 + F_2 + Cl?$	6.3	No	6.5	MS	168
	SF_5Cl	$F^- + ?$	8.0	No	9.4	MS	168
	SeF_6	$F^- + SeF_5$	0.05	No		MS	52
	SeF_6	$F^- + SeF_5$	0.4	No	1.9	MS	119
	SeF_6	$F^- + SeF_5$		No	6.5	MS	169
	TeF_6	$F^- + TeF_5$		No	~7.2	MS	169
	XeF_4	$F^- + XeF_3$		No	0	MS	185
	XeF_4	$F^- + XeF_2 + F?$		No	~7	MS	185
	XeF_6	$F^- + XeF_5$		No	0	MS	185
	XeF_6	$F^- + XeF_4 + F?$		No	~5	MS	185
	XeF_6	$F^- + ?$		No	~8.5	MS	185
	LiF	$F^- + Li$	3.55	No		MS	187
	LiF	$F^- + ?$	6.5	No		MS	187
	NaF	$F^- + Na$	2.55	No		MS	187
	NaF	$F^- + ?$	5.25	No		MS	187
	KF	$F^- + K$	2.40	No		MS	187
	KF	$F^- + ?$	5.60	No		MS	187
	CrO_2F_2	$F^- + CrO_2F$	0.95	No		MS	196
	CrO_2F_2	$F^- + CrOF + O$	5.39	No		MS	196
	MoF_6	$F^- + MoF_5$		No	~1.0	MS	184
F_2^-	BF_3	$F_2^- + BF$	10.2	Yes		MS	25, 30
	BF_3	$F_2^- + BF$	10.5	No	~10.9	MS	150
	COF_2	$F_2^- + CO$	2.6	No	3.1	MS	20, 117
	NF_3	$F_2^- + NF?$	0	No		MS	140
	NF_3	$F_2^- + N + F?$	3.9	No	5.6	MS	140
	SiF_4	$F_2^- + SiF_2$	10.55	No	11	MS	158
	PF_3	$F_2^- + PF$	10.9	No	~11.5	MS	150
	SO_2F_2	$F_2^- + SO_2$		No	3.8	MS	165
	XeF_4	$F_2^- + XeF_2$		No	0	MS	185
	XeF_4	$F_2^- + ?$		No	~4.5	MS	185
	XeF_6	$F_2^- + XeF_4$		No	0	MS	185
	XeF_6	$F_2^- + ?$		No	~6	MS	185
	CrO_2F_2	$F_2^- + CrO_2$	5.7	No		MS	196
	CrO_2F_2	$F_2^- + CrO + O$	10.3	No		MS	196
O^-	O_2	$O^- + O$	3.45	No	6.5	MS	70
	O_2	$O^- + O$		No	5.62	MS	18
	O_2	$O^- + O$	4.63			TI	54
	O_2	$O^- + O$	4.3	No	6.5	TI	53
	O_2	$O^- + O$	4.4	Yes	6.7	TI	59, 36, 60, 61
	O_2	$O^- + O$	4.53	No	5.98	MS	47
	O_2	$O^- + O$	4.4	Yes	6.7	MS	36
	O_2	$O^- + O$	4.0	No	~6.7	MS	56
	O_2	$O^- + O$		No	~15	MS	57
	O_2	$O^- + O$	6.0	Yes		MS	62
	O_3	$O^- + O_2$	0.42	Yes	~1.3	MS	64
	NO	$O^- + N(^4S)$	5.0	No		MS	76
	NO	$O^- + N$	6.7	No	8.1	MS	63
	NO	$O^- + N$	6.6	No	8.6	MS	63
	NO	$O^- + N(^1D)$	6.99	No	7.9	MS	71[b]
	NO	$O^- + N(^1D)$	7.43	No	8.1	MS	70[b]
	NO	$O^- + N(^2D)$	7.50	Yes	~7.8	MS	74[b]
	NO	$O^- + N(^2D)$	7.39	No	~7.8	MS	75[b]
	NO	$O^- + N(^2D)$	6.5	Yes	7.5	MS	62[b]
	NO	$O^- + N^*(^2D)$		No	7.6	MS	57
	NO	$O^- + ?$		No	~14	MS	57
	NO	$O^- + ?$		No	~16	MS	57
	N_2O	$O^- + N_2$	0.15	Yes	0.15	MS	80
	N_2O	$O^- + N_2$	~0.2	No		MS	62
	N_2O	$O^- + N_2$	0	No	0.5	MS	79
	N_2O	$O^- + N_2$	~0	No	0.6	TI	63

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
O^-	N_2O	$O^- + N_2^*$	0	Yes	0.7	TI	77
	N_2O	$O^- + N_2^*$	0	Yes	0.7	MS	78
	N_2O	$O^- + N_2$		No	2.2	TI	63
	N_2O	$O^- + N_2$		Yes	2.25	MS	80
	N_2O	$O^- + N_2$		No	2.25	MS	57
	N_2O	$O^- + N_2$		No	2.4	MS	79
	N_2O	$O^- + N_2^{**}$		Yes	2.23	TI	77
	N_2O	$O^- + N_2^{**}$	~1.0	Yes	2.3	MS	78
	N_2O	O^- + ?		No	8.4	MS	57
	N_2O	$O^- + N_2$		No	10	TI	63
	N_2O	O^- + ?		No	~13	MS	57
	NO_2	O^- + NO	1.3	No	1.9	MS	82
	NO_2	O^- + NO	1.35	No	1.9	MS	81
	NO_2	O^- + NO	~2.5	No	3.0	MS	81
	NO_2	O^- (impurity)	7.5	No	8.75	MS	81
	CO	O^- + C	9.0	No	9.9	TI	63
	CO	O^- + C	9.3		10.2	TI	61
	CO	O^- + C	9.35	Yes	10	TI	85
	CO	O^- + C	9.3			MS	97
	CO	O^- + C	9.4	Yes	10.1	TI	59
	CO	O^- + C	9.39	Yes	10	TI	86
	CO	O^- + C	9.6	Yes	10	MS	41
	CO	O^- + C	9.63			MS	83
	CO	$O^- + C(^3P)$		No	9.6	MS	57
	CO	$O^- + C(^3P)$	9.7	Yes	9.8	MS	74
	CO	$O^- + C(^3P)$	9.7			MS	76
	CO	$O^- + C^*(^1D)$		No	10.9	MS	57
	CO	$O^- + C(^1D)$	10.95	Yes		MS	74
	CO	$O^- + C(^1D)$	10.88			MS	83
	CO	O^- + ?		No	~15.5	MS	57
	CO	O^- + ?		No	~18	MS	57
	CO_2	O^- + CO	3.6	Yes	4.3	TI	61
	CO_2	O^- + CO	3.6	No	4.3	TI	63
	CO_2	O^- + CO	3.83	Yes	4.4	TI	88
	CO_2	O^- + CO	3.85	No	4.4	TI	37, 59
	CO_2	O^- + CO		Yes	3.9	MS	62
	CO_2	O^- + CO	3.96	No		MS	91
	CO_2	O^- + CO		Yes	7.9	MS	62
	CO_2	O^- + CO	6.6	Yes	8.2	TI	59
	CO_2	O^- + CO	6.75	Yes	8.3	TI	61
	CO_2	O^- + CO	7.0	No		MS	91
	CO_2	O^- + CO	~7.0	No	8.1	TI	63
	CO_2	O^- + CO	7.1	No	8.2	TI	37
	CO_2	O^- + CO	~7.1	Yes	8.4	TI	88
	C_3O_2	$O^- + C_3O$	5.2			MS	97
	C_3O_2	$O^- + C_2$ + CO	10.6			MS	97
	H_2O	$O^- + H_2$	4.4	No	6.5	MS	65
	H_2O	$O^- + H_2$	6.4	No	6.9	MS	66
	H_2O	$O^- + H_2$?	7.0	No	8.4	MS	65
	H_2O	$O^- + H_2$?	7.4	No	9.15	MS	68
	H_2O	O^- + H + H?	8	No	9	MS	66
	H_2O	O^- + 2H?	8.5	No	11.2	MS	65
	H_2O	O^- + 2H?		No	11.25	MS	58
	H_2O	O^- + H + H?		No	11.5	MS	66
	CH_3OH	O^- + (or from H_2O?)	6.6	No		MS	100
	CH_3OH	O^- + (or from H_2O?)	9.3	No		MS	100
	C_2H_5OH	O^- + (or from H_2O?)	8.3	No		MS	100
	n-C_3H_7OH	$O^- + C_3H_8$	6.2	No	7.0	MS	127
	n-C_3H_7OH	O^- + ?		No	10	MS	127
	n-C_3H_7OH	O^- + ?		No	11	MS	127
	i-C_3H_7OH	$O^- + C_3H_8$?	6.4	No	7.1	MS	127
	i-C_3H_7OH	O^- + ?		No	10	MS	127
	$C_2H_2O^a$	$O^- + C_2H_2$	3.95	No	4.8	MS	130
	$C_2H_2O^a$	O^- + ?	6.48	No	8.3	MS	130
	$C_2H_2O^a$	O^- + ?	8.95	No	10.0	MS	130
	$C_2H_2O_2{}^c$	$O^- + C_2H_2O$?	3.7	No	7.0	MS	131
	$C_2H_2O_2{}^c$	O^- + ?		No	10.0	MS	131

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
O^-	$C_4H_6O_2$[d]	$O^- + C_4H_6O$?	5.6	No	7.1	MS	131
	$C_4H_6O_2$[d]	O^- + ?		No	9.1	MS	131
	C_4H_4O[e]	O^- + ?	9.2	No	9.7	MS	133
	C_4H_8O[f]	$O^- + C_4H_8$?	5.8	No	7.0	MS	129
	C_4H_8O[f]	O^- + ?	7.7	No	9.9	MS	129
	$C_4H_{10}O_3$[g]	O^- + ?	3.5	No	3.8	MS	128
	$C_4H_{10}O_3$[g]	O^- + ?	3.8	No	4.3	MS	128
	$C_4H_{10}O_3$[g]	O^- + ?	5.7	No	6.0	MS	128
	$C_4H_{10}O_3$[g]	O^- + ?	6.5	No	7.0	MS	128
	CH_3NO_2	$O^- + CH_3NO$	3.0	No	6.5	MS	124
	CH_3NO_2	$O^- + O + CH_3N$?	8.3	No	9.5	MS	124
	CH_3NO_2	O^- + ?	3.5	No	5.5	MS	126
	$C_2H_5NO_2$	O^- + ?	3.7	No	5.9	MS	126
	$C_2H_5NO_2$	$O^- + C_2H_5NO$	3.0	No	6.7	MS	124
	$C_2H_5NO_2$	$O^- + C_2H_5N + O$?	8.6	No	10.2	MS	124
	C_2H_5ONO	O^- + ?	4.5	No	5	MS	126
	C_2H_5ONO	O^- + ?		No	6.5	MS	126
	C_2H_5ONO	O^- + ?		No	7.5	MS	126
	1-$C_3H_7NO_2$	$O^- + C_3H_7NO$	3.1	No	6.6	MS	124
	1-$C_3H_7NO_2$	$O^- + C_3H_7N + O$?	8.7	No	10.1	MS	124
	2-$C_3H_7NO_2$	$O^- + C_3H_7NO$	3.1	No	6.5	MS	124
	2-$C_3H_7NO_2$	$O^- + C_3H_7N + O$	8.6	No	10.0	MS	124
	$C_2H_5ONO_2$	O^- + ?	1.9	No	2.1	MS	126
	$C_2H_5ONO_2$	O^- + ?	5.2	No	6.0	MS	126
	$C_2H_5ONO_2$	O^- + ?		No	8	MS	126
	$C(NO_2)_4$	O^- + ?	1.5	No	2.0	MS	126
	$C(NO_2)_4$	O^- + ?		No	3.8	MS	126
	$C(NO_2)_4$	O^- + ?		No	8.0	MS	126
	$C_6H_5NO_2$	O^- + ?	3.5	No	5	MS	126
	CH_2BrCH_2OH	O^- + ?		No	7.4	MS	62
	CH_2BrCH_2OH	O^- + ?		No	11	MS	62
	$(CH_3)_2SO$[h]	O^- + ?	3.1	No	4.7	MS	134
	$(CH_3)_2SO$[h]	O^- + ?	6.7	No	8.1	MS	134
	SO_2	$O^- + SO$	3.2	Yes	4.6	MS	62
	SO_2	$O^- + SO$		No	4.3	MS	165
	SO_2	$O^- + SO$		No	7.0	MS	165
	SO_2	O^- + ?		No	~8.0	MS	62
	COS	O^- + CS	4.0	No	5.2	MS	90
	COS	O^- + ?	7.6	No	8.9	MS	90
	CrO_2Cl_2	$O^- + CrOCl_2$	3.34	No		MS	196
	CrO_2Cl_2	O^- + CrOCl + Cl	6.58	No		MS	196
	CrO_2F_2	$O^- + CrOF_2$	3.17	No		MS	196
	CrO_2F_2	O^- + CrOF + F	7.13	No		MS	196
O_2^-	O_3	O_2^- + O	~0	Yes	~1.7	MS	64
	NO_2	O_2^- + N	~3.2	No	~4.4	MS	82
	$C_4H_{10}O_3$[g]	$O_2^- + C_4H_{10}O$	0	No	1.7	MS	128
	CrO_2F_2	$O_2^- + CrF_2$	4.0	No		MS	196
	CrO_2F_2	O_2^- + CrF + F	9.5	No		MS	196
OH^-	H_2O	OH^- + H	4.7	No	6.1	MS	68
	H_2O	OH^- + H	6.0	No	~7	MS	66
	H_2O	OH^- + H?		No	8.5	MS	68
	H_2O	OH^- + H		No	8.8	MS	66
	H_2O	OH^- + H		No	11	MS	66
	H_2O	OH^- + H?		No	11.2	MS	68
	CH_3OH	$OH^- + CH_3$	6.5	No		MS	100
	CH_3OH	$OH^- + CH + H_2$?	7.8	No		MS	100
	CH_3OH	OH^- + ?	9.7	No		MS	100
	$C_2H_2O_2$[c]	$OH^- + C_2HO$?	3.3	No	7.0	MS	131
	n-C_3H_7OH	$OH^- + C_3H_7$	6.5	No	9.0	MS	127
	i-C_3H_7OH	$OH^- + C_3H_7$	7.6	No		MS	100
	i-C_3H_7OH	$OH^- + C_3H_7$	6.7	No	8.5	MS	127
	$C_4H_6O_2$[d]	$OH^- + C_4H_5O$?	5.4	No	6.9	MS	131
	$C_4H_{10}O_3$[g]	$OH^- + C_4H_9O_2$	0.5	No	0.9	MS	128
	CH_3NO_2	OH^- + ?	3.2	No	4.0	MS	126
	CH_3NO_2	OH^- + ?		No	5.5	MS	126
	CH_3NO_2	OH^- + ?		No	8.8	MS	126
	$C_2H_5NO_2$	OH^- + ?	3.5	No	5.8	MS	126
	C_2H_5ONO	OH^- + ?	0.7	No	1.1	MS	126
	C_2H_5ONO	OH^- + ?	4.5	No	5	MS	126

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
OH^-	$C_2H_5ONO_2$	$OH^- + ?$	0	Yes	0.3	MS	126
	$C_6H_5NO_2$	$OH^- + ?$	3.5	No	4.2	MS	126
	$C_6H_5NO_2$	$OH^- + ?$	6	No	6.7	MS	126
	CH_2BrCH_2OH	$OH^- + ?$		No	7.4	MS	62
	$(CH_3)_2SO^h$	$OH^- + ?$	3.3	No	4.7	MS	134
OF^-	CF_3OF	$OF^- + CF_3$	3.9	No	6.0	MS	117
NH^-	NH_3	$NH^- + ?$	9	No	11	MS	62
	NH_3	$NH^- + 2H?$	~8.2	No		MS	135
	CH_3NH_2	$NH^- + CH_3 + H?$		No	9.37	MS	139
	$(CH_3)_2NH$	$NH^- + ?$		No	7.38	MS	139
	$(CH_3)_3N$	$NH^- + ?$		No	8.35	MS	139
NH_2^-	NH_3	$NH_2^- + H$	3.5	No		MS	135
	NH_3	$NH_2^- + H$	~4.5	No	5.60	MS	137
	NH_3	$NH_2^- + H$	4.8	No	6.0	MS	62
	NH_3	$NH_2^- + H$	5.45	Yes	5.65	MS	136
	NH_5	$NH_2^- + H$		No	5.95	MS	138
	NH_3	$NH_2^- + H$		No	9.68	MS	138
	NH_3	$NH_2^- + ?$	8.6	No	10.0	MS	62
	NH_3	$NH_2^- + H$		Yes	10.5	MS	136
	NH_3	$NH_2^- + H?$		No	12.05	MS	138
	ND_3	$ND_2^- + D$	~4.5	No	5.80	MS	137
	ND_3	$ND_2^- + D$	5.45	Yes	5.65	MS	136
	ND_3	$ND_2^- + D$		Yes	10.5	MS	136
	CH_3NH_2	$NH_2^- + CH_3$		No	5.37	MS	139
	CH_3NH_2	$NH_2^- + CH_3$		No	6.42	MS	138
	CH_3NH_2	$NH_2^- + CH_3?$ $(CH_2 + H?)$		No	9.96	MS	138
	CH_3NH_2	$NH_2^- + CH + 2H?$		No	11.86	MS	138
	CH_3ND_2	$ND_2^- + CH_3$		No	6.42	MS	138
NF^-	NF_3	$NF^- + 2F?$	0	No	2.8	MS	140
NO^-	NO_2	$NO^- + O$	~2.4	No	~3.3	MS	82
	$C_2H_5ONO_2$	$NO^- + ?$	0	No	0.5	MS	126
	$C(NO_2)_4$	$NO^- + ?$	1.6	No	2.8	MS	126
	$C(NO_2)_4$	$NO^- + ?$		No	8.0	MS	126
NO_2^-	NO_2	NO_2^-		No		MS	81
	$C(NO_2)_4$	$NO_2^- + C(NO_2)_3$	1.5	Yes	3.2	MS	126
	$C(NO_2)_4$	$NO_2^- + ?$		No	8.0	MS	126
	CH_3NO_2	$NO_2^- + CH_3$	0.3	Yes	0.7	MS	126
	CH_3NO_2	$NO_2^- + CH_3?$		No	<3	MS	124
	CH_3NO_2	$NO_2^- + CH_3^*$	4	No	4.6	MS	124
	CH_3NO_2	$NO_2^- + ?$	8	No	8.5	MS	124
	$C_2H_5NO_2$	$NO_2^- + C_2H_5$	0.4	Yes	1.0	MS	126
	$C_2H_5NO_2$	$NO_2^- + C_2H_5?$		No	<3	MS	124
	$C_2H_5NO_2$	$NO_2^- + CH_2 + CH_3?$		No	5.5	MS	124
	$C_2H_5NO_2$	$NO_2^- + ?$	7.1	No	9.7	MS	124
	$C_2H_5ONO_2$	$NO_2^- + C_2H_5O$	0	Yes	0.3	MS	126
	$1\text{-}C_3H_7NO_2$	$NO_2^- + C_3H_7$		No	<3	MS	124
	$1\text{-}C_3H_7NO_2$	$NO_2^- + ?$	4	No	5.5	MS	124
	$1\text{-}C_3H_7NO_2$	$NO_2^- + ?$	6.8	No	9.8	MS	124
	$2\text{-}C_3H_7NO_2$	$NO_2^- + C_3H_7$		No	<3	MS	124
	$2\text{-}C_3H_7NO_2$	$NO_2^- + ?$	4	No	5.5	MS	124
	$2\text{-}C_3H_7NO_2$	$NO_2^- + ?$	6.8	No	9.9	MS	124
	$C_6H_5NO_2$	$NO_2^- + C_6H_5$	1.0	Yes	1.5	MS	126
	$C_6H_5NO_2$	$NO_2^- + ?$	2.5	No	4	MS	126
	$C_6H_4ClNO_2$	$NO_2^- + C_6H_4Cl$	~0	No	0.9	MS	121
	$C_6H_4ClNO_2$	$NO_2^- + C_6H_4Cl$		No	3.3	MS	121
	$C_6H_4INO_2$	$NO_2^- + C_6H_4I$	~2.0	No	4.1	MS	121
NO_3^-	$C(NO_2)_4$	$NO_3^- + ?$	1.5	No	3.0	MS	126
	$C(NO_2)_4$	$NO_3^- + ?$		No	8.0	MS	126
HNO^-	$C_2H_5ONO_2$	$HNO^- + ?$	0	No	0.3	MS	126
	C_2H_5ONO	$HNO^- + C_2H_4O$	0	Yes	0.3	MS	126
HNO_2^-	$C_2H_5ONO_2$	$HNO_2^- + C_2H_4O$	0	Yes	0.2	MS	126
C^-	CO	$C^- + O$	10.20	No	10.4	MS	83
	CO	$C^- + O$	10.9	No	11.1	MS	83
	C_3O_2	$C^- + 2CO$	4.5	Yes		MS	97
	C_3O_2	$C^- + 2CO?$	8.7	Yes		MS	97
	CH_4	$C^- + ?$				MS	100
	C_2H_2	$C^- + ?$	13.2			MS	100
	CS_2	$C^- + S_2$	5.4	No	6.8	MS	90

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
C_2^-	C_3O_2	$C_2^- + CO_2$?	9.9	Yes		MS	97
	C_2H_2	$C_2^- + H_2$?	7.6			MS	100, 101
	C_2H_2	$C_2^- +$ 2H?	11.8			MS	100
	C_2H_4	$C_2^- +$?	10.4			MS	100
	$C_2H_2O^a$	$C_2^- + H_2O$	6.57	No	8	MS	130
	$C_2H_2O^a$	$C_2^- +$?	8.79	No	10.2	MS	130
	CF_2CH_2	$C_2^- +$ 2HF?	3.5		5.3	MS	105
	CF_2CH_2	$C_2^- +$?	6.1		7.0	MS	105
CH^-	CH_4	$CH^- + H_2 + H$?	9.6			MS	100
	CH_4	$CH^- + H_2 + H$?	10.6			MS	99
	C_2H_4	$CH^- + CH_3$	7.0		7.9	MS	105
	C_2H_4	$CH^- + CH_3$	7.3			MS	100
	C_2H_4	$CH^- + CH_2 + H$?	8.4		10.1	MS	105
	C_2H_4	$CH^- + CH_2 + H$?	9.0			MS	101
	C_2H_4	$CH^- +$?	8.7			MS	100
	$CH_2CH(CH_3)CH_3$	$CH^- +$?	7.9			MS	100
	$C_2H_2O^a$	$CH^- + CO + H$	9.10	No	10.3	MS	130
	C_2H_5OH	$CH^- +$?	7.8	No		MS	100
CH_2^-	CH_4	$CH_2^- + H_2$?	9.6			MS	99
	CH_4	$CH_2^- + H_2$?		No	~10.3	TI	102
	CH_4	$CH_2^- + H_2$?	8.3			MS	100
	CH_4	$CH_2^- +$ 2H?	9.3			MS	100
	C_2H_4	$CH_2^- + CH_2$	7.8		8.1	MS	105
	C_2H_4	$CH_2^- +$?	8.8			MS	100
	C_2H_4	$CH_2^- + CH + H$	9.1		10.3	MS	105
	C_2H_6	$CH_2^- +$?	9.2			MS	100
	C_3H_6	$CH_2^- +$?	6.1			MS	100
	C_3H_6	$CH_2^- +$?	7.3			MS	100
	C_3H_6	$CH_2^- +$?	7.8			MS	100
CH_2^-	$CH_2CH(CH_3)CH_3$	$CH_2^- +$?	7.8			MS	100
	$CH_2{=}CHCH_2CH_3$	$CH_2^- +$?	7.3			MS	100
	$CH_2{=}CHCH_2CH_3$	$CH_2^- +$?	7.8			MS	100
	CH_3OH	$CH_2^- +$ HOH	9.9	No		MS	100
	$C_2H_2O^a$	$CH_2^- + CO^*$	2.9	No	4.0	MS	130
	$C_2H_2O^a$	$CH_2^- + CO^*$?	4.6	No	5.8	MS	130
CH_3^-	C_3H_8	$CH_3^- + C_2H_5$?	7.6			MS	100
	$CH_2CH(CH_3)CH_3$	$CH_3^- +$?	7.4			MS	100
	$i\text{-}C_4H_{10}$	$CH_3^- + C_3H_7$?	7.5			MS	100
	C_2H_5OH	$CH_3^- + CH_2OH$?	6.2	No		MS	100
	$i\text{-}C_3H_7OH$	$CH_3^- +$?	6.1	No		MS	100
	$i\text{-}C_3H_7OH$	$CH_3^- +$?	6.9	No		MS	100
	$C_4H_6O_2{}^d$	$CH_3^- + C_3H_3O_2$	3.3	No	5.2	MS	131
	$C_4H_{10}O_3{}^g$	$CH_3^- + C_3H_7O_3$	1.7	No	2.3	MS	128
	$C_2H_5ONO_2$	$CH_3^- +$?	0	No	0.3	MS	126
C_2H^-	C_2H_2	$C_2H^- + H$	2.8			MS	100
	C_2H_2	$C_2H^- + H$	2.8			MS	101
	C_2H_2	$C_2H^- + H$?	6.0			MS	100
	C_2H_4	$C_2H^- + H_2 + H$	6.9			MS	101
	C_2H_4	$C_2H^- + H_2 + H$	6.9		8.5	MS	105
	C_2H_4	$C_2H^- +$?	7.1			MS	100
	C_2H_4	$C_2H^- +$?	8.8		9.5	MS	105
	C_2H_4	$C_2H^- +$?	9.8		10.7	MS	105
	C_2H_4	$C_2H^- +$ 3H	9.9			MS	101
	C_2H_4	$C_2H^- +$?	10.0			MS	100
	C_6H_6	$C_2H^- +$?	8.3			MS	100
	C_6H_6	$C_2H^- +$?	10.5			MS	100
	C_2H_3F	$C_2H^- +$ 2H + F	9.1			MS	101
	CF_2CH_2	$C_2H^- +$ HF + F(?)	5.5		7.0	MS	105
	CF_2CH_2	$C_2H^- +$ 2F + H(?)	10.0		11.6	MS	105
	$C_2H_2O^a$	$C_2H^- +$ OH	6.26	No	7.8	MS	130
	$C_2H_2O^a$	$C_2H^- +$ H + O	8.84	No	9.8	MS	130
	C_2H_5OH	$C_2H^- +$?	2.4	No		MS	100
	C_2H_5OH	$C_2H^- +$?	7.7	No		MS	100
	$C_4H_4O^e$	$C_2H^- +$?	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_2H^- +$?	9.2	No	9.7	MS	133
	$C_6H_5NO_2$	$C_2H^- +$?	4.2	No	4.5	MS	126
	$C_6H_5NO_2$	$C_2H^- +$?	4.7	No	5	MS	126
	$C_6H_5NO_2$	$C_2H^- +$?	6	No	7	MS	126

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
C_2H^-	C_2H_3Cl	$C_2H^- + H + HCl$	6.2			MS	101
	C_2H_3Cl	$C_2H^- + H_2 + Cl$					
	$C_2H_3SiCl_3$	$C_2H^- + ?$	6.2	No		MS	154
	$C_2H_3SiCl_3$	$C_2H^- + ?$	7.4	No		MS	154
	$C_4H_4S^i$	$C_2H^- + ?$	5.55	No	5.9	MS	133
	$C_4H_4S^i$	$C_2H^- + ?$	8.25	No	8.55	MS	133
	$C_5H_6S^j$	$C_2H^- + ?$	8.0	No	8.5	MS	133
	$C_5H_6S^k$	$C_2H^- + ?$	5.45	No	5.7	MS	133
	$C_5H_6S^k$	$C_2H^- + ?$	8.1	No	8.5	MS	133
	$C_6H_8S^l$	$C_2H^- + ?$		No	~8	MS	133
	$C_7H_{10}S^m$	$C_2H^- + ?$		No	8.4	MS	133
	$C_7H_{10}S^n$	$C_2H^- + ?$	5.3	No	5.6	MS	133
	$C_7H_{10}S^n$	$C_2H^- + ?$	7.9	No	8.45	MS	133
	$C_4H_4Se^o$	$C_2H^- + ?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$C_2H^- + ?$	7.5	No	7.8	MS	133
$C_3H_3^-$	$CH_2CH(CH_3)CH_3$	$C_3H_3^- + ?$	5.8			MS	100
	$CH_2CH(CH_3)CH_3$	$C_3H_3^- + ?$	7.0			MS	100
	$C_4H_4O^e$	$C_3H_3^- + ?$	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_3H_3^- + ?$	9.2	No	9.7	MS	133
	$C_4H_4S^i$	$C_3H_3^- + ?$	8.25	No	8.55	MS	133
$C_3H_5^-$	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	1.4	No	1.7	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	1.7	No	2.1	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	2.1	No	2.6	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	7.4	No	7.7	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	7.7	No	8.0	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	7.9	No	8.4	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	8.3	No	9.1	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_5^- + ?$	8.8	No	9.9	MS	128
C_4H^-	$C_4H_4O^e$	$C_4H^- + ?$	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_4H^- + ?$	9.2	No	9.7	MS	133
	$C_4H_4S^i$	$C_4H^- + ?$	5.55	No	5.9	MS	133
	$C_4H_4S^i$	$C_4H^- + ?$	8.25	No	8.55	MS	133
	$C_5H_6S^j$	$C_4H^- + ?$	8.0	No	8.5	MS	133
	$C_6H_8S^l$	$C_4H^- + ?$	~5.2	No		MS	133
	$C_7H_{10}S^m$	$C_4H^- + ?$		No	8.8	MS	133
	$C_5H_6S^k$	$C_4H^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$C_4H^- + ?$	7.9	No	8.45	MS	133
	$C_4H_4Se^o$	$C_4H^- + ?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$C_4H^- + ?$	7.5	No	7.8	MS	133
$C_4H_3^-$	C_6H_6	$C_4H_3^- + C_2H_3$	8.5			MS	100
	$C_5H_6S^j$	$C_4H_3^- + ?$	8.0	No	8.5	MS	133
	$C_7H_{10}S^m$	$C_4H_3^- + ?$		No	8.4	MS	133
	$C_5H_6S^k$	$C_4H_3^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$C_4H_3^- + ?$	7.9	No	8.45	MS	133
	$C_4H_4Se^o$	$C_4H_3^- + ?$	7.5	No	7.8	MS	133
$C_5H_5^-$	$Ti(C_5H_5)_2Cl_2$	$C_5H_5^- + TiC_5H_5Cl_2$		No	3.6	MS	204
	$Zr(C_5H_5)_2Cl_2$	$C_5H_5^- + ZrC_5H_5Cl_2$		No	4.7	MS	204
	$Hf(C_5H_5)_2Cl_2$	$C_5H_5^- + HfC_5H_5Cl_2$		No	1.7	MS	204
	$Hf(C_5H_5)_2Cl_2$	$C_5H_5^- + ?$		No	5.0	MS	204
	$Hf(C_5H_5)_2Cl_2$	$C_5H_5^- + ?$		No	8.1	MS	204
$C_6H_5^-$	C_6H_6	$C_6H_5^- + H$	5.8			MS	100
CF^-	C_2F_4	$CF^- + F_2 + CF?$	10.0	No	11.9	MS	107
CF_2^-	C_2F_4	$CF_2^- + CF_2$	2.9	No	3.7	MS	107
	CF_3COCF_3	$CF_2^- + F + CO + CF_3?$	4.25	No	5.25	MS	108
CF_3^-	CF_4	$CF_3^- + F$	5.4	No	7.2	MS	158
	C_2F_4	$CF_3^- + CF$	3.0	No	4.3	MS	107
	C_2F_6	$CF_3^- + CF_3$	1.6	No	1.9	MS	106
	C_2F_6	$CF_3^- + ?$	2.2	No	2.5	MS	106
	C_2F_6	$CF_3^- + ?$	2.7	No	3.9	MS	106
	C_2F_6	$CF_3^- + CF_3$	2.8		3.75	MS	109
	C_3F_8	$CF_3^- + C_2F_5?$	2.0			MS	114
	C_3F_8	$CF_3^- + C_2F_5$	2.2		3.4	MS	109
	C_4F_8	$CF_3^- + C_3F_5?$	3.0		5.0	MS	109
	CF_3OF	$CF_3^- + O + F$	4.4	No	6.3	MS	117
	CF_3COCF_3	$CF_3^- + CF_3CO$	3.0	No	4.3	MS	108
	CF_3COCF_3	$CF_3^- + CO + CF_2 + F?$	5.4	No	6.7	MS	108
	CF_3COCF_3	$CF_3^- + ?$	8.2	No	8.6	MS	108
	CF_3COCF_3	$CF_3^- + ?$	10.5	No	11.0	MS	108

