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SOME THEORETICAL BASES FOR SELECTION OF MOLECULAR ION PROPELLANTS AND A SURVEY OF MOLECULAR PLASMA COLLISION PROCESSES

by John V. Dugan, Jr.

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • FEBRUARY 1964

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SOME THEORETICAL BASES FOR SELECTION OF MOLECULAR ION PROPELLANTS AND A SURVEY OF MOLECULAR PLASMA COLLISION PROCESSES

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SUMMARY

The advantages of using heavy molecules as propellants for an electron-bombardment ion thrustor are recounted. Fragmentation of molecules under electron impact in the discharge chamber is a serious obstacle to the attainment of a heavy ion beam and is discussed theoretically. The nature of localized chemical bonding in diatomic molecules is explained in detail by use of the familiar potential-energy curves. Polyatomic molecules with their complex energy-state structure are discussed in an analogous manner, and their possible fates under electron impact are enumerated with respect to ionization and dissociation phenomena.

A procedure is included to predict ionization cross sections from atom polarizability values. For sample heavy-molecule propellants, total ionization cross sections should be at least an order of magnitude larger than for the mercury atom.

All collisions of interest in the molecular plasma of the heavy-molecule ion thrustor are discussed including ion-electron recombination and ion-molecule reactions. Relative collision numbers of some discharge encounters have been estimated for representative residence times of the ionic species.

Comparison of molecular bonding types indicates that aromatic organics are the most suitable class of readily available compounds for heavy-molecule-propellant material. Suggestions are made for ultimate selection of likely aromatics, and a quantum-mechanical method is outlined for calculation of the stabilities of promising compounds.

The status of mass spectrometric data on compounds of interest is included, and some necessary fundamental investigations are indicated.

INTRODUCTION

The desirability of operating more efficient, versatile ion thrustors has prompted the study of heavy-molecule propellants (ref. 1). Below specific impulses I_s of 4000 seconds, the efficiency of the mercury ion thrustor drops

rapidly (ref. 2), but it would be advantageous to operate thrustors at lower specific impulses to fulfill certain mission requirements if high efficiency were attainable (ref. 1). Certain molecular species ranging in molecular weight from 500 atomic mass units, two and one-half times the atomic weight of mercury, to several thousand atomic mass units, the upper limit of reasonable availability exclusive of polymeric substances and colloidal particles, may be suitable for attaining lower values of specific impulse at high efficiency.

The process of charging heavy molecules via electron bombardment introduces many problems, especially molecular fragmentation under impact, which has been given some preliminary consideration (ref. 3). This report proposes (1) to consider the nature of these problems, (2) to suggest calculations on a general class of suitable propellants, and (3) to calculate the relative probabilities of various discharge processes.

Fragmentation of molecular species will unavoidably accompany ionization of molecules by electron bombardment. The interactions that occur when 10- to 100-volt electrons collide with large molecules are extremely difficult processes to treat theoretically. Moreover, most molecules of interest have not yet been studied experimentally.

The first section of the report contains an enumeration of the possible electron collision consequences for polyatomic molecules in order to reach some basis for deciding on desirable propellant characteristics. The second section of the report discusses semiempirical methods of molecular quantum mechanics, which can be readily applied to species that appear to have desirable molecular characteristics. These approaches are particularly useful for calculations on aromatic organic molecules, an important class of compounds for propellant consideration.

Ionization cross sections Q_I are measures of the ionization probability for molecular species in the initial bombardment act. Useful correlation methods are available for estimating some of these Q values. New ionic species may be formed in secondary processes in the discharge, such as ion-molecule reactions and multiple inelastic impacts by plasma electrons. Ion-electron recombination might take place sufficiently fast to inhibit net ionization severely. Contributions of all these collision processes will ultimately determine the average mass of the ion beam. The third part of the report consists of an assessment of the relative rates of collision processes

PROPELLANT SELECTION

Early Thrustor Experiments

A few preliminary tests of heavy-molecule ion-propulsion devices have been conducted at the Lewis Research Center. Propellants were initially chosen primarily on the basis of their high molecular weights. Little vapor pressure data were available for those substances in the range of achievable boiler operating temperatures. Significant vapor pressures, however, are necessary to sustain the ion-source discharge. Furthermore, only the presence of strong interatomic links

may ensure survival of a significant fraction of heavy, positively charged species after exposure of the molecule to the various impact processes occurring in the discharge of the ion source.

Thermal Decomposition of Molecules

Molecules and ions may fragment from electron and ion impact or simply because of high temperature. Strengths of chemical bonds between adjacent atoms in molecules and molecular ions are generally at least 2 electron volts, which correspond to temperatures greater than 20,000° K. Thermal decomposition of a molecule or large ion through bond breakage will occur at a particular site along the atomic "chain" only if vibrational energy equal to the bond energy becomes somehow localized in that interatomic link. The likelihood that this event will take place in a thermal equilibrium can be considered proportional to the Boltzmann factor $e^{-E_D/kT}$, where E_D is the bond dissociation energy and k and T denote the Boltzmann constant and absolute temperature, respectively (refs. 4 and 5). The hot filament cathode in the ion chamber is the only region where significant decomposition of neutrals or ions can transpire via thermal decomposition or pyrolysis. The filament temperature at usual emission conditions is ≈2400° K, while other parts of the ion source probably remain about 500° K. Effects of crystalline changes in heating on any other results of decomposition in the boiler region are not considered herein, but it can safely be concluded that thermal decomposition will be insignificant in the discharge region.

Ion Impact on Discharge Surfaces

The final class of fragmenting collision to be mentioned requires a separate series of fundamental experiments. If molecular ions with a temperature of several volts happen to strike surfaces, they may dissociate. However, aromatic ions should efficiently randomize the energy received in collision with a surface, and it is therefore likely that, at the temperatures encountered, this process will be negligible for the compounds of interest. If the molecular species, charged or uncharged, actually "stick" to the surface in a chemisorption process, the fates of these entities could be quite different through dissociation because of atom-to-surface bonding greater than the intramolecular forces.

Molecular Fragmentation by Electron Impact

The most important source of fragmentation is electron impact in the process of ion formation.

In an elastic "billiard-ball" collision where there is no change in internal energy, the electron can only transfer the fraction $(2m_e/M)$ of its kinetic energy to the molecule (where m_e is the electronic mass and M is the molecular mass). The largest value of m_e/M that is of concern is 4×10^{-6}, so that elastic energy transfer is negligible.

Not only do electrons with kinetic energies from 20 to 100 electron volts have some significant probability of causing ionization by collision when passing through a gas, but these electrons are also capable of simultaneously breaking a molecule apart into charged and uncharged fragments. The pattern of this fragmentation process is virtually impossible to predict theoretically for large molecules because of the complicated electronic structure of these many-atom systems. Experimentally, a beam of monoenergetic electrons produces a distribution of charged species of varying mass when incident upon target gas molecules. The form of this distribution of products depends on the variable amounts of kinetic energy transferred inelastically to the target molecules in the individual impacts.

There will probably be two distributions of electrons in the molecular discharge (ref. 6) just as in the mercury thrustor. The fast electrons are those that come directly from the cathode, while the slow electrons are assumed to be either fast electrons which have lost most of their energy through collision, or slow secondaries from ionized neutrals.

It will be assumed throughout this report that the probability that a fast electron with 10 to 100 volts kinetic energy only excites a neutral molecule is on the same order as the probability that such an electron will ionize the molecule. To simplify the theoretical discussion, it is assumed that the chance of such a molecular excitation resulting in dissociation to solely neutral fragments is relatively small for the group of high-energy electrons coming directly from the cathode. This will be true if the upper electronic states of the molecule are not strongly dissociative. This process will not be discussed, although it could be treated with the same type of potential-energy curves adopted to explain ion formation. Neutral fragments formed in such dissociation would be subject to the same collision processes as any other neutrals in the chamber.

Generally, only the higher electronic states of the excited molecules are dissociative. These states could be reached by successive inelastic impacts as well as by one collision, although the time between inelastic impacts is generally large enough to permit radiation of excitation energy. It is further postulated that excited neutrals will not be dissociated to any extent by either fast or slow electrons. Ionization from these excited states is one of the many possible secondary processes. Some mention of the excitation phenomenon is included in the treatment of cross sections and collision frequencies: it is a more important consideration for unstable neutral fragments such as free radicals.

Both charged and uncharged fragments thus have some probability of being ionized and/or dissociated by the relatively fast filament electrons and slow randomized electrons during the interval elapsing between formation and departure from the ion chamber. The residence time of the neutral fragments is governed by a free-molecular-flow process, whereas the ions migrate under the influence of the various potentials in the discharge chamber and depend on the withdrawal field of the accelerator potential for their extraction and eventual acceleration as a charged beam. En route to the exit region of the ion source, all these entities are exposed to a whole variety of collision processes.

Desired Behavior of Heavy-Molecule Propellants

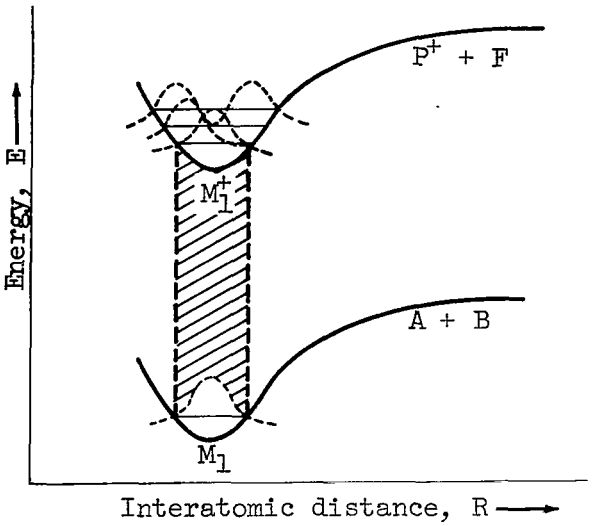
In the light of the fragmentation problems noted, it is instructive to consider the characteristics sought in a heavy-molecule propellant. The density in the ion source is about 10^{12} particles per cubic centimeter with ions, electrons, and neutrals at different temperatures. The ionizing voltages may be 10 to 50 volts; the effective accelerating voltage of interest is in the range from 2500 to 20,000 volts. The specimen in the heavy-molecule discharge will probably be subject to an environment similar to that in the source of the mercury thrustor. The ideal propellant would lose only one electron and suffer no fragmentation while in the ionizer under electron bombardment. Such a molecular entity appears to be completely hypothetical. However, a satisfactory propellant should be capable of supplying mainly heavy ions despite some unavoidable loss of atoms or groups of atoms. Since the interatomic bonds in large molecules are never more than about 5 electron volts (ref. 7), the initial formation of molecular ions is usually unavoidably accompanied by the dissociative production of neutral fragments. Many electrons will deliver some excess energy above the ionization potential of the molecule, which will affect the molecule in a complex fashion. A short discussion of the arrangement of molecular energy levels as related to fragmentation is given in appendix B. A more detailed description of the intricate ionization consequences of electron impact is given in appendix C.

POSSIBLE CONSEQUENCES OF ELECTRON BOMBARDMENT

The possible major consequences of electron bombardment of polyatomic molecules will be outlined in terms of potential energy curves. The discussion includes three different types of the final molecular ion states: completely binding, completely dissociative, and partly dissociative.

Parent Ion Formation

The troughs of the curves in sketches (a) to (c) indicate the degree of molecular binding, and their significance is fully explained in appendix B. In sketch (a), the vertical transition region determined by the turning points of the lower energy curve describes a simple ionization of the parent molecule M_1 to a distribution of excited vibrational states of the upper curve of the parent ion M_1^+. In quantum-mechanical language, the square of the vibrational wave function ψ_v^2 for the simple harmonic oscillator for a specified vibrational quantum number gives the probability of finding the center of mass of the oscillator at a specific point in the particular state. The curves drawn in the various vibrational levels of sketches (a) and (b) are the vibrational ψ_v functions for the initial and final states of the system. The probability of transition between states in the collision process is proportional to $(\int \psi_a \psi_b \, d\tau)^2$, where ψ_a and ψ_b are the vibronic wave functions (product of electronic and vibrational) for the molecular and ionic states, respectively (ref. 8). This integral of $\psi_a \psi_b$ is taken over the volume accessible to the electron $d\tau$ and is known as the overlap integral. Unfortunately, satisfactory

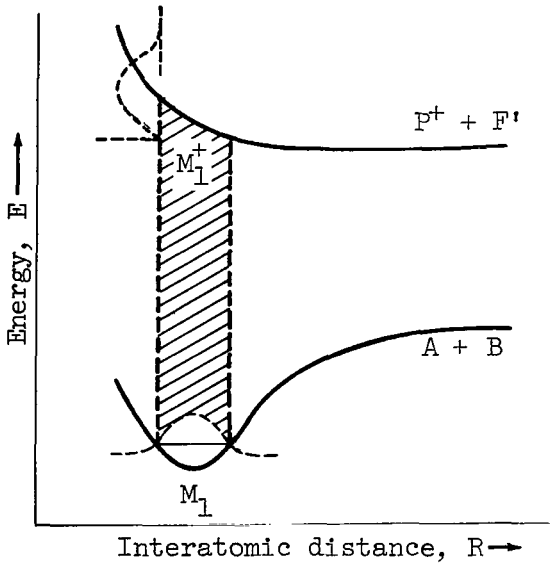


(a) Potential energy curves for molecule and molecular ion with vibrational wave functions (dashed curves).

wave functions cannot usually be written for heavy molecules of interest, so transition probabilities can rarely be predicted theoretically.

Simple Dissociation of Molecular Ions

Sketch (b) illustrates a simple instantaneous dissociation of the molecule

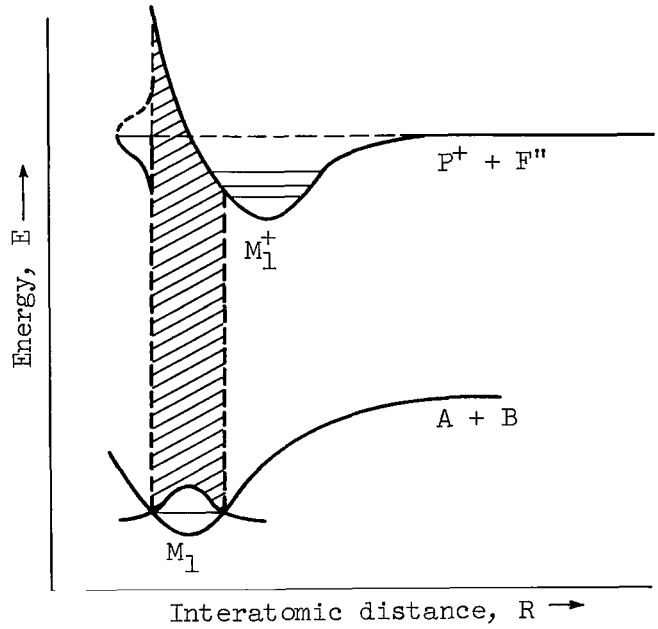


(b) Franck-Condon region for transition to a completely dissociative state of the molecular ion.