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
C_2F^-	CF_2CH_2	$C_2F^- + H_2 + F$	4.9		7.0	MS	105
	CF_2CH_2	C_2F^- ?	8.3		10.2	MS	105
$C_2F_3^-$	C_2F_4	$C_2F_3^- + F$	3.2	No	4.9	MS	107
	C_2F_4	$C_2F_3^- + F$?	6.4	No	6.9	MS	107
$C_2F_5^-$	C_2F_6	$C_2F_5^- + F$	4.0	No	4.8	MS	106
	C_2F_6	$C_2F_5^- + F$	5.8	No	6.1	MS	106
	C_2F_6	$C_2F_5^- + F$?	12.0			MS	106
	C_2F_6	$C_2F_5^- + F$?	15.0			MS	106
	C_3F_8	$C_2F_5^- + CF_3$?	1.7			MS	114
	C_3F_8	$C_2F_5^- + CF_3$	2.1		3.2	MS	109
$C_3F_6^-$	CF_3COCF_3	$(CF_3)_2C^- + O$	5.1	No	6.4	MS	108
$C_3F_7^-$	C_3F_8	$C_3F_7^- + F$	2.4			MS	114
$C_4F_6^-$	C_4F_6[p]	$C_4F_6^-$	0	No	0	MS	122
$C_4F_8^-$	c-C_4F_8	$C_4F_8^-$	0			MS	110
	C_4F_8[q]	$C_4F_8^-$	0	No	0	MS	122
$C_5F_8^-$	C_5F_8[r]	$C_5F_8^-$	0	No	0	MS	122
$C_6F_5^-$	C_6F_5Cl	$C_6F_5^- + Cl$	~0	No	0.2	MS	121
	C_6F_5Br	$C_6F_5^- + Br$	~0	No	0.06	MS	121
	C_6F_5I	$C_6F_5^- + I$	~0	No	0	MS	121
	C_6F_5CHO	$C_6F_5^- + CHO$?	~0	No	0.4	MS	121
	C_6F_5CHO	$C_6F_5^-$ + ?	2.8	No	3.8	MS	121
	$Hg(C_6F_5)_2$	$C_6F_5^- + Hg(C_6F_5)$		No	15	MS	205
$C_6F_6^-$	C_6F_6	$C_6F_6^-$	0	No		MS	121
	C_6F_6[s]	$C_6F_6^-$	0	No		MS	122
$C_nF_y^-$	C_6F_{10}[t]	$C_6F_{10}^-$	0	No		MS	122
	C_6F_{12}[x]	$C_6F_{12}^-$	0	No		MS	122
	C_7F_8[u]	$C_7F_8^-$	0	No		MS	122
	c-C_7F_{14}	$C_7F_{14}^-$	0.15			TI	111
	c-C_7F_{14}	$C_7F_{14}^-$	1.2			MS	112
	C_7F_{14}[v]	$C_7F_{14}^-$	0	No		MS	122
	$C_8F_{16}O$[w]	$C_7F_{14}^- + CF_2O$	0.4			MS	118
	$C_8F_{16}O$[x]	$C_7F_{14}^- + CF_2O$	0.4			MS	118
C_2O^-	C_3O_2	$C_2O^- + CO$	4.2			MS	97
	C_3O_2	$C_2O^- + O + C$	12.8			MS	97
	C_2H_2O[a]	$C_2O^- + H_2$	5.22	No	6.1	MS	130
	C_2H_2O[a]	$C_2O^- + 2H$?	8.89	No	10.2	MS	130
	$C_2H_2O_2$[c]	$C_2O^- + H_2O$?	3.4	No	6.7	MS	131
CHO^-	CH_3OH	CHO^- + ?	6.1	No	7.0	MS	100
	CH_3OH	CHO^- + ?	7.4	No	8.5	MS	100
	n-C_3H_7OH	CHO^- + ?	7.4	No		MS	100
	$C_2H_2O_2$[c]	$CHO^- + CHO$	3.0	No	4.1	MS	131
CH_3O^-	CH_3OH	$CH_3O^- + H$	2.8	No	3.5	MS	100
	CH_3OH	$CH_3O^- + H$?	5.8	No	6.8	MS	100
	CH_3OH	CH_3O^- + ?		No	8.1	MS	100
	CH_3OH	CH_3O^- + ?		No	11.0	MS	100
	$C_4H_{10}O_3$[g]	$CH_3O^- + C_3H_7O_2$	1.1	No	2.4	MS	128
C_2OH^-	C_2H_5OH	C_2OH^- + ?	7.9	No		MS	100
	C_2H_5OH	C_2OH^- + ?	14.8	No		MS	100
	i-C_3H_7OH	C_2OH^- + ?	5.8	No		MS	100
	i-C_3H_7OH	C_2OH^- + ?	7.7	No		MS	100
	C_2H_2O[a]	$C_2OH^- + H$	2.03	No	2.9	MS	130
	C_2O_2O[a]	$C_2OH^- + H$		No	6	MS	130
	C_4H_4O[e]	C_2OH^- + ?	5.4	No	5.6	MS	133
	C_4H_4O[e]	C_2OH^- + ?	9.2	No	9.7	MS	133
	C_4H_8O[f]	$C_2OH^- + C_2H_5 + H_2$?	6.2	No	7.6	MS	129
	$C_4H_6O_2$[d]	$C_2OH^- + C_2H_5O$?	3.9	No	7.0	MS	131
	$C_2H_2O_2$[c]	$C_2OH^- + HO$	2.6	No	6.6	MS	131
	$C_2H_5ONO_2$	$\left.\begin{matrix}C_2H_3N^-\\C_2HO^-\end{matrix}\right\}? + ?$	0	No	0.3	MS	126
	$C_2H_5ONO_2$	$\left.\begin{matrix}C_2H_3N^-\\C_2HO^-\end{matrix}\right\}? + ?$	0.5	No	1.1	MS	126
$C_2H_3O^-$	C_2H_5OH	$C_2H_3O^- + H_2$?	5.8	No		MS	100
	C_2H_5OH	$C_2H_3O^- + 2H$	8.1	No		MS	100
	i-C_3H_7OH	$C_2H_3O^-$ + ?	5.9	No		MS	100
	i-C_3H_7OH	$C_2H_3O^-$ + ?	7.2	No		MS	100
	$C_2H_5ONO_2$	$C_2H_3O^- + H_2NO_2$	0	Yes	0	MS	126
	C_2H_5ONO	$C_2H_3O^- + H_2NO$?	0	Yes	0.3	MS	126
$C_2H_5O^-$	C_2H_5OH	$C_2H_5O^- + H$	2.6	No		MS	100
	C_2H_5OH	$C_2H_5O^- + H$	5.6	No		MS	100

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
$C_2H_5O^-$	$C_2H_5ONO_2$	$C_2H_5O^- + NO_2$	0	Yes	0.5	MS	126
	C_2H_5ONO	$C_2H_5O^- + NO$	0	Yes	0.3	MS	126
$C_3H_xO^-$	$n\text{-}C_3H_7OH$	$C_3H_3O^- + ?$	7.3	No		MS	100
	$C_4H_{10}O_3{}^g$	$C_3H_4O^-$ (or $C_2O_2^-$) $+ ?$	0	No	0.5	MS	128
	$n\text{-}C_3H_7OH$	$C_3H_5O^- + H_2 + H$	5.8	No		MS	100
	$n\text{-}C_3H_7OH$	$C_3H_5O^- + 3H$	7.0	No		MS	100
	$i\text{-}C_3H_7OH$	$C_3H_5O^- + H_2 + H$	5.8	No		MS	100
	$i\text{-}C_3H_7OH$	$C_3H_5O^- + 3H$	7.9	No		MS	100
	$C_4H_{10}O_3{}^g$	$C_3H_5O^- + CH_3OH + OH$	0.3	No	1.2	MS	128
	$n\text{-}C_3H_7OH$	$C_3H_7O^- + H$	2.6	No		MS	100
	$n\text{-}C_3H_7OH$	$C_3H_7O^- + H$	5.7	No		MS	100
	$i\text{-}C_3H_7OH$	$C_3H_7O^- + H$	2.6	No		MS	100
	$i\text{-}C_3H_7OH$	$C_3H_7O^- + H$	5.7	No		MS	100
	$C_4H_{10}O_3{}^g$	$C_3H_7O^- + CH_2O + OH$	0	No	0.5	MS	128
$C_4H_xO^-$	$C_4H_4O^e$	$C_4OH^- + ?\ C_4OH^-$	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_4OH^- + ?$	9.2	No	9.7	MS	133
	$C_4H_4O^e$	$C_4OH_2^- + ?$	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_4OH_2^- + H_2?$	9.2	No	9.7	MS	133
	$C_4H_4O^e$	$C_4OH_3^- + H$	5.4	No	5.6	MS	133
	$C_4H_4O^e$	$C_4OH_3^- + H$	9.2	No	9.7	MS	133
	$C_4H_{10}O_3{}^g$	C_4H_9O (or $C_3H_5O_2^-$) $+ ?$	0	No	0.4	MS	128
	$C_4H_{10}O_3{}^g$	$C_4H_9O^- + ?$	0.2	No	1.0	MS	128
	$C_4H_{10}O_3{}^g$	$C_4H_9O^- + ?$		No	1.4	MS	128
$C_xH_yO_z^-$	$C_2H_2O_2{}^c$	$C_2HO_2^- + H$	2.5	No	3.7	MS	131
	$C_2H_2O_2{}^c$	$C_2H_2O_2^-$	0	No	0.15	MS	131
	$C_4H_{10}O_3{}^g$	$C_3H_7O_2^- + CH_3O$	0	No		MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_7O_2^- + ?$		No	0.9	MS	128
	$(CH_3CO)_2$	$(CH_3CO)_2^-$		No		MS	182
	$C_4H_6O_2{}^d$	$C_4H_6O_2^-$	0	No	0.15	MS	131
	$C_4H_{10}O_3{}^g$	$C_4H_9O_2^- + OH$	0	No	0.2	MS	128
	$C_4H_{10}O_3{}^g$	$C_2H_7O_3^- + ?$	0	No	0.2	MS	128
	$C_4H_{10}O_3{}^g$	$C_2H_9O_3^-$ (or $C_4O_2H^-$) $+ ?$	0	No	0.2	MS	128
	$C_4H_{10}O_3{}^g$	$C_3H_7O_3^- + CH_3$	0	No	0.6	MS	128
	$C_4H_{10}O_3{}^g$	$C_4H_8O_3^- + H_2$	0	No	1.1	MS	128
CFO^-	COF_2	$CFO^- + F$	2.8	No	3.3	MS	20, 117
	CF_3COCF_3	$CFO^- + CF_2 + CF_3?$	3.0	No		MS	108
	CF_3COCF_3	$CFO^- + C_2F_3 + 2F?$	5.3	No	6.6	MS	108
CF_3O^-	CF_3OF	$CF_3O^- + F$	0	No	0.6	MS	117
	CF_3OF	$CF_3O^- + ?$	3.6	No	6.4	MS	117
	CF_3OF	$CF_3O^- + ?$	~7.2			MS	117
	CF_3OF	$CF_3O^- + ?$	~8.5			MS	117
	CF_3OF	$CF_3O^- + ?$	~10.2			MS	117
$C_2F_3O^-$	CF_3COCF_3	$CF_3CO^- + CF_3$	3.1	No	4.1	MS	108
$C_3F_5O^-$	CF_3COCF_3	$CF_3COCF_2^- + F$	3.1	No	4.2	MS	108
$C_3F_6O^-$	CF_3COCF_3	$CF_3COCF_3^-$	0	No		MS	108, 113
	$CF_3COCF_3 + e^{-\,y}$	$CF_3COCF_3^-$	0			MS	116
$C_xF_yO_z^-$	$C_8F_{16}O^w$	$C_5F_9O^- + ?$	0.8			MS	118
	$C_8F_{16}O^x$	$C_5F_9O^- + ?$	0.8			MS	118
	C_6F_5OH	$C_6F_4O^- + HF?$	~0	No	0.11	MS	121
	C_6F_5OH	$C_6F_4O^- + HF?$		No	0.73	MS	121
	$C_6F_5OCH_3$	$C_6F_4O^- + CH_3F?$	~0	No	0.1	MS	121
	$C_6F_5OCH_3$	$C_6F_4O^- + CH_3 + F?$		No	0.8	MS	121
	$C_6F_5OCH_3$	$C_6F_5O^- + CH_3?$	~0	No	1.1	MS	121
	$C_6F_5OCH_3$	$C_6F_5O^- + ?$	~3	No	4.4	MS	121
	C_6F_5OH	$C_6F_5O^- + H$	~0	No	0.5	MS	121
	$C_8F_{16}O^w$	$C_8F_{16}O^-$	0.2			MS	118
	$C_8F_{16}O^x$	$C_8F_{16}O^-$	0.2			MS	118
$C_6F_4NH_2^-$	$C_6F_5NH_2$	$C_6F_4NH_2^- + F$	~0	No	1.1	MS	121
$C_6F_5X^-$	C_6F_5Cl	$C_6F_5Cl^-$	~0	No		MS	121
	C_6F_5Br	$C_6F_5Br^-$	~0	No		MS	121
	C_6F_5CN	$C_6F_5CN^-$	0	No		MS	121
	C_6F_5CHO	$C_6F_5CHO^-$	0	No		MS	121
CN^-	HCN	$CN^- + H$	1.8	No	2.5	MS	142
	$(CN)_2$	$CN^- + CN$	4.4	No		MS	141
	$(CN)_2$	$CN^- + CN$	4.4	No	5.3	MS	142
	$(CN)_2$	$CN^- + CN$		No	4.4	MS	144
	$CNCl$	$CN^- + Cl$		No	0.4	MS	144
	$CNBr$	$CN^- + Br$		No	0	MS	144
	CNI	$CN^- + I$		No	0	MS	144

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
CN^-	$C(NO_2)_4$	$CN^- + ?$	1.2	No	3.8	MS	126
	$C(NO_2)_4$	$CN^- + ?$		No	9	MS	126
	$C(NO_2)_4$	$CN^- + ?$		No	13	MS	126
	CH_3CN	$CN^- + CH_3$		No	<2.0	MS	145
	CH_3CN	$CN^- + CH_3$	5.6	No		MS	141
	CH_3CN	$CN^- + ?$	5.3	No	~ 8.0	MS	145
	C_2H_5CN	$CN^- + C_2H_5$		No	<2.0	MS	145
	C_2H_5CN	$CN^- + ?$	5.0	No	~ 8.5	MS	145
	$HC{\equiv}C{-}CN$	$CN^- + C_2H$		No	6.0	MS	143
	$NC{-}C{\equiv}C{-}CN$	$CN^- + C_3N$		No	0.8	MS	143
	$NC{-}C{\equiv}C{-}C{\equiv}C{-}CN$	$CN^- + C_5N$		No	2.0	MS	143
	CH_3NH_2	$CN^- + ?$		No	2.52	MS	138
	CH_3NH_2	$CN^- + ?$		No	8.34	MS	138
	CH_3ND_2	$CN^- + ?$		No	1.95	MS	138
	CH_3ND_2	$CN^- + ?$		No	8.88	MS	138
	CH_3NO_2	$CN^- + ?$	1.0	No	1.8	MS	126
	CH_3NO_2	$CN^- + H_2O + OH?$		No	<3	MS	124
	CH_3NO_2	$CN^- + ?$	3.5	No	5	MS	125
	CH_3NO_2	$CN^- + ?$	7.5	No	10	MS	125
	$C_2H_5NO_2$	$CN^- + ?$	1.6	No	2.0	MS	126
	$C_2H_5NO_2$	$CN^- + ?$		No	<3	MS	125
	$C_2H_5NO_2$	$CN^- + ?$		No	5	MS	126
	$C_2H_5NO_2$	$CN^- + ?$	~ 5	No	8.5	MS	125
	$C_2H_5NO_2$	$CN^- + ?$		No	8	MS	126
	$1\text{-}C_3H_7NO_2$	$CN^- + ?$		No	<3	MS	125
	$1\text{-}C_3H_7NO_2$	$CN^- + ?$	4.5	No	10	MS	125
	$2\text{-}C_3H_7NO_2$	$CN^- + ?$		No	<3	MS	125
	$2\text{-}C_3H_7NO_2$	$CN^- + ?$	4	No	10.5	MS	125
	$C_6H_5NO_2$	$CN^- + ?$	2.8	No	4	MS	126
C_2N^-	CH_3CN	$C_2N^- + H_2 + H?$	7.3	No	~ 9	MS	145
	C_2H_5CN	$C_2N^- + ?$	6.9	No	~ 9	MS	145
C_3N^-	$HC{\equiv}C{-}CN$	$C_3N^- + H$		No	3.5	MS	143
	$NC{-}C{\equiv}C{-}CN$	$C_3N^- + CN$		No	1.6	MS	143
	$NC{-}C{\equiv}C{-}C{\equiv}C{-}CN$	$C_3N^- + C_3N$		No	4.0	MS	143
	C_2H_5CN	$C_3N^- + ?$	~ 9.4	No	~ 10.2	MS	145
	C_2H_5CN	$C_3N^- + ?$	~ 13.9	No	~ 17	MS	145
C_5N^-	$NC{-}C{\equiv}C{-}C{\equiv}C{-}CN$	$C_5N^- + CN$		No	3.0	MS	143
$C_6N_2^-$	$NC{-}C{\equiv}C{-}C{\equiv}C{-}CN$	$C_6N_2^-$		No	0	MS	143
HCN^-	CH_3CN	$HCN^- + ?$		No	~ 2	MS	145
	C_2H_5CN	$HCN^- + ?$		No	~ 2	MS	145
	CH_3CN	$HCN^- + ?$	6.0	No	~ 8.5	MS	145
	C_2H_5CN	$HCN^- + ?$	5.0	No	~ 9.0	MS	145
H_2CN^-	CH_3NH_2	$CH_2N^- + ?$		No	5.26	MS	139
	CH_3NH_2	$CH_2N^- + ?$		No	7.72	MS	139
H_4CN^-	CH_3NH_2	$CH_3NH^- + H$		No	5.55	MS	138
	CH_3NH_2	$CH_3NH^- + H$		No	4.87	MS	139
	$(CH_3)_2NH$	$CH_3NH^- + CH_3$		No	4.86	MS	139
	CH_3ND_2	$CH_3ND^- + D$		No	5.55	MS	138
HC_2N^-	CH_3CN	$CHCN^- + ?$	2.3	No	4	MS	145
	C_2H_5CN	$CHCN^- + ?$	6.5	No	9.5	MS	145
	CH_3CN	$CHCN^- + ?$	7.0	No	~ 10	MS	145
$H_2C_2N^-$	CH_3CN	$CH_2CN^- + H$	~ 1.8	No	3.5	MS	145
$H_6C_2N^-$	$(CH_3)_2NH$	$(CH_3)_2N^- + H$		No	4.75	MS	139
$H_5C_7N^-$	C_6H_5CN	$C_6H_5CN^-$	0	No		MS	121
CNO^-	$C(NO_2)_4$	CNO^-	1.0	No	2.5	MS	126
	$C(NO_2)_4$	CNO^-		No	4.3	MS	126
	$C(NO_2)_4$	CNO^-		No	8.0	MS	126
	CH_3NO_2	$CNO^- + ?$	0.8	No	1.0	MS	126
	CH_3NO_2	$CNO^- + ?$		No	2.1	MS	126
	CH_3NO_2	$CNO^- + ?$		No	3.8	MS	126
	CH_3NO_2	$CNO^- + H_2O + H?$	3.0	No	5.3	MS	125
	CH_3NO_2	$CNO^- + ?$	6.5	No	9	MS	126
	CH_3NO_2	$CNO^- + ?$	~ 7.5	No	9.8	MS	125
	$C_2H_5NO_2$	$CNO^- + CH_3OH + H?$	3.0	No	5.3	MS	125
	$C_2H_5NO_2$	$CNO^- + ?$	3	No	5	MS	126
	$C_2H_5NO_2$	$CNO^- + ?$		No	8	MS	126
	$C_2H_5NO_2$	$CNO^- + ?$	~ 7.0	No	8.6	MS	125
	$1\text{-}C_3H_7NO_2$	$CNO^- + C_2H_5OH + H?$	2.5	No	5.3	MS	125
	$1\text{-}C_3H_7NO_2$	$CNO^- + ?$	~ 6.7	No	9.4	MS	125

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
CNO^-	$2\text{-}C_3H_7NO_2$	$CNO^- + C_2H_5OH + H?$	3.0	No	5.8	MS	125
	$2\text{-}C_3H_7NO_2$	$CNO^- + ?$	~6.7	No	8.1	MS	125
$C_wH_xN_yO_z^-$	$C(NO_2)_4$	$CNO_2^- + ?$	1.8	No	3.4	MS	126
	$C(NO_2)_4$	$CNO_2^- + ?$		No	8.4	MS	126
	$C(NO_2)_4$	$C(NO)_2^-$	1.5	No	2.1	MS	126
	$C(NO_2)_4$	$C(NO_2)_2^- + 2NO_2$	0.8	No	3.0	MS	126
	$C(NO_2)_4$	$C(NO_2)_3^- + NO_2$	0.8	Yes	2.1	MS	126
	CH_3NO_2	$CH_2NO^- + HO$	3.1	No	4	MS	126
	CH_3NO_2	$CH_2NO^- + ?$	6.8	No	8	MS	126
	$C_2H_5NO_2$	$CH_2NO_2^- + CH_3$	7.3	No	9.7	MS	124
	$1\text{-}C_3H_7NO_2$	$CH_2NO_2^- + C_2H_5$	7.3	No	9.7	MS	124
	$2\text{-}C_3H_7NO_2$	$CH_2NO_2^- + C_2H_5$	7.4	No	9.8	MS	124
	$C_2H_5NO_2$	$C_2H_3NO_2^- + H_2?$	0	No	0.2	MS	126
	$C_6H_5NO_2$	$C_6H_4NO_2^- + H$	2.8	No	3.8	MS	126
	$C_6H_5NO_2$	$C_6H_4NO_2^- + H$	~6	No	7.2	MS	126
	$C_6H_5NO_2$	$C_6H_5NO_2^-$	0	No		MS	121
	$C_6H_5NO_2$	$C_6H_5NO_2^-$	0	Yes	0.15	MS	126
	$C_6H_5NO_2$	$C_6H_5NO_2^-$		No	0	MS	182
	$C_2H_5ONO_2$	$CH_2NO_3^- + CH_3$	0	No	0.3	MS	126
	$C_2H_5ONO_2$	$C_2H_4NO_3^- + H$	0	No	0.3	MS	126
$B_xH_y^-$	B_5H_9	$B_3H_5^- + ?$		No	0.3	MS	147
	B_4H_{10}	$B_3H_7^- + ?$		No	<2.0	MS	149
	$B_{10}H_{14}$	$B_3H_8^- + ?$		No	2.6	MS	147
	B_5H_9	$B_4H_4^- + ?$		No	4.8	MS	147
	B_5H_9	$B_4H_5^- + BH_3 + H?$		No	7.9	MS	147
	B_5H_9	$B_4H_6^- + BH_3?$		No	2.8	MS	147
	B_4H_{10}	$B_4H_8^- + H_2?$		No	~3	MS	149
	B_4H_{10}	$B_4H_9^- + H$		No	~3	MS	149
	B_4H_{10}	$B_4H_{10}^-$	~2.0	No	~3	MS	149
	B_5H_9	$B_5H_8^- + H$		No	0.8	MS	147
	B_5H_9	$B_5H_9^-$		No	0.3	MS	147
	$B_{10}H_{14}$	$B_8H_8^- + ?$		No	11.7	MS	147
	$B_{10}H_{14}$	$B_9H_{11}^- + BH_3?$		No	0.7	MS	147
	$B_{10}H_{14}$	$B_{10}H_{14}^-$		No	0	MS	147
BF_2^-	BF_3	$BF_2^- + F$	~7.6	No		MS	150
Cl^-	Cl_2	$Cl^- + Cl$	1.6	No	2.4	MS	46, 47
	HCl	$Cl^- + H$	0.62	No	0.77	MS	50
	CCl_4	$Cl^- + CCl_3$	0	No		MS	18
	CCl_4	$Cl^- + CCl_3$	0	Yes		MS	25
	CCl_4	$Cl^- + CCl_3$	0	No		MS	62
	CCl_4	$Cl^- + CCl_3$	0	No	0	MS	170
	CCl_4	$Cl^- + CCl_3$	0	No	0.02	TI	51
	CCl_4	$Cl^- + ?$		No	0.8	MS	18
	CCl_4	$Cl^- + CCl_3$	0.2	No	1.6	MS	119
	CCl_4	$Cl^- + CCl_3$	0.2	No	1.62	MS	52
	CCl_4	$Cl^- + ?$		No	3.0	MS	119
	CCl_4	$Cl^- + CCl_3$		No	4.0	MS	141
	CCl_4	$Cl^- + ?$		No	6	MS	18
	CCl_4	$Cl^- + CCl_2 + Cl$		Yes	6.1	MS	62
	CH_3Cl	$Cl^- + CH_3?$		No	0.5	MS	62
	CH_3Cl	$Cl^- + ?$		No	7.3	MS	62
	CH_3Cl	$Cl^- + CH_3$	3.2	No	~8	MS	120
	CH_2Cl_2	$Cl^- + CH_2Cl$	0	Yes		MS	25
	CH_2Cl_2	$Cl^- + CH_2Cl$	0			MS	62
	CH_2Cl_2	$Cl^- + ?$		No	7.3	MS	62
	$CHCl_3$	$Cl^- + CHCl_2$	~0			MS	62
	$CHCl_3$	$Cl^- + ?$		No	6.4	MS	62
	C_2H_5Cl	$Cl^- + C_2H_5?$	3.5	No	7.5	MS	120
	C_2H_5Cl	$Cl^- + ?$	8.2	No	9.5	MS	120
	$C_2Cl_4H_2$	$Cl^- + ?$		No	~6.5	MS	62
	$n\text{-}C_3H_7Cl$	$Cl^- + ?$	4.1	No	8	MS	120
	$i\text{-}C_3H_7Cl$	$Cl^- + ?$	4.3	No	9	MS	120
	CCl_3F	$Cl^- + CCl_2F$	0	Yes	0.2	MS	32
	CCl_3F	$Cl^- + CCl_2F$	0.1	No	1.6	MS	119
	CCl_3F	$Cl^- + CCl_2F$	0.1	No	1.60	MS	52
	CCl_2F_2	$Cl^- + CClF_2$	0.5	No	2.0	MS	52
	CCl_2F_2	$Cl^- + CClF_2$	0.5	No	2.1	MS	119
	C_2F_3Cl	$Cl^- + C_2F_3$	0.9	No	~2.8	MS	52
	C_2F_3Cl	$Cl^- + C_2F_3$	0.9	No	2.8	MS	119

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
Cl^-	CF_2ClCF_2Cl	$Cl^- + C_2F_4Cl$	0.2	No	2.1	MS	119
	$CHCl_2F$	$Cl^- + CHClF$	0.9	No	2.1	MS	52, 119
	$CNCl$	$Cl^- + CN$		No	6.7	MS	144
	$CNCl$	$Cl^- + ?$		No	0	MS	144
	m-$C_6H_4ClNO_2$	$Cl^- + C_6H_4NO_2$	~ 0	No	0.9	MS	121
	m-$C_6H_4ClNO_2$	$Cl^- + ?$		No	3.4	MS	121
	o-C_6H_4ClF	$Cl^- + C_6H_4F$	~ 0	No	0.24	MS	121
	m-C_6H_4ClF	$Cl^- + C_6H_4F$	~ 0	No	0.26	MS	121
	m-C_6H_4ClBr	$Cl^- + C_6H_4Br$	~ 0	No	0.31	MS	121
	m-C_6H_4ClI	$Cl^- + C_6H_4I$	~ 0	No	0.1	MS	121
	C_6F_5Cl	$Cl^- + C_6F_5?$	~ 0	No	0.2	MS	121
	S_2Cl_2	$Cl^- + S_2Cl?$		No	0	MS	62
	S_2Cl_2	$Cl^- + ?$		Yes	4.0	MS	62
	$SiCl_4$	$Cl^- + SiCl_3$	0	No		MS	154
	$SiCl_4$	$Cl^- + SiCl_3?$		No	2.5?	MS	62
	$SiCl_4$	$Cl^- + SiCl_2 + Cl?$	1.4	No		MS	154
	$SiCl_4$	$Cl^- + SiCl_3$	1.4	No	3.5	MS	153
	$SiCl_4$	$Cl^- + SiCl_2 + Cl?$	2.4	No	4	MS	153
	$SiCl_4$	$Cl^- + SiCl + Cl_2?$	6.1	No		MS	154
	$SiCl_4$	$Cl^- + ?$		No	7.0	MS	62
	$SiCl_4$	$Cl^- + SiCl + Cl_2?$	8.2	No	9.7	MS	153
	$(CH_3)_2SiCl_2$	$Cl^- + (CH_3)_2SiCl$	0	No		MS	154
	$(CH_3)_2SiCl_2$	$Cl^- + ?$	1.6	No		MS	154
	$(CH_3)_2SiCl_2$	$Cl^- + ?$	6.5	No		MS	154
	$(CH_3)_3SiCl$	$Cl^- + (CH_3)_3Si$	0	No		MS	154
	$(CH_3)_3SiCl$	$Cl^- + CH_3 + Si(CH_3)_2$	1.9	No		MS	154
	$(CH_3)_3SiCl$	$Cl^- + ?$	6.4	No		MS	154
	$C_2H_3SiCl_3$	$Cl^- + C_2H_3SiCl_2$	0.5	No		MS	154
	$C_2H_3SiCl_3$	$Cl^- + ?$	3.8	No		MS	154
	$C_2H_3SiCl_3$	$Cl^- + ?$	6.0	No		MS	154
	CH_3SiCl_3	$Cl^- + CH_3SiCl_2$	0	No		MS	154
	CH_3SiCl_3	$Cl^- + ?$	1.4	No		MS	154
	CH_3SiCl_3	$Cl^- + ?$	6.5	No		MS	154
	$C_6H_5SiCl_3$	$Cl^- + C_6H_5SiCl_2?$	0.5	No		MS	154
	$C_6H_5SiCl_3$	$Cl^- + ?$	3.8	No		MS	154
	$C_6H_5SiCl_3$	$Cl^- + ?$	6.1	No		MS	154
	PCl_3	$Cl^- + PCl_2$		No	0.05	MS	161
	$POCl_3$	$Cl^- + POCl_2$		No	0.05	MS	161
	$POCl_3$	$Cl^- + ?$		No	8	MS	161
	SF_5Cl	$Cl^- + SF_3 + F_2$	4.0	No		MS	168
	SF_5Cl	$Cl^- + SF_2 + 3F?$	7.6	No	9.1	MS	168
	$SbCl_3$	$Cl^- + SbCl_2$		No	~ 0	TI	164
	$TlCl$	$Cl^- + Tl$		No	1.9	MS	194
	$PbCl_2$	$Cl^- + Pb + Cl$		No	~ 2.7	MS	189–191
	$ZnCl_2$	$Cl^- + ZnCl$		No	~ 5	MS	163
	$HgCl_2$	$Cl^- + HgCl$		No	~ 3	MS	163
	$NbCl_5$	$Cl^- + NbCl_4$		No	4.7	MS	163
	$TaCl_5$	$Cl^- + TaCl_4$		No	5.5	MS	163
	$TiCl_4$	$Cl^- + TiCl_3$	0.1	Yes	0.96	TI	53
	$TiCl_4$	$Cl^- + TiCl_3?$		No	6.4	TI	53
	$TiCl_4$	$Cl^- + TiCl_3?$		No	6.5	MS	163
	$TiCl_4$	$Cl^- + ?$		No	10.9	TI	53
	$Ti(C_5H_5)_2Cl_2$	$Cl^- + Ti(C_5H_5)_2Cl$		No	0.1	MS	204
	$Ti(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	2.55	MS	204
	$Ti(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	8	MS	204
	$Zr(C_5H_5)_2Cl_2$	$Cl^- + Zr(C_5H_5)_2Cl$		No	0.3	MS	204
	$Zr(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	4.2	MS	204
	$Zr(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	8.5	MS	204
	$Hf(C_5H_5)_2Cl_2$	$Cl^- + Hf(C_5H_5)_2Cl$		No	0.8	MS	204
	$Hf(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	4.4	MS	204
	$Hf(C_5H_5)_2Cl_2$	$Cl^- + ?$		No	8.8	MS	204
	CrO_2Cl_2	$Cl^- + CrO_2Cl$	0	No		MS	196
	CrO_2Cl_2	$Cl^- + CrO_2 + Cl$	3.46	No		MS	196
	$LiCl$	$Cl^- + Li$	3.36	No		MS	187
	$LiCl$	$Cl^- + ?$	5.60	No		MS	187
	$NaCl$	$Cl^- + Na$	2.90	No		MS	187
	KCl	$Cl^- + K$	2.60	No		MS	187
	KCl	$Cl^- + ?$	4.50	No		MS	187