M_1 into a primary ion P^+ and a neutral fragment F'. The ratio of the masses of the charged and uncharged segments is a function of the nature of the excited ionic state, which is the upper state of interest. In this instance the dissociative state is completely repulsive, and the reflection of the square of the ground-state wave function of the lower curve illustrates the probability distribution for the initial energy of the fragments (ref. 8). The range of difference in energy between the Franck-Condon intersections (shaded areas explained in appendix B) and the asymptote of the upper state sets the relative energy distribution, mainly kinetic, to be shared by the two fragments. Multiple fragmentations such as $P^+ + F + F'$ are also possible in a single impact.

Combination of Stable Ion Formation and Dissociation

Sketch (c) illustrates a dissociation, but there is also a substantial prob-



(c) Franck-Condon region for transition to a partly dissociative state of the molecular ion.

ability of the formation of stable, vibrationally excited ions. A combination of the reasoning employed in sketches (a) and (b) is sufficient to explain the effects observed from such an impact. The reflected square of the ground-state wave function ψ gives a truncated distribution of energies in the upper state, which determines the range of relative energies of the fragments. The overlap integral of ψ_a and ψ_b again determines the occupation of vibrational states in which the parent molecular ions are to be found.

General Remarks on Fragmentation of Polyatomic Molecules

The diverse interactions of the outer electrons of the asymptotic entities P^+ and F directly determine the nature of the molecular binding in any ionic state. The upper electronic states of the molecular ion, which are reached under impact, can either be the ground or various excited states. Similar nuclear configurations of initial and final molecular states, such as those shown in sketch (a), have large values of the overlap integral and are said to be "strongly coupled" under electron impact. Excited states of the parent molecular ion naturally require more energy to be formed, since bound electrons must be "kicked up" in addition to the energy required to remove the most loosely bound orbital electron.

Useful generalizations can be made about the manner in which certain dissociative processes proceed and the possible distributions of kinetic energies and excited electronic energy among fragments. Multicenter bond breakage, producing more than two fragments, usually gives products with excess internal energy, but one-center breaks do not (ref. 8). In the second case the excess energy is found to be mainly translational energy of the fragments. Prediction of fragmentation in any detail would require a complete analysis of the normal mode vibrations of the intermediate ion involved in dissociation. With the present state of knowledge this would be a completely speculative approach and hardly worthwhile for a large molecule.

Some useful information can be obtained from the values of the lowest potentials at which various ions appear in the mass spectrum, that is, appearance-potential studies and collection-efficiency studies of the resulting charged fragments. Quantum-mechanical description of the activated ionic complex, which is the precursor of the fragment ion, is impossible, and only qualitative guesses can be made in regard to its structure. In addition, energetics of particular bond breakage processes are such that some dissociations actually require molecular ions in highly excited electronic states.

Experimental Results of Impact on Polyatomic Systems

With little refined knowledge available on molecular detail, a priori postulates of the distribution of ion products for experimentally untested molecules are impossible. Prediction of electron impact patterns for as yet untested large molecules must necessarily be gathered from trends in experimental data on similar small molecules (ref. 9). Mass spectrometric studies of molecules give relative intensities of all product ions that are formed in bombardment at a particular electron energy within the limits of instrumental detection. Molecules will "break down" when subjected to electron bombardment in a manner determined by the fashion in which bound electrons are linked to the atomic array. The molecular weight of the fragment, which retains the charge in a $P^+ + F$ type dissociation, will thus depend critically on the type of bonding responsible for the stability of the molecular species. Many tables, called cracking patterns, which contain a list of ions formed and their relative abundances, are available for various chemical compounds, especially hydrocarbons. Heavy inorganic molecules have not been well studied as yet.

COMPARISON OF MOLECULAR BONDING TYPES

Since fragmentation of the propellant by electron impact is a problem in the molecular ion thrustor, it is valuable to investigate the advantages of employing promising compounds that are relatively stable under impact. First, however, the bonding in small molecules will be discussed, and then the special organic bonding will be considered. Aromatic organic bonding is a particularly interesting case.

Diatomic Molecules

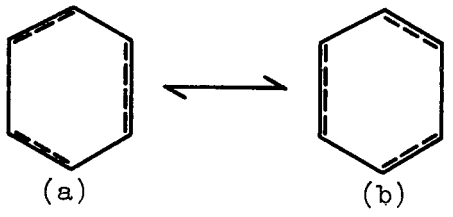
The pairing of electrons with opposite spins from two atoms accounts for the stability of diatomic molecules, such as hydrogen (H_2) and nitrogen (N_2) (ref. 7). These localized electrons, formerly describing a more random motion in the free atoms, are usually the most easily removable electrons in the diatomic molecule and hence are the electrons of interest in the ionization of such molecules.

Aliphatic and Alicyclic Organic Molecules

The concept of electron pairing must be modified to cover the field of carbon chemistry. Localized electron pairs with the concept of directed bonding satisfactorily explain stability of most aliphatic and alicyclic compounds. These are chain and ring compounds in which all carbon atoms have four single bonds, such as C_3H_8, which has the structural formula $CH_3{-}CH_2{-}CH_3$. Complete treatment of bonding in this class involves the inclusion of spin terms of electrons in adjacent bonds and the additional utilization of the concept of equivalent pairing or hybrid bonding. Extended quantum-mechanical discussion of this unusual bonding is beyond the scope of this report (ref. 10).

Aromatic Organic Molecules

Aromatic hydrocarbons such as benzene (C_6H_6) and its derivatives display a further unique behavior. Electrons in the highest bound levels cannot be paired together in any preferential fashion and must be considered as completely delocalized. The six electrons filling the three highest orbitals in the molecule are free to migrate throughout the regular hexagonal ring, which is comprised of the six stably bonded carbon atoms (ref. 11). The resultant so-called resonance structures are depicted in sketch (d) (carbon atoms are at vertices).



(d) Resonating structures for benzene molecule

The actual structure of benzene is a simultaneous superposition of the two structures (a) and (b). The solid-line bonds are formed by stationary electron pairs, but the dashed-line bonds are identical links producing a "streamer" of charge around the ring.

Bonding in Inorganic and Organometallic Compounds

Chemical binding in inorganic molecules generally consists of localized electron pairs with the exception of systems that have some π-electrons. In any case, the π-electron network does not extend over the entire molecule. Since these molecules can have only a partial aromatic character, they will have bonding that is a composite of aliphatic and aromatic bonding. There is no subclass of such compounds that shows any definite trend in enhanced stability among neutral molecules.

Organometallic compounds are molecules composed of metal atoms with attached organic groups. The metal-metal bonds are the strength of the usual inorganic bonds, that is, several volts, while the metal-organic bonds are usually of a polarization type and weaker than the conventional inorganic bonds. The overall bonding is much like that of the aliphatics except where the metal-organic bonds are of a weak π-electron type.

GENERAL MECHANISM OF FRAGMENTATION IN ORGANICS

A general discussion has already been presented of the complicated fragmentation that will accompany ionization of polyatomic molecules, and the changes produced in electronic energy have been considered. Now, a more particular topic comes into consideration: fragmentation behavior in organic compounds.

Energy Randomization Requirements for Ion Stability After Impact

In aliphatic hydrocarbons, the branching of the molecular chain determines the breakdown of the molecule into charged and neutral fragments. Two possible fragmentation paths for $C_3H_8^+$ are:

$$C_3H_8^+ \rightarrow C_3H_6^+ + H_2$$

$$C_3H_8^+ \rightarrow C_2H_5^+ + CH_3$$

Inasmuch as violent movement of adjoining atoms results in dissociation, the yields of various ions will be governed by the capability of the bombarded entity to randomize excess energy and the number of certain bonds available as sinks for the dissipation process. Resonance stabilized aromatic hydrocarbons are not as susceptible to bond disruption as the saturated aliphatics and alicyclics, as shown by electron impact studies (ref. 12). Energy flowing freely between the coupled oscillators allows for rapid migration of energy rather than localization with consequent bond breakage.