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
Cl^-	RbCl	$Cl^- + Rb$		No	~2	MS	189
Cl_2^-	CCl_4	$Cl_2^- + CCl_2$	2.3	Yes		MS	25, 30
	CCl_4	$Cl_2^- + CCl_2$?	0.5	No	1.5	MS	62
	$C_2Cl_4H_2$	$Cl_2^- +$?	4.5	No	6.5	MS	62
	S_2Cl_2	$Cl_2^- + S_2$?		No	3.5	MS	62
	S_2Cl_2	$Cl_2^- +$?		No	6.2	MS	62
	$SiCl_4$	$Cl_2^- + SiCl_2$	0	No		MS	154
	$SiCl_4$	$Cl_2^- + SiCl + Cl$?	6.5	No		MS	154
	$SiCl_4$	$Cl_2^- + SiCl_2$?		No	7.0	MS	62
	CH_3SiCl_3	$Cl_2^- + CH_3SiCl$	7.0	No		MS	154
	$(CH_3)_2SiCl_2$	$Cl_2^- +$?	6.7	No		MS	154
	$C_2H_5SiCl_3$	$Cl_2 +$?	6.3	No		MS	154
	$C_2H_5SiCl_3$	$Cl_2^- +$?	7.2	No		MS	154
	CrO_2Cl_2	$Cl_2^- + CrO_2$	2.74	No		MS	196
HCl_2^-	$CHCl_3$	$HCl_2^- + CCl$?	0.5	No	1.7	MS	62
FCl^-	SF_5Cl	$FCl^- + SF_2 + 2F$?	7.6	No	9.1	MS	168
ClO_x^-	CrO_2Cl_2	$OCl^- + CrOCl$	3.79	No		MS	196
	ClO_3F	$ClO_3^- + F$	0.2	No	1.8	MS	119
CCl_x^-	$CHCl_3$	$CCl_2^- + HCl$?	0.5	No	1.7	MS	62
	CCl_4	$CCl_2^- + Cl_2$?		No	1.7	MS	62
	CCl_4	$CCl_2^- +$?		No	6.4	MS	62
	CCl_4	$CCl_3^- + Cl$	0.5	No	1.7	MS	62
	CCl_3F	$CCl_3^- + F$	2.75	Yes	3.2	MS	32
S^-	H_2S	$S^- + H_2$	2.03		2.67	MS	28
	H_2S	$S^- + 2H$?	5.2		5.9	MS	28
	H_2S	$S^- + 2H$?	7.8		9.2	MS	28
	CS_2	$S^- + CS$	2.5	Yes	3.7	MS	62
	CS_2	$S^- + CS$	2.9	No	3.7	MS	90
	CS_2	$S^- + C + S$	5.4	No	6.3	MS	90
	CS_2	$S^- +$?		No	6.4	MS	62
	CS_2	$S^- + C + S$?	7.2	No	7.9	MS	90
	CS_2	$S^- +$?		No	8.1	MS	62
	COS	$S^- + CO$	1.3	No	2.05	MS	90
	COS	$S^- +$?	6.7	No	7.4	MS	90
	COS	$S^- +$?	9.2	No	10.8	MS	90
	COS	$S^- + C + O$	13.2	No	14.1	MS	90
	CH_3SH	$S^- + CH_4$	1.0		1.4	MS	28
	CH_3SH	$S^- +$?	3.2		3.4	MS	28
	CH_3SH	$S^- +$?	5.2		5.4	MS	28
	CH_3SH	$S^- +$?	7.4		8.3	MS	28
	CH_3SCH_3	$S^- + 2CH_3$	4.7		5.1	MS	28
	CH_3SCH_3	$S^- + 2CH_3$?	7.1	Yes	7.8	MS	28
	SO_2	$S^- + O_2$?	3.0	No	4.1	MS	62
	SO_2	$S^- +$?		No	8	MS	62
	S_2Cl_2	$S^- +$?	~2	No	3.0	MS	62
	S_2Cl_2	$S^- +$?		No	5.1	MS	62
	S_2Cl_2	$S^- +$?		No	8	MS	62
	C_3H_5SH	$S^- +$?	4.8		5.6	MS	28
	C_3H_5SH	$S^- +$?	5.9		6.6	MS	28
	C_3H_5SH	$S^- +$?	7.6		8.8	MS	28
	C_6H_5SH	$S^- +$?	4.9		5.4	MS	28
	C_6H_5SH	$S^- +$?	7.5		8.7	MS	28
	$C_6H_5CH_2SH$	$S^- +$?	4.8	Yes	5.8	MS	28
	$C_6H_5CH_2SH$	$S^- +$?	7.5		8.5	MS	28
	CH_3SSCH_3	$S^- +$?	4.79		5.4	MS	28
	CH_3SSCH_3	$S^- +$?	7.1		7.6	MS	28
	$(C_3H_5S)_2$	$S^- +$?	4.4		5.37	MS	28
	$C_4H_4S^i$	$S^- +$?	5.55	No	5.9	MS	133
	$C_4H_4S^i$	$S^- +$?	8.25	No	8.55	MS	133
	$C_5H_6S^j$	$S^- +$?	5.25	No	5.5	MS	133
	$C_5H_6S^j$	$S^- +$?	8.0	No	8.5	MS	133
	$C_6H_8S^l$	$S^- +$?	~5.2	No		MS	133
	$C_6H_8S^l$	$S^- +$?		No	~8	MS	133
	$C_7H_{10}S^m$	$S^- +$?	0	No	5.2	MS	133
	$C_7H_{10}S^m$	$S^- +$?		No	8.4	MS	133
	$C_5H_6S^k$	$S^- +$?	5.45	No	5.7	MS	133
	$C_5H_6S^k$	$S^- +$?	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$S^- +$?	5.3	No	5.6	MS	133

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
S^-	$C_7H_{10}S^n$	$S^- + ?$	7.9	No	8.45	MS	133
	$(CH_3)_2SO^h$	$S^- + ?$	3.6	No	4.6	MS	134
S_2^-	CS_2	$S_2^- + C?$	5.3	No	6.5	MS	62
	CS_2	$S_2^- + C$	5.2	No	6.3	MS	90
	S_2Cl_2	$S_2^- + ?$		No	4	MS	62
	S_2Cl_2	$S_2^- + ?$		No	7.5	MS	62
	$(C_3H_5S)_2$	$S_2^- + (C_3H_5)_2$	0.0			MS	28
	$(C_3H_5S)_2$	$S_2^- + 2C_3H_5?$	1.2		2.09	MS	28
	$(C_3H_5S)_2$	$S_2^- + ?$	4.0		5.09	MS	28
SH^-	H_2S	$SH^- + H$	1.56		2.27	MS	28
	CH_3SH	$SH^- + CH_3$	2.0		2.5	MS	28
	CH_3SH	$SH^- + ?$	7.9		8.3	MS	28
	CH_3SH	$SH^- + ?$	8.7	Yes	9.5	MS	28
	CH_3SCH_3	$SH^- + C_2H_5?$	1.8		2.4	MS	28
	CH_3SCH_3	$SH^- + CH_3 + CH_2?$	8.1		9.0	MS	28
	C_3H_5SH	$SH^- + C_3H_5$	0.6	Yes	1.19	MS	28
	$(C_3H_5S)_2$	$SH^- + ?$	0.58	Yes	1.26	MS	28
	C_6H_5SH	$SH^- + C_6H_5$	0.4	Yes	0.9	MS	28
	C_6H_5SH	$SH^- + C_6H_5?$	1.4	Yes	2.3	MS	28
	C_6H_5SH	$SH^- + C_6H_5?$	3.9	Yes	4.4	MS	28
	C_6H_5SH	$SH^- + C_6H_5?$	4.6	Yes	5.0	MS	28
	C_6H_5SH	$SH^- + C_6H_5?$	5.4	Yes	6.3	MS	28
	C_6H_5SH	$SH^- + C_6H_5?$	7.5	Yes	8.9	MS	28
	$C_6H_5CH_2SH$	$SH^- + C_6H_5CH_2$	0.41	Yes	0.92	MS	28
	$C_4H_4S^i$	$SH^- + ?$	5.55	No	5.9	MS	133
	$C_4H_4S^i$	$SH^- + ?$	8.25	No	8.55	MS	133
	$C_5H_6S^j$	$SH^- + ?$	5.25	No	5.5	MS	133
	$C_5H_6S^j$	$SH^- + ?$	8.0	No	8.5	MS	133
	$C_6H_8S^l$	$SH^- + ?$	$\sim$5.2	No		MS	133
	$C_6H_8S^l$	$SH^- + ?$		No	$\sim$8	MS	133
	$C_7H_{10}S^m$	$SH^- + ?$		No	5.2	MS	133
	$C_7H_{10}S^m$	$SH^- + ?$		No	8.4	MS	133
	$C_5H_6S^k$	$SH^- + ?$	5.45	No	5.7	MS	133
	$C_5H_6S^k$	$SH^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$SH^- + ?$	5.3	No	5.6	MS	133
	$C_7H_{10}S^n$	$SH^- + ?$	7.9	No	8.45	MS	133
	$(CH_3)_2SO^h$	$SH^- + ?$	0	No	0.8	MS	134
	$(CH_3)_2SO^h$	$SH^- + ?$	3.4	No	4.7	MS	134
SF_x^-	SF_4	$SF_3^- + F$	0.7	No	1.35	MS	167
	SF_5Cl	$SF_3^- + 2F + Cl$	7.9	No	8.9	MS	168
	SF_4	SF_4^-	0.0	No	0.4	MS	166, 167
	SF_6	$SF_4^- + 2F$	5.0	No	6.0	MS	167
	SF_5Cl	$SF_4^- + F + Cl$	4.1	No	4.65	MS	168
	SF_5Cl	$SF_5^- + Cl$	0.2	No	0.7	MS	168
	CF_3SF_5	$SF_5^- + CF_3$	0.2	No	1.8	MS	119
	CF_3SF_5	$SF_5^- + ?$	3.9	No	5.4	MS	119
	SF_6	$SF_5^- + F$	0.05	No		MS	119
	SF_6	SF_6^-	0	No	0	MS	18
	SF_6	SF_6^-	0.0	No		MS	119
	SF_6	SF_6^-	0.03			TI	111
	SF_6	SF_6^-		No	0	MS	184
	SF_6	SF_6^-	0	No	0	MS	170, 182
	SF_6	SF_6^-	0	No	0	MS	169
	SF_6	SF_6^-	0	No	0	MS	51
SO^-	SO_2	$SO^- + O$	3.8	No	4.8	MS	62
	SO_2	$SO^- + O(^3P)?$		No	4.6	MS	165
	SO_2	$SO^- + O$	4.9	No	6.5	MS	119
	SO_2	$SO^- + O(^1D)?$		No	7.2	MS	165
	SO_2	$SO^- + ?$		No	8	MS	62
	COS	$SO^- + C?$	4.5	No	5.7	MS	90
	$(CH_3)_2SO^h$	$SO^- + ?$	2.8	No	4.6	MS	134
	$(CH_3)_2SO^h$	$SO^- + ?$	7.9	No	8.9	MS	134
$SO_xF_y^-$	SO_2F_2	$SO_2F^- + F$		No	2.3	MS	165
	SO_2F_2	$SO_2F_2^-$		No	$\sim$0	MS	165
CS^-	CS_2	$CS^- + S$	5.0	No	6.1	MS	62
	CS_2	$CS^- + S$	5.3	No	6.3	MS	90
	COS	$CS^- + O$	5.6	No	6.9	MS	90
CHS^-	$(CH_3)_2SO^h$	$CHS^- + ?$	3.0	No	4.7	MS	134
	$C_5H_6S^k$	$CHS^- + ?$	8.1	No	8.5	MS	133

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
CHS^-	C_5H_6S[j]	$CHS^- + ?$	8.0	No	8.5	MS	133
	C_4H_4S[i]	$CHS^- + ?$	8.25	No	8.55	MS	133
CH_2S^-	CH_3SH	$CH_2S^- + H_2$	0.33		0.68	MS	28
	C_3H_5SH	$CH_2S^- + C_2H_4$	1.3		1.75	MS	28
	CH_3SCH_3	$CH_2S^- + CH_3 + H$	8.1		8.9	MS	28
	CH_3SSCH_3	$CH_2S^- + CH_3SH$	0.35	Yes	0.7	MS	28
	$(CH_3)_2SO$[h]	$CH_2S^- + ?$	3.2	No	4.8	MS	134
CH_3S^-	CH_3SH	$CH_3S^- + H$	0.58		1.0	MS	28
	CH_3SH	$CH_3S^- + H?$	1.44		2.1	MS	28
	C_3H_5SH	$CH_3S^- + C_2H_3$	0.8		1.39	MS	28
	CH_3SCH_3	$CH_3S^- + CH_3$	0.6		1.0	MS	28
	CH_3SCH_3	$CH_3S^- + CH_2 + H$	7.2		7.8	MS	28
	CH_3SSCH_3	$CH_3S^- + SCH_3$	0.6	Yes	1.0	MS	28
	$(CH_3)_2SO$[h]	$CH_3S^- + ?$	3.5	No	4.9	MS	134
C_2HS^-	C_4H_4S[i]	$SC_2H^- + ?$	5.55	No	5.9	MS	133
	C_4H_4S[i]	$SC_2H^- + ?$	8.25	No	8.55	MS	133
	C_5H_6S[j]	$SC_2H^- + ?$	5.25	No	5.5	MS	133
	C_5H_6S[j]	$SC_2H^- + ?$	8.0	No	8.5	MS	133
	C_6H_8S[l]	$SC_2H^- + ?$		No	2.8	MS	133
	C_6H_8S[l]	$SC_2H^- + ?$	~5.2	No		MS	133
	$C_7H_{10}S$[m]	$SC_2H^- + ?$		No	8.4	MS	133
	C_5H_6S[k]	$SC_2H^- + ?$	5.45	No	5.7	MS	133
	C_5H_6S[k]	$SC_2H^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S$[n]	$SC_2H^- + ?$	5.3	No	5.6	MS	133
	$C_7H_{10}S$[n]	$SC_2H^- + ?$	7.9	No	8.45	MS	133
$C_2H_2S^-$	$(C_3H_5S)_2$	$C_2H_2S^- + ?$	0.0		0.80	MS	28
	C_4H_4S[i]	$SC_2H_2^- + C_2H_2$	5.55	No	5.9	MS	133
	C_4H_4S[i]	$SC_2H_2^- + C_2H_2?$	8.25	No	8.55	MS	133
	C_5H_6S[j]	$SC_2H_2^- + ?$	5.25	No	5.5	MS	133
	C_5H_6S[j]	$SC_2H_2^- + ?$	8.0	No	8.5	MS	133
	C_6H_8S[l]	$SC_2H_2^- + ?$	~5.2	No		MS	133
	C_5H_6S[k]	$SC_2H_2 + ?$	5.45	No	5.7	MS	133
	C_5H_6S[k]	$SC_2H_2^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S$[n]	$SC_2H_2^- + ?$	7.9	No	8.45	MS	133
$C_2H_xS^-$	$C_7H_{10}S$[m]	$SC_2H_4^- + ?$		No	5.2	MS	133
	CH_3SSCH_3	$CH_3SCH_2^- + HS$	0.46		0.8	MS	28
$C_3H_xS^-$	$(C_3H_5S)_2$	$C_3H_2S^- + ?$	0.36		0.97	MS	28
	C_5H_6S[j]	$SC_3H_3^- + C_2H_3?$	8.0	No	8.5	MS	133
	C_5H_6S[k]	$SC_3H_3^- + C_2H_3?$	5.45	No	5.7	MS	133
	C_5H_6S[k]	$SC_3H_3^- + C_2H_3?$	8.1	No	8.5	MS	133
	$C_7H_{10}S$[n]	$SC_3H_3^- + ?$	5.3	No	5.6	MS	133
	$C_7H_{10}S$[n]	$SC_3H_3^- + ?$	7.9	No	8.45	MS	133
	C_3H_5SH	$C_3H_4S^- + H_2$	0.04	Yes	0.47	MS	28
	C_3H_5SH	$C_3H_4S^- + 2H\ ?$	1.2		1.59	MS	28
	$(C_3H_5S)_2$	$C_3H_4S^- + HSC_3H_5$	0.07	Yes	0.49	MS	28
	$C_7H_{10}S$[m]	$C_3H_4S^- + ?$		No	5.2	MS	133
	$(C_3H_5S)_2$	$C_3H_5S^- + SC_3H_5$	0.6	Yes	1.28	MS	28
	C_3H_5SH	$C_3H_5S^- + H$	0.65	Yes	1.28	MS	28
	$C_6H_5CH_2SH$	$C_3H_5S^- + ?$	0.42		0.97	MS	28
$C_4H_xS^-$	C_4H_4S[i]	$SC_4H^- + ?$	8.25	No	8.55	MS	133
	C_5H_6S[j]	$SC_4H^- + ?$	8.0	No	8.5	MS	133
	C_6H_8S[l]	$SC_4H^- + ?$		No	~8	MS	133
	$C_7H_{10}S$[m]	$SC_4H^- + ?$		No	8.4	MS	133
	C_5H_6S[k]	$SC_4H^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S$[n]	$SC_4H^- + ?$	7.9	No	8.45	MS	133
	C_4H_4S[i]	$SC_4H_2^- + H_2?$	8.25	No	8.55	MS	133
	C_5H_6S[j]	$SC_4H_2^- + ?$	8.0	No	8.5	MS	133
	$C_7H_{10}S$[m]	$SC_4H_2^- + ?$		No	8.4	MS	133
	C_5H_6S[k]	$SC_4H_2^- + ?$	5.45	No	5.7	MS	133
	C_5H_6S[k]	$SC_4H_2^- + ?$	8.1	No	8.5	MS	133
	$C_7H_{10}S$[n]	$SC_4H_2^- + ?$	7.9	No	8.45	MS	133
	C_4H_4S[i]	$SC_4H_3^- + H$	5.55	No	5.9	MS	133
	C_4H_4S[i]	$SC_4H_3^- + H$	8.25	No	8.55	MS	133
	C_5H_6S[j]	$SC_4H_3^- + CH_3?$	5.25	No	5.5	MS	133
	C_6H_8S[l]	$SC_4H_3^- + C_2H_5?$	~5.2	No		MS	133
	C_6H_8S[l]	$SC_4H_3^- + C_2H_5?$		No	~8	MS	133
	$C_7H_{10}S$[m]	$SC_4H_3^- + ?$		No	8.4	MS	133
	C_5H_6S[k]	$SC_4H_4^- + CH_2?$	5.45	No	5.7	MS	133

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
$C_4H_xS^-$	$C_7H_{10}S^n$	$SC_4H_3^- + ?$	5.3	No	5.6	MS	133
	$C_7H_{10}S^n$	$SC_4H_3^- + ?$	7.9	No	8.45	MS	133
$C_5H_xS^-$	$C_5H_6S^j$	$SC_5H_4^- + H_2$	8.0	No	8.5	MS	133
	$C_6H_8S^l$	$SC_5H_4^- + CH_3 + H$		No	~8	MS	133
	$C_7H_{10}S^m$	$SC_5H_4^- + ?$		No	8.4	MS	133
	$C_5H_6S^k$	$SC_5H_4^- + H_2?$	5.45	No	5.7	MS	133
	$C_5H_6S^k$	$SC_5H_4^- + H_2?$	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$SC_5H_4^- + ?$	7.9	No	8.45	MS	133
	$C_5H_6S^j$	$SC_5H_5^- + H$	5.25	No	5.5	MS	133
	$C_5H_6S^j$	$SC_6H_5^- + H$	8.0	No	8.5	MS	133
	$C_6H_8S^l$	$SC_5H_5^- + CH_3$	~5.2	No		MS	133
	$C_7H_{10}S^m$	$SC_5H_5^- + C_2H_5?$		No	5.2	MS	133
	$C_7H_{10}S^m$	$SC_5H_5^- + C_2H_5?$		No	8.4	MS	133
	$C_5H_6S^k$	$SC_5H_5^- + H$	5.45	No	5.7	MS	133
	$C_5H_6S^k$	$SC_5H_5^- + H$	8.1	No	8.5	MS	133
	$C_7H_{10}S^n$	$SC_5H_5^- + C_2H_5?$	5.3	No	5.6	MS	133
	$C_7H_{10}S^n$	$SC_5H_5^- + C_2H_5?$	7.9	No	8.45	MS	133
$C_6H_xS^-$	C_6H_5SH	$C_6H_5S^- + H$	0.04		0.24	MS	28
	C_6H_5SH	$C_6H_5S^- + H?$	0.34		0.75	MS	28
	C_6H_5SH	$C_6H_5S^- + H?$	0.6		1.32	MS	28
	$C_6H_5CH_2SH$	$C_6H_5S^- + CH_3$	0.15	Yes	0.95	MS	28
	$C_6H_8S^l$	$SC_6H_7^- + H$		No	~8	MS	133
	$C_6H_8S^l$	$SC_6H_7^- + H$	~5.2	No		MS	133
$C_7H_xS^-$	$C_6H_5CH_2SH$	$C_6H_5CHS^- + H_2$	0		0.2	MS	28
	$C_6H_5CH_2SH$	$C_6H_5CHS^- + 2H\ ?$			0.7	MS	28
	$C_6H_5CH_2SH$	$C_6H_5CHS^- + 2H\ ?$			1.1	MS	28
	$C_6H_5CH_2SH$	$C_6H_5CH_2S^- + H$	0.35		0.9	MS	28
	$C_7H_{10}S^m$	$SC_7H_9^- + H$		No	5.2	MS	133
	$C_7H_{10}S^m$	$SC_7H_9^- + H$		No	8.4	MS	133
	$C_7H_{10}S^n$	$SC_7H_9^- + H?$	5.3	No	5.6	MS	133
	$C_7H_{10}S^n$	$SC_7H_9^- + H$	7.9	No	8.45	MS	133
$C_xH_yS_2^-$	CH_3SSCH_3	$CH_2S_2^- + CH_4$	0.02		0.3	MS	28
	CH_3SSCH_3	$CH_3S_2^- + CH_3$	0.36	Yes	0.8	MS	28
	$(C_3H_5S)_2$	$C_3H_4S_2^- + C_3H_6$	0.0		0.18	MS	28
	$(C_3H_5S)_2$	$C_3H_5S_2^- + C_3H_5$	0.02	Yes	0.77	MS	28
$C_xH_yO_zS^-$	$(CH_3)_2SO^h$	$CHSO^- + ?$	4.2	No	4.8	MS	134
	$(CH_3)_2SO^h$	$CHSO^- + ?$	7.5	No	9.1	MS	134
	$(CH_3)_2SO^h$	$CH_3SO^- + CH_3$	0	No	0.4	MS	134
	$(CH_3)_2SO^h$	$CH_3SO^- + CH_3?$	2.5	No	4.4	MS	134
	$(CH_3)_2SO^h$	$(C_2H_5)SO^- + H$	0.9	No	1.7	MS	134
SCl^-	S_2Cl_2	$SCl^- + SCl?$		No	6.0	MS	62
PH_x^-	PH_3	$P^- + ?$	5.7	No	6.7	MS	152
	PH_3	$P^- + H_2 + H$	5.8	No		MS	160
	PH_3	$P^- + 3H?$	8.3	No	9.7	MS	152
	PH_3	$P^- + 3H?$	8.4	No		MS	160
	PH_3	$P^- + ?$	13.4	No		MS	160
	PH_3	$PH^- + H_2?$	2.1	No	3	MS	152
	PH_3	$PH^- + H_2$	2.2	No		MS	160
	PH_3	$PH^- + 2H$	6.3	No		MS	160
	PH_3	$PH^- + 2H?$	6.3	No	7.5	MS	152
	PH_3	$PH^- + 2H?$	8.1	No	9.5	MS	152
	PH_3	$PH^- + 2H$	8.2	No		MS	160
	PH_3	$PH_2^- + H$	2.3	No	3	MS	152
	PH_3	$PH_2^- + H$	2.2	No		MS	160
	PH_3	$PH_2^- + H$	5.2	No		MS	160
	PH_3	$PH_2^- + H?$	5.2	No	6.5	MS	152
	PH_3	$PH_2^- + H$	8	No		MS	160
PX_y^-	PF_3	$PF^- + 2F?$	11.4	No	~12	MS	150
	PF_3	$PF_2^- + F$	10.3	No	~10.5	MS	150
	PCl_3	$PCl_2^- + Cl$		No	0.4	MS	161
	$POCl_3$	$PCl_2^- + ?$		No	0.05	MS	161
SiH_x^-	SiH_4	$Si^- + ?$	8.2	No		MS	152
	SiH_4	$Si^- + ?$	8.5	No		MS	151
	SiH_4	$Si^- + ?$	12.5	No		MS	151
	CH_3SiH_3	$Si^- + CH_4 + 2H$	8.2	No		MS	156
	CH_3SiH_3	$Si^- + CH_3 + 3H?$	13.3	No		MS	156
	Si_2H_6	$Si_2^- + ?$	~5	No	~7	MS	151
	SiH_4	$SiH^- + H_2 + H?$	7.7	No		MS	151
	SiH_4	$SiH^- + ?$	7.9	No		MS	152

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
SiH_x^-	SiH_4	$SiH^- + ?$	11.5	No		MS	151
	CH_3SiH_3	$SiH^- + CH_4 + H?$	7.1	No		MS	156
	Si_2H_6	$SiH^- + ?$	~5	No	~7	MS	151
	SiH_4	$SiH_2^- + H_2?$	2.5	No		MS	151
	SiH_4	$SiH_2^- + 2H?$	7.7	No		MS	151
	SiH_4	$SiH_2^- + 2H?$	8.4	No		MS	152
	SiH_4	$SiH_2^- + 2H?$	~13	No		MS	151
	CH_3SiH_3	$SiH_2^- + CH_4?$	7.1	No		MS	156
	Si_2H_6	$SiH_2^- + ?$	~5	No	~7	MS	151
	SiH_4	$SiH_3^- + H$	2.5	No		MS	151
	SiH_4	$SiH_3^- + H?$	6.7	No		MS	151
	SiH_4	$SiH_3^- + H?$	7.0	No		MS	152
	SiH_4	$SiH_3^- + H$	11.0	No	8.5	MS	151
	CH_3SiH_3	$SiH_3^- + CH_3$	7.1	No		MS	156
	Si_2H_6	$SiH_3^- + SiH_3?$	~5	No	~7	MS	151
$Si_2H_x^-$	Si_2H_6	$Si_2H^- + ?$	~5	No	~7	MS	151
	Si_2H_6	$Si_2H_2^- + ?$	~5	No	~7	MS	151
	Si_2H_6	$Si_2H_3^- + ?$	~5	No	~7	MS	151
	Si_2H_6	$Si_2H_4^- + 2H?$	~5	No	~7	MS	151
	Si_2H_6	$Si_2H_5^- + H$	~5	No	~7	MS	151
SiX_x^-	SiF_4	$SiF_3^- + F$	10.55	No	11.2	MS	158
	$SiCl_4$	$SiCl_2^- + Cl_2 ?$	0.8	No	~2	MS	153
	$SiCl_4$	$SiCl_2^- + Cl_2$	0	No		MS	154
	$SiCl_4$	$SiCl_2^- + 2Cl?$	6.7	No		MS	154
	CH_3SiCl_3	$SiCl_2^- + CH_3Cl$	6.3	No		MS	154
	$(CH_3)_2SiCl_2$	$SiCl_2^- + 2CH_3$	6.3	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_2^- + C_2H_3Cl$	0	No		MS	154
$SiCl_x^-$	$C_2H_3SiCl_3$	$SiCl_2^- + ?$	3.8	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_2^- + ?$	5.7	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_2^- + ?$	6.3	No		MS	154
	$SiCl_4$	$SiCl_3^- + Cl$	0	No		MS	154
	$SiCl_4$	$SiCl_3^- + Cl?$	1.7	No		MS	154
	$SiCl_4$	$SiCl_3^- + Cl?$	5.9	No		MS	154
	CH_3SiCl_3	$SiCl_3^- + CH_3$	1.3	No		MS	154
	CH_3SiCl_3	$SiCl_3^- + CH_2 + H?$	6.6	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_3^- + C_2H_3$	0	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_3^- + ?$	3.7	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_3^- + ?$	5.7	No		MS	154
	$C_2H_3SiCl_3$	$SiCl_3^- + ?$	6.5	No		MS	154
	$C_6H_5SiCl_3$	$SiCl_3^- + C_6H_5$	3.7	No		MS	154
	$C_6H_5SiCl_3$	$SiCl_3^- + ?$	5.6	No		MS	154
	$C_6H_5SiCl_3$	$SiCl_3^- + ?$	6.1	No		MS	154
	$SiCl_4$	$SiCl_4^-$	0	No		MS	154
	$SiCl_4$	$SiCl_4^-$	0	No		MS	155
$SiC_xH_y^-$	CH_3SiH_3	$SiCH_3^- + ?$	7.1	No		MS	156
	CH_3SiH_3	$SiCH_4^- + ?$	7.1	No		MS	156
	CH_3SiH_3	$CH_3SiH_2^- + H$	7.1	No		MS	156
$SiC_xH_yCl^-$	$C_2H_3SiCl_3$	$C_2SiCl^- + ?$	7.2	No		MS	154
	CH_3SiCl_3	$CH_2SiCl^- + ?$	7.0	No		MS	154
	$(CH_3)_2SiCl_2$	$CH_2SiCl^- + ?$	6.2	No		MS	154
	$C_2H_3SiCl_3$	$C_2HSiCl^- + ?$	3.9	No		MS	154
	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl^- + Cl$	6.6	No		MS	154
	$(CH_3)_3SiCl$	$C_3H_7SiCl^- + H_2$	2.7	No		MS	154
	$(CH_3)_3SiCl$	$C_3H_7SiCl^- + 2H?$	6.5	No		MS	154
$SiC_xH_yCl_2^-$	CH_3SiCl_3	$CH_3SiCl_2^- + Cl$	6.1	No		MS	154
	$(CH_3)_2SiCl_2$	$CH_3SiCl_2^- + CH_3$	6.2	No		MS	154
	$C_2H_3SiCl_3$	$C_2SiCl_2^- + ?$	5.9	No		MS	154
	$C_2H_3SiCl_3$	$C_2SiCl_2^- + ?$	6.9	No		MS	154
	$C_2H_3SiCl_3$	$C_2HSiCl_2^- + ?$	4.1	No		MS	154
	$C_2H_3SiCl_3$	$C_2HSiCl_2^- + ?$	5.6	No		MS	154
	$(CH_3)_2SiCl_2$	$C_2H_4SiCl_2^- + H_2$	8.2	No		MS	154
	$(CH_3)_2SiCl_2$	$C_2H_5SiCl_2^- + H$	2.2	No		MS	154
	$(CH_3)_2SiCl_2$	$C_2H_5SiCl_2^- + ?$	6.6	No		MS	154
	$C_6H_5SiCl_3$	$C_6H_5SiCl_2^- + Cl$	5.9	No		MS	154
	$C_6H_5SiCl_3$	$C_6H_5SiCl_2^- + ?$	6.3	No		MS	154
$SiC_xH_yCl_3^-$	$C_2H_3SiCl_3$	$CSiCl_3^- + ?$	0	No		MS	154
	$C_2H_3SiCl_3$	$CSiCl_3^- + ?$	4.0	No		MS	154
	$C_2H_3SiCl_3$	$CSiCl_3^- + ?$	6.0	No		MS	154
	$C_2H_3SiCl_3$	$CSiCl_3^- + ?$	7.4	No		MS	154

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
$SiC_xH_yCl_3^-$	CH_3SiCl_3	$CHSiCl_3^- + H_2$	7.4	No		MS	154
	CH_3SiCl_3	$CHSiCl_3^- + 2H$	8.3	No		MS	154
	$C_2H_3SiCl_3$	$CHSiCl_3^- + CH_2$	3.8	No		MS	154
	$C_2H_3SiCl_3$	$CHSiCl_3^- + ?$	6.1	No		MS	154
	$C_2H_3SiCl_3$	$CHSiCl_3^- + ?$	7.3	No		MS	154
	CH_3SiCl_3	$CH_2SiCl_3^- + H$	1.9	No		MS	154
	$C_2H_3SiCl_3$	$C_2SiCl_3^- + ?$	4.0	No		MS	154
	$C_2H_3SiCl_3$	$C_2SiCl_3^- + ?$	5.9	No		MS	154
	$C_2H_3SiCl_3$	$C_2SiCl_3^- + ?$	7.2	No		MS	154
	$C_2H_3SiCl_3$	$C_2H_3SiCl_3^-$	0	No		MS	154
	$C_6H_5SiCl_3$	$C_6H_4SiCl_3^- + H$	6.4	No		MS	154
	$C_6H_5SiCl_3$	$C_6H_4SiCl_3^- + ?$	7.2	No		MS	154
	$C_6H_5SiCl_3$	$C_6H_5SiCl_3^-$	0	No		MS	154
$SiC_xH_yCl_{12}^-$	$C_{12}H_{36}Si_6$	$C_{12}H_{36}Si_6^-$	~5	No		MS	157
Br^-	Br_2	$Br^- + Br$	0	No	0.03	MS	46
	HBr	$Br^- + H$	0.10	No	0.21	MS	50
	CH_2Br_2	$Br^- + CH_2Br$	0	Yes		MS	25
	CNBr	$Br^- + CN$		No	4.1	MS	144
	CNBr	$Br^- + CN$		No	0	MS	144
	CH_2BrCH_2OH	$Br^- + ?$		No	7	MS	62
	m-C_6H_4ClBr	$Br^- + C_6H_4Cl$	~0	No	0	MS	121
	C_6F_5Br	$Br^- + C_6F_5$	~0	No	0.1	MS	121
	LiBr	$Br^- + Li$	4.85	No		MS	187
	NaBr	$Br^- + Na$	3.75	No		MS	187
	KBr	$Br^- + K$	3.80	No		MS	187
	RbBr	$Br^- + Rb$	3.85	No		MS	187
	$ZnBr_2$	$Br^- + ZnBr$		No	~5	MS	163
	$HgBr_2$	$Br^- + HgBr$		No	~3	MS	163
	$PbBr_2$	$Br^- + Pb + Br$		No	~2	MS	190
	InBr	$Br^- + In$		No	~1.5	MS	193
Br_2^-	CBr_4	$Br_2^- + CBr_2$	0	Yes		MS	30
SeX_n^-	SeF_6	$Se^- + ?$		No	0	MS	169
	$C_4H_4Se^o$	$Se^- + ?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$Se^- + ?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeH^- + ?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$SeH^- + ?$	7.5	No	7.8	MS	133
	SeF_6	$SeF_3^- + ?$		No	8	MS	169
	SeF_6	$SeF_4^- + 2F$		No	7	MS	169
	SeF_6	$SeF_5^- + F$		No	0	MS	169
	$C_4H_4Se^o$	$SeC^- + ?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeCH^- + ?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeC_2H^- + ?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$SeC_2H^- + ?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeC_4H^- + ?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeC_4H_2^- + H_2?$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$SeC_4H_2^- + H_2?$	7.5	No	7.8	MS	133
	$C_4H_4Se^o$	$SeC_4H_3^- + H$	5.1	No	5.2	MS	133
	$C_4H_4Se^o$	$SeC_4H_3^- + H$	7.5	No	7.8	MS	133
AsH_x^-	AsH_3	$As^- + H_2 + H?$	5.3	No	6.3	MS	152
	AsH_3	$As^- + 3H?$	7.8	No	9.4	MS	152
	AsH_3	$AsH^- + H_2$	2.0	No	2.7	MS	152
	AsH_3	$AsH^- + 2H$	6.2	No	7.3	MS	152
	AsH_3	$AsH^- + ?$		No	~9.0	MS	152
	AsH_3	$AsH_2^- + H$	2.0	No	2.7	MS	152
	AsH_3	$AsH_2^- + H$	5.2	No	6.2	MS	152
XeF_x^-	XeF_4	$XeF^- + F_2 + F?$		No	0	MS	185
	XeF_4	$XeF^- + 3F?$		No	~4.5	MS	185
	XeF_6	$XeF^- + ?$		No	0	MS	185
	XeF_6	$XeF^- + ?$		No	~7	MS	185
	XeF_4	$XeF_2^- + F_2?$		No	0	MS	185
	XeF_4	$XeF_2^- + 2F?$		No	~4.5	MS	185
	XeF_6	$XeF_2^- + ?$		No	0	MS	185
	XeF_6	$XeF_2^- + ?$		No	~5	MS	185
	XeF_4	$XeF_3^- + F$		No	~0	MS	185
	XeF_4	$XeF_3^- + F?$		No	~6	MS	185
	XeF_6	$XeF_3^- + F_2 + F?$		No	0	MS	185
	XeF_6	$XeF_3^- + 3F$		No	~4.7	MS	185
	XeF_6	$XeF_4^- + F_2?$		No	0	MS	185
	XeF_6	$XeF_4^- + 2F?$		No	~4.7	MS	185

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
I^-	I_2	$I^- + I$	0.03	No	0.34	MS	46–49
	HI	$I^- + H$	0.03	No	0.05	MS	50
	CH_2I_2	$I^- + CH_2I$	0	Yes		MS	25
	C_6F_5I	$I^- + C_6F_5$	0	No	0	MS	121
	m-C_6H_4ClI	$I^- + C_6H_4Cl$	~0	No	0	MS	121
	$C_6H_4INO_2$	$I^- + C_6H_4NO_2$	~0	No	0	MS	121
	$C_6H_4INO_2$	$I^- + C_6H_4NO_2$		No	0.8	MS	121
	$C_6H_4INO_2$	$I^- + C_6H_4NO_2$		No	3.1	MS	121
	CNI	$I^- + CN$		No	2.6	MS	144
	LiI	$I^- + Li$	3.95	No		MS	187
	NaI	$I^- + Na$	3.25	No		MS	187
	KI	$I^- + K$	3.20	No		MS	187
	RbI	$I^- + Rb$	3.30	No		MS	187
	HgI_2	$I^- + HgI$		No	~3	MS	163
I_2^-	CI_4	$I_2^- + CI_2$	0	Yes		MS	30
	CHI_3	$I_2^- + CHI$	0	Yes		MS	30
TeX_n^-	TeF_6	$TeF_4^- + 2F$?		No	~7	MS	169
	TeF_6	$TeF_5^- + F$		No	0	MS	169
	TeF_6	$TeF_5^- + F$?		No	~6	MS	169
		Metals					
		Alkali Metals					
$Li_yX_n^-$	LiF	$Li^- + F$	5.71	No		MS	187
	LiF	$Li^- + ?$	7.66	No		MS	187
	LiCl	$Li^- + Cl$	4.63	No		MS	187
	LiCl	$Li^- + ?$	6.10	No		MS	187
	LiBr	$Li^- + Br$	4.09	No		MS	187
	LiBr	$Li^- + ?$	5.35	No		MS	187
	LiI	$Li^- + I$	3.27	No		MS	187
	LiI	$Li^- + ?$	4.55	No		MS	187
	Li_2F_2	$LiF^- + Li + F$?	7.65	No		MS	187
	Li_2Cl_2	$LiCl^- + Li + Cl$?	6.08	No		MS	187
	Li_2Br_2	$LiBr^- + Li + Br$?	5.25	No		MS	187
	Li_2I_2	$LiI^- + Li + I$?	4.30	No		MS	187
	Li_2F_2	$Li_2F^- + F$	6.7	No		MS	187
	Li_2Cl_2	$Li_2Cl^- + Cl$	5.41	No		MS	187
	Li_2Br_2	$Li_2Br^- + Br$	4.80	No		MS	187
	Li_2I_2	$Li_2I^- + I$	4.08	No		MS	187
$Na_yX_n^-$	NaF	$Na^- + F$	4.66	No		MS	187
	NaF	$Na^- + ?$	6.30	No		MS	187
	NaCl	$Na^- + Cl$	4.04	No		MS	187
	NaBr	$Na^- + Br$	3.36	No		MS	187
	NaI	$Na^- + I$	2.84	No		MS	187
	Na_2F_2	$NaF^- + Na + F$?	6.30	No		MS	187
	Na_2Cl_2	$NaCl^- + Na + Cl$	5.08	No		MS	187
	Na_2Br_2	$NaBr^- + Na + Br$	4.38	No		MS	187
	Na_2I_2	$NaI^- + Na + I$	3.54	No		MS	187
	Na_2F_2	$Na_2F^- + F$	5.85	No		MS	187
	Na_2Cl_2	$Na_2Cl^- + Cl$	4.76	No		MS	187
	Na_2Br_2	$Na_2Br^- + Br$	4.08	No		MS	187
	Na_2I_2	$Na_2I^- + I$	3.26	No		MS	187
$K_yX_n^-$	KF	$K^- + F$	4.78	No		MS	187
	KCl	$K^- + Cl$	3.93	No		MS	187
	KBr	$K^- + Br$	3.36	No		MS	187
	KI	$K^- + I$	2.85	No		MS	187
	K_2F_2	$KF^- + K + F$	6.20	No		MS	187
	K_2Cl_2	$KCl^- + K + Cl$	5.02	No		MS	187
	K_2Br_2	$KBr^- + K + Br$	4.63	No		MS	187
	K_2I_2	$KI^- + K + I$	3.63	No		MS	187
	K_2F_2	$K_2F^- + F$	5.73	No		MS	187
	K_2Cl_2	$K_2Cl^- + Cl$	4.68	No		MS	187
	K_2Br_2	$K_2Br^- + Br$	4.00	No		MS	187
	K_2I_2	$K_2I^- + I$	3.36	No		MS	187
$Rb_yX_n^-$	RbCl	$Rb^- + Cl$	4.00	No		MS	187
	RbBr	$Rb^- + Br$	3.44	No		MS	187
	RbI	$Rb^- + I$	2.9	No		MS	187
	Rb_2Cl_2	$RbCl^- + Rb + Cl$	4.90	No		MS	187
	Rb_2Br_2	$RbBr^- + Rb + Br$	4.44	No		MS	187
	Rb_2I_2	$RbI^- + Rb + I$	3.65	No		MS	187

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
$Rb_yX_n^-$	Rb_2Cl_2	$Rb_2Cl^- + Cl$	4.55	No		MS	187
	Rb_2Br_2	$Rb_2Br^- + Br$	4.05	No		MS	187
	Rb_2I_2	$Rb_2I^- + I$	3.42	No		MS	187
CsX_n^-	CsF	$Cs^- + F$	5.10	No		MS	187
	CsCl	$Cs^- + Cl$	4.10	No		MS	187
	CsBr	$Cs^- + Br$	3.55	No		MS	187
	CsI	$Cs^- + I$	3.01	No		MS	187
	$CsPbCl_3$	$CsCl^- + PbCl_2$		No	0.5	MS	191
		Transition and Other Metals					
TiX_n^-	$TiCl_4$	$TiCl_3^- + Cl$		No	5.5	MS	163
	$Ti(C_5H_5)_2Cl_2$	$Ti(C_5H_5)_2Cl^- + Cl$		No	0.25	MS	204
	$Ti(C_5H_5)_2Cl_2$	$Ti(C_5H_5)Cl_2^- + C_5H_5$		No	2.95	MS	204
	$Ti(C_5H_5)_2Cl_2$	$Ti(C_5H_5)_2Cl_2^-$		No	0.08	MS	204
ZrX_n^-	$Zr(C_5H_5)_2Cl_2$	$Zr(C_5H_5)Cl_2^- + C_5H_5$		No	3.75	MS	204
	$Zr(C_5H_5)_2Cl_2$	$Zr(C_5H_5)_2Cl_2^-$		No	0.08	MS	204
HfX_n^-	$Hf(C_5H_5)_2Cl_2$	$Hf(C_5H_5)_2Cl_2^-$		No	0.08	MS	204
NbX_n^-	$NbCl_5$	$NbCl_4 + Cl$		No	2.3	MS	163
TaX_n^-	$TaCl_5$	$TaCl_4 + Cl$		No	2.6	MS	163
CrX_n^-	$Cr(CO)_6$	$Cr^- + 6CO$	6.85	No	8.7	MS	197
	$Cr(CO)_6$	$Cr^- + 6CO$		No	8.3	MS	200
	CrO_2F_2	$CrF^- + O_2 + F$	8.60	No		MS	196
	CrO_2F_2	$CrF^- + 2O + F$	13.61	No		MS	196
	CrO_2F_2	$CrF_2^- + O_2$	2.89	No		MS	196
	CrO_2F_2	$CrF_2^- + 2O$	8.10	No		MS	196
	CrO_2Cl_2	$CrO^- + O + Cl_2$	8.88	No		MS	196
	CrO_2Cl_2	$CrO^- + O + 2Cl$	11.42	No		MS	196
	CrO_2F_2	$CrO^- + O + 2F$	13.74	No		MS	196
	CrO_2Cl_2	$CrO_2^- + Cl_2$	2.69	No		MS	196
	CrO_2Cl_2	$CrO_2^- + 2Cl$	4.97	No		MS	196
	CrO_2F_2	$CrO_2^- + 2F$	7.22	No		MS	196
	CrO_2F_2	$CrOF^- + F + O$	8.05	No		MS	196
	CrO_2F_2	$CrOF_2^- + O$	2.56	No		MS	196
	CrO_2F_2	$CrO_2F^- + F$	1.87	No		MS	196
	CrO_2F_2	$CrO_2F_2^-$	0.03	No		MS	196
	CrO_2Cl_2	$CrCl^- + O_2 + Cl$	7.22	No		MS	196
	CrO_2Cl_2	$CrCl^- + 2O + Cl$	12.36	No		MS	196
	CrO_2Cl_2	$CrCl_2^- + O_2$	2.28	No		MS	196
	CrO_2Cl_2	$CrCl_2^- + 2O$	7.06	No		MS	196
	CrO_2Cl_2	$CrOCl^- + ClO$	4.12	No		MS	196
	CrO_2Cl_2	$CrOCl^- + Cl + O$	6.61	No		MS	196
	CrO_2Cl_2	$CrO_2Cl^- + Cl$	1.22	No		MS	196
	CrO_2Cl_2	$CrOCl_2^- + O$	2.36	No		MS	196
	CrO_2Cl_2	$CrO_2Cl_2^-$	~0	No		MS	196
	$Cr(CO)_6$	$Cr(CO)^- + 5CO$	6.0	No	7.9	MS	197
	$Cr(CO)_6$	$Cr(CO)^- + 5CO$		No	8.2	MS	200
	$Cr(CO)_6$	$Cr(CO)_2^- + 4CO$	4.5	No	5.9	MS	197
	$Cr(CO)_6$	$Cr(CO)_2^- + ?$	6.5	No	8.5	MS	197
	$Cr(CO)_6$	$Cr(CO)_2^- + 4CO$		No	8.1	MS	200
	$Cr(CO)_6$	$Cr(CO)_3^- + 3CO$	3.0	No	4.2	MS	197
	$Cr(CO)_6$	$Cr(CO)_3^- + 3CO$		No	4.8	MS	200
	$Cr(CO)_6$	$Cr(CO)_4^- + 2CO$	0.6	No	1.5	MS	197
	$Cr(CO)_6$	$Cr(CO)_4^- + ?$	2.9	No	3.8	MS	197
	$Cr(CO)_6$	$Cr(CO)_4^- + 2CO$		No	3.7	MS	200
	$Cr(CO)_6$	$Cr(CO)_5^- + CO$		No	2.4	MS	200
	$Cr(CO)_6$	$Cr(CO)_5^- + CO$	0.1	No	0.3	MS	197
MoX_n^-	$Mo(CO)_6$	$Mo^- + 6CO$		No	10.9	MS	200
	MoF_6	$MoF_4^- + 2F?$		No	~7.5	MS	184
	MoF_6	$MoF_5^- + F$		No	1.0	MS	184
	MoF_6	MoF_6^-		No	0.25	MS	184
	MoF_6	MoF_6^-		No	1.0	MS	184
	$Mo(CO)_6$	$Mo(CO)^- + 5CO$		No	9.8	MS	200
	$Mo(CO)_6$	$Mo(CO)_2^- + 4CO$	7.4	No	~10	MS	197
	$Mo(CO)_6$	$Mo(CO)_2^- + 4CO$		No	7.5	MS	200
	$Mo(CO)_6$	$Mo(CO)_3^- + 3CO$	2.3	No	~3.8	MS	197
	$Mo(CO)_6$	$Mo(CO)_3^- + ?$	3.7	No	~4.7	MS	197
	$Mo(CO)_6$	$Mo(CO)_3^- + ?$		No	4.1	MS	200
	$Mo(CO)_6$	$Mo(CO)_4^- + 2CO$	0.7	No	2.7	MS	197
	$Mo(CO)_6$	$Mo(CO)_4^- + ?$		No	3.0	MS	200

TABLE I (continued)

Ion	Molecule	Products	AP	KE	Max	Method	Ref
MoX_n^-	$Mo(CO)_6$	$Mo(CO)_5^- + CO$	0	No	0.3	MS	197
	$Mo(CO)_6$	$Mo(CO)_5^- + ?$		No	2.2	MS	200
WX_n^-	$W(CO)_6$	$W(CO)^- + 5CO$		No	10.8	MS	200
	$W(CO)_6$	$W(CO)_2^- + 4CO$		No	7.5	MS	200
	$W(CO)_6$	$W(CO)_2^- + 4CO$	2.6	No	$\sim$3.4	MS	197
	$W(CO)_6$	$W(CO)_2^- + ?$	6.5	No	$\sim$8.7	MS	197
	$W(CO)_6$	$W(CO)_3^- + 3CO$		No	3.6	MS	200
	$W(CO)_6$	$W(CO)_3^- + 3CO$	2.4	No	$\sim$4.3	MS	197
	$W(CO)_6$	$W(CO)_3^- + ?$	6.0	No	$\sim$7.3	MS	197
	$W(CO)_6$	$W(CO)_4^- + 2CO$		No	2.6	MS	200
	$W(CO)_6$	$W(CO)_4^- + 2CO$	1.0	No	$\sim$1.5	MS	197
	$W(CO)_6$	$W(CO)_4^- + ?$	2.1	No	$\sim$3.3	MS	197
	$W(CO)_6$	$W(CO)_5^- + CO$		No	1.8	MS	200
	$W(CO)_6$	$W(CO)_5^- + CO$	0.15	No	$\sim$0.3	MS	197
ReX_n^-	ReF_6	$ReF_3^- + F_2 + F$		No	0	MS	184
	ReF_6	$ReF_3^- + 3F?$		No	$\sim$4.7	MS	184
	ReF_6	$ReF_5^- + F$		No	0	MS	184
	ReF_6	$ReF_5^- + ?$		No	5.5	MS	184
	ReF_6	ReF_6^-		No	0	MS	184
FeX_n^-	$Fe(CO)_5$	$Fe^- + 5CO$		No	8.3	MS	200
	$Fe(CO)_5$	$Fe(CO)^- + 4CO$	5.0	No	$\sim$6.7	MS	197
	$Fe(CO)_5$	$Fe(CO)_2^- + 3CO$	2.8	No	4.7	MS	197
	$Fe(CO)_5$	$Fe(CO)_2^- + 3CO$		No	4.0	MS	200
	$Fe(CO)_5$	$Fe(CO)_3^- + 2CO$	0.55	No	1.8	MS	197
	$Fe(CO)_5$	$Fe(CO)_3^- + ?$		No	3.0	MS	200
	$Fe(CO)_5$	$Fe(CO)_4^- + CO$	0.1	No	0.5	MS	197
	$Fe(CO)_5$	$Fe(CO)_4^- + ?$		No	2.0	MS	200
NiX_n^-	$Ni(CO)_4$	$Ni^- + 4CO$		No	5.3	MS	200
	$Ni(CO)_4$	$Ni(CO)^- + 3CO$		No	4.5	MS	200
	$Ni(CO)_4$	$Ni(CO)_2^- + 2CO$		No	2.6	MS	200
	$Ni(CO)_4$	$Ni(CO)_3^- + CO$		No	2.0	MS	200
ZnX_n^-	$ZnBr_2$	$ZnBr^- + Br$		No	$\sim$4.5	MS	163
HgX_n^-	C_2Cl_3HgCl	$HgCl_2^- + C_2Cl_2?$		No	3	MS	206
InX_n^-	$InBr$	$In^- + Br$		No	$\sim$5.5	MS	193
TlX_n^-	$TlCl$	$Tl^- + Cl$		No	3.9	MS	194
	$TlBr$	$Tl^- + Br$		No	2.4	MS	194
	TlI	$Tl^- + I$		No	2.9	MS	194
PbX_n^-	$CsPbCl_3$	$Pb^- + CsCl + Cl_2?$		No	3.5	MS	191
	$PbCl_2$	$PbCl^- + Cl$		No	$\sim$2.2	MS	189–191
	$PbBr_2$	$PbBr^- + Br$		No	$\sim$2	MS	190
	$CsPbCl_3$	$PbCl_2^- + Cs + Cl$		No	2.9	MS	191
	$NaPbCl_3$	$NaPbCl_2^- + Cl$		No	2.5	MS	191
	$RbPbCl_3$	$RbPbCl_2^- + Cl$		No	2.0	MS	191
UX_n^-	UF_6	$UF_5^- + F$		No	2.2	MS	184
	UF_6	UF_6^-		No	0	MS	184

[a] Ketene. [b] These data are equivalent; differences arise from *IE* curve interpretation and calibration. [c] Glyoxal. [d] Biacetyl. [e] Furan. [f] Tetrahydrofuran. [g] 2-Methoxy-2-hydroperoxypropane. [h] Dimethyl sulfoxide. [i] Thiophene. [j] 2-Methylthiophene. [k] 3-Methylthiophene. [l] 2-Ethylthiophene. [m] 2-Propylthiophene. [n] 3-Propylthiophene. [o] Selenophene. [p] Perfluorocyclobutene. [q] Octafluorocyclobutane. [r] Perfluorocyclopentene. [s] Hexafluorobenzene. [t] Perfluorocyclohexene. [u] Octafluorotoluene. [v] Perfluoromethylcyclohexane. [w] Perfluoro-2-propyltetrahydropyran. [x] Perfluoro-2-butyltetrahydrofuran. [y] Secondary electron capture process, negative ion current second order in pressure. [z] Perfluorocyclohexane.

6. *Carbon Oxides*

CO, CO_2

Oxygen negative ion is detected in CO using mass spectrometric[41,74,76,83] and total ionization (Lozier type) apparatus.[59,61,63,84–86] Chantry[74] has shown that two processes contribute to O^- production using the kinetic energy analysis technique.[36] The single dissociative capture peak for total negative ion current collected was shown[74] to correspond to O^- formation plus ground-state (^3P) carbon and excited-state (^1D) carbon. The experimental energy difference 1.25 eV is in good agreement with the calculated value, 1.22 eV. Recent energetic measurements[83] have also indicated a second process at 10.88 eV where carbon is produced in an excited ^1D state.

Although O^- is detected from two different CO^{-*} states, at $\sim$10 eV, Rempt,[87] using electron impact excitation, has suggested that a temporary negative ion state of CO^- exists in the energy range 1.8–3.0 eV. The CO^- ion is short-lived, and, from the variation in "trapped electron" current below 3.0 eV, Rempt[87] estimates EA(CO) = −1.8 eV. Peaks at near 10 eV are associated

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with the dissociative attachment processes reported by Chantry.[74]

The only ion detected[37,59,61-63,88] in CO_2 is O^- *via* dissociative capture at low energies. Two capture maxima are observed at 4.4 and 8.2 eV. Spence and Schulz[37] have found that the energy integrated cross sections at 4.4 and 8.2 eV are little changed from 300 to 550°K, but that from 550 to 1000°K the values increase. In addition the dissociative capture onset values decrease while the capture peak width increases with increasing temperature. The broadening of the cross section is attributed to vibrational excitation of a CO_2 bending mode which has a broader level than the ground-state mode. It is reasonable that the reduced appearance potential is due to vibrational and rotational excitation.[37,88] For accurate evaluation of the onset energy where ions are produced without excess kinetic energy and for use of this value in calculating electron affinities, it is shown[88] that onset values must be extrapolated to 0°K. These results bring into question the electron affinities of other ions, O_2^-, etc., where the O_2^- ion is formed with no translational energy. Although CO_2^- was not detected, a compound state of CO_2^-, lifetime about 10^{-15} sec at 4.4 eV, contributes to the dissociative process. This compound state is also important in vibrational excitation of CO_2.[89] This observation is consistent with the explanation for temperature effects in O^- production from CO_2.[37,88]

Recently a long-lived CO_2^- ion was detected[89a] in organic molecules containing bent CO_2 moieties as a basic unit. Long-lived CO_2^- is attributed to two factors. First an unfavorable Franck-Condon overlap exists between the CO_2^- ion (bent, 134°) and the linear neutral molecule, CO_2. Secondly the potential energy curve of CO_2^- ($^2A_1$) is below that of CO_2 ($^1A_1$, bent, 134°); *i.e.*, the ion has a positive vertical detachment energy.

MacNeil and Thynne[90] have investigated the formation of negative ions at low pressures in COS and CS_2. In contrast to the limited ion formation processes in CO_2 (O^- only), a variety of negative ions are formed in COS[90] and CS_2.[90,91] The abundant ion at high electron energies is S^-. The CS_2^- ion is formed[90] at low energies with a maximum in the ionization efficiency curve at 6.3 eV. Kraus[92] suggested that CS_2^- was formed *via* charge transfer with CS^- which has a maximum at 6.3 eV. If CS_2^- were formed by direct capture it would be expected at near 0 eV. On the other hand, MacNeil and Thynne[90] suggest that the ion observed is an excited metastable state of CS_2^{-*} which fragments to produce S^-, S_2^-, C^-, and CS^-. The dependence of ion current on pressure was not measured for CS_2^-.[90] It is not established which of these interpretations is correct.

In carbonyl sulfide no COS^- ion was observed.[90] In addition to primary ions S^-, O^-, and CS^-, other ions, SO^- and S_2^-, are detected in low abundance. The S_2^- ion is produced by pyrolysis on the filament *via* an ion-molecule reaction of S^- with COS. The formation of SO^- is unexplained. Ion-molecule reactions are suggested.

$$S^- + COS \rightarrow SO^- + CS \quad (19)$$

$$O^- + COS \rightarrow SO^- + CO \quad (20)$$

but are discounted based on a comparison of the ionization efficiency curves for O^- and S^- with SO^-. A rearrangement process is excluded on energetic arguments.

7. Carbon Compounds

The simplest member of this class, C^-, has been detected in dissociative processes from CO.[83] Although the cross section for C^- formation is small, the appearance potential for C^- was obtained, and it was suggested that C^- and O^- could be formed from different compound states of CO^-. Polyatomic carbon ions C_n^- (n = 1–8) have been detected[93] in sublimation processes of graphite. The C_2^- ion is the most abundant species and C_8^- the least abundant. In high-frequency discharge experiments, C_n^- ions (n = 48,[94] 33,[95] 10[96]) have been detected, but no accurate electron affinities have been determined. Honig[93] has computed electron affinities from heats of sublimation and pressure ratios for C_2 and C_3 where the C_2^- and C_3^- species are assumed to be parent negative ions. The values are $EA(C_2) = 3.1$ eV and $EA(C_3) = 1.8$ eV.

Botter[97] has studied the negative ions in carbon suboxide, C_3O_2, at electron energies down to about 3.0 eV. The molecular negative ion was observed and C_2O^- was the dominant ion at 70 eV. $C_3O_2^-$ was no doubt formed at 70 eV by secondary electron capture but was not observed at low energies presumably because the lowest energy studied was 3 eV.

The majority of investigations of negative ions in hydrocarbons and their derivatives have been concerned with halocarbons. Such an emphasis is due to the variety and abundance of negative ions formed where electronegative groups are present. However, some studies of negative ions in hydrocarbons have been reported.

Studies on hydrocarbons have indicated that the most abundant ion at low electron energies[62,98,99] and *via* ion-pair processes[98,99] is H^- as shown in Table I. There is disagreement on whether the ion-pair process occurs. Melton and Hamill[98] report H^- formation *via* the ion-pair process, while Dorman[62] does not observe H^- at higher energies (~10 eV). Ion-pair processes have been suggested for some fragment ions in methane.[99]

Fragment ions produced *via* dissociative processes in a series of hydrocarbons have been identified.[100] In general, a large variety of negative ions is noted. The dominant ion is H^-. Fragment ions usually are produced by the loss of H, H_2, and hydrocarbon fragments, CH_2, CH_3, etc. Abundant hydrocarbon ions at low energies are CH_3^-, C_2H^-, CH_2^-, for simple four-carbon alkanes, alkenes, and alkynes.[100]

Appearance potential measurements have been used to evaluate limits for the electron affinities of various $C_nH_y^-$ species.[100,101] There is some disagreement in the results, perhaps because the true appearance potential has not been measured; *i.e.*, no attempt was made to evaluate or to measure excess energy.[100,101] In addition, the processes suggested for fragment negative ion formation are highly speculative and include postulation of

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excited electronic states in the negative ion.[101] The values quoted are EA(CH) = 2.6,[101] ≥ 3.1;[100] EA(C_2) = 3.3,[101] ≥ 2.9;[100] EA(C_2H) = 2.1,[101] ≥ 2.8 eV.[100]

An investigation[102] of the dissociative capture process in methane and methane-d_4 has revealed that H^- and D^- are abundant ions at about 9 eV. An inverse isotope effect was reported for the cross-section ratio of $H^-(CH_4)/D^-(CD_4) \cong 0.8$. By contrast, a large direct isotope effect was observed for CH_2^- (CH_4), CD_2^- (CD_4) ion formation in the energy region 8-13 eV. The cross section for CD_2^- (CD_4) production is reportedly at least 250 times smaller than that for CH_2^- (CH_4).

More complex hydrocarbons have been studied using electron swarm and beam techniques.[10,103,104] Molecular negative ions in aromatic hydrocarbons are formed *via* nondissociative electron attachment processes. It is of interest to note that one of the aromatic hydrocarbons which had a large electron attachment cross section[104] is also slightly carcinogenic. The authors caution against extrapolating such correlations to condensed-phase systems where medium effects are important to the biological activity of a molecule.

8. *Fluorocarbons, Nitro Compounds, Alcohols*

In fluorocarbon negative ion spectra, F^- is usually the dominant ion at 70 eV and often in the low-energy dissociative attachment processes.[105-109] For some fluorocarbons parent negative ions have been detected[108-113] at near zero electron energies and at high energies by secondary electron capture. Interest in the electron affinities[105-108,114] of various fluorocarbon species has prompted measurement of appearance potentials of negative fragment ions. In most of these measurements, however, excess energy contributions are assumed to be small or zero and are therefore neglected. From the limited number of measurements of excess energy for complex molecules and particularly for fluorocarbons, it seems that this neglect is unjustified. The fragmentation processes suggested, from which limits to the electron affinity are calculated, appear reasonable for simple fragment ions, *i.e.*, fragmentation involving loss of F, CF_2, CF_3, HF, F_2 neutrals, while other suggested processes are highly speculative. Other investigations have emphasized the use of negative ion appearance potential measurements to evaluate or set limits for bond energies.[101,105,109,115] However, in these studies no measurement of translational energy was carried out, and the values deviate from bond energies obtained thermochemically.

In addition to parent ion and fragment ion formation by direct electron impact, it has been observed that ions are formed by secondary electron capture. The secondary electron is a de-energized electron, produced in ionization yielding positive ions or by excitation of a molecule above its ground state. As Melton,[1] Thynne,[108,116] and others have pointed out, negative ion current produced *via* this process should exhibit second-order pressure dependence. Secondary electron capture has been reported in the production of the hexafluoroacetone parent negative ion.[108,116] McNeil and Thynne[106] have reported that the formation of F^- from hexafluoroethane obeys second-order pressure behavior. It was suggested[106] that the process is the result of a secondary electron capture, thermalized by electronic excitation of C_2F_6 at 16 eV. The F^- ion is the fragment ion produced from a compound state of ($C_2F_6^{-}*$) according to the reactions

$$C_2F_6 + e^- \rightarrow C_2F_6^* + \mathbf{e}^- \qquad (21)$$

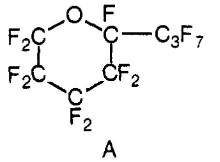
$$\mathbf{e}^- + C_2F_6 \rightarrow (C_2F_6^{-}*) \rightarrow F^- + C_2F_5 \qquad (22)$$

where $\mathbf{e}^-$ represents a thermalized or low-energy electron. Secondary electron formation *via* positive ionization is ruled out since the appearance potentials of fragment ions are too high and the parent positive ion, $C_2F_6^+$, is not detected. The secondary electron capture process was supported by observing formation of F^- at lower energies in butane–hexafluoroethane and butene-2-hexafluoroethane mixtures due to secondary electrons arising from the appearance of fragment and molecular positive ions. The possibility of F^- formation *via* ion–molecule reactions was not ruled out.