Present Status of Electron Impact Studies

Fragmentation patterns for saturated straight and branched chain hydrocarbons have been reported (ref. 8). These compounds have been studied extensively because of obvious industrial interest. There is a more limited amount of data available relating to impact studies on large chain-type unsaturates, for example, 1,3,5-hexatriene ($CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$). Large ring aromatic hydrocarbons are not readily synthesized and have low vapor pressures, so consequently little mass spectral data have been taken on this class of compounds. Recent studies indicate that amino acids will generally have cracking patterns (ref. 13) much like aliphatics unless large aromatic segments are involved. High molecular weight inorganic compounds have been virtually ignored in bombardment investigations.

Fragmentation of Saturated Hydrocarbons

Localization of the paired electronic motion in individual chemical bonds gives rise to normal mode vibrations that generally produce fracture in the molecular ion states. The breakdown of saturated hydrocarbons upon electron impact is such that their distribution of ionic fragmentation products has an average mass to charge ratio M/q much smaller than the singly ionized parent ion. For example, the compound 3-ethyltetracosane (mol. wt. = 367 amu) gives an average ionic mass of less than 40 (ref. 12). Multiple electron impacts upon parent ions and neutral fragments can only serve to dissociate molecular entities to an even greater degree. In view of this combined behavior, the aliphatic and alicyclic saturated hydrocarbons are not promising as propellants for the heavy-molecule thrustor. The fragmentation patterns of polymeric substances should parallel those of the saturated hydrocarbons unless there is considerable cross-linking of the molecular chain. Moreover, the sublimation of the polymer layers will give a distribution of sizes of neutrals even before bombardment or charging.

Fragmentation of Unsaturated Hydrocarbons

Alternating double-bond compounds, both straight chain polyenes and the ring-type unsaturated class of aromatic compounds, offer the most promise for molecular stability and high average molecular weight of product ions from the discharge. The aromatic molecules are generally more stable than chain-type polyenes of the same molecular weight because the 120° angle between the adjoining carbons in the hexagonal aromatic ring enhances the stability of the benzene-type structures (ref. 10). The unique hybrid bonding of sp^2 equivalent orbitals acquires its most comfortable configuration with minimum bond strain in the planar benzene arrangement (ref. 11). Such a situation provides maximum bonding energy for the atoms.

Behavior of Inorganics Under Impact

There is no reason to believe that inorganic molecules should be unusually stable under impact. Those molecules with only a few constituent atoms offer a

narrow choice of paths for fragmentation. Many-atom systems will break down much like aliphatics and alicyclics because of the localized bonding (ref. 12). If the preferred dissociative mode of the predominant molecular ion corresponds to formation of a large ion and a small neutral fragment, the problem of efficient beam collection remains. The residence time of primary ions must be minimized to extract a satisfactory amount of ions from the chamber. Organometallic compounds should generally fragment like aliphatics because of normal localized bonds and weaker polarization bonds between organic groups and metal atoms (ref. 14). There is no straightforward approach to obtaining a promising inorganic or organometallic compound, since no subclass of these compounds displays aromatic behavior. However, similar atom systems such as the selenium octamer Se_8 and SnI_4 could have unique fragmentation patterns under impact because of symmetry.

POSSIBLE EMPLOYMENT OF AROMATIC PROPELLANTS

Since the aromatic compounds appear to be the most promising propellants, it would appear profitable to investigate specific molecules.

Ring Systems and Delocalization Energy

Benzene, the single-ring aromatic, is the basic unit from which many polyring systems are synthesized. Generally, the smaller polyring compounds behave much like benzene upon electron bombardment. The electronic characteristics of benzene have been well studied and satisfactorily explained via experiment (ref. 15). Fused polyring systems have not been investigated in detail past anthracene, the three-ring molecule whose mass spectra have been reported for bombardment with 70-volt electrons (ref. 16). These molecules give parent ions whose structures usually resemble those of the neutral molecules. The quantitative degree of stability for aromatics can be expressed in terms of the delocalization energy associated with the mobile π-electrons (ref. 10). The delocalization energy can be defined as the calculated additional binding energy that results from delocalization of electrons originally constrained to isolated double bonds. This energy value oscillates somewhat on a per-electron basis on going from C_6H_6 to $C_{14}H_{10}$ and through the larger ring compounds. The delocalization energies for some aromatic hydrocarbons are given in table I. Nonbenzenoid type aromatics, whose ring units have more or less than six carbon atoms, have been excluded from consideration because they generally have lower delocalization energies than the benzene compounds.

Two General Classes of Likely Heavy Molecules

The preceding discussion indicates that high-molecular-weight aromatics, or aromatic derivatives, would be most suitable as heavy-molecule propellants. Large polyring compounds with molecular weights greater than 400 atomic mass units could be used. Alternatively, compounds of high molecular weight, but composed of only a few rings, may be prepared chemically by the substitution of heavy atoms for the hydrogens on the component rings. However, the stability of the latter group is questionable.

Preparation of Large Polyring Systems - "Aromaticity" Principle

The usefulness of polyring compounds can be assessed by extension of molecular fragmentation studies to specially prepared polyring molecules. These electron impact tests have been initiated (ref. 2), and preliminary results include the qualitative nature of the molecular cracking patterns, some of which can be theoretically explained on the basis of the aromaticity principle (ref. 17). This principle has been satisfactorily employed to explain the stability of many molecules in the gas phase and molecular ions in the solution. The principle states that stable electron configurations exist for aromatic molecular structures when they have $(4n + 2)$ π-electrons (ref. 17). The concept has a theoretical basis in the molecular orbital theory of chemical bonding. The ground-state energy level in this electron pairing scheme is nondegenerate and accommodates only two electrons. All other electronic levels are considered filled if occupied by four electrons, and these orbitals are designated doubly degenerate.

There are limitations to the strict application of the aromaticity criterion for molecular stability, both among neutrals and molecular ions. For example, the pyrene molecule with 16 π-electrons does not fulfill the $(4n + 2)$ requirement, and yet it is stable. Symmetric aromatics, unchanged by reflection in the plane normal to the rings, have an even number of electrons, so their singly charged ions cannot have $(4n + 2)$ electrons; however, doubly charged ions with $(4n + 2)$ π-electrons may be desirable impact products. Since formation of doubly charged ions is relatively improbable, the desirability of ions with $(4n + 2)$ π-electrons suggests the use of asymmetric molecules that have $(4n + 3)$ π-electrons, since their parent ions may be unusually stable. Ovalene, a stable compound of 13 rings with 32 π-electrons, could be a promising propellant. However, it has yet to be subjected to electron impact at conventional thrustor ionizing voltages.

Preparation of the Halogenated Derivatives of Polyring Systems

The usefulness of heavy-atom substituted polyring compounds can be estimated by considering the effects of replacing a ring hydrogen with a halogen atom. Such a substitution will alter the electronic behavior and associated chemical properties of the benzene ring. Halogen atoms such as bromine and iodine are preferred for substitution, since they not only bind stably to ring systems but also have much higher molecular weights than other group choices such as hydroxyl (OH), nitro (NO_2), amino (NH_2), and so forth. The electronic condition of the attaching group is critical in predicting the effects of chemical substitution on the ring (ref. 15). One class of attaching groups withdraws negative charge from the ring, and another class provides an additional electronic charge. In the substitution reaction, the former type (electrophilic) seeks sites of high electron density, while the latter (nucleophilic) prefers the ring locations of lowest electron density. The presence of additional halogens on the ring more drastically alters the characteristics of the π-electron skeleton, that is, delocalization energy and accompanying ring stability.

Iodine (at. wt., 127) would be the preferred halogen atom for substitution. It is considerably heavier than the next number of this electronegative family,

bromine (at. wt., 80). However, each halogen will bind to the ring to a degree dependent upon its electron affinity. This quantity is roughly proportional to the exothermicity of the gaseous reaction, $X + e^- \rightarrow X^-$. The electron affinities of bromine and iodine are 3.55 and 3.30 electron volts, respectively, and therefore bromine will bind more stably to the ring (ref. 10).