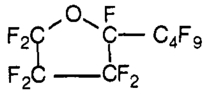
In studies of hexafluoroacetone[108] it was noted that ion–molecule reactions between O^- (SO_2, the calibrating gas) and CF_3COCF_3 produced the fragment ions $CF_3COCF_2^-$, CF_3^-, and F^-. The process was envisioned as a charge transfer from O^- to CF_3COCF_3 followed by subsequent fragmentation of $CF_3COCF_3^{-}*$. It is interesting to note that these experiments were carried out[108] at "low pressures" where ion–molecule reactions would be expected to make a small contribution to ion-formation reactions.

Appearance potential studies have been extended[20,117] to COF_2 and CF_3OF to estimate bond energies and electron affinities. A high-energy process (~10 eV) for CF_3O^- formation has been observed, and a secondary electron capture process has been suggested[117] similar to that noted in C_2F_6.[108]

A measure of the abundance of negative ions and appearance potentials in $C_8F_{16}O$ compounds has led to an identification of five- and six-membered ring components which were separated by gas chromatography.[118] The fragmentation of perfluoro-2-pyran (A) and furan (B) compounds were considered.



A



B

The differentiation was based on differences in abundance for $C_7F_{14}^-$ and $C_4F_8O^-$ ions. The $C_7F_{14}^-$ ion could be formed by loss of CF_2O from either compound to produce $C_7F_{14}^-$. The $C_4F_8O^-$ ion could be produced directly from compound A by two different bond cleavages, while in B a rearrangement process would be required. For the $C_4F_7O^-$ ion which is more abundant in B,

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the ions of the butyl group could be responsible for $C_4F_7O^-$ formation. For A, $C_4F_7O^-$ formation would necessitate loss of F and opening of the six-membered ring to eliminate C_4F_8 or a rearrangement process where C_4F_9 is lost. Ease of C_4F_9 loss in B is suggested as support for the formulation of A and B as indicated.

A number of investigators have examined negative ion processes in other halogenated hydrocarbons. Total ionization measurements were reported and total cross sections calculated.[54] Several mass spectrometric studies[62,119,120] have been reported, appearance potentials measured, and ion formation processes predicted for a variety of chloro compounds. The thermal energy of the molecules affected the measured relative ion intensities for $Cl^-(CCl_3F)$ at low energies and was attributed[119] to alterations in gas density with temperature. However, for Cl^- from CCl_4 a complex behavior is observed for ion current in the low electron energy process (1.8 eV). The Cl^- ion decreases with increasing temperature while Cl^- for a higher energy reaction (2.6 eV) increases with increasing temperature. This latter behavior is consistent with the formation of thermally excited CCl_4 molecules. A similar explanation was advanced for the variation of SF_6^- and SF_5^- (SF_6) ion current behavior as a function of temperature.[119]

It is reported that in halogenated gases[119,120] at low energies (0–10 eV) only X^- (Cl^-, Br^-, etc.) ions were detected. No ions containing carbon, hydrogen, and/or the halogen were observed *via* dissociative electron attachment processes. This is in contrast to the observations of abundant and rich negative ion chemistry in highly fluorinated hydrocarbons. More recent studies[31] have shown that X_2^- ions are formed in carbon tetrahalides and other selected halogenated compounds (see Table I and references therein). It is reasonable to suggest that the presence of the highly electronegative fluorine atoms and CF_3 groups present in the fluorocarbons contributes to fragment negative ion stability.

A careful and informative study of the dissociative and resonance capture processes in substituted benzene molecules has been published.[121,122] Two classes of temporary negative ions are suggested. One class includes those molecules which form parent negative ions with lifetimes greater than 1 μsec. Ions with lifetimes of this magnitude live long enough to be detected in the mass spectrometer. The second ion class is composed of molecular negative ions whose lifetimes are less than 1 μsec and whose real lifetimes are expected to be of the order of 10^{-15}–10^{-13} sec, *i.e.*, about one vibrational period. It should be pointed out that intermediate lifetimes between 1 μsec and 10^{-13} sec are theoretically reasonable. Ions in this second class are not detected in the mass spectrometer. Their existence in transient negative ion states is affirmed from electron-scattering experiments. In the scattering experiments the electron is lost from the temporary negative ion state by autodetachment and possesses essentially thermal (near-zero) energy. If a molecule which captures thermal electrons, say, SF_6, is mixed with the material of interest, then measurement of the SF_6^- ion current reflects the autodetachment process for the temporary negative ion.

Long-lived molecular negative ions are formed by electron capture into a vacant bound energy level where the energy of the captured electron may be distributed among the vibrational degrees of freedom. Since negative ion formation is influenced by charge density on the benzene ring in substituted systems, two factors will be important: the inductive and the resonance effect. Electron-donating and withdrawal effects by substituent atoms or groups will greatly affect the energy of the unoccupied orbitals and thereby influence the formation of negative ions. A characteristic measure of the donating or withdrawal effect is the dipole moment, and it is expected that a correlation between dipole moment and negative ion formation may exist. Parent ion production in C_6F_5X and C_6H_5X molecules was found[121] to correlate with the dipole moment of C_6H_5X.

For monosubstituted benzenes (halogens, aldehydes, etc.) only nitrobenzene and benzonitrile form long-lived parent ions[121] (see Table I). This is attributed to two factors: (a) that the NO_2 and CN substituents add low-energy vacant π levels to the molecule and (b) the much greater electron-withdrawing power of NO_2 and CN compared to other substituents. Although the aldehyde group CHO has electron-withdrawing resonance and inductive effects, no molecular negative ion was formed at low energies. Also no $C_6H_5X^-$ ions were noted for X = Cl, Br, or I even though halogen substitution enhances electron-withdrawing inductive effects and electron-donating resonance effects. It is found[121] that for molecules with dipole moments greater than about -4 D, long-lived parent negative ions are formed (a negative moment indicates a greater electron density on the substituent than on the remainder of the molecule).

In pentafluoro-substituted benzene molecules C_6F_5X molecular negative ions were detected when X = CN, CHO, H, Cl, and Br. For pentafluorobenzene it was suggested[121] that the five fluorines altered the electron affinity to a positive value. For OH substitution the electron-withdrawing power is sufficiently less than that for halogen substitution so that a stable negative ion $C_6F_5OH^-$ is not formed.

When iodine was the substituent on the benzene ring, no parent negative ion was observed,[121] although dissociative processes were recorded at low electron energies. It was suggested that weak benzene–iodine bonding and the presence of at least one additional low-level π-electronic state are responsible for the behavior. It appears that the second low-lying π resonance state leads to dissociation rather than capture.

Support for the suggestion that negative ion stability with respect to autodetachment is related to the distribution of energy among the vibrational degrees of freedom is provided from lifetime measurements.[121,122] An increase in the autodetachment lifetime with the number of degrees of vibrational freedom was noted for fluorocarbons[122] and substituted benzenes.[121] Of particular interest is the increase in the lifetime of nitrobenzene upon deuteration.[121] This result is in agreement with the fact that the vibrational spacing in $C_6D_5NO_2^-$ is expected to be smaller than in $C_6H_5NO_2^-$, and thus the density of states would be greater for $C_6D_5NO_2^-$. This fact contributes to the greater $C_6D_5NO_2^-$ lifetime.

Dissociative attachment processes are also observed[121] in substituted benzenes, C_6F_5X. It is noted that both parent and fragment ion formation occurs in approximately the same energy region (see Table I). This observation is consistent with the suggestion that dissociation occurs from the long-lived molecular negative ion state. However, it was shown that the dissociative capture process occurred rapidly after electron impact and that, after about 2 μsec, autodetachment was the dominant unimolecular decomposition process. Two possible explanations are offered:[121] either (a) dissociative at-

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tachment from $C_6F_5X^-$ occurs from a state different from the long-lived state or (b) autodetachment of a long-lived state occurs when the electron energy is less than the threshold of dissociation.

In disubstituted benzene molecules, C_6H_4XY, dissociative capture processes producing both X^- and Y^- (except where $Y = F$) are observed at comparable electron energies.[121] It is suggested that the two dissociation processes occur from the same negative ion state. Slight deviations between capture maxima are noted where $X =$ Cl and $Y =$ Br or I. These differences are attributed to a combination of effects: differences in electron affinities of the X and Y species and differences in C–X and C–Y bond energies.

Investigations of the fragment and molecular negative ions formed at low electron energies from nitroalkanes[123-126] have permitted estimates of the electron affinities of various species including NO_2,[126] CH_2NO_2,[124] C_2H_5O,[126] $C(NO_2)_3$,[126] CN,[125] and CNO.[125] In the dissociative resonance process at less than 3.0 eV, NO_2^- is the most intense ion. Jäger and Henglein[126] have measured the onset energies for NO_2^- to be 0.3 eV from nitromethane and 0.4 eV from nitroethane. Dissociative capture processes for NO_2^- were not reported[126] at energies greater than 3 eV for the monosubstituted alkyl nitro compounds although resonance maxima were detected[124] for NO_2^- at about 5.5 and 9.8 eV. The higher energy processes occur with much smaller cross sections than the dissociative capture at near 0 eV. Unfortunately the data of Tsuda, *et al.*,[124] are limited to electron energies above 3.0 eV. It was demonstrated from measurements of ion current as a function of source pressure[124] that fragment ions NO_2^-, O^-, CN^-, and CNO^- exhibited first-order behavior and were therefore produced by unimolecular processes. From the onset energy and the measured excess translational energy a value of $EA(NO_2) = 3.0$ eV is calculated.[126] This value is lower than previously updated values. The discrepancy is possibly due to internal excitation of NO_2^- and/or CH_3, or C_2H_5.[126]

An important ion observed in the alkyl nitro compounds, except nitromethane, is $CH_2NO_2^-$.[124] The resonance maxima occur at about 9.7 eV. The $CH_2NO_2^-$ ion was not detected in nitroethane by other workers[126] and could result because its intensity is reportedly low.[124] From the suggested dissociation process which involves fragmentation of the alkyl moiety, $EA(CH_2NO_2) \simeq 0.5$ eV is calculated. Excess energy in the fragment ions was not measured for the $CH_2NO_2^-$ ions.[124]

Unlike the nitro-substituted compounds, the dominant ion formed *via* dissociation capture in ethyl nitrite is $C_2H_5O^-$.[126] The unusual production of the very intense rearrangement ion NOH^- at near 0 eV suggests[126] that the reaction

$$C_2H_5ONO + e^- \rightarrow HNO^- + C_2H_4O \qquad (23)$$

is exothermic.

In ethyl nitrate[126] the dominant ions at low energies are NO_2^- and $C_2H_3O^-$, which are formed according to the reactions

$$C_2H_5ONO_2 + e^- \rightarrow NO_2^- + C_2H_5O \qquad (24)$$

$$C_2H_5ONO_2 + e^- \rightarrow C_2H_3O^- + H_2NO_2$$
$$\text{(or } H_2 + NO_2,\ H_2O + NO) \qquad (25)$$

In competition with these reactions are the complementary dissociative processes

$$C_2H_5ONO_2 + e^- \rightarrow C_2H_5O^- + NO_2 \qquad (26)$$

$$C_2H_5ONO_2 + e^- \rightarrow HNO_2^- + C_2H_4O \qquad (27)$$

The latter hydrogen rearrangement process is similar to that noted for the formation of NOH^- in ethyl nitrite.

In the studies[123-126] parent negative ions were observed for nitrobenzene[126] and $C(NO_3)_4$.[126] From pressure-dependent ion current studies it is clear that these ions are formed *via* direct electron capture. In ethyl nitrite, however, it was suggested that the parent negative ion was formed *via* electron transfer from a primary ion, $C_2H_5O^-$, $C_2H_3O^-$, or NOH^-.

The electron affinity for $C(NO_2)_3$ was estimated to be about 3.8 eV. The $EA[C(NO_2)_3]$ is calculated[126] from the difference of the appearance potentials for NO_2^- and $C(NO_2)_3^-$ and the measured excess translational energies. In the measurements it was not possible to take into account contributions from internal excitation of the neutrals or the fragment ions.

Dissociative ionization processes have been reported in aliphatic alcohols.[100,127] In the lower molecular weight alcohols (methyl to propyl) the dominant ions at low energies are[100] O^- in methanol, CH^- in ethanol, and OH^- in *n*-propyl and isopropyl alcohols. At energies above 70 eV the dominant ions in methanol are[100] O^-, OH^-, H^-, and CH_3O^-; those in ethanol[100] are O^-, CH^-, H^-, $C_2H_3O^-$, and $C_2H_5O^-$. In the isomeric propyl alcohols the major ions at 80 eV are[127] O^-, OH^-, and C_2H^-; in isopropyl alcohol the important ions are[127] OH^-, O^-, and C_2H^-. Because of the approximately equal strength of the C–O bonds, the dissociative capture processes for each of the O^-, OH^-, and $C_nH_{2n-1}O^-$ ions appear at about the same energies in the compounds studied.[100,127] It should be noted that the OH^- and O^- ions reported and their appearance potentials[100] are believed to arise to some extent from water as an impurity or background in the instrument. It is curious that the appearance potentials for OH^- and O^- determined by Tsuda, *et al.*,[127] are in agreement with those of von Trepka and Neuert.[100]

The interesting $C_nH_{2n+1}O^-$ ions are observed *via* two dissociative capture processes at 2.8 and 5.7 eV in the four simple alcohols investigated.[100] From the appearance potentials and assuming that excess energy contributions are small, the electron affinities of the $C_nH_{2n+1}O$ species are all about 1.5 eV.

Additional studies of dissociative capture processes in hydrocarbon systems have been published on hydroperoxy derivatives of propane[128] on selected fragment ions in tetrahydrofuran,[129] ketene,[130] and diketones.[131] Parent ions are noted[131] in the diketones at near zero energy where the ionization efficiency curves for glyoxal and biacetyl ions are identical with that for SF_6^-. In the 80-eV spectrum of tetrahydrofuran[129] C_2H^-, O^-, and C_2HO^- are the most intense. The O^- and C_2HO^- are also observed *via* dissociative capture processes. Above about 6 eV, the C_2H^- ion is only detected *via* an ion-pair process at about 24 eV. It is noted[128] that the dominant fragmentation process in the hydroperoxide occurs from the

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$(CH_3)_3OCO^-$ ion, *via* competitive reactions involving the loss of CH_3OH and CH_2O. The formation of fragment ions is extremely rich at near 0 eV as indicated in Table I.

A limited number of investigations of the negative ion mass spectra and appearance potentials in mercaptans have shown that HS^- is a dominant ion[28] for disulfides. The fragment ion formed by sulfur-sulfur bond cleavage and hydrogen migration to the neutral fragment is important in the dissociative attachment energy region. An ion-pair process has been suggested[132] for the formation of S^- and HS^- from thiophene, and dissociative electron capture energies have been measured.[133] Translational energies of the fragment ions have been measured, and limits for the electron affinities of CH_3S, CH_3S_2, S_2, and $C_3H_5S_2$ have been calculated.[28]

Negative ion formation in dimethyl sulfoxide has been studied.[134] At low energies SO^- and O^- are the dominant ions, while at 50 eV $C_2H_5SO^-$ is most abundant. Ion-pair processes for O^- and OH^- were suggested. The parent negative ion was not detected.

9. Nitrogen Compounds

Several studies of the negative ions produced from ammonia[135-138] and substituted amines[138,139] *via* electron impact have been reported. Negative ions from deuterated ammonia have been studied.[136,137] In ammonia and ammonia-d_3 two dissociative capture processes are noted at 5.65 and 10.5 eV,[136] with the peak at 5.65 eV about 30 times more intense. Direct isotope effects were noted for $NH_2^-:ND_2^-$ at both energies but only at the higher energy for $H^-:D^-$. This result is explained[136] by suggesting that for ND_3 the ion ND_3^- spends time in a potential region where electron ejection is possible. As a result, the likelihood of fragment negative ion production is decreased and the $NH_3:ND_3$ ion production ratio is greater than one.

The appearance potentials for NH_2^- and H^- were measured,[136] and excess energy for H^- was determined.[136] Two resonance maxima are noted for each ion at 5.65 and 10.5 eV. Two processes are postulated for H^- and NH_2^- formation: (a) $H^- + NH_2$ in their ground states and with or without excess translational energy and (b) $H^- + NH_2^*$ with NH_2 in an excited electronic state and H^- with excess translational energy. Similar processes would be predicted for the $NH_2^- + H$ reaction. From translational energy measurements[136] it is suggested that at 5.65 eV NH_2^- and H^- and the neutrals H and NH_2 are formed in their ground states and that at 10.5 eV the reaction is $H^- + NH_2^*$ with excess translational energy in H^- and electronic excitation energy in NH_2. The plausibility of excited NH_2^{-*} formation at 10.5 eV is mentioned although not confirmed experimentally.[136]

The spectrum of NF_3 has also been reported.[140] The dominant ion is F^- but F_2^- and NF^- are also detected. In contrast to NH_3, no NF_2^- ion was detected. In addition, the dissociative capture processes for F^- and NF^- ions occur at energies below about 4 eV while that for F_2^- is at about 5.0 eV. The importance of F_2^- observation in NF_3 and in other fluorinated molecules is that F_2 must have a rather high electron affinity. The value of the electron affinity of F_2 has been established as about 3.0 eV.[30,378]

From studies of the dissociative resonance processes in methylamine and methylamine-*N,N*-d_2, it was possible to distinguish[138] the loss of H from the methyl group and from the nitrogen. Three low-energy resonances are detected for H^-, 5.5, 6.8, and 9.5 eV. From a comparison with the deuterated compound, H^- formation can be ascribed to the following processes

$$CH_3NH_2 \rightarrow H^- + CH_3NH \text{ (5.5 eV)} \quad (28)$$

$$CH_3ND_2 \rightarrow D^- + CH_3ND \text{ (5.8 eV)} \quad (29)$$

$$CH_3NH_2 \rightarrow H^- + CHNH_2 + H \text{ (6.83 eV)} \quad (30)$$

$$CH_3ND_2 \rightarrow H^- + CHND_2 + H \text{ (6.30 eV)} \quad (31)$$

$$CH_3ND_2 \rightarrow D^- + CH_3 + ND \text{ (7.30 eV)} \quad (32)$$

$$CH_3NH_2 \rightarrow H^- + CH_2 + NH_2 \text{ (9.50 eV)} \quad (33)$$

$$CH_3ND_2 \rightarrow H^- + CH_2 + ND_2 \text{ (9.71 eV)} \quad (34)$$

$$CH_3ND_2 \rightarrow D^- + H + CH_2ND \text{ (9.53 eV)} \quad (35)$$

Additional ions detected in the amines CH_3NH^- and CH_3ND^- occur *via* a competitive process with H^- or D^- formation at about 5.65 eV. NH_2^- and ND_2^- are also noted at about 6.0 eV. It is suggested[138] that NH_2^- formation reactions at about 9.9 and 11.8 eV lead to excited states of NH_2^-.

Negative ions in cyanogen,[141-144] alkyl cyanides,[145,146] and cyanogen halides[144] have been studied. In all studies an important ion in the spectrum is CN^-. The ion is produced *via* dissociative attachment and ion-pair processes. In the spectrum of dicyanodiacetylene[143] an intense molecular negative ion is detected at near 0 eV. In methyl and ethyl cyanide the rearrangement ion HCN^- is detected with maxima at two electron energies about 2 and 9 eV.[145] The first resonance peak is very weak while the second dissociative capture process is rather intense and occurs over a broad energy range, $\simeq$5 to 25 eV.[145] In methyl cyanide a molecular negative ion was reported[146] at 40 and 80 eV. Owing to experimental difficulties, 0 eV could not be attained.[145,146] Although in none of the reports has excess translational energy been measured, small quantities of excess energy are predicted in the dissociative attachment processes in the cyanogen halides. Using appearance potential data, limits for electron affinities have been calculated.

10. Boron

The 70-eV negative ion mass spectra of several boron hydrides have been published.[147,148] The fragmentation

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processes generally involve the loss of 2H or H_2 and BH_3. The reported relative intensities of the major fragment ions in diborane and pentaborane(9) show some discrepancies.[147,148] As noted earlier this is probably not crucial because experimental conditions and mass spectrometric operational parameters were not identical. Appearance potentials are reported for the major ions in decaborane(14) and pentaborane(9).[147] For both compounds molecular negative ions were detected at 0.3 eV.[147] Formation of fragment ions produced *via* dissociative attachment and ion-pair processes could be rationalized by loss of H_2 or 2H and BH_3 neutrals. The possibility of secondary processes was not ruled out although ion source pressures were maintained at $<10^{-5}$ Torr.

Dunbar[149] has suggested that "stable", B_nH_{n+4}, and "unstable", B_nH_{n+6}, boron hydrides may be conveniently classified on the basis of their negative ion mass spectra. In the "stable" hydrides the most abundant ion is $(M - 1)^-$ plus an ion corresponding to the loss of one boron and hydrogen, and hydrogen atoms. The spectra of the "unstable" hydrides are unique in that the most intense ion at low energies is $(M - BH_3)^-$. Thus Dunbar's suggestion of a convenient way of differentiating the two classes of compounds appears reasonable.

The mass spectrum of BF_3[30,150] is similar to that for other fluoro compounds. The dominant ion is F^- with smaller abundances of F_2^- and BF_2^-. It is reported[30,150] that F_2^- is formed *via* a unimolecular process at about 10.5 eV, and *via* a secondary process[150] at 11.5 eV. From measurements of excess energy it has been shown[30] that BF is formed in an electronically excited state at 10.5 eV.

$$BF_3 + e^- \rightarrow F_2^- + BF^* \qquad (36)$$

$$F^- + BF_3 \rightarrow F_2^- + BF_2 \qquad (37)$$

Other ions in the spectrum except BF_4^- appear to be formed by unimolecular processes.

11. Silicon, Germanium

Appearance potential measurements and high-energy mass spectra have been reported for silane,[151,152] disilane,[151] silicon tetrachloride,[153-155] alkylsilanes,[156,157] silicon tetrafluoride,[158] and germanium tetrafluoride.[159] The negative ions in SiH_4 correspond to the loss of hydrogen atoms from SiH_4^- (not observed)[151,152] and include Si^-, SiH^-, SiH_2^-, and SiH_3^-. The most intense ion at low energies is SiH_3^-.[151,152] Each ion has a characteristic dissociative capture ionization efficiency curve and unique appearance potential. On the other hand, in disilane a similar situation regarding the types of ions formed exists; *i.e.*, all possible ions except $Si_2H_6^-$ are detected. The unusual behavior in Si_2H_6 is that the same energy dependence is observed for formation of each fragment ion. The ionization efficiency curves are characterized by a large maximum at about 7 eV and less intense maxima at 15 and 25 eV. The cross sections for the various ions are not identical, however. The interpretation of this result is that upon electron capture a highly excited $Si_2H_6^-$ ion is formed such that all dissociation pathways are energetically feasible. The alterations in ion intensity must be due to the nature of the potential energy functions of the fragment ions.

In halosilanes[154,155] and alkyl-substituted halosilanes[154] typical ion formation processes involve the loss of the groups attached to silicon. Intramolecular fragmentation processes are noted for the formation of Cl_2^-. In the alkylsilanes no hydrogen migration processes are reported. It is noteworthy that in $SiCl_4$,[154,155] $Si(NCO)_4$,[155] $C_2H_3SiCl_3$,[154] and $C_6H_5SiCl_3$[154] abundant molecular negative ions are formed. That these species are produced *via* primary electron capture processes is confirmed by the first-order variation of ion current with pressure.

Thynne and coworkers[158,159] have studied the negative ions produced in SiF_4 and GeF_4. The abundant ions include F^-, F_2^-, SiF_3^- (SiF_4),[158] GeF_2^-, and GeF_3^- (GeF_4).[159] The SiF_5^- and GeF_5^- ions were detected in the gas phase and apparently are formed *via* ion–molecule reactions. In addition, polymeric germanium negative ions $Ge_2F_4^-$ and $Ge_2F_8^-$ were noted.[159] Although not verified experimentally, it was postulated that the polygermanium ions $Ge_2F_4^-$ and $Ge_2F_8^-$ are generated *via* reactions of GeF_3^- and GeF_5^-, respectively, with the parent molecule, GeF_4.

$$GeF_3^- + GeF_4 \rightarrow Ge_2F_4^- + 3F \qquad (38)$$

$$GeF_5^- + GeF_4 \rightarrow Ge_2F_8^- + F \qquad (39)$$

Other investigators have also reported the detection of gaseous negative ions which have the same chemical composition as anions generated in solution. Gohlke[157] has detected the anion of dodecamethylcyclohexasilane at near zero energies in the mass spectrum of the parent compound, $C_{12}H_{36}Si_6$.

12. Phosphorus, Arsenic, Antimony

Phosphine has been studied[152,160] at low electron energies where PH_2^- is the dominant negative ion. The agreement for the appearance potential measurements in the two studies[152,160] is excellent. Two maxima are noted in the PH_2^- ionization efficiency curve. It has been suggested[160] that the second maximum corresponds to the formation of PH_2^- in an excited electronic state. The excess translational energy was not measured.[160] Additional ions in the low-energy spectrum, 0–10 eV, are PH^-, P^-, and H^-.[152,160] In phosphorus trifluoride[150] and phosphorus trichloride[161,162] the most intense ion is X^-, and PX_2^- is the second most abundant. The ionization efficiency curves for PX_2^- and X^- occur in the same energy region, suggesting a competitive dissociation process from some state of PX_3^-. In PCl_3,[162] PCl_3^- was detected in low abundance. It was suggested that PCl_3^- was produced *via* an ion–molecule reaction, with Cl^- as the primary ion. Such a process indicates $EA(PCl_3) > EA(Cl)$. In PF_3 no parent negative ion was observed under any conditions.[150]

Negative ions in $POCl_3$ have been detected[161-163] and appearance potentials reported.[161,162] As with the PX_3 compounds, X^-, in this case Cl^-, is the most intense

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ion. However, an abundant $POCl_2^-$ ion was formed *via* dissociative ionization. Formation of PCl_3^- was not observed, indicating the preferred dissociative pathway for the parent ion, $POCl_3^{-*}$ (not detected). This is not surprising since the P–O bond is expected to be stronger than the P–Cl bond in the $POCl_3^{-*}$ ion.

For the heavier elements, arsenic and antimony, the negative ion mass spectrum has been reported for AsH_3.[152] Arsine behaves like phosphine at low energies in that AsH_2^- is the dominant ion.

The negative ions in $SbCl_3$[164] have been studied using a total ionization tube. An intense negative ion signal is observed at near zero energy. It is suggested that the negative ion formed at low energies is probably Cl^-.

13. Sulfur, Selenium, Tellurium

Negative ions from sulfur-containing molecules including SO_2,[52,84,91,108,119,165] SF_4,[166,167] SF_6,[168-182] SF_5CF_3,[119] SF_5Cl,[168] and dimethyl sulfoxide[183] have been studied. In SO_2 the O^- and SO^- are both produced at two electron energies, about 4.5 and 7.0 eV.[91,108,165] It is suggested[165] that the dissociation of SO_2^{-*} (not detected) at the lower energy produces ions and neutrals in ground states, while the formation at about 7 eV yields either excited state neutrals or ions with excess kinetic energy or both. A recent determination[84] of excess translational energy indicates that SO is produced in its ground state and O^- is formed with excess translational energy.

Probably the most thoroughly studied sulfur-containing molecule is SF_6, because of its unique characteristics as a gaseous dielectric. Sulfur hexafluoride forms a molecular negative ion at 0 eV. At 70 eV, all ions produced by the loss of atomic fluorine, SF_n^- (n = 6–0), are observed[167] as well as F^- and F_2^-. The energy width of the capture cross section is extremely narrow so that measurement of SF_6^- ion current at 0 eV is a measure of the thermal energy distribution on the electron beam.[111,119,170] The near zero energy capture has also been used for calibrating the electron energy scale, but Schulz[175] has warned that under certain conditions the calibration using SF_6^- may be in error. It has been noted that SF_5^- is also produced at low energies in SF_6. The SF_5^-/SF_6^- ion current ratio increases with increasing temperature.[52,119,171] This behavior is attributed to the formation of SF_6^- in higher vibrational energy states which are open channels for SF_5^- production. The activation energy for SF_5^- formation has been measured to be 0.43 eV from a determination of the rate of SF_5^- formation as a function of temperature.[171] The F^- ion is also noted[181] in very low abundance at 0 eV. The measured appearance potential and excess energy for F^- have been used to evaluate[181] $D(SF_5\text{–}F)$.

The rate of attachment of electrons to SF_6 has been studied in a flowing afterglow[171] in swarm experiments,[10,172-174,177] with a TOF mass spectrometer,[179] and a microwave cavity.[178] The rate of attachment is found to be independent of temperature and pressure.[171] It appears[173,174] that buffer gases are equally efficient at stabilizing the SF_6^{-*} ion. In some cases SF_6^- has been produced by the reaction of highly excited atomic species Ar** with SF_6.[180] The autodetachment lifetime for SF_6^{-*} has been a variable of some interest.[170,172,176,178,179,182] The lifetime has been measured in a TOF mass spectrometer,[182] using a microwave cavity resonance method,[179] and in an icr mass spectrometer.[176] The value ranges from 10 to 500 μsec depending on the mode of SF_6^- formation. In conventional low-pressure ion sources the lifetime is 10–25 μsec.[179,182] Henis and Mabie[176] have introduced a technique where an analysis of peak widths in the icr instrument permits an evaluation of the detachment lifetime. The lifetime of SF_6^{-*} is critically dependent on electron energy. The long lifetime (500 μsec) measured in the icr experiment is attributed to capture of electrons trapped in the icr cell.[176]

Anticipating that other group VIa hexafluorides should form MF_6^- ions at low energies, Brion[169] and others[52,119] investigated the formation of negative ions in SeF_6 and TeF_6. In Brion's[169] work the electron energy distribution was reduced by incorporating a 127° electrostatic velocity analyzer on the electron gun. Surprisingly SeF_6^- or TeF_6^- was not detected[169] under conditions where ion–molecule collision events were known to be absent. The dominant ions formed *via* dissociative attachment were SeF_5^- in SeF_6 and F^- from TeF_6. In experiments where SF_6 and the molecules SeF_6 and TeF_6 were present, SeF_6^- and TeF_6^- were detected in rather large abundance. Brion[169] has suggested that collisional stabilization by SF_6 is responsible for the formation of SeF_6^- and TeF_6^-.

Fragment ions have been detected in substituted SF_6 molecules, SF_5CF_3[52,119] and SF_5Cl.[168] No molecular negative ions are noted in either compound. The important fragment ions are SF_5^- and additional SF_x^- species. Additional fragment ions formed *via* dissociative attachment include F_2^- and ClF^- from SF_5Cl.[168]

In SF_4, the molecular negative ion SF_4^- was noted[166,167] at low energies. The measured autodetachment lifetime is shorter than that for SF_6^-. This observation is in agreement with the model[121,182] which considers that the lifetime is related to the number of vibrational degrees of freedom. It is also suggested[166] that the availability of unoccupied d orbitals in sulfur enhances SF_4^- formation.

Stockdale, Compton, and Schweinler[184] have studied negative ions in a number of MF_6 molecules, M = S, Se, Te, Mo, Re, and U. Molecular negative ions, MF_6^-, are observed at low (near 0 eV) energies for SF_6, MoF_6, and ReF_6. SeF_6^-, TeF_6^-, and UF_6^- were detected when SF_6 was present. It is reported[184] that these ions are formed *via* electron transfer reactions (charge exchange) with SF_6^-. This explanation is in contrast to the collisional stabilization reaction suggested by Brion.[169] From unpublished swarm experiments[184] (ref 12), no evidence can be obtained for collisional stabilization.

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The fact that SF_6 forms a long-lived SF_6^- ion ($\tau > 10^{-6}$ sec), whereas SeF_6^- and TeF_6^- do not, is attributed to a Jahn–Teller effect in SF_6. The calculated[184] electronic levels in SF_6 are such that electron capture occurs in a degenerate orbital leaving the orbital partially occupied. This event results in a Jahn–Teller effect in the negative ion. By comparison, capture of an electron in SeF_6 and TeF_6 is into orbitals which are split by spin–orbit coupling so that no Jahn–Teller effect is possible in the ion. Furthermore, the Jahn–Teller effect is not noted in the neutral hexafluoride molecules.

It is suggested[184] therefore that where a Jahn–Teller effect is possible in the ion but not in the neutral (and *vice versa*) that electron capture occurs. A similar situation might occur when distortion is present both in the ion and in the molecule. Nevertheless, it is believed,[184] that alterations in potential for the nuclei provide an effective coupling between nuclear and electronic motions, thus capturing the electron.

14. Xenon Fluorides

The negative ion mass spectra of XeF_6,[185] XeF_4,[185] and $XeOF_4$[186] have been reported. The XeF_6^- and XeF_5^- ions are not observed in the spectrum of XeF_6. An important decomposition process is a competitive formation of F_2^- and XeF_4^- at near 0 eV. XeF_3^- was an abundant ion in the spectrum of both XeF_6 and XeF_4. In the high-energy negative ion spectrum of $XeOF_4$, the abundant ions are XeF_2^- and XeF_3^-. XeF_4^- and $XeOF_3^-$ are also observed. This behavior is in contrast to fragmentation processes in oxyfluorides where loss of fluorine is important.

15. Metal-Containing and Organometallic Compounds

Dissociative attachment and ion-pair processes have been reported for group Ia halides.[187,188] Fragment negative ions are produced from monomer, MX, and dimer, M_2X_2, species.[187] No molecular negative ions, $M_2X_2^-$, are observed, but M_2X^- and MX^- ions are detected. From measured appearance potentials of MX^- and M^-, the electron affinities of many MX and M (M = group Ia metal; X = group VIIa halides) species have been calculated.[187]

Studies of other metal halide compounds indicate dissociative attachment processes which correspond to the reaction

$$MX_n^- \rightarrow MX_{n-1}^- + X \qquad (40)$$

and the competitive process forming X^-

$$MX_n^- \rightarrow X^- + MX_{n-1} \qquad (41)$$

Metals whose halides (usually the chlorides) have been studied are lead(II),[189-191] iron(II),[192] cobalt(II),[192] nickel(II),[192] aluminum(III),[193] gallium(I),[193] indium(I),[193] thallium(I),[193,194] titanium(IV),[163] niobium(V),[163] and tantalum(V).[163] In high-temperature Knudsen cell studies of $PbCl_2$ mixtures with group Ia chlorides,[191] the $PbCl_2^-$ ion is detected *via* dissociative attachment from $CsPbCl_3$. From AP($PbCl_2^-$)[191] the electron affinity of $PbCl_2$ = 3.2 eV. Additionally, $CsPbCl_2^-$ and $CsCl^-$ species were observed *via* dissociative attachment. Limits for the electron affinities were calculated from appearance potential data. In the negative ion mass spectra[192] of $NiCl_2$, $FeCl_2$, and $CoCl_2$ (recorded at an unspecified electron energy and source pressure) molecular negative ions were detected. In $FeCl_2$, $FeCl_3^-$ was observed. No explanation for its observation was offered.

The negative ions from osmium and ruthenium tetroxides[195] are formed by oxygen atom loss. The important metal-containing ions are MO_3^-, MO_2^-, and MO^-. Approximate appearance potentials have been recorded.[195] In chromium oxychloride and oxyfluoride, CrO_2X_2, the mass spectra are rich in metal-containing negative ions.[196] Reaction processes involving loss of oxygen atoms and halogen atoms from $CrO_2X_2^-$ have been identified. In addition the CrO_3X^- and $CrOX_3^-$ ions are noted and their formation is accounted for by atom abstraction processes.

$$CrO_2X^- + CrO_2X_2 \rightarrow CrO_3X^- + CrOX_2 \qquad (42)$$

$$CrOX_2^- + CrO_2X_2 \rightarrow CrOX_3^- + CrO_2X \qquad (43)$$

The identification of the reactant ions is accomplished from a comparison of ionization efficiency curves for the secondary and primary ions.[196] The formation of $CrO_2X_2^-$, the molecular negative ion, in both compounds (X = Cl, F) could arise from charge exchange, direct capture, or atom abstraction. The latter process is suggested as the most probable reaction.

Metal carbonyls have received the greatest attention in investigations of negative ions in organometallic systems. Low-energy dissociative attachment processes have been investigated for $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$.[197] The $M(CO)_{n-1}^-$ ion is observed at near zero where the shape and width of the ionization efficiency curve is similar to that for SF_6^-. In no case was the molecular negative ion detected at any electron energy. The fragmentation process appears to involve successive loss of CO groups, a sequence of reactions similar to that noted in the positive ion spectra. Two resonance peaks are observed for the $M(CO)_{n-2}^-$ ions. Of two possible explanations, secondary electron capture and neutral formation in an excited state, the latter appears most reasonable. Excitation of the ion and neutral was not considered. Although translational energies were not measured and internal energy was not accounted for in the fragment ions, the electron affinities of the $M(CO)_{n-1}$ species were calculated[197] to be less than about 2.0 eV.

The unimolecular decomposition process for negative ions in metal carbonyls has received attention.[198-200] The suggestion[200] that loss of carbonyl groups from a pseudo-parent ion, $(M - CO)^-$, is the dominant decomposition process has been confirmed for the hexacarbon-

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yls of chromium,[198,199] molybdenum,[198] and tungsten.[198] Transitions were observed in a double-focusing mass spectrometer using the normal[198] and the defocused[199] electrostatic sector mode of study. The metastables noted for chromium hexacarbonyl support the process[200]

$$Cr(CO)_5^- \rightarrow Cr(CO)_4^- \rightarrow Cr(CO)_3^- \rightarrow Cr(CO)_2^- \rightarrow Cr(CO)^- \quad (44)$$

Presumably similar consecutive decomposition processes occur in the carbonyls of molybdenum and tungsten where only two and a single transition were noted,[198] respectively.

Fragmentation of the dimetallic carbonyls $Mn_2(CO)_{10}$ and $Co_2(CO)_8$[201] also involves successive loss of CO as the electron energy is increased from near 0 eV. However, abundant ions arising from M–M bond cleavage in the fragment ions was also an important process for negative ion formation.

An explanation as to why a parent negative ion is not observed in the diamagnetic carbonyls of chromium and nickel, but is for vanadium hexacarbonyl, has been offered by Kiser and coworkers.[202] Molecular orbital calculations indicate that the captured electron in $Cr(CO)_6$ and $Ni(CO)_4$ would be placed in an antibonding molecular orbital. For paramagnetic $V(CO)_6$ the captured electron would be located in a bonding orbital. This is consistent with observations in solution. The extension to the gas phase is reasonable and the molecular ion $V(CO)_6^-$ has been observed[202] in the 70-eV spectrum of $V(CO)_6$; secondary electron capture and resonance electron capture are suggested as possible processes for $V(CO)_6^-$ formation. Low energy measurements were not reported.

Studies of substituted metal carbonyls $C_5H_5M(CO)_x$ (M = Co, Mn, V; x = 2, 3, 4)[203] support the suggestion that loss of CO groups is the dominant fragmentation process. Unfortunately, it was not possible to assign m/e values more accurate than ±3 amu so it is not known whether fragmentation of the cyclopentadienyl ligand occurs. Investigation of group IVb dicyclopentadienyl dichlorides[204] indicates that molecular negative ions are formed at 0 eV and that fragmentation of the cyclopentadienyl groups is not important. The observation of molecular negative ions $M(C_5H_5)_2Cl_2^-$ might be expected since the $Ti(C_5H_5)_2Cl_2^-$ ion is isoelectronic with paramagnetic $V(C_5H_5)_2Cl_2$ which is stable in solution.

Other studies of organometallic compounds have centered on perfluoroaromatic[205] and chloroaliphatic[206] mercury compounds. An interesting halogen migration reaction is noted for C_6F_5HgCl[205] to produce an intense ion $C_6F_5Cl^-$. An approximate measurement of the appearance potential was presented.[205] In the chloroalkylmercury compounds a similar process was observed for the production of $HgCl_2^-$ according to the reaction[206]

$$C_2Cl_3HgCl \rightarrow HgCl_2^- + C_2Cl_2 \quad (45)$$

In $(C_2Cl_3)_2Hg$[206] the $HgCl_2^-$ ion is observed above 10 eV, presumably due to an ion-pair process. At higher ion source pressures ion–molecule reactions occur and the $HgCl_3^-$ and $C_4Cl_7Hg^-$ ions were observed. No details of the secondary ion formation process were given.

B. Photodetachment-Dissociative Resonance Ions

Over the past years measurements of photodetachment thresholds have provided the most accurate and reliable results for evaluating electron affinities in atomic systems. The detachment process occurs *via* vertical transitions from atomic negative ion to neutral atom. In atomic systems the photodetachment process usually corresponds to the detachment of an electron from the ground-state ion to the ground-state neutral atom. In some instances[10] excited states of negative ions have been reported.

The extension of the photodetachment technique to polyatomic ions in principle should yield accurate values for electron affinities. The requirement for accuracy is that the negative ion can be formed in its ground state (electronic, vibrational, and rotational), and the product neutral formed by detachment is also formed in its ground state. However, for polyatomic negative ions photodetachment may not, and in general will not, yield the neutral in its ground state. Thus the use of photodetachment for polyatomic negative ions suffers from the same limitations as any other method which involves vertical transitions.

Brauman and coworkers[207,208] have reported the use of an icr mass spectrometer to measure the photodetachment energy of negative ions. The negative ion current is monitored as a function of the photon energy which passes down the length of the icr cell. The measured electron affinities of OH^- and SH^- [207] are in agreement with values previously reported.[2] In a recent publication[208] a tunable laser beam was passed through the icr cell, and the photodetachment energies for NH_2^- and PH_2^- were reported. The measured electron affinities are $EA(NH_2) = 0.74$ eV, and $EA(PH_2) = 1.26$ eV. The value for PH_2 represents a new value, but the value for NH_2 is less than that tabulated by Berry[2] from Page's[209] measurement using the magnetron technique. All ions are produced *via* dissociative capture processes at low electron energies.

Recent studies[487-489] involving laser photodetachment and photoelectron spectroscopy should provide accurate electron affinities for polyatomic negative ions.

C. Ion-Pair Processes

The formation of negative ions *via* ion-pair processes occurs at electron energies around 10 eV and above. The reaction involves the production of a positive fragment ion and a negative fragment ion.

$$AB + E \rightarrow A^+ + B^- \quad (46)$$

The energy source, E, is commonly an energetic electron but more definitive studies have been carried out using photoionization techniques. The identification of an ion-pair process is accomplished when the onset energy (appearance potential) for the positive ion, A^+, and the negative ion, B^-, are identical. There are reports in the literature which attribute the formation of various negative ions to an ion-pair process without measuring the appearance potentials of the positive and negative ions involved. In this review we consider only those investigations in which an ion-pair process is established from energetic measurements for positive and negative ions.

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Generally the reports discussed employ photoionization methods for ion formation, and the studies have been carried out for simple diatomic or polyatomic molecules.

1. *Diatomic and Nonmetal Compounds*

Frost and McDowell[46,47] measured the appearance potentials for Cl^+ and Cl^- from Cl_2 using RPD techniques. The onset energies for Cl^+ and Cl^- were 11.86 and 11.93 eV, respectively. The calculated dissociation limit for Cl^- and Cl^+ using more recent thermochemical data[2,210] is 11.91 eV in excellent agreement with the measured value. The ion-pair process occurs *via* a transition from ground-state Cl_2 to an excited state of Cl_2 where the dissociation limit is at 11.91 eV. Similar dissociation processes were noted for I_2,[47] and two ion-pair processes were detected in Br_2.[46] The ion-pair processes in Br_2 differ in the excited state formed and the channels available for dissociation. In the first instance, an excited Br_2 state at the dissociation limit is involved while for the second ion-pair process an excited unstable Br_2 level is involved.

In oxygen[47] two processes are detected at 17.28 and 20.60 eV. For both processes O^- is formed in its ground state and O^+ in the ground state ^4S_u and the excited state ^2D_u. However, in photoionization studies[211,212] of the ion-pair process in O_2 only one process is reported. The reported onset energy[211] (17.24 eV) is in excellent agreement with the RPD electron-impact value.[40] In a recent electron-impact study,[213] where deconvolution is employed using a model function, a number of ion-pair processes were reported. The transitions were assigned to the various excited states of O^+ and the ground state of O^- ^2P_u.

Accurate bond dissociation energies for F_2 and HF have been of interest recently. Electron impact[45] and photoionization[214-217] investigations have been carried out to evaluate $D(F_2)$ and $D(HF)$. In some instances, excess energy has been measured[45,217] for the ion-pair process

$$F_2 \rightarrow F^+ + F^- \qquad (47)$$

Dibeler, *et al.*,[214,215] have measured the onset value to be 801 Å while Berkowitz, *et al.*,[216] have determined the onset as 798 Å. From measurements of translational energy, Chupka and Berkowitz[217] suggest that at onset F^+ is produced in its ground state but that above threshold (787 Å) F^+ is produced in an excited $^3P_0$ state.

Dibeler, *et al.*,[214,215] point out that the threshold process observed is spin forbidden and that the onset at 801 Å is well above the thermodynamic onset. Berkowitz, *et al.*,[216,217] have argued that the ion-pair onset at about 800 Å is the thermodynamic threshold. It was pointed out[216] from an examination of the potential energy diagram for F_2 and F_2^+ that the ion-pair process proceeds through some intermediate state. The state must cross some potential energy curve which correlates with $F^+(^3P) + F^-(^1S)$, the ion-pair onset. The intermediate state suggested is a Rydberg level which crosses the $^3\Sigma_u^+$ ionic state. The $^3\Sigma_u^+$ correlates with the ground-state ionic species, F^+ and F^-. Thus Berkowitz, *et al.*,[216] emphasize that transitions from ground-state neutrals to ground-state ionic products can be allowed and the true threshold is attained if Rydberg states exist (in the correct region) and cross ionic states near threshold.

A second ion-pair process is detected in F_2.[216,217] The process produced excited F^+ (^1D) and ground-state F^- (^1S). This higher energy process, onset at about 18.93 eV, is interpreted as an allowed transition to Rydberg states which converge to $^2\Pi_u$. The Rydberg states cross an ionic state, $^1\Sigma_u^+$, which correlates with F^+ (^1D) + F^- (^1S). The energy (18.93 eV) is sufficient to permit the initial absorption process to occur, and the crossing yields the ionic products.

Of interest here is the use of the ion-pair process for evaluating $D_0(F_2)$. From the threshold ion-pair appearance potentials using photoionization techniques[216,217] and the accepted ionization potential[210] and electron affinity[217a] of fluorine, $D_0(F_2)$ = 1.59 eV. The value (D_0) calculated from electron impact measurements[45] is 1.59 eV.

Similar measurements have been carried out for HF.[214-217] Onset appearance potential values and translational energy measurements yield $D_0(HF)$[216,217] = 5.87 eV.

Dibeler, *et al.*,[218] have detected an ion-pair process in ClF. The process reported corresponds to the reaction $ClF \rightarrow Cl^+ + F^-$. This represents the lowest energy process of the two ion-pair reactions possible. The complementary process $ClF \rightarrow Cl^- + F^+$ was not reported,[218] although the threshold for ground-state ion formation is calculated[2,210,218] to be 16.37 eV.

Additional studies of ion-pair processes in hydrocarbons and substituted hydrocarbons have been reported using electron impact[98,99,101,219-221] and photoionization methods.[222-224] In simple alkane hydrocarbons only the H^- ion is reported.[98,223,224] In another report[99] ion-pair processes were reported for C^-, CH^-, CH_2^-, and H^-. Approximate[220] appearance potentials for negative ions have been measured in methane and methyl halides for the reaction

$$CH_3X \rightarrow CH_3^+ + X^- \qquad (48)$$

Photoionization appearance potential data[222] for CH_3Cl indicate identical onset values and nearly identical ionization efficiency curve shapes for CH_3^+ and Cl^-. However, the measured appearance potential is higher than the value calculated from known thermochemical data. In other studies of hydrocarbons,[219,221] ethers,[219] halides,[219,221] and nitro[219] compounds, ion-pair processes are predicted, but appearance potentials for the negative ions were not measured. A comparison[223] of the photoionization and electron impact (RPD) results indicate that ionization probabilities differ and that interpretation

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of the ionization efficiency data suggests the formation of different ionic states. It is noted[223] that many of the breaks in the positive ion RPD curve, interpreted as the formation of fragment ions in different states, are not supported by the photoionization result, and it is emphasized that linear segments should be rare in electron-impact ionization efficiency curves. Measurement of ionization efficiency curves for the negative ions using monoenergetic electrons could aid in clarifying the apparent discrepancies.

Investigations of ion-pair processes in electron-impact mass spectrometers have been reported for a number of simple molecules including H_2,[213] CO,[86,213,225] NO,[213] H_2O,[68] C_3O_2,[97] NF_3,[140] PCl_3,[161-163] $POCl_3$,[161,162] and PCl_5.[162] The majority of the ion-pair reactions involve the formation of the negative ion of the most electronegative element, *i.e.*, Cl, O, F, etc. A number of ion-pair processes were suggested in water[68] for the formation of H^-, O^-, and OH^-.

Interest in the electron affinity of CN has prompted several studies in which ion-pair processes were reported. An electron-impact study on cyanogen halides[144] has indicated that both complementary ion-pair processes occur, *i.e.*

$$CNX \rightarrow CN^- + X^+ \quad (49)$$

$$CNX \rightarrow CN^+ + X^- \quad (50)$$

From the measured appearance potentials a value of EA(CN) = 3.21 eV was obtained.

Page[226] has used a revised value for ΔH_f(CN) to re-evaluate EA(CN) from magnetron data. The revised value is 3.18 eV. In a photoionization study[227] of HCN, a combination of the ion-pair process $HCN \rightarrow H^+ + CN^-$ and the dissociative ionization process $HCN \rightarrow H^+ + CN$ was used to evaluate EA(CN) = 3.82 eV. This latter value has been selected by Berry[2] as the most reliable value for EA(CN).

2. *Metal and Noble Gas Halides*

An ion-pair process has been noted in XeF_2.[228] The appearance potential for the dissociative process $XeF_2 + h\nu \rightarrow Xe^+ + F^- + F$ has been used to evaluate $\Delta H_f°$ (XeF_2). The formation of F^- appears to occur *via* a predissociation process similar to that suggested for ion-pair formation in F_2 and HF.[216] In the excitation-crossing process it is suggested that the ionic products are produced in their ground states at threshold. No evidence for ion-pair processes was obtained for XeF_4 and XeF_6.[228]

Binary halides of thallium(I) have been investigated using photoionization[229,230] and electron impact.[194] The only ion-pair processes reported correspond to the reaction

$$TlX \rightarrow Tl^+ + X^- \quad (51)$$

The complementary ion-pair reaction forming Tl^- and X^+ was not reported,[194,229,230] but the low-energy dissociation capture process $TlX \rightarrow Tl^- + X$ was observed.[194] The agreement between the photoionization[229] and electron impact[194] onset values is good. Dimer species Tl_2X_2 are detected,[229] but it is evident that X^- is not produced *via* an ion-pair process from Tl_2X_2 because the appearance potentials of X^- are below those for Tl_2X^+ ions. The ion yield curves for Tl_2F^+ and F^- were shown,[229] and it is presumed that onset behavior for the other halides was the same.[229,230]

In other high-temperature studies,[190] ion-pair processes in $PbBr_2$ and $PbCl_2$ were reported. Ion-pair reactions forming PbX^+ and X^- are identified from appearance potential measurements. The PbX^- ions are also detected at high energies, ≈8–10 eV, but it is not clear whether these ions arise from secondary electron capture or ion-pair reactions. Two onset potentials were measured[190] for Cl^- and Br^- corresponding to the reactions

$$PbX_2 \rightarrow PbX^+ + X^- \quad (52)$$

$$PbX_2 \rightarrow Pb^+ + X + X^- \quad (53)$$

D. Fragmentation Patterns

Melton[1] suggested that negative ion mass spectrometry might be useful as an aid in determining molecular structures. Since negative ion spectra usually contain fewer ions, it was expected that the simplicity of the spectra would lead to greater ease in interpretation. However, a number of problems are inherent in measuring negative ion spectra. Because high energies (70 eV) are commonly used ions may be formed not only by resonance and ion-pair processes but also by secondary electron capture. In an effort to increase the detectability of negative ions, the pressure in the ionization chamber is usually increased so that the possibility of secondary electron capture is increased, and the likelihood of ion–molecule reactions is enhanced. As already mentioned the energy distribution of the electron beam and electron beam collimation may also affect the abundances measured for negative ions. Thus because of the difficulties of ion detection, the low cross sections for negative ion formation, and the critical dependence on electron energy of the ion formation processes, there has been little widespread interest in molecular structure determinations using negative ion mass spectra. Nevertheless, some studies attempting to catalog mass spectra based on the functional group present have been published in the literature. It is often difficult to eliminate secondary processes (secondary electron, capture and/or ion–molecule reactions), and in this discussion only unimolecular processes will be considered unless specified otherwise.

To aid in the problem of *m/e* assignments in negative ion mass spectra, Gohlke and Thompson[231] have reported that perfluorokerosene (PFK) produces a rich negative ion spectrum at 70 eV. The mass range extends from *m/e* 19 to at least 940. The advantage of PFK is that its *m/e* values do not occur where nonperfluorinated molecules yield *m/e* values for negative ions.

In analytical applications negative ion spectra have been used to measure the chlorine isotope ratios.[232] Advantages of measuring the negative ion intensities are little or no interference from background peaks and the fact that the measurement is made on the two isotopes directly. Negative ion intensities have been used to measure subnanogram quantities of iodine. The technique permits the measurement of small quantities of ^{129}I in the presence of ^{127}I. Some possible interference at *m/e* 129 from species such as BrO_3^- or $H_2{}^{127}I^-$ was noted.[233] The information on negative ion mass spectra has been generated in the attempt to elucidate molecular structures.

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The utility of negative ion mass spectrometry in structure elucidation and in functional group analysis has been investigated for simple organic compounds. The compounds studied include hydrocarbons,[234] esters,[234,235] nitriles,[234] nitro compounds,[234,236-242] acids,[234] ketones,[234] alcohols,[234,244] aldehydes,[244] halides,[120,245-247] *N*-oxides,[243,248] heterocyclic molecules,[133,248,249] and group IVb molecules.[243]

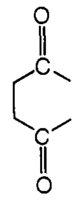
The high-energy (50–100 eV) negative ion mass spectrum has been reported for methane[250,251] in a study of the total ionization process upon radiolysis. The negative ion mass spectrum of diazocyclopentadiene-2-carboxylic acid[252] yields a weak peak (0.4%) at *m/e* 63 which corresponds to the dehydrocyclopentadienyl anion, $C_5H_3^-$. This anion is postulated as an intermediate in the thermal and photochemical decomposition of the diazocyclopentadiene-2-carboxylate anion. The detection of *m/e* 63 is suggested as evidence for the $C_5H_3^-$ ion as an intermediate in the reaction.

Initial studies of negative ion spectra[234] showed that the most abundant ion in selected aromatic hydrocarbons was C_2H^-, *m/e* 25. Derivatives of benzene,[234] benzonitrile, aniline, nitrobenzene, and methyl benzoate yielded $(M - 1)^-$ ions. In nitrogen-containing molecules,[234] benzonitrile and aniline, the CN^- ion was the base peak. The spectra of simple aliphatic acids were characterized by the O^- ion and the $(M - 1)^-$ negative ion. The ease of formation of the $(M - 1)^-$ ions was related to the ionic dissociation constants in aqueous solution.[234]

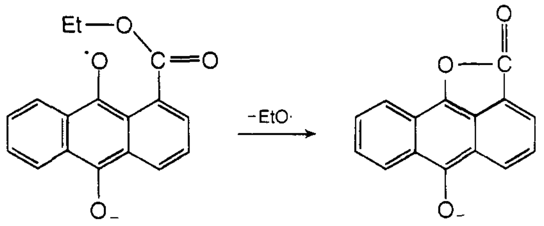
General observations were[234] that fragmentation processes corresponding to hydrogen stripping were important. When heteroatoms were present in the molecule, the stable anions O^-, OH^-, NO_2^-, CN^-, etc., were abundant. It was noted that there was a remarkable similarity between the spectra for all the compounds investigated and that fragmentation processes did not clearly lead to functional group analysis. The fragment ions only indicated the heteroatom present. Thus, from this study[234] it was suggested that negative ion spectra (20–70 eV) had little utility for structure determination, molecular weight measurements, or functional group analysis.

Bowie and coworkers[235,236,240,241,253] have taken an approach to the study of negative ion mass spectra in which the molecule in question is "tagged," so to speak, with a group or substituent which "stabilizes" the negative ion.[235] Four properties and functions of the tag are suggested as important:[235] (1) the substituent must aid in producing an abundant parent ion at high electron energies (70 eV); (2) fragmentation of the added substituent must not be significant; (3) the substituent must enhance the unimolecular decomposition of the functional group of interest; and (4) the spectrum must be easily obtained at low ion source pressures, 1×10^{-7} Torr, where ion-molecule processes are eliminated.

The substituent selected by Bowie, *et al.*,[235] is the dicarbonyl unit

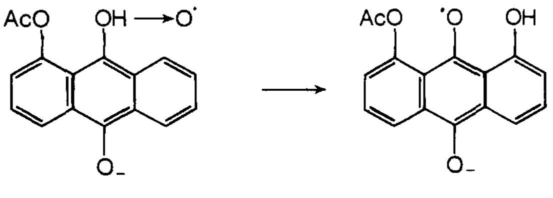


where electron capture occurs without using antibonding molecular orbitals. The moiety used for the study of esters[235] and ethers[253] was anthraquinone. With the ester function, CO_2R ($R = CH_3$, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9), at the 2 position in anthraquinone, the dominant negative ion was the molecular ion. Although the quoted pressure is $1\text{-}3 \times 10^{-7}$ Torr, it is likely that the molecular ions are formed *via* secondary processes, such as capture of secondary electrons. Fragmentation processes occurring by loss of $RCO_2\cdot$ and loss of R followed by elimination of CO_2 were confirmed by metastable transitions. When the ester group, $CO_2C_2H_5$, is present in the 1 position, an abundant ion corresponding to the loss of $C_2H_5O\cdot$ is detected. This ion is not present in the spectrum of the 2 isomer and is due to a proximity effect with the carbonyl of anthraquinone. A postulated process for the formation of the *m/e* 235 species, $[M - C_2H_5O]^-$, is



This process is not possible for the 2 isomer and thus the spectra permit differentiation of the two isomers.

Fragmentation processes for acetate derivatives of anthraquinone[235] also show proximity effects. The 1 isomers eliminate ketene, $[M - CH_2CO]^-$, while 2 isomers lose the acetyl radical, $[M - CH_3CO\cdot]^-$. Successive loss of ketene was also reported in 1,8- and 1,5-diacetoxyanthraquinones,[235] where it was proposed that the second loss proceeds only after hydrogen transfer. In 1,2-diacetoxyanthraquinone, a "double-proximity" effect is suggested where the major fragmentation pathway involves loss of two ketene molecules. The loss of ketene appears to be prominent when a phenoxy radical (or anion) is adjacent to the acetoxy group. If none is present, loss of the acetyl radical is noted.



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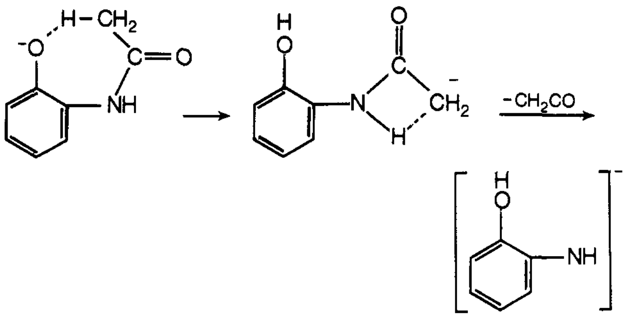
The selection of substituents has been extended to include electron-withdrawing groups, namely nitro substituents. Initial investigations[236] of aryl nitro compounds were carried out to discover the preferred fragmentation process for substituents containing carbonyl and nitro groups. The spectra of isomers of nitrobenzaldehydes and nitrobenzoic acid reveal the preferential loss of NO. The intensity of the $[M - NO]^-$ ion is related to the power of the electron-withdrawing substituent. The stronger the withdrawing power, the larger the $[M - NO]^-$ ion, an observation which aids in identifying ortho, meta, and para isomers. Another process which permits differentiating between ortho, meta, and para substitution is the decomposition of the $[M - NO]^-$ ion. The $[M - NO]^-$ ion in the ortho isomer of nitro benzoic acid eliminates CO_2 while nitrobenzaldehyde eliminates CO. These processes occur by a proximity effect at the ortho position. Elimination of neutral molecules (CO_2 and CO) is not observed for meta and para isomers. The process thus provides a convenient method for identifying the ortho isomer.

Negative ion spectra of other aryl nitro compounds $RC_6H_4NO_2$, where R = OH, OCH_3, NH_2, $NHCOCH_3$, and $OCOCH_3$, have been investigated.[236] Postulated mechanisms and fragmentation characteristics useful in identifying ortho, meta, and para isomers have been presented for nitrophthalic anhydrides,[240] nitrophenyl trifluoroacetamides,[241] nitroanilines,[237] and aromatic azoxy compounds, nitrones, and *N*-oxides.[242]

The spectrum of *o*-nitroacetanilide provides evidence for hydrogen scrambling in negative ions.[236] The molecular negative ion of *o*-nitroacetanilide eliminates NO, and the fragment ion $(M - NO)^-$ loses ketene. Selective deuterium substitution on N and on the CH_3 carbon shows loss of CH_2CO and CHDCO and loss of CD_2CO and CHDCO, respectively. The ratios are respectively 2:1 CH_2CO:CHDCO and CD_2CO:CHDCO, in both cases. To explain this result it is suggested that in the fragmentation process (1) a terminal hydrogen is transferred to the anion center (in this case oxygen), (2) randomization of the remaining three hydrogens occurs, and (3) ketene is lost as summarized below. Both processes were substantiated by observation of metastable peaks.



When the methyl group in nitrophenylacetamides is fluorinated, the fragmentation processes for this class of compounds are altered significantly.[241] Loss of CF_2CO from the $[M - NO\cdot]^-$ ion is not observed for these isomers. This is understandable since it is reasonable that the fluorine would not be strongly attracted to the phenoxide ion. A fragmentation process characteristic of all isomers is the loss of a hydrogen atom from the amide nitrogen and elimination of HNO_2. The loss of HNO_2 is supported by a metastable process, but a metastable for the loss of NO_2 from the $(M - H\cdot)^-$ ion was not observed. It was shown that the H atom involved was originally bound to nitrogen. No mechanism was postulated for this unusual elimination process.

Although there are similar fragmentation processes, the spectra of the ortho, meta, and para isomers are dissimilar,[241] and it is possible to differentiate among the species. The ortho isomer loses OH *via* a proximity effect involving the amine nitrogen and the nitro group. The $[M - OH]^-$ ion is the base peak in the spectrum. The para isomer is characterized by elimination of HF followed by H loss. The $[M - HF]^-$ ion is the most abundant ion in the spectrum. The loss of HF involves the nitrogen hydrogen while the second hydrogen lost comes specifically from the position ortho to the trifluoroacetamido group. The meta compound also loses HF but the $[M - HF]^-$ ion eliminates a hydroxy radical. This is in contrast to the $[M - HF]^-$ ion in the para isomer which loses a hydrogen atom. No labeling evidence was presented to discover the hydrogen atom involved in OH loss in the meta compound.[241]

Studies of substituted trinitromethanes,[238] $XC(NO_2)_3$, X = halogen, CH_3, NO_2, reveal that the molecular ion is not detected at any electron energy. The 70-eV spectra of the halogen derivatives show the relative stabilities of the C–X and C–N bonds. The $X\text{-}C(NO_2)_2^-$ ion is more abundant than the $C(NO_2)_3^-$ ion except for the iodo derivative. The intensity of the $C(NO_2)_3^-$ ion depends on the bond strength of X and its electron affinity. If the $XC(NO_2)_2^-$ ion intensity is taken as a measure of stability, the order is Br > Cl > F > I.