Preparation of stable molecules in the range of desired molecular weight will be difficult, but it is an encouraging fact that certain monohalogenations proceed more rapidly with larger ring systems than they do with benzene (refs. 17 and 18). The methods available in synthetic organic chemistry assure the preparation of the compounds of interest. The important question that remains, however, is whether a polysubstituted compound and its ions would be sufficiently stable to provide a heavy ion beam.

Since polyhalogenated benzenes, for example, tetrabromobenzene, have been prepared and are thermally stable, it is possible that extensive halogenation will be no problem. It seems likely that polyring structures such as anthracene could accommodate 6 to 10 halogens, although the reaction yield of these molecules might be low. Steric effects will undoubtedly limit the maximum number of halogens, since large atoms tend to overlap, and the mutual repulsion of their electron clouds strains the ring conformation (ref. 15). The method to be employed for calculating molecular stability is outlined in appendix D.

IONIZATION CROSS SECTIONS

Fundamental studies must be undertaken to obtain the mass spectra of any large molecules that show promise as heavy-molecule propellants. The relative amounts of ions eventually constituting the beam will be indirectly determined by the cross sections for ionization at the bombarding electron energy. The ionizing voltages for bombarding electrons in these fundamental studies should be those required for a stable thrustor discharge as determined experimentally. The cross section topic will now be discussed in some detail and will ultimately be related to the probability of formation of the various charged species in the discharge.

The probability of obtaining ions by impact is proportional to the total molecular ionization cross section Q_T, which is made up of the cross sections for formation Q_i of particular product ions.

These ionization cross sections Q_i are measures of the "effective" areas that the negative charge clouds of molecules present to an incident electron of some given energy for formation of a particular product ion. This "size" is indicative of the ease of removal of electrons whose binding energy or ionization potential is equal to or less than the kinetic energy of the impacting electron. The magnitude of Q_i is consequently critically dependent on the energy of the incident electron, and plots of this dependence are quite valuable (ref. 19).

Reliable theoretical predictions of cross section dependencies for the formation of specific ions are not readily performed. A complete quantum-mechanical treatment of collisions in molecular systems requires exact wave functions, which

at least describe the behavior of the most easily removable electrons in the polyatomic framework. Such necessary wave functions are known exactly only for the hydrogen atom. It is extremely difficult to obtain them because an exact potential for a many-electron system cannot be constructed. Such a potential is required for the molecular Hamiltonian $H\psi = E\psi = (K + V)\psi$, where K and V are the total kinetic and potential energies, respectively. Another Hamiltonian operator, needed to describe the interaction of the two systems (incident electron and atom) between initial and final states ψ_i and ψ_f, is even less well known and can at best be only crudely approximated (ref. 20).

The theoretical Born approximation describes atomic scattering of elèctrons but is valid only when the amount of energy lost in the collision can be neglected with respect to the kinetic energy of the electron previous to collision (ref. 19), which is not a case of interest for this report. When validly employed, this approximation gives a virtually exact interaction potential. Other theoretical methods, such as the partial wave scattering treatment (ref. 21), would be applicable for low-energy interactions, if the molecular wave functions were known.

Ionization Cross Section Estimates

Since useful theoretical approaches are presently not available, experimental semiempirical methods must be relied on.

Values of the total cross section for ionization Q_T have been obtained for many molecules via mass spectrometer experiments (refs. 22 and 23). The values given are the sums of the cross sections for all possible routes of ion formation at a constant electron-bombardment energy, that is, $Q_T = \sum_i Q_i$, where the previously introduced Q_i is the ionization cross section for a specific product ion. The percentage of total ionization attributed to the most abundant ion will, however, vary over a wide range depending on the type of molecule and the incident electron energy. The values of Q_i for a propellant molecule will determine the initial amount of ions of varying mass and charge that is formed in the discharge before the occurrence of secondary processes or multiple impacts by the free electrons. For a steady-state description of the discharge, it is obviously quite important also to know the ionization cross sections for both neutral and charged fragments. If all these Q_i values are known, the distribution of ions arriving at the accelerator after all possible collision processes have taken place can be predicted in principle. It is possible to estimate total cross sections since there is good evidence that the Q_T value at a fixed bombardment energy is primarily a function of α, the polarizability of the molecule.

Studies on Molecular Radicals and Formation of Doubly Charged Ions

Unfortunately, many large molecules under consideration as potential propellants for the heavy-molecule thrustor have not yet been subjected to electron im-

pact in low-pressure (10^{-6} mm Hg) mass spectrometer experiments. Smaller molecular fragments, such as C_2H_4, have been relatively well studied, and Q_T values have been reported for species in at least two independent investigations (refs. 22 and 23). However, organic free radicals, entities with no net charge but in a condition of unsatisfied valence, cannot be retained for sufficiently long periods to make extensive studies. Very little data are available on such fragments of any more molecular complexity than the methyl ($CH_3\cdot$) or phenyl ($C_6H_5\cdot$) radicals. There are virtually no electron impact data on molecular ions.

Experimental methods whose employment will overcome this lack of satisfactory cross section data are currently available. Flash photolysis techniques employing high-intensity, pulsed ultraviolet and visible light do give free radicals in abundance and are a source of spectroscopic data. Double mass spectrometers, utilizing two ion chambers, one for ion formation via bombardment and the other for scattering of electrons by only the ions, are necessary to obtain ionization cross sections for molecular ions. Detection of significant product ion currents is a problem, and only the advent of a-c modulated cross-beam techniques offers hope of satisfactory measurements (ref. 24).

Of necessity, semiempirical treatments, such as those of reference 22 or 23, must be employed in the absence of experimental data to estimate the Q_T values for all neutrals including free radicals. Use of these approaches is confined to correlating Q_T values with effective atomic radii or atomic polarizability for a specific electron-bombardment energy. This polarizability method cannot be confidently applied to compute Q_T values for charged molecular species because of lack of information on molecular ions. Molecular ion fields naturally extend to larger distances than do the fields of the neutral species, and, if the ionization potential in the process $M_1^+ + e^- \rightarrow M_1^{++} + 2e^-$ is nearly equal to the molecular ionization potential, it is expected that Q_T will be at least as large as the predicted values for the parent molecule (ref. 25).

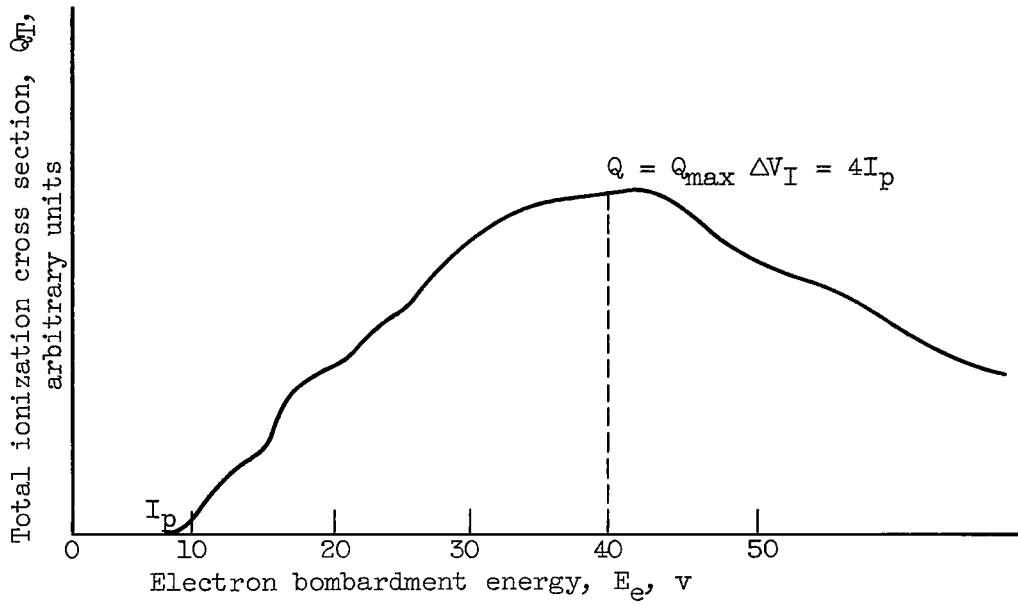
Ionization Cross Section Curves

The general energy dependence of Q_T for simple polyatomic molecules resembles the case shown in sketch (e). Many more ions are possible as products from polyatomic systems that can arise from atoms in the same range of bombardment energy. The various ions resulting from the parent molecular ion via dissociation will display roughly the same $Q_i = f(E_e)$ dependence from their threshold point or characteristic appearance potential. In some narrow region of ionizing voltage just above the onset of ion current, it may be possible to obtain sufficient heavy ions without excessive breakup.

It should not be expected that the entire ion beam current will be due to the parent ion (i.e., the molecule divested of one electron with no loss of component atoms) over the range of ionizing voltage ΔV_I.

Values of Q_i

Magnitudes of Q_i for large molecules may be 100 times Q_{max}, the maximum ionization cross section for the mercury atom. At 75 electron volts, the total ionization cross section for mercury reaches its maximum of about 7×10^{-16} square centimeter (ref. 26). Total cross sections for some small polyatomic molecules studied in the mass spectrometer are as much as five times as large at this ionizing energy (ref. 23). Larger and heavier polyatomic molecules would be expected to have even larger cross sections. It is only possible to estimate Q_i near the threshold, since the initial slope of the curve of Q_i against E_e



(e) Curve illustrating general form of dependence of cross section on electron energy.

will determine Q_i in the area of low ionizing energy. The following two methods are available for predicting $Q_T = \sum_i Q_i$ to within 10 to 15 percent of observed values (refs. 22 and 23).

Method of Atomic Additivity

The authors of reference 22 have adopted an additivity principle for atomic contributions to calculate Q_T for organic and inorganic molecules (ref. 22). Their work demonstrates that within a class of compounds it can be safely assumed that Q_T for a molecule is the sum of the cross sections of the constituent atoms obtained from the mean-square electronic radii of atomic electrons. Values calculated for organic molecules generally fall within 15 percent of the experimental values, but it is not clear what interpretation should be made of experimental disagreement.

Semiempirical Method

The authors of reference 23 have semiempirically related Q_T to the known molecular polarizability at a constant electron energy. The mean molecular polarizability $\bar{\alpha}$ is a measure of the deformability of the electron cloud or the ease with which positive and negative charge centers can be separated. Theoretically, the cross section can be related to $\bar{\alpha}$ through a quantum-mechanical matrix element, so the connection between the two quantities is not unexpected. Experimental polarizabilities may be written in terms of the polarization P, which is obtained from refraction studies. The following expression is utilized:

$$P = \frac{4}{3}\pi N_o \bar{\alpha} = \frac{n_\infty^2 - 1}{n_\infty^2 + 2}\frac{MW}{\rho} = P_E + P_A$$

where MW is the gram molecular weight, ρ the density, N_o the Avogadro number, n_∞ the index of refraction at infinite wavelength, P_E the electronic polarization, and P_A the atomic polarization. For practical reasons, data are obtained from the visible rather than the infrared (essentially infinite wavelength) spectral region. Since visible light displaces only the outer electrons, thereby inducing a dipole moment, only P_E contributes to the measured P. The motion of the ion core is unaffected by visible light, so experimentally P_A is zero. Actually, the expected P_A with infrared light would be a few percent of the observed P_E. Group polarizabilities can be added to give $\bar{\alpha}$ for all types of hydrocarbons. Tabulated values of α are available for (CH_2), (CH_3), (C=H) (aliphatic), (C–H) (aromatic), and numerous other groups. The empirical relation between cross section and polarizability (ref. 23) is $Q_T = A\bar{\alpha}$; the constant $A = 1.8\times10^8$ per centimeter for 70-volt electrons. This value is obtained from a fitted plot of 20 substances. The value of the constant can only be estimated at the lower electron energies required for thrustor operation, that is, 15 to 20 volts. Allowing for nearly the same A value to describe the dependence of Q_T on $\bar{\alpha}$ at low bombardment energies yields the values of predicted Q_T in the range from 50 to 200×10^{-16} square centimeters. This value suggests a greatly enhanced probability of ion formation for certain molecular propellants over that of the atomic propellants. It must be kept in mind that extrapolation of the $Q = \bar{\alpha}$ relation to ionizing energies below 70 electron volts still predicts the total ionization cross section, and, since the pattern of the molecular ion dissociation is highly specific, the Q_i for the parent ion can be much less than Q_T.

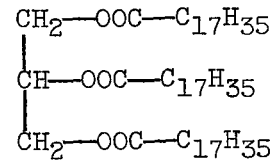
Polarizabilities have been computed for some compounds already investigated as possible thrustor propellants. An $\bar{\alpha}$ value for SnI_4 of 3.25×10^{-23} cubic centimeter is given in reference 27. For small polyatomic molecules the cross section at 20 volts can be taken as 0.75 of the Q_T for 70 volts from the general form of the curves for Q_T against E_e. The new A is then

$$A' = 0.75\times1.8\times10^8 \text{ per centimeter} = 1.35\times10^8 \text{ per centimeter}$$

and

$$Q_T(SnI_4) = A'\bar{\alpha} = 44\times10^{-16} \text{ square centimeter}$$

The principle of the additivity of group polarizabilities was utilized to get $\bar{\alpha}$ for glycerine tristearate, which has the following structural formula:



For glycerine tristearate there are three CH_3 groups: ($\bar{\alpha} = 22.6\times10^{-25}$ cm^3), 51 CH_2 groups ($\bar{\alpha} = 18.2\times10^{-25}$ cm^3), and three $\left(-\overset{O}{\overset{\|}{C}}-O-\right)$ groups ($\bar{\alpha} = 30.0\times10^{-25}$ cm^3). The total $\bar{\alpha} = 1.08\times10^{-22}$ cubic centimeter, so that Q_T equals 146×10^{-16} square centimeter (1.35×10^{8} per centimeter times 1.08×10^{-22} cubic centimeter), which again is a very large cross section value.

General Remarks on Aromatics

Some general remarks can be made about the nature of dissociation processes for large molecules.

Loss of small fragments, such as H_2, from large molecular ions is a favored process because of a relatively low energy expenditure (ref. 8). An abundance of heavy ions for beam acceleration could still result, despite production of numerous ionic products, if important dissociative paths corresponded to the loss of small groups of neutrals. In the molecular weight range of interest among organic compounds (i.e., 300 to 1000 amu), it is impossible to predict an ionic breakdown pattern quantitatively. Extended conjugated structures (alternating single and double bonds) do seem the most suitable propellants, qualitatively, from inspection of their breakdown patterns (ref. 9). Ionization potentials for these compounds range from 5 to 10 electron volts, so extrapolations of the visible and ultraviolet excitation spectra may supply information on unknown ionization potentials. Although these molecules have not been thoroughly investigated in the mass spectrometer, much data are available concerning their physical properties.

DISCUSSION OF VARIOUS COLLISIONS IN DISCHARGE

A complete analysis of discharge phenomena in the molecular ion rocket must include simple molecular excitation and all possible secondary effects for any molecular propellant. Excitation of molecules, molecular ions, and all types of

charged and neutral fragments will have interrelated effects in the discharge. The previously mentioned interstate crossings (appendix B) also follow collisional excitation and will generally occur before a second impact or a radiative transition. In regard to the radiative transition, emission of a light quantum between certain states of large molecules is dependent on certain selection rules. The description of these emission phenomena is exceedingly complicated even in diatomic molecules (ref. 28), and analysis of the spectra of large molecules is clearly a formidable task. This situation precludes any reliable prediction of the total excitation cross section from optical spectra.

It is an empirical fact that for high-pressure molecular gases, which are subjected to irradiation by high-energy charged particles, X-rays or γ-rays, there is an energy absorption equivalent to 32.5 electron volts required on the average to produce an ion pair (ref. 29). Since ionization potentials are generally under 10 electron volts for the molecules of interest, it is concluded that the remaining 20 electron volts are used up in several excitations (refs. 29 and 30). This rule of thumb must be applied with care to the case of impacts due to plasma electrons, but it seems fairly certain that there are at least as many excitations as there are ionizations.

The average energy required to produce an ion increases at lower average particle energies because of the increasing ratio of excitation to ionization, and this trend may set a lower limit on electron-volt per ion values.

Collision Frequencies

The probability of occurrence of secondary events can be estimated through the cross sections for collisions of various species after ions have been formed during initial bombardment.

Collision frequencies ν_{Mj} and ν_{jM} are defined as equal to $N_j Q_{Mj} v_{Mj}$ and $N_M Q_{jM} v_{jM}$, respectively, where $Q_{Mj} = Q_{jM}$ and $v_{Mj} = v_{jM}$. For the electron neutral collisions, the relative velocity of the pair is the velocity of the electron. In electron-neutral inelastic collision the Q_{eM} is $Q_T + Q_{ex}$, where Q_{ex} is the total molecular excitation cross section and Q_T has been defined previously. This Q_{eM} accounts for total ionization and excitation and is characteristically less than Q_{iM} the ion-molecule collision cross section. The electron velocity to be chosen for a collision frequency calculation, however, is at least

$$v_e = \left(\frac{2E_p}{m_e}\right)^{1/2} \qquad \text{cm/sec}$$

where E_p is the first excitation potential of the molecule and by definition has a value less than the first ionization potential. The lower limit to v_e for an inelastic molecule-electron collision is about 2×10^8 centimeters per second with $N_e = 10^{11}$ per cubic centimeter plus $Q_{eM} = 10^{-14}$ square centimeter; so

$\nu_{Me} = 10^{11} \cdot 10^{-14} \cdot 2\times10^{8} = 2\times10^{5}$ per second. This value of ν_{Me} when multiplied by a residence time for a neutral of less than 10^{-3} second (ref. 31) gives as many as 200 inelastic collisions per neutral, some of which certainly result in fragmentation. Since the v_e value is rather high, it would seem advantageous to lower it, but the velocities of electrons tend to remain this order of magnitude in these low-density molecular plasmas. Despite the somewhat rough choices of values, these figures again suggest that the residence time of neutral species in the discharge (which hopefully became heavy ions in one of the inelastic collisions) should be reduced if possible.

Ion-Molecule Collision Frequencies

The collision frequency for inelastic ion-neutral and neutral-neutral collisions will be less than inelastic electron-ion and electron-neutral events because the electron velocity is relatively high; that is, $v_e \gg v_i > v_M$. In experimental plasmas, fractional ionization of about 10 percent is commonly achieved so it is a good approximation to, for example, $N_e = N_i \approx 10^{-1} N_M$, where N_e, N_i, and N_M are the electron, ion, and neutral number densities, respectively. Pressures in the ionization chamber are as high as 10^{-3} millimeter of mercury (ref. 32), and the neutral density at that pressure combined with a representative ion-neutral collision cross section of 10^{-13} square centimeter gives an order of magnitude $\nu_{iM} = 10^{12}$ per cubic centimeter times 10^{-13} square centimeter times 5×10^{4} centimeters per second $= 5\times10^{3}$ per second for each ion. For a typical ion residence time of 5×10^{-4} second (ref. 33) there are 2.5 collisions. It appears that molecule-ion collisions will not be important in the discharge in view of the relatively large ν_{Me} values compared with

$$\nu_{Mi} = \frac{N_i}{N_M} \nu_{iM}$$

where the mean ion residence time is taken to be one-half that of the neutral residence time.

Ion-Molecule Reactions

The consequences of collision between ions and neutrals will be very efficient ion-molecule reactions in which every spiraling collision is a reaction. These encounters will be governed by the ion-induced dipole potential $\varphi(r) = -\bar{\alpha}e^2/2r^4$ where r is the distance between molecule and ion, and $\bar{\alpha}$ has been defined previously. The microscopic cross section for ion-molecule reactions can be written as

$$Q_{iM} = \left(\frac{4\bar{\alpha}q^2}{m}\right)^{1/2} \frac{\pi}{v_{iM}}$$

where q is the unit electron charge, M is the reduced mass, and v_{iM} is the relative velocity of the ion-molecule pair. Large polarizabilities at relatively low velocities mean large reaction cross sections, for example, $Q_{iM} > 10^{3}$ square angströms $= 10^{-13}$ square centimeter (ref. 34). These reactions could affect the

escape rate of primary and secondary ions. The ionic mobility in an effective field is inversely dependent on Q_d, the diffusion cross section, which is essentially the macroscopic average of Q_{iM} over the velocity distribution (ref. 35). Diffusion is a volume process only slightly affected by penetration of the accelerating field into the ion chamber. This field withdraws ions from a small volume near the discharge screen (ref. 32). Elastic collisions of electrons with both ions and molecules are of concern in one aspect. The ions scatter electrons over a sphere of Debye radius, and these coulombic encounters determine the plasma conductivity at these low pressures.

Electron-Ion Recombination

Certain collisions between electrons and ions will result in mutual charge neutralization rather than further ionization or excitation.

The magnitude of recombination can be assessed first by disregarding pure radiative recombination $M^+ + e^- \rightarrow M' + (hw/2\pi)$ (ref. 36), where w is the frequency of the emitted light in radians per second and h is the Planck constant. It is shown in reference 35 that the main recombination mechanism is $M^+ + e^- + e^- \rightarrow M' + e^-$. This equation describes an event wherein one free electron gives up most of its kinetic energy to another electron, and the resulting slow electron is captured into some excited electronic level of the molecule without emission. Dissociative recombination, whereby the molecular ion breaks up as it captures an electron, is a probable variation of the recombination mechanism but need not be discussed separately. An expression has been derived in reference 36 for the recombination coefficient γ of a proton-electron plasma as a function of electron temperature and electron (ion) number density in the range $N_e = 10^9$ to 10^{13} particles per centimeter. If the recombination coefficient γ is 10^{-10} cubic centimeter per second for the highly ionized, relatively low pressure gas, the recombination rate

$$R_{rec} = -\frac{dN_e}{dt} = \gamma(N_e)^2 = 10^{-10}(10^{11})^2 = 10^{12}\ \text{cm}^{-3}\ \text{sec}^{-1}$$

for a 1-electron-volt plasma (ref. 6), which corresponds to a temperature T_e of 11,600° K. The associated frequency factor for recombination is

$$\nu_{rec} = \frac{R_{rec}}{N_e} = \frac{10^{12}}{10^{11}} = 10^1\ \text{sec}^{-1}$$

Electron temperatures will undoubtedly be lower for these molecular plasmas than for the mercury discharges because of additional energy sinks in vibrational and rotational degrees of freedom and closely arranged electronic states. The γ value for heavy molecular ions may be very large and might give a recombination rate larger than the ionization rate, and consequently it may be difficult to sustain a discharge.

It should be noted that the slow or low-velocity electrons may have a Maxwellian energy distribution around a temperature T_e of at most several volts, although the ionizing voltage ΔV_I for operation may be from 20 to 75 volts.