The overall unimolecular decomposition process is suggested as a quartet of competitive processes from the excited molecular ion (not observed) where neutral substituents are lost to form the ions (X^-, NO_2^-) and ions which are formed by loss of X, where X = CH_3, H, and NO_2. The dominant fragment ion is NO_2^-. The fragmentation processes observed are similar to photolysis reactions for nitromethanes wherein the initial decomposition is C–N bond fracture.

Mass spectral studies of complex organosulfur compounds are limited.[254,255] The spectra of β-thioketo thiolesters[255] are characterized by a base peak produced by the loss of RSH and the low abundance of molecular ions. In contrast to the positive ion spectra, the negative ion spectra are independent of the ester group. The fragmentation patterns of thioglycollic esters, *S*-alkylthioglycollic acids, and arylsulfinylamines are useful for diagnostic purposes in that molecular ions are detected in relatively high abundance.[254] In the acids, hydrogen rearrangement processes, originating by transfer of the carboxyl hydrogen, followed by cleavage of the C–S bond yield the $CH_2CO_2^-$ and/or RSH^- ions. In the esters no hydrogen migrations are noted. For the sulfinylaniline derivatives, the molecular ion is always the most intense ion in the spectrum. The spectra of the ortho, meta, and para isomers are not distinguishable although the nature of a substituent may be determined.[254]

The significance of obtaining molecular ions in highly fluorinated organic compounds has prompted studies of the negative ion mass spectra of this class of compounds. Since molecular ion formation, *via* resonance attachment, was noted for other highly fluorinated compounds, namely hexafluoroacetone[116] and perfluorotetrahydrofuran derivatives,[118] it appeared reasonable that a similar situation might exist for other organic fluorine molecules. The spectra of selected fluorinated compounds have been characterized at energies where ion-pair processes are dominant.[247] It is observed that among halogen compounds negative ion formation is

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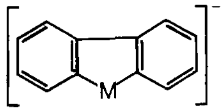
more extensive in chlorine-containing compounds. In substituted hydrocarbon species, mixed ions, CHX^- (X = Cl or F), are not abundant, but a large number of halogenated molecules form X_2^-. In perfluorinated molecules[245,246] molecular negative ions were noted for a variety of compounds. Many were detected at high electron energies, no doubt *via* either charge transfer with SF_6^- or by secondary electron capture. In all spectra, F^- was an important ion with a relative abundance usually greater than 10% and often the base peak. The general conclusion is that negative ion spectra are not helpful for structure studies or compound identification for highly fluorinated compounds.

Negative ion mass spectra have also been reported for compounds containing other nonmetal elements and for some metal-containing materials. Specifically a number of investigators have measured the mass spectra of other group IV elements, particularly silicon and tin.[243,256-262] The spectra[243,256] of tetramethylsilane and tetramethyltin show an abundant $(M - H)^-$ ion. The stability of these ions is attributed to $d\pi$–$p\pi$ bonding of the central atom (Si, Sn) d orbitals with p orbitals on carbon. The negative fragment ions and the observation of a molecular negative ion were used to characterize the molecule, $(CF_3C{\equiv}C)_4Si$.[257] The positive ion spectrum did not contain the molecular ion. Loss of CF_3 was an important decomposition pathway from M^-. Unusual rearrangement ions were reported.[257]

Negative ions from tetraphenyl compounds of germanium, tin, and lead have been reported.[261] The important decomposition process for the group IV tetraphenyl compounds[261] and the group V triphenyl molecules[259,261] occurs by loss of C_6H_5. However, the spectrum of $Si(C_6H_5)_4$ is an exception[261] and the base peak is the $(M - C_{12}H_{10})^-$ ion. The $[Si(C_6H_5)_2]^-$ ion behaves in a fashion similar to that for the group V $M(C_6H_5)_2^-$ ions. Bowie and Nussey[259,261] have suggested that loss of H_2 from $M(C_6H_5)_2^-$ is preceded by hydrogen scrambling in the ion. Deuterium-labeling studies were carried out and indicate that hydrogen scrambling does not occur upon loss of C_6H_5 or $C_{12}H_{10}$, but only upon H_2 loss from $M(C_{12}H_{10})^-$. A cyclic structure for $As(C_{12}H_{10})^-$ and $Si(C_{12}H_{10})^-$ is suggested[259,261] where the arsenic species is an even-electron ion, while the silicon entity is an odd-electron ion.



M = Si ·; As

It is pointed out that other intermediate structures would also be possible.

Reports of the formation of negative ions in water[263] and in xenon difluoride dioxide[264] have been presented. In XeO_2F_2 only XeF^-, $XeOF^-$, and XeF_2^- were detected. The observation of predominant loss of atomic oxygen compared to the loss of atomic fluorine compares with the spectrum noted for other xenon oxyfluorides.[186]

In an effort to make the study of negative ion mass spectra more useful, von Ardenne, Steinfelder, and Tümmler have developed the technique of "Elektronenanlagerung" (electron attachment) mass spectrometry or EA mass spectrometry.[265-269] The analysis method centers around a low-energy gas discharge source operated at relatively high pressures, 10^{-2} Torr. An inert gas such as argon is present in the source as a buffer gas. Samples may be introduced into the instrument as gases, liquids, or solids. In the study of organic molecules it has been observed that for many compounds an abundant ion is the molecular ion. Under such conditions very little fragmentation is noted. This observation appears reasonable in that the ions formed initially in the source could be collisionally stabilized at high ion source pressures. However, it is also noted that ion–molecule reactions occur, producing ions at m/e values greater than the molecular ion. The reactions usually involve an ion transfer process where the atomic or polyatomic reactant negative ion is incorporated into the molecule of interest. Reaction of hydrocarbons, alcohols, acids, etc., with a variety of ions, O^-, OH^-, Cl^-, etc., have been studied.[267,268]

In addition to ion transfer and molecular ion formation, fragmentation processes in the EA mass spectrometer have been used to characterize complex organic materials. EA spectra have been reported for organosulfur compounds,[270] natural products,[271-276] vitamins,[277] amino acids,[278] antibiotics,[279] complex organic acids,[280] metabolites,[281] transition metal phthalocyanines,[282] and other transition metal[265] and nonmetal compounds.[265]

The analytical applications of EA mass spectrometry have been emphasized.[268,283] The determination of the number of carbon atoms in petroleum hydrocarbons is accomplished by ^{13}C analysis of $(M + 1)^-$ ions. Hydrocarbon mixtures have also been analyzed and yield results comparable to gas chromatographic results.[268] Studies of the thermal behavior of polymers indicates[268] that the EA mass spectrum is critically dependent on temperature. This factor may nevertheless provide a useful technique for elucidating polymer constituents and structure.

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Another technique for producing intense, reproducible and interpretably useful negative ion mass spectra has been suggested by Dougherty.[284] The technique is based on the formation of secondary electrons due to the formation of positive ions from an unreactive added gas, such as N_2, and subsequent electron capture by the molecule of interest. The ion source is operated at high pressures, and the negative ions are produced by resonance and dissociative resonance capture of the secondary electrons. Using the technique, intense spectra of benzene, naphthalene, and anthracene were reported. The intensity of the molecular negative ion increased with increasing electron affinity of the molecule.[284]

E. Doubly Charged Negative Ions

Thus far in the discussion we have considered only the formation of singly charged negative ions. Multiply charged positive ions are detected in the mass spectrometer, and it is well known that multiply charged negative ions are present in crystals and in solutions, where crystal fields and solvation effects stabilize the ions. The question then arises: should one expect to observe multiply charged negative ions in the gas phase? There are theoretical reasons for expecting that only singly charged negative ions would be observed in the gas phase. First, the affinity of atoms and polyatomic molecules for a single electron is small (the largest electron affinity reported is less than 4.0 eV[2]), and, secondly, the presence of a second electron in a species, MX_n^{2-}(g) would experience strong Coulomb repulsion. Nevertheless, doubly charged negative ions have been reported in mass spectrometric studies using a variety of mass spectrometers.

Stuckey and Kiser[285,286] first reported doubly charged negative ions in studies of halocarbons using an omegatron mass spectrometer.[16] The doubly charged negative ions observed include the ions X^{2-} (X = F, Cl, Br, O, and CN). As a result of the ion flight times in the omegatron, the lifetime of these ions must be at least 10^{-4} sec. Since doubly charged negative ions are not detected in conventional mass spectrometric studies, the possibility that simultaneous capture of two electrons occurs is eliminated. The formation of the doubly charged ions appears to be a second-order process involving one of two possible modes.[285,286]

In the omegatron instrument nonresonant ions are forced to pass back through the electron beam; thus when X^{2-} is in resonance, X^- is passing through the electron beam. A possible process for X^{2-} is therefore that X^- captures a second electron upon interaction with the electron beam. Alternatively an ion–ion collision of two nonresonant X^- ions could produce X^{2-} *via* electron transfer. For either process the ion current of X^{2-} would vary as the square of the electron beam current. It is just this behavior which is observed.[285,286] The report of Stuckey and Kiser has been challenged by Fremlin[287] who offers alternate explanations as to why the peaks corresponding to X^{2-} ions are observed. The first alternative is that negative ions which are lost by collisional processes produce high-energy neutral species. It is suggested[287] that these neutrals are ionized on the surfaces in the omegatron and are collected at the frequency corresponding to X^{2-}. The second alternate explanation is that the X^{2-} ions arise from singly charged ions that under certain conditions gain energy from the rf field and that these ions would be collected at the X^{2-} ion apparent mass. It is pointed out that the conditions for this latter phenomena would be extremely critical and that this explanation is less likely.

There are conditions where doubly charged ions would be stable and should therefore be detected in conventional mass spectrometers. If the binding energy of the second electron exceeds the Coulomb repulsion energy, the doubly charged ion would be stable with respect to electron ejection. Under such conditions the ion would have an infinite lifetime or the ion could dissociate with a finite lifetime. On the other hand, if the binding energy is less than the Coulomb repulsion energy, the lifetime of the unstable ion could be as short as 10^{-15} sec but will depend on the strength of the interaction which causes autodetachment.

Recently[288] the observation of doubly charged negative ions using a Penning ion source and a 60° sector magnetic mass analyzer was reported. The ions detected were X^{2-}, where X = O, Te, Bi, F, Cl, Br, and I. That these ions do not arise from metastable processes, $X_2^- \rightarrow X^- + X$, was demonstrated by deflecting the ions in an electric field. Such deflection experiments confirmed the existence of doubly charged negative ions. It was also observed that the intensity of the doubly charged negative ion increased with increasing mass of the element. A doubly charged negative ion has been reported for *m/e* 26 from N_2F_2,[245] but it is possible that this *m/e* 26 ion may be produced from an impurity and is actually CN^-. Dougherty[289] has reported the observation of a doubly charged negative ion in the spectrum of benzo[*cd*]-pyrene-6-one (I). The peak at *m/e* 254.5 was attributed to the ^{13}C isotope of the doubly charged dimer of the parent molecule (I). The spectrum was recorded at high ion source pressures and electron beam currents. It was suggested that *m/e* 254.5 arises from an ion–ion or a doubly charged ion–molecule reaction in the source.

F. Theoretical Studies: Quantitative and Qualitative

Theoretical expressions have been derived to evaluate cross sections for dissociative attachment.[44,290-297] A detailed review[290b] of the theoretical treatments of dissociative attachment has appeared, so only a brief outline of the approaches taken in the calculations will be given here. The important dissociative attachment processes for diatomic molecules occur *via* Franck–Condon transitions from a stable state of the neutral molecule to a continuum of the molecular negative ion.

Dissociative attachment has been described[290,290a] as a coupling of terms between nuclear and electronic motions. This coupling arises because the constituent nuclei must absorb the energy imparted by the captured elec-

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tron and separate from one another in the process. The distorted wave treatment[290] involves a one-center expansion to obtain an equation where the total energy of the system is the sum of products of wave functions which include the relative nuclear motions. The effective nuclear potential, approximated as a Morse function, is obtained by including diagonal coupling terms in the electron energy. The magnitude of the cross section for dissociative attachment in H_2 calculated by Chen[290] is in agreement with the experimental value and predicts two resonance processes at about 9 and 13 eV.

A second approach treats dissociative capture as a resonance phenomenon.[44,291-293] A coupling of nuclear and electronic motion is not required because in the resonance region the wave function takes on resonance character. The process is viewed as an electronic transition from a continuum to a discrete electronic state (degenerate with the continuum), which leads to dissociation. Thus the AB^{-*} state is not a bound state in the conventional sense, but a resonance state. An expression, derived from a general rearrangement formalism using projection operators on the resonance state, permits an evaluation of the dissociative attachment cross section. It is indicated that the resonance states are usually narrow in energy, $\sim$ 0.1 eV. O'Malley comments that the processes treated, except H_2, are consistent with a compound ion type process. An application of the theoretical expression[291] to the temperature dependence for dissociative attachment in O_2 was successful.[292] The variation is attributed to a rapidly varying survival probability and its effect on excited vibrational states. The theory has also been used to explain inverse isotope effects on dissociative capture processes for deuterated molecules.[293]

The concept of expressing the dissociative capture cross section as a product of a survival probability and the capture cross section was shown not to be a general expression.[44] A more accurate expression is given as a sum of products of survival probability and capture cross section for the various states of the nuclei. The treatment has been applied to dissociative capture in H_2.[44]

In complex polyatomic molecules the dissociative attachment cross section is found[295] to be strongly dependent on electron energy. Three classes of molecules are designated. Two classes are identified by the relationship between the energy of the capture cross section maximum, ϵ_m, and the known energy of excited electronic states, ϵ_n, in the neutral molecule. For class I where $\epsilon_m < \epsilon_n$, the effect of autodetachment on the total cross section is small, while for class II, $\epsilon_m > \epsilon_n$, autoionization is significant. For class III the dissociative attachment cross section is small, and a vertical onset for dissociative attachment is noted. For class III autoionization is a significant channel for ion loss. The dissociative attachment cross section and its dependence on energy have been discussed in view of the classifications.[295]

In complex aromatic molecules the dissociative capture process is envisioned[296] as a two-step process. It is argued[296] that the initial electron capture leads to the formation of the molecular anion in an attractive state. A transition to a higher repulsive state of symmetry different from the molecular anion state is required as the second step. This second step requires an activation energy which is offered as an explanation of temperature effects in dissociative capture.[296] In addition it is suggested that a change from Π^7 to Π^6 type symmetry is required for dissociative capture. A collisional process implying a pressure dependence is suggested as a reasonable manner for altering the symmetry. This latter suggestion conflicts with experimental results which have shown that most dissociative attachment processes are first order in pressure.

Application of theoretical approaches to the calculation of ion abundances of normal and metastable ions produced by dissociative processes and unimolecular fragmentation processes at 70 eV have been published.[200,298-300] Winters and Kiser[200] applied the statistical theory of mass spectra to describe unimolecular decomposition processes in metal carbonyls. A consecutive unimolecular decomposition process corresponding to the loss of carbonyl groups was suggested as the principal mode of ion formation. The agreement between calculated and experimentally measured ion abundance is quite good and demonstrates the applicability of the statistical theory to negative ion spectra.

Breakdown curves for parent, metastable, and fragment ions have been calculated at low energies (0–1 eV) for SF_6 and several fluorocarbons.[298,299] The general features of the breakdown curves show[298] a decrease of parent ion, increase of fragment ion, and a maximum in the metastable ion as the electron energy is increased. The metastable ion curves are broader than for SF_6^- due to the greater thermal energy distribution. It is found that the autoionization rate is not a significantly large quantity for these particular fluorocarbons and that dissociations of the parent ion by loss of CF_3 and F are the most important reactions.

An application[300] of a statistical treatment to superexcited negative ion states has been applied to dissociation processes in SF_6. At equilibrium by the principle of microscopic reversibility the electron attachment rate constant, k_e, is related to the autodetachment rate constant, k_a. Accurate measurements of k_a can lead to an evaluation of the density of states in the excited negative ion since $k_e p^0$ is equal to $k_a p^-$; P^0 and P^- are the density of states for the ion and its fragments. The dominant parameter in determining P^0/P^- is the electron affinity. It is emphasized[300] that in evaluating lower limits of electron affinities[182] it is necessary only to have accurate rate constants at thermal energies.

IV. Negative Ions at High Pressures, $>10^{-5}$ Torr

At source pressures 10^{-7}–10^{-6} Torr, in conventional mass spectrometers, unimolecular decomposition of molecular and fragment negative ions occurs. Upon increasing the source pressure the mean free paths of the ions decrease and the likelihood of collisional processes is enhanced. These processes commonly are described as ion–molecule reactions, and it is usually implied that this process produces a new ion and a neutral species as

$$AB^- + CD \rightarrow ACD^- + B$$

However, for negative ions an ion–molecule collision may produce a variety of products *via* a number of different reactions. In addition, it is reasonable that electron molecule reactions at high pressures may be unlike those occurring at low pressures. The variety of reactions involving negative ions and processes for the formation of negative ions at high pressures have been summarized by McDaniel,[301] Melton,[302] Christophorou,[10] and others. The important processes are summarized below

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Charge transfer

$$AB^- + CD \rightarrow AB + CD^-$$

Abstraction or transfer

$$\text{Ion: } AB^- + CD \rightarrow CDA^- + B$$

$$AB^- + CD \rightarrow A + BCD^-$$

$$\text{Atom: } AB^- + CD \rightarrow ABC^- + D$$

Attachment

$$AB^- + CD \rightarrow ABCD^-$$

Dissociation

$$AB^- + CD \rightarrow AB + C + D^-$$

$$AB^- + CD \rightarrow A + B^- + CD$$

Detachment

$$\text{Collisional: } AB^- + CD \rightarrow AB + CD + e^-$$

$$\text{Associative: } AB^- + CD \rightarrow ABCD + e^-$$

In addition to the processes involving molecules, a number of important reactions with electrons at high pressures will be considered. These reactions of interest are electron scattering

$$AB + e^- \rightarrow AB^* + \mathbf{e}^-$$
$$\mathbf{e}^- + CD \rightarrow CD^-$$

where e^- represents an energetic electron and $\mathbf{e}^-$ is a thermalized electron, and third body collisions

$$e^- + M + M \rightarrow M_2^-$$
$$e^- + M + M \rightarrow M^- + M^*$$

The great interest in ion-molecule reactions stems from an attempt to describe ionic events in the upper atmosphere and the reactions of ions which occur in flames and gaseous discharges and in radiation chemistry. The greatest interest for negative ions is no doubt in the first area, aeronomy. The discussion of reactions involving upper atmospheric ions and neutrals is included in the next section. In this section ionic reactions which are potentially important in other areas are discussed.

Recently two monographs on ion-molecule reactions have been published.[303,304] Methods for studying ion-molecule reactions using single ion source mass spectrometers, ion cyclotron resonance instruments, various tandem geometries and beam methods, and flowing afterglow methods are discussed. Melton[305,306] has discussed the design and function of the mass spectrometer as a chemical laboratory, and papers contributed at the September 1966 ACS symposium on ion-molecule reactions have been collected.[307] The use of ion cyclotron resonance for ion-molecule studies including negative ions has been described.[308,309] A detailed discussion of the use of the flowing afterglow apparatus[310,311] for studying reactions at thermal energies and the importance of such studies in atmospheric research have been summarized.[312]

Two important points should be recognized regarding ion-molecule reactions; most of the well-studied reactions are very fast and the processes proceed with little or no activation energy. In general the reactions which have been studied are exothermic processes. Recently there has been active interest in measuring the threshold energy for endoergic ion-molecule reactions. The threshold values are important in evaluating electron affinities of atoms and molecules.

Negative ion-molecule reactions have been studied in conventional mass spectrometers. In the instrument ions are removed from the ionization chamber by applying an electrostatic potential to the repeller plate to give a field strength E_r. Upon acceleration through the ionization chamber the ions have a probability of reacting with the neutral gaseous molecules yielding secondary ions. The expression to describe the probability of reaction reflects the attenuation of the primary ion beam due to the reaction in question as the primary ion travels through the ionization chamber. The expression is

$$i_s/i_p = (1 - e^{-nlQ})$$

where i_s and i_p are the secondary and primary ion currents, respectively, n is the neutral gas number density, l is the distance of ion travel toward the ion exit slit, and Q is the phenomenological cross section.[313] The value of Q may be determined by measuring i_s/i_p as a function of pressure when l is known.

Variation of the repeller potential gives Q as a function of E_r, but the true microscopic cross section, $\sigma(E)$, variation with E is masked because the primary ions have a range of energies from 0 to (lE_r).

The rate constant, which conveys a reaction probability for some distribution of ion energies, is related to the cross section by the expression $k = vQ$, where v is the mean relative velocity of the ion. This relationship holds only when it can be shown that Q varies as v^{-1}.[314] The measured cross section is a function of excess energy in the reactant ion, including translational and internal vibrational and electronic energy.

Another measure of the reaction rate constant in single source mass spectrometers involves a measure of i_s/i_p as a function of reaction time. The measurements are carried out in pulsed source instruments where ions are formed by a short pulse of electrons of known energy. After a time t, the delay time, the reaction is quenched by rapidly extracting the ions from the ionization chamber and into the mass spectrometer for analysis of primary and secondary ions. The relationship between i_s and i_p is

$$i_s/i_p^0 = (1 - e^{-nkt})$$

where i_s is the number of secondary ions at time t, i_p^0 is the number of primary ions at time = 0, k is the rate constant, t is the delay time, and n is the gas number density. Under these conditions the reactions occur with thermal energies unless the primary ions are formed with excess energy in the initial ionization-dissociation process.

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A. Organic Compounds

The important ion–molecule reactions observed in hydrocarbons and their derivatives are proton transfer or hydrogen atom abstraction processes. The reactions have been investigated in flowing afterglow systems, in icr instruments, and in conventional single source mass spectrometers.

If a homologous series of neutrals and ions is examined and the direction of proton transfer determined, a scale of relative acidities may be obtained. The scale is established from the values of proton affinities. Thus if $PA(A^-) > PA(B^-)$, then the acidities of the parent acids are $HB > HA$. The advantage of such measurements in the gas phase is that intrinsic acid values may be obtained which are independent of solvation phenomena and counterion effects. From the gas-phase experiments it is noted that the relative order of gas-phase acidities for several molecules[317] is the reverse of the order determined from solution studies.

If sufficient thermochemical information is available, proton-transfer reactions may be used to set limits on electron affinities. From the proton-transfer reaction

$$A^- + HB \rightarrow HA + B^- \qquad (54)$$

the sign of ΔH (or ΔG) may be determined by carrying out the forward and the reverse reactions independently.

If the reactions are carried out at thermal or near-thermal energies, then only exothermic or approximately thermoneutral reactions processes will be observed. The sign of the free energy change for the reaction may be derived. If entropy is neglected, then the enthalpy change is obtained.

The enthalpy change for the reaction is given by the expression

$$\Delta H_r = D(HB) - D(HA) - EA(A) + EA(B) \qquad (55)$$

If the sign of ΔH is known from the experiment and if values for all of the variables but one are known, then a limit for this unknown may be obtained. It is the electron affinity of A or B which is of interest.

The experiments may be conveniently carried out using a flowing afterflow apparatus where the reactant ion may be generated up stream and the reactant neutral introduced into the flow. The icr instrument is equally well suited for these studies using the pulsed double resonance technique.[315,316] A tandem mass spectromer[317] is also suitable, and by varying the reactant ion energy the onset or minimum energy required for an endoergic reaction may be determined.

The first measurement of relative gas-phase acidities was accomplished by Brauman and Blair[316] using an icr mass spectrometer. The acidities were determined from (1) the observation of and (2) the inability to observe proton-transfer reactions. The acidity decreased in the order $CH_3COCH_2COCH_3$ (90% enol form) $> CH_3COCN > HCN$. This order is established from the fact that acetyl cyanide transfers a proton to CN^- but proton transfer from HCN to CH_2COCN^- is not observed. Similarly proton transfer is detected from acetylacetone to CN^- and CH_2COCN^-. Proton transfer from CH_3COCN to the acetylacetonate anion is not observed. Thus from the experiments in mixtures of HCN and CH_3COCN the relative proton affinities are $PA(CN^-) > PA(CH_2COCN^-)$, and thus the relative acidities are $CH_3COCN > HCN$. In the second experiments the results indicate $PA(CH_2COCN^-) > PA(CH_3COCHCOCH_3^-)$ and thus the acidities are $CH_3COCH_2COCH_3 > CH_3COCN$.

The relative acidities of simple alcohols have also been determined[318,319] from icr measurements and in a tandem mass spectrometer.[317] Using the double resonance technique to investigate forward and reverse reactions,[318,319] it is reported that the acidity decreases with decreasing carbon chain length in normal alcohols. The order is opposite to that reported from solution studies. Tiernan and Hughes[317] have measured the rate constants for forward and reverse proton-transfer reactions of the type

$$C_nH_gO^- + C_{n+1}H_{g+2}OH \underset{k_r}{\overset{k_f}{\rightleftarrows}} C_nH_gOH + C_{n+1}H_{g+2}O^- \qquad (56)$$

for simple alcohols at 0.3-eV ion energies. From the calculated equilibrium constants, $K_{eq} = k_f/k_r$, the relative acidities vary in the same manner as that reported from the icr measurements. Similar results have been obtained in flowing afterglow experiments.[320] It has been suggested[317-320] that the reversal of the relative acidities in the gas phase compared to that from solution studies may result from several factors including alkoxide ion–solvent dipole interactions, hydrogen bonding, steric factors, specific solvation effects, and dispersion forces.

The reactions of a number of simple negative ions with methyl chloride have been studied[321] in the continuing effort to describe reactions of organic molecules in the gas phase where solvent effects are removed. Reaction of O^-, OH^-, alkoxide, phenyl, and benzylic anions, Y^-, with methyl chloride indicate that the dominant reaction channel is the formation of chloride ion. The reaction processes are envisioned as substitution reactions since other probable processes

$$Y^- + CH_3Cl \rightarrow Cl^- + HY + CH_2$$

dissociative charge transfer

$$Y^- + CH_3Cl \rightarrow Cl^- + CH_3 + Y$$

etc., are calculated to be endothermic. The thermodynamic evaluation for the substitution process

$$Y^- + CH_3Cl \rightarrow Cl^- + CH_3Y$$

could only be confirmed for $Y^- = O^-$ and OH^-. It is presumed that for the other anions a similar reaction occurs.

The rate constants[321] fall roughly into two categories depending on the nature of the nucleophile. It is noted that when charge localization can be reasonably predicted in the nucleophile, as in the case of O^- and OH^-, the rate constants are large. On the other hand, if the charge is delocalized, on the ring, as in the benzyl anion, the rate constants are low by roughly a factor of 40 compared to the phenyl anion, $C_6H_5^-$. These results compare favorably with the known behavior in solutions, where correlation between reactivity of an anion and the nature of its charge distribution is observed.

Additional reports of relative gas-phase acidities and studies of proton- and atom-transfer reactions have been

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presented for hydrogen,[322] aliphatic amines,[323,324] ethyl nitrate,[325] nitroethane,[126] mercaptans[28,326] and other sulfur-containing molecules,[134] phosphine,[327] binary hydrides,[328-330] and alcohols.[100,331,332] Hydrogen atom transfer is observed[333] in the reaction of O^- with ammonia[333] and with alcohols.[334] The reactions of O^- with a variety of organic and inorganic molecules have been studied and atom-transfer ($O^- + I_2 \rightarrow OI^- + I$), proton-transfer, and charge-transfer processes were noted.[335]

Using the flowing afterglow technique, Bohme and Young[336] have investigated proton-transfer reactions in benzene and toluene. With the anion radicals $(M - H)^-$, H^-, OH^-, and $C_3H_5^-$ as reactant ions, the electron affinities of C_6H_5 and $C_6H_5CH_2$ were bracketed at $1.2 \leq EA(C_6H_5) \leq 1.6$ and $0.4 \leq EA(C_6H_5CH_2) \leq 0.9$. The value of $EA(C_6H_5)$ is lower than that obtained using the magnetron technique,[209] and it is suggested that the affinity evaluated from proton transfer corresponds to ground-state $C_6H_5^-$.[336] The reactions of oxygen ions (O^-) and of hydroxide ions with hydrocarbons have also been studied. Two processes, hydrogen atom and proton-transfer reactions, are noted in the reaction of O^- with simple olefins,[337] while only hydrogen atom abstraction occurs with saturated hydrocarbons.[338] Simple olefins,[337] except ethylene, react with OH^- *via* hydrogen abstraction, while OH^- reactions with saturated hydrocarbons were not observed.[338] From the observation that neither the sp^3 nor the sp^2 hydrogen is abstracted from ethane and ethylene, respectively, it is postulated[337] that the allylic proton is transferred from the olefins producing the allylic carbanion.

Hydrocarbon anions react with molecular oxygen *via* electron transfer, hydride ion transfer, and rearrangement.[337] The propynyl anion, $C_3H_3^-$, reacts with O_2 to yield C_2HO^- and H_2CO (formaldehyde), but electron transfer does not occur. The formation of the products is envisioned as O_2 addition to the carbon-carbon single bond in the propynyl anion followed by fracture of the carbon-carbon and oxygen-oxygen bonds. That the electron transfer does not occur is presumably because $EA(C_3H_3) > EA(O_2)$. For the allyl anion, $C_3H_5^-$, the reaction with O_2 proceeds almost exclusively by electron transfer. These two different modes of reaction illustrate the higher electron affinity of the propynyl radical. This result is consistent with a greater electronegativity of the sp-hybridized propynyl radical compared to the sp^2-hybridized allyl radical. For $C_4H_7^-$ ions, reaction with oxygen proceeds by hydride ion transfer and electron transfer. The hydride ion transfer reaction is the more important of the two processes. It is reasoned that the hydride ion transfer predominates due to the formation of 1,3-butadiene.[337]

The results of Bohme[337] have been substantiated in a study of the reactions of O^- with simple hydrocarbons[339] and OH^- with C_2H_4.[337] The associative detachment process for O^- with C_2H_4 was postulated for reactants at thermal energies.[337]

Studies of other processes in hydrocarbon and substituted hydrocarbon systems have been reported. Evidence has been presented for hydrogen migration in the formation of dimer anions in formic acid.[340] Reactions in chlorocarbon derivatives have been reported.[341-343] The dominant product at high pressures is Cl^-. Investigations of the reactions in acetonitrile[344,345] have shown that CN^- reacts with CH_3CN to produce $CH(CH)_2^-$ and C_3N^-. In mixtures of acetonitrile and water, OH^- reacts with CH_3CN by proton abstraction and by oxide ion transfer accompanied by H atom transfer to yield OCN^- and CH_4. Polymeric species have been observed at high pressures in the spectrum of cyanogen and in cyanogen-xenon mixtures.[346] Enhancement of the negative ion signal upon addition of xenon is attributed to secondary electrons and reaction of $(CN)_2$ with excited Xe to produce CN radicals which capture electrons.[346] Reactions of fluorocarbon negative ions in perfluoropropane with xenon have been studied.[347] The reactant ion energy is varied in a tandem mass spectrometer so that upon collision with xenon dissociative decay of the CF_n^- ions occurs. The dissociation of CF_3^- and $C_2F_5^-$ occurs according to the reaction

$$CF_n^- + Xe \rightarrow Xe + F^- + CF_{n-1} \qquad (57)$$

The reactions are endothermic, and thus the reaction cross section increases with increasing primary ion energy. Charge-transfer reactions from temporary negative ions of fluorocarbons to CS_2, NO_2, and O_2 have been reported.[348] All fluorocarbon anions transfer an electron to NO_2 while the heavier fluorocarbon species, $C_6F_{10}^-$ and $C_7F_{14}^-$, transfer an electron to CS_2 or O_2. That electron transfer occurs with NO_2 and not with CS_2 may be due to extended interaction time with NO_2 which has a permanent dipole moment. Charge transfer from O^- to hexafluoroacetylacetone has been reported.[108] Secondary negative ions in acetone are produced by CH_3 transfer to the $(M - H)^-$ primary ion.[349] Negative ions up to about *m/e* 140 have been reported in acetone. It is suggested that the heavy ions are bound by weak intermolecular forces.[350]

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B. Inorganic Compounds

The reactions of various negative ions with water have been studied. The reaction of water with D^- and H^-

$$H^- + H_2O \rightarrow OH^- + H_2 \tag{58}$$

has been studied[351,352] under field-free ion source conditions where the reactant ion translational energy is that provided *via* dissociative capture from D_2 or H_2, *i.e.*, about 2.0 eV. The reaction has also been studied[353,354] where the ions obtain translational energy from a repeller field and thus possess a range of ion energies. The reaction cross section measured for 2-eV ions[351,352] is larger by about a factor of 17 than the value determined for constant repeller field[353] where the total ion energy is about 4 eV. These data are consistent with the fact that the reaction cross section decreases with increasing ion energy for an exothermic reaction.