PRIMARY ION SPECTRUM WITH SAMPLE PROPELLANT RECOMBINATION PRODUCTS

The initial distribution of molecular ions and recombination reactions of these ions determine the state of the plasma period to the occurrence of secondary impacts.

The primary ion spectrum for anthracene is given in table II (ref. 16). The electron energy is higher than what would be used in an electron-bombardment thrustor and undoubtedly produces more fragmentation. From these data, probable secondary recombination processes can be deduced for ionic species excluding electron impact (table III). Nevertheless, these two tables, combined with neutral fragment bombardment data, should furnish some general background for a sample survey of discharge phenomena in a hypothetical ion source where all molecular entities suffer an average of only one collision with electrons and none with ions. It should be noted that the discharge phenomena are quite complicated and that processes aside from electron impact give rise to new products that only serve to make treatment of the system more difficult. The detailed effects of all secondary processes, which have been outlined, must be included for the complete description of the plasma and the desired estimate of ion beam composition (i.e., M/q value). Primary ions that leave the discharge and recombine preferentially with slow electrons have a high probability of dissociating, giving rise to two or more neutral fragments (ref. 37). Negative ion states of the molecule have been disregarded throughout the study, although the presence of halogens in molecular systems may render that approximation invalid (ref. 38). Some investigators have reported negative ion concentration of atomic halogen of the order of positive ion concentrations in discharge columns (ref. 39). Free radicals will be the predominant neutral fragment products of dissociative recombination. All these entities can suffer inelastic collisions with electrons in transit. Reactions between molecular ions and molecules are also ignored in the construction of table II. These reactions will produce an entire spectrum of secondary ion products.

CONCLUDING REMARKS

Extensive fundamental experimentation is clearly required for any understanding of the ionization chamber processes in heavy-molecule thrustor systems. Large polyring aromatic compounds, or smaller halogenated derivatives, should exhibit the most desirable molecular characteristics of known compounds as heavy-molecule propellants. Minimum fragmentation should occur in the ion source for these species. The possibility of preparation of new compounds with exotic bonding has not yet been scrutinized to any extent. Residence times of all species in the discharge throughout bombardment are the most critical parameters in the determination of ion beam composition and may affect the design of the ion source. For example, the electron bombardment source as conventionally designed

(ref. 2) has ion residence times that are long enough for significant fragmentation of even an "ideal" propellant to occur. Reduction of these residence times tends to favor efficient production of heavy ion beams.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, September 18, 1963

APPENDIX A

SYMBOLS

C_{rj} coefficient of rth atomic orbital in j^{th} molecular orbital

D representative atomic dimension

E total energy of molecular system, ev

E_e electronic bombardment energy, ev

E_D molecular bond dissociation energy, ev

E_j calculated quantum-mechanical energy for molecular ground state

E_o actual ground-state energy of molecule, ev

E_p first molecular excitation potential, ev

H Hamiltonian total energy operator

H_{rr} coulombic energy integral of the rth atomic orbital

H_{rs} resonance energy integral between r^{th} and s^{th} atomic orbitals

h Planck constant, 4.1×10^{-15} (ev)(sec)

h_1 adjustment factor for heteroatomic coulombic energy

I_m minimum ionization potential, ev

I_s specific impulse, sec

K kinetic energy, ev

k Boltzmann constant, 9.1×10^{-5} (ev)/(molecule)(^{o}K)

k_1 adjustment factor for heteroatomic resonance energy

M molecular mass

m_e electronic mass

N_e electron number density, particles/cm^3

N_i ion number density (N_e), particles/cm^3

N_j	number density of jth species, particles/cm^3
N_M	neutral number density, particles/cm^3
N_o	Avogardro number, 6.023×10^{23} molecules, $(g\text{-mole})^{-1}$
n	number of π-electrons
n_∞	index of refraction at infinite wavelength
Q_{eM}	electron-molecule collision cross section (same as Q_{Me}), cm^2
Q_{ex}	total molecular excitation cross section, cm^2
Q_i	cross section for formation of particular ionic species, cm^2
Q_{im}	ion-molecule collision cross section (same as Q_{Mi}), cm^2
Q_T	total ionization cross section, cm^2
Q_{Mj}, Q_{jM}	collision cross section of molecule with j^{th} species, cm^2
q	unit of electronic charge, 4.8×10^{-10} esu
R	interatomic distance
R_{rec}	recombination rate
S_{rs}	overlap integral between atomic orbitals r and s
T	absolute temperature, ^oK
T_e	electron temperature, ev
V	potential energy, ev
V_I	accelerating voltage
ΔV_I	anode-cathode potential difference; effective ionizing voltage
v	vibrational quantum number
v_e	velocity of incident electron, cm/sec
v_{eM}	equal to electron velocity, cm/sec
v_{jM}	velocity of jth species relative to neutral molecule, cm/sec
v_{Mj}	velocity of neutral molecule relative to j^{th} species taken equal to v_{jM}, cm/sec

α	molecular polarizability, cm^3
$\bar{\alpha}$	mean molecular polarizability, cm^3
α_o	coulombic integral for carbon 2p atomic orbital
α_{rr}	coulombic integral for r^{th} atomic orbital
α_1	coulombic integral for substituted atomic orbital
β_o	resonance integral between carbon 2p atomic orbitals
β_{rs}	resonance integral between atomic orbitals r and s
β_1	resonance integral between carbon 2p atomic orbital and substituted atomic orbital
γ	recombination coefficient, cm^3/sec
ν_{iM}	collision frequency of ion with molecules, sec^{-1}
ν_{jM}	collision frequency of jth species with molecules, sec^{-1}
ν_{Me}	collision frequency of molecule with electrons, sec^{-1}
ν_{Mi}	collision frequency of molecule with ion, sec^{-1}
ν_{Mj}	collision frequency of molecule with j^{th} species, sec^{-1}
$d\tau$	volume element for electron
τ_c	characteristic time
$\varphi(r)$	ion molecule potential function
φ_r	wave function of rth atomic orbital
φ_s	wave function of sth atomic orbital
ψ	total molecular wave function
ψ_a	final-state molecular wave function of state a (vibronic)
ψ_b	final-state molecular wave function of state b (vibronic)
ψ_f	final-state molecular wave function
ψ_i	initial-state molecular wave function
ψ_v	vibrational wave function

APPENDIX B

DESCRIPTION OF MOLECULAR ENERGY STATES

To discuss the problem of fragmentation of molecules by impact, it is first necessary to describe the arrangement of the various molecular energy states.

Electronic States of Molecules

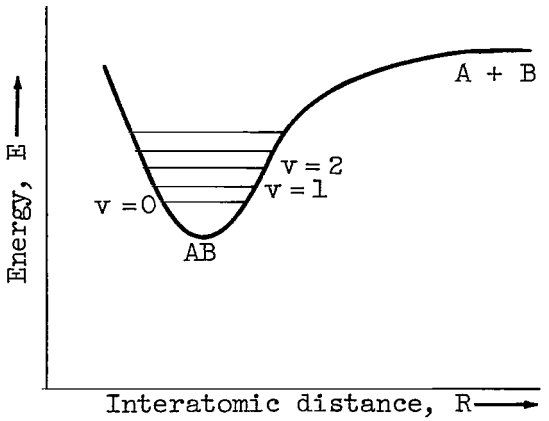
Since many different electrons in polyatomic molecules have similar excitation energies, there is a vast number of densely yet discretely arranged electronic energy levels extending from very near the molecular ground state to its ionization continuum. Singly and doubly charged ions of the parent molecule have levels similarly distributed above their lowest energy states. The ground-state levels of these ions correspond to one and two electrons removed from the parent molecule with all other electrons remaining in the lowest, most strongly bound levels.

Vibrational and Rotational States

Each electronic level has groups of associated nuclear vibrational and rotational levels. The characteristic ranges of spacings