The reaction of O^- with water producing the hydroxide ion and hydroxy radical has been studied for O^- ion energies from 0.5 eV[354] to about 200 eV.[355] There is some discrepancy between the reaction cross sections for comparable ion energies. An alteration in the energy dependence for OH^- formation at high ion energies, ~5 eV, is attributed[354] to dissociation of the OH radical.

Atom-transfer and charge-transfer reactions involving sulfur in simple carbon sulfides with a number of negative ions, S^-, NH_2^-, etc., have been reported.[90,91,356,357] Reactions of sulfur-containing negative ions with CNCl have been studied.[358] The dominant reaction produces CN^- and SCN^- by reaction of S^- or HS^- with CNCl. Additional reactions of S^- with CNCl involve charge transfer and dissociative ionization.

The reactions of simple inorganic and organometallic compounds with negative ions have been studied in the gas phase where the absence of solvent effects is important to an understanding of the intrinsic chemical properties and reactivity of the species. In addition, it is possible to generate in the gas phase reactant ions which are relatively unstable in solutions or cannot be formed at all. Certainly ion-molecule reactions in inorganic chemistry provide an exciting area of investigation where formal oxidation states of central atoms of neutrals can be varied and where atoms in the same formal oxidation state may have different structures. Studies of ligand replacement and nucleophilic reactions with the central atom are of importance. Additional reasons for the interest in inorganic systems have been cited in the literature.[359-361]

For inorganic compounds other than nonmetal oxides negative ion-molecule reactions have been studied in iron pentacarbonyl,[359] nonmetal fluorides,[150,158,159,360-365] silicon halides,[154,158,361] and boron hydrides,[366] and halides.[367]

The nucleophilic reactions[359] of F^- and $C_2H_5O^-$ with $Fe(CO)_5$ produce four-coordinate organometallic anions. The elimination of two carbonyl groups occurs upon addition of the anion to the metal carbonyl.

Investigations of the reactions in nonmetal fluorides indicate that stable product anions are produced by fluoride ion transfer to the neutral. Incorporation of the fluoride ion produces stable inorganic anions of the type BF_4^-, PF_6^-, PF_4^-, POF_4^-, SiF_5^-, etc. Three anions have been observed to transfer fluoride ions to nonmetal fluorides. Formation of BF_4^- occurs in the reaction of SF_6^- [361] and F_2^- [150,363] with BF_3. In SiF_4, the pentafluorosilicate anion has been produced by reactions of SiF_4 with SF_6^- [361] and with SiF_3^-.[158,364] It is interesting that SiF_3^- is selected as the primary ion in SiF_4 since the ionization efficiency curves for F_2^- and SiF_3^- in SiF_4 are almost identical.[158] The formation of GeF_5^- and polymeric germanium ions $Ge_2F_4^-$ and $Ge_2F_8^-$ have been reported.[159] The formation of GeF_5^- and $Ge_2F_4^-$ reportedly[159] occurs by the reaction of GeF_4 and GeF_3^-. It is postulated that $Ge_2F_8^-$ occurs *via* the reaction of GeF_5^- with GeF_4.

It is of interest[361,362] that the reaction cross sections for fluoride ion transfer do not vary in the manner expected from the ion induced dipole model for ion-molecule reactions. It is suggested[362] that the reaction cross section may be related to the Lewis acidity of the neutral molecule. In the reactions of SF_6^- with a number of molecules,[361,362,365] charge transfer was not observed. In SF_6-C_4F_8 mixtures[365] charge transfer was not observed from SF_6^- or from $C_4F_8^-$. It is suggested that the delocalization of charge in the molecular negative ion presents a barrier to charge transfer. The reactions of SF_6^- with substituted chlorosilanes[154] produce Cl^- as the predominant secondary ion. The reaction[352] of SF_6^- with HCl yields F_2Cl^-, and the interaction[352] of $HCOO^-$ with SF_6 produces SF_5^- and HCOOF. Substitution reactions

$$O^- + SiCl_4 \rightarrow SiCl_3O^- + Cl \tag{59}$$

and exchange reactions

$$O^- + SiCl_4 \rightarrow Cl^- + SiCl_3O \tag{60}$$

have been shown[154] to be important processes in chlorosilanes and their derivatives.

The negative ion chemistry of boron compounds has been investigated with the idea that (1) concepts employed in carbon chemistry may be employed to interpret the results[366] and (2) ion-molecule chemistry may be able to provide insight into the reactivity of the "stable" and "unstable" boron hydrides.[149] An important reaction in diborane is

$$BH_4^- + B_2H_6 \hookrightarrow B_2H_7^- + BH_3 \tag{61}$$

Detailed analysis[366] of the double resonance signal indicates that the boron in BH_3 is produced from the ion and the neutral reactants. This observation indicates equivalence of the boron atoms in the intermediate. It is suggested[366] that short-lived tautomeric structures involving cleavage and formation of boron-hydrogen bridge and normal bonds are present in the intermediate. Reactions of diborane and H_2S *via* pyrolysis on the filament yield BS_2^- and H_3BSH^- ions which are isoelectronic with CS_2

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and CH_3SH. Reactions in more complex boron hydrides are characterized[149] by successive addition of BH units to the molecular ion. The ions responsible for BH addition were not identified.

C. Solvation–Hydration Reactions

An important study of negative ions in the gas phase is that involving solvation, particularly hydration reactions. Kebarle[367,368] has presented the arguments for the importance of the study of solvation phenomena. From examination of the solvated ions as a function of solvent pressure, free-energy changes and the respective equilibrium constants may be evaluated. When the equilibria are studied as a function of temperature, enthalpy and entropy changes for stepwise solvation may be obtained. The important experiments involve a comparison of the solvation of cations and anions by the same solvent, comparison of solvation behavior for isoelectronic ions, and examination of competitive solvation processes where different ions and/or different solvents are present in the reaction chamber. The solvation reactions studied have considered water,[368-375] carbon tetrachloride,[369] and chloroform[369] as solvents and the halide ions[369-371,373] and other common anions, CN^- [368] and OH^-.[368,372,374] A comparison of solvation of Cl^- by CCl_4 and $CHCl_3$ shows[369] stronger attachment by chloroform presumably due to ion–dipole attraction. The extent of solvation of halide ions[370,371,373] decreases with increasing ion size as expected. Fluoride ion, $F(H_2O)_n^-$, is solvated to the greatest extent, $n = 6$ at 1.0 Torr water pressure and 292°K, while a maximum of four water molecules solvated I^-. For fluoride ion the most abundant ion was $F(H_2O)_5^-$, while for iodide ion, $I(H_2O)_2^-$ was most intense. A similar limitation in the extent of hydration was noted[367] for BCl^- and B_2Cl^- compared to Cl^-. The enthalpies of hydration for the first water molecule in NO_2^-, NO_3^-, and CN^- are slightly greater[368] than for the halogens, except fluoride. This result is expected since the water molecule may selectively hydrogen bond to the electronegative groups in the ions. An examination[373] of the variation of hydration numbers and heats of hydration for positive (alkali metal) and negative (halide) ions has led to the suggestion that for $X(H_2O)_n^-$, where n is small, the water molecule is bound through both hydrogens. For larger values of n, the crowding of water molecules is relieved by the attachment of water through only one hydrogen atom. This suggestion comes in part from a calculation of the electrostatic potential energy of the solvated ions. A comparison of solvation enthalpies for isoelectronic positive–negative ion pairs indicates that the initial hydration of the smaller positive ion is greater than for the negative ion. However, as the number of water molecules is added to the anion, the ability to attach the water molecules with small water–water repulsion enhances the hydration process, and the interaction at higher n values becomes larger for the negative ions. Recent molecular orbital calculations indicate[375] that for hydration of OH^- chain-like structures are more favorable than cyclic structures.

TABLE II. Electron Affinities Determined by Endothermic Charge-Transfer Reactions

Molecule	Electron affinity	Ref
O_2 ($I^- + O_2$)	≥ 0.45	377
O_2 ($Br^- + O_2$)	≥ 0.40	377
O_2 ($O^- + O_2$)	≥ 0.45	355, 377
O_2 ($S^- + O_2$)	≥ 0.57	377
O_2 ($I^- + O_2$)	0.48	379
O_2 ($ND_2^- + O_2$)	$1.05 \leq EA \leq 1.2$	380
O_3 ($I^- + O_3$)	1.96	379
F_2 ($F^- + F_2$)	≥ 3.07	378
F_2 ($Br^- + F_2$)	3.10	378
F_2 ($I^- + F_2$)	3.06	378
Cl_2 ($Br^- + Cl_2$)	2.35	378
Cl_2 ($I^- + Cl_2$)	2.41	378
Br_2 ($Br^- + Br_2$)	2.53	378
Br_2 ($I^- + Br_2$)	2.48	378
I_2 ($Br^- + I_2$)	2.57	378
I_2 ($I^- + I_2$)	2.59	378
IBr ($I^- + Br_2$)	2.63	378
IBr ($Br^- + I_2$)	2.83	378
NO ($I^- +$ NO)	0.09	379
NO_2 ($Cl^- + NO_2$)		355
NO_2 ($Cl^- + NO_2$)	2.25	376
NO_2 ($Br^- + NO_2$)	2.36	376
NO_2 ($I^- + NO_2$)	2.04	379
NO_2 ($SH^- + NO_2$)		355
NO_3 ($I^- + HNO_3 \rightarrow HI + NO_3^-$)	≥ 2.48	379
SF_6 ($Cl^- + SF_6$)	$0.43 \leq EA \leq 1.0$	376

D. Endothermic Charge-Transfer Reactions

In conventional mass spectrometers reactant ions acquire an average kinetic energy due to the manner of dissociation and from the repeller field. In tandem mass spectrometers the negative ion is formed by electron impact, and the primary ion energy can be varied from about 0.3 to several eV.[376,377] If the primary ions are produced *via* ion-pair processes using photoionization methods,[378,379] the primary ion energy is varied from near zero to several electron volts. This capability provides a method for studying endothermic reactions. In particular, investigations of endothermic charge-transfer reactions have been reported[376-379] and electron affinities have been calculated from the measured threshold energy. Dissociative ion-transfer reactions have also been detected in the reactions of halide ions and halogen molecules.[378] The results of endothermic charge-transfer reactions have provided electron affinities of the halogen molecules,[378] O_2,[355,377,379,380] various nitrogen oxides,[355,376,379] and SF_6.[376] The calculated affinities and the endothermic charge-transfer reactions studied are summarized in Table II.

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E. Reactions of Atmospheric Interest

$$O_2 + M^- \rightarrow \text{products} \qquad (62)$$

The reaction of H^- with O_2 has been studied by a number of workers.[380-386] Three product ions are formed. O_2^- is formed *via* charge transfer, and O^- and OH^- are formed by ion–molecule reactions. Total reaction cross sections have been measured for a range of ion energies. Examination of the reaction of H^- with O_2 using the flowing afterglow technique[385] at 300°K has revealed that only the associative attachment process is important. An accurate knowledge of the impacting H^- ion energy has been questioned.[385] It is reasoned that the reaction channels producing O^-, O_2^-, and OH^- become important above some threshold ion energy. Thus these alternate reactions are observed only where the H^- ion has initial translational energy. It is also reported that C^- in the ^2D excited state charge transfers to O_2,[387] whereas no charge transfer by thermal ground-state C^- ion was noted.[388] The excited-state ^2D, C^- ion is produced[387] by secondary electrons at 10^{-3} Torr of CH_4, CO_2, and CO. Reaction cross sections for the reaction of OH^- with oxygen have also been reported.[382,383]

Because of the importance of O^- and O_2^- in the atmosphere and in the upper atmosphere, there is a great interest in the interaction of O_2^- and O^- with O_2 in binary and three-body reactions.[312,389-392] The reactions produce O_2^-, O_3^-, and O_4^- depending on the pressure and energy of the O^- ion. The reactions include three-body attachment and ion-molecule processes,[383-406] charge exchange,[353,383,407,408] collisional and associative detachment,[409-411] and other reactions including clustering processes.[406,412-414] The significance of these processes in aeronomy has been emphasized by Ferguson.[312,390] Phelps has reviewed the techniques for studying collisional processes of interest in the upper atmosphere[389] and some important processes for negative ion formation.

The electron attachment process in oxygen is envisioned as the formation of O_2^-, which is vibrationally excited, followed by collisional stabilization.[393] Conway[398,399] suggested that the nature of the collision pair should be important and that negative ion complexes might be formed. In the case of O_2^{-*}, stabilized by O_2, O_4^- would be the anticipated negative ion complex. O_4^- has been reported[399] in the high-pressure spectrum of O_2. The efficiency for collisional stabilization has been found[395] to be larger for water than for C_2H_4 or O_2 by about a factor of 4 to 5. More recent studies[404] indicate that acetone is even more effective than water in the stabilizing collision.

In drift tube studies[402] of electron attachment in mixtures of O_2 and CO_2, evidence for an attachment-detachment equilibrium involving the formation of CO_4^- is presented. In a series of experiments in mixtures containing O_2 and 0.23% CO_2, the concentration of the new negative ion, CO_4^-, appeared to be in equilibrium with O_2^-. In other O_2–CO_2 mixtures containing 2.5% O_2, the concentration of the CO_4^- ion was apparently in equilibrium with the free electron concentration and the O_2^- concentration. Equations 63a and 63b summarize these two equilibria. Mass analysis was not employed[402] but an m/e corresponding to CO_4^- has been reported.[403,406]

$$O_2^- + CO_2 \rightleftarrows CO_4^- \qquad (63a)$$

$$CO_2 + O_2 + e^- \rightleftarrows CO_4^- \qquad (63b)$$

O_2^- may also be formed by charge transfer or ion-atom interchange with O^-.[353,383,391,407,408] The pressures used in these studies were low so that no O_3^- or O_4^- ions were detected. Paulson[353] has obtained the rate constants for charge-transfer and ion–atom interchange by studying the reaction in mixtures of $^{16}O_2$ and $^{18}O_2$. It is reported[353] that the rate of charge transfer is greater than that for ion–atom interchange by about a factor of 3 for primary ions with kinetic energy from 3.6 to 7.6 eV (sum of initial O^- translational energy and repeller field contribution). Resonance charge transfer in the reaction of O_2^- with O_2 is also reported.[383,407,408] The charge-transfer cross section increases with decreasing ion energy. Charge-transfer reactions were noted in the reaction of ND_2^- and SO^- with O_2.[380]

Ferguson, *et al.*,[409] have investigated the interaction of O^- with O_2 at thermal energies in the flowing afterglow and observe no reaction of O^- with O_2. This result is consistent with the endothermic nature of the charge transfer. Reactions of O^- and O_2^- ions with oxygen atoms have been reported.[409,410] The dominant process is the associative detachment process.

Important clustering processes for oxygen negative ions, O_2^- and O^-,[406,412,413] and the reactions of the clustered species with various neutrals[412] have been reported. Clusters of O_2^- with water, $O_2^-(H_2O)_x$, where x = 1–5, have been detected.[406] In the flowing after-

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glow[412] with He as a buffer gas, clusters of O_2^- and O^- with H_2O, O_2, and CO_2 have been observed. The reactions of cluster ions with NO, CO_2, CO, N_2, and N_2O have been published.[412] An important result of these studies is the evaluation of the equilibrium constants for the processes under the conditions present in the experiments. Equilibrium constants were obtained for processes of the type

$$O^-\cdot CO_2 + NO \rightleftarrows O^-\cdot NO + CO_2 \qquad (64a)$$

$$O_2^-\cdot O_2 + CO_2 \rightleftarrows O_2^-\cdot CO_2 + O_2 \qquad (64b)$$

and others. It is emphasized[412] that care must be used in interpreting the results and whether the equilibrium constants refer to ground-state ions. It is believed that the equilibrium constant for reaction 64a above does not correspond to the ground states for ions. Specifically it is suggested that NO_2^- maintain most of its excitation energy until it reacts with CO_2 again. Additional evidence is presented[412] to support the formation of excited-state cluster ions. NO_3^- exhibited different reactivities toward NO depending on the mode of formation, *e.g.*, (a) $O_4^- + NO \rightarrow NO_3^- + O_2$ and (b) $NO_2^- + NO_2 \rightarrow NO_3^- + NO$. NO_3^- produced *via* process a reacted with NO to give NO_2^-, whereas NO_3^- produced by the reaction b did not.

Reactions of negative ions and CO_2,[388,406,415,416] CO,[385,406] and other carbon-containing compounds[417] have been reported. Some of these processes were discussed above. The formation of CO_4^- and CO_3^- *via* three-body processes with O_2^- and O^- in CO_2 has been noted.[406] It is suggested[415] that the associative detachment process, $CO_2 + O^- \rightarrow CO_3 + e^-$, is endothermic from an estimate of the upper limit for the rate constant of 1×10^{-13} cm^3/sec. Paulson[416] has studied the interaction of O^-, NO^-, and O_2^- with CO_2. With O^-, NO^-, and O_2^-, CO_2^- is an important product. The $NO^- + CO_2$ reaction has the largest cross section. In addition to CO_2^-, O_2^- is formed in the reaction with O^-, and CO_3^- in the reaction with O_2^-. The reaction cross sections peak in the ion energy range 8–15 eV for the primary ion. From the threshold for the ion–molecule reaction, the electron affinity of CO_2 is estimated to be a negative value. The fact that a nonzero cross section is observed in these systems implies that higher values of the CO_2 electron affinity must exist. Recent studies[89a] indicate that CO_2^- can have a positive vertical detachment energy.

The rate for associative detachment of H^- and CO has been measured.[385] The reaction of C^- (^4S) with CO_2 ($^1\Sigma$) at thermal ion energies yields no observable ion product, and associative detachment yielding two CO's ($^1\Sigma$) or C_2O_2 is suggested.[388] The reaction of C^- (^4S) with CO ($^1\Sigma$) is a factor of 10 faster than the C^- reaction with CO_2 and also yields no ion products. C_2O ($^3\Sigma$) is suggested as the neutral product. If the reactants are formed in the states as indicated, the reaction of C^- with CO_2 violates spin conservation while the reaction with CO corresponds to a spin-allowed channel. It is argued[388] that the relative rates of reaction may be associated with the fact that one process is a spin-allowed channel while the other is not.

A number of studies of negative ion formation in N_2O have been published. Studies using a microwave cavity have suggested[418] that the interaction of an electron with N_2O produces N_2O^- *via* a three-body attachment process. The reaction of O^- and N_2O has been studied[311,352,353,419-423] and a number of important reactions have been observed.

$$O^- + N_2O \rightarrow NO^- + NO \qquad (65)$$

$$O^- + N_2O \rightarrow O_2^- + N_2 \qquad (66)$$

In addition, charge transfer from NO^- to yield N_2O^- has been reported.[419,420] The formation of NO_2^- reported earlier has been attributed to impurities.[353] At high ion source pressure (0.3–8.0 Torr) dimer and solvated negative ion species were detected.[423] The important ions $N_2O_2^-$ [$(NO)_2^-$] and $N_3O_2^-$ [$(NO^-\cdot N_2O)$] are produced *via* three-body reaction processes of O^- and NO^-, respectively, with N_2O.[423]

The energy dependence of the reaction cross section for process 65 has been studied.[419] The cross section falls monotonically with increasing O^- ion energy. On the other hand, the cross section for reaction 66 is near zero for thermal O^- ions and rises to a maximum where the O^- kinetic energy is about 8 eV.[419] In the reaction of O^- with 0.65 eV of kinetic energy, only reaction 65 is observed.[352] Only reaction 65 is detected for the reaction at thermal energies using icr techniques.[421] Based on the most recent[488] EA(NO) = 0.024 eV, reaction 65 is just slightly endothermic (0.5 kcal/mol). On the other hand, reaction 66 is exothermic by 54 kcal/mol (EA(O_2) = 0.44 eV[487]). It is curious that the most frequently observed reaction is the slightly endothermic process, whereas the highly exothermic reaction is not observed. It is of importance that the cross section for the exothermic reaction 66 reaches a maximum at 8 eV ion energy. It is implied[419] that such unusual behavior is indicative of an energy barrier in the atom-transfer reaction and may be related to the accessible spectroscopic levels of the intermediate ion, presumably $N_2O_2^-$.

The formation of N_2O^- by the reaction with NO^- has been studied at higher pressures.[419,420,423] The pressure dependence for N_2O^- formation is initially third order but changes to fourth order, while the pressure dependence for NO^- formation is initially second order changing to third order.[420] The pressure dependence is consistent with the reactions

$$N_2O + O^- \rightarrow NO^- + NO \qquad (67)$$

$$NO^- + N_2O \rightarrow N_2O^- + NO \qquad (68)$$

where isotopic substitution studies have indicated that reaction 67 is a dissociative charge-transfer process[353] and reaction 68 is electron transfer.[419]

Reaction of C^- with N_2O at thermal energies, 300°K, occurs *via* associative detachment.[388] Six possible arrangements of products CO + N_2 and CN + NO in various electronic states are suggested. No process is confirmed. The reaction of H^- with N_2O proceeds at thermal energies by oxygen atom abstraction.[385] The reaction of H^- with NO has also been studied.[385]

Studies of reactions of NO_2 with negative ions have been primarily concerned with a determination of the electron affinity of NO_2. The popular charge transfer reaction

$$O^- + NO_2 \rightarrow NO_2^- + O \qquad (69)$$

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is exothermic and obeys a second-order pressure dependence.[335,353,424] The reaction of O^- formed with excess translational energy from various oxygen compounds has been reported.[352] The variation of reaction cross section for charge transfer to NO_2 from a number of primary ions, SO^-, S^-, CS^-, and O^-, has been measured[425] for different ion energies. Reactions of O^-, O_2^-, O_3^-, and OH^- with NO_2 have also been reported.[408] A decrease in the reaction cross section with increasing ion energy is consistent with the exothermicity of the charge-transfer reaction.[334,352,425] An additional reaction in NO_2 yields[353] O_2^- according to the process

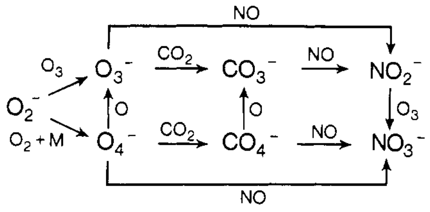
$$O^- + NO_2 \rightarrow NO + O_2^- \cdot \tag{70}$$

Attempts to elucidate the mechanism of O_2^- formation using $^{18}O_2$ in NO_2–O_2 mixtures failed[353] because of isotope exchange in the reservoir.

The importance of negative ion reactions discussed above and others in the description of the negative ion chemistry of the lower ionosphere has been summarized by Ferguson.[312,426-428] The interesting feature appears to be the formation of NO_3^- as a terminal ion product. It has been demonstrated[426-429] that NO_3^- is very unreactive. It appears[426] that NO_3^- is destroyed by ion recombination processes or photodetachment and not through reactions with other species present in the D region. It is suggested[426] that NO_3^- may solvate with water or other species in the region, and this form may be the most important species present.

The first reports[430,431] of negative ion reactions of D region species presented the results of associative detachment[430] and ion–molecule reactions.[430,431] Reactions of O^- and O_2^- with nitrogen and oxygen atoms proceeded *via* associative detachment while reactions with O_3 occurred by charge transfer. The reactions of CO_3^- and O_3^- were also studied. A significant reaction is the conversion of NO_2^- to NO_3^- by O_3.[431] In the scheme summarized by Ferguson, *et al.*,[312,427,428,430] the important reactant neutrals are CO_2, NO, O, O_2, and O_3. These neutrals react in the processes collected below to produce NO_3^-. The initial reaction is the three-body attachment reaction yielding O_2^- (Scheme I).

SCHEME I



The final product ions NO_2^- and NO_3^- are lost by recombination with positive ions or photodetachment. A discussion of various models for describing the ion chemistry of the D region has been presented.[432] The basis of the model relies on the laboratory measurements of the reactions of negative ions at thermal energies.[312,426-428] Various papers have appeared[433-439] which consider the implication of the reactions observed, the measured rate constants, and photochemical behavior of atmospheric negative ions and the results of the determination of negative ions in the upper atmosphere from rocket probe experiments. The discussion of these results is outside the scope of this review.

A significant negative ion reaction process which has no counterpart in positive ion reactions is the associative detachment process

$$A^- + B \rightarrow AB + e^-$$

Some of the reactions of importance to the ion chemistry of D region have been discussed. Reactions in other systems have been studied. A complementary process, collisional detachment, has been found to be important in negative ion chemistry.

Associative detachment reactions were first reported by Fehsenfeld, *et al.*,[440] using the ESSA flowing afterglow apparatus. The reactions of O^-, Cl^-, O_2^-, OH^-, H^-, and NO^-[440,441] with a number of molecules and atoms were investigated. A general result is that exothermic reactions appear to be very fast at thermal energies. Reactions calculated to be endothermic were either not observed or proceeded at very slow rates. The rates of reaction of O^- and O_2^- with O_2 $(^1\Delta_g)$[442] are both fast, and the products are ozone and O_2, respectively. It is interesting to note that the endothermic reaction of O^- with ground-state O_2[440] was not observed and an upper limit of 1×10^{-12} cm^3/sec was set for the rate constant. The reaction of O^- with NO, CO, and H_2 has been reported.[406,443] The results of the drift tube measurements[406,443] compare with the results from the flowing afterglow.[440,444] In order to explain the slow rates of some exothermic associative detachment reactions, two cases have been considered.[445] The slow rate for O^-

$$O^- + N_2 \rightarrow N_2O + e^- \tag{71}$$

is rationalized on the basis that a compound negative ion state of N_2O^- is formed initially. The slow detachment process results from a change in geometry in going from bent N_2O^- to linear N_2O.[446] For the insertion reaction

$$OH^- + N \rightarrow HNO + e^- \tag{72}$$

the rate is slow, and it is suggested[445] that an activation energy is required for the insertion. The model proposed[445] assumes the formation of a stable molecule which autodetaches, *i.e.*

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$$A^- + BC \rightarrow [BAC^-] \rightarrow BAC + e^- \quad (73)$$

To predict the relative reaction rates one examines the balance between the energy required for nuclear deformation ΔE_d (bond lengthening) and the decrease in electronic energy ΔE_r due to the formation of BAC^-. If $\Delta E_d > \Delta E_r$, then the rate is predicted to be slow, and conversely. In the reactions

$$S^- + H_2 \rightarrow H_2S + e^- \quad (74)$$

$$S^- + O_2 \rightarrow SO_2 + e^- \quad (75)$$

where $\Delta E_d > \Delta E_r$, the reactions are slow while for the reaction

$$O_2^- + N \rightarrow NO_2 + e^- \quad (76)$$

$\Delta E_r > \Delta E_d$, and the process is fast. Thus the experimental results support the simple criteria. A more extensive theoretical treatment of associative detachment processes has been presented.[447-449]

Collisional detachment occurs with negative ions and neutrals at higher ion energies. Selected reports of collisional detachment processes

$$AB^- + X \rightarrow X + AB + e^- \quad (77)$$

and dissociative collision reactions

$$AB^- + X \rightarrow A + B^- + X \quad (78)$$

include studies of negative ions in SF_6,[450] NO_2,[450] and O_2.[451,452] Detachment processes of halide negative ions[453-455] and O^-[453,456-458] with N_2[455,457,458] and noble gas atoms[453,454,456] have been reported. From the variation of the collisional detachment cross section with ion energy, threshold values for detachment were obtained.[456] The onset values were in approximate agreement with the known electron affinities of the species studied.

F. Inelastic Electron Scattering

Electronic states of various neutral species and temporary states of negative ions have been studied by electron scattering techniques. Electrons which have been slowed to thermal energies by inelastic scattering processes are detected using a scavenger molecule with a large cross section for thermal electron capture, *i.e.*, SF_6. By measuring the SF_6^- ion current as a function of bombarding electron energy, the threshold energy for excited-state formation in the neutral can be determined.[103,459-461] The reactions occur as shown

$$e^-(E_e) + M \rightarrow M^* + e^-(E_t\text{: thermal}) \quad (79)$$

$$e^-(E_t) + SF_6 \rightarrow SF_6^- \quad (80)$$

where E_e is the incident electron energy, and E_t represents thermal energy of the electron after excitation of M. The method is useful for detecting optically forbidden transitions in M. Detection of electrons with nonthermal energies may be accomplished by use of a scavenger which captures electrons of higher energies and produces a characteristic negative ion.

The limiting factor in the precision is the measurement of the electron energy, while the resolution is dependent on the energy spread of the bombarding electron beam. The RPD method[459,460] and an electron velocity selector[169,462,463] have been used to reduce the electron energy spread. Other scavenger molecules which have been used include CH_3I (I^-)[461] and CCl_4 (Cl^-).[464] Investigation of electronic levels using the "SF_6^- scavenger technique" have been reported using magnetic,[459,460] time-of-flight,[460] icr,[464,465] and monopole[18,462,463] mass spectrometers. The compounds studied include noble gas atoms,[460-463,465,466] simple diatomic molecules, N_2,[459,464,465,467] CO,[468] CO_2,[469] and polyatomic species, benzene,[103,470,471] halogenated benzenes,[103,471,472] hydrocarbons,[465,473] pyridine,[474] ammonia,[137] and N_2O.[469,475] The recent measurements of Brion and Olsen[463] indicate that in noble gases optically forbidden transitions represent an important contribution to threshold excitation. The identification of temporary negative ion states, *i.e.*, molecular negative ions with lifetimes shorter than about 10^{-6} sec, have been discovered in N_2O,[475] benzene,[470,471] ethylene,[470] halogenated benzenes,[471] perfluorocarbons,[122,472] pyridine,[474] and carbon monoxide.[468] Temporary negative ion states have also been detected in fluorinated benzenes.[122] It is further noted[122] that the peak resonance energy decreases approximately linearly with the addition of fluorine to the ring. From this variation of temporary negative ion resonance energy an additive effect upon the molecular electron affinity is suggested. Specifically the addition of fluorine to the ring increases[122] the electron affinity of the molecule by approximately 0.4 eV per fluorine.

The results of other SF_6^- scavenger studies have been summarized and discussed in detail by Christophorou.[10] A comparison of the trapped electron method and other methods with the scavenger technique is also presented.[10]

V. Additional Negative Ion Studies

Not included in this review are studies relating the role

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of negative ions in flames and combustion processes and in gaseous discharges. These topics have been discussed recently.[303,476] In addition the studies of negative ions using the magnetron method are not covered in this review. A complete and detailed discussion has been presented by Page.[209] Furthermore, the excellent work by Christophorou, Compton, and coworkers using electron swarm and beam techniques for negative ion studies has not been reviewed here in detail. A comprehensive and detailed discussion of the many experiments reported has recently been published by Christophorou.[10] Discussions of surface[477-482] and field ionization[483] have been omitted. A number of interesting studies of the formation of negative ions on metallic surfaces have been published.[477-482] The techniques employed have included ion bombardment and thermal methods. The thermal electron attachment method of Wentworth has not been included. A recent summary of the important aspects of this method has been published.[484,485]

VI. Future Studies

The wealth of information on gaseous negative ions is somewhat surprising, yet in several areas where negative ions may be important a complete understanding of the likelihood of ion formation and of the subsequent reactions of negative ions is not established. In concluding this review a few areas of additional negative ion studies will be mentioned.

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Certainly further studies of the reactions of negative ions in organic and inorganic molecular systems will be important. Such studies are vital to an understanding of intrinsic acid-base properties of molecules and ions. Detailed investigations of ion-molecule reactions using icr, flowing afterglow, and tandem mass spectrometric methods will be significant in evaluating gaseous equilibrium constants and thermodynamic quantities. No doubt studies of ion-molecule reactions will clarify the role of negative ions in electrical discharges and in combustion processes.

The use of negative ion reactants in chemical ionization mass spectrometry should prove useful in analytical mass spectrometry. Extension of the EA mass spectrometric method may provide a significant aid in molecular structure elucidation studies. The extension of these studies to inorganic compounds is obvious. Of importance also to analytical applications are investigations of metastable negative ions in unimolecular decomposition reactions and the excess energies which accompany negative ion formation. Further evaluation[10] of the probable role of negative ions in biological systems and in health related problems is certainly of interest.

It is anticipated that the electron affinities of molecules and radicals may be measured with greater accuracy. The laser-icr technique of Brauman[207,208] and coworkers certainly is promising. In addition the method of Hall and coworkers[486-489] involving laser induced detachment accompanied by kinetic energy analysis of the ejected electrons should yield meaningful electron affinities for polyatomic species.

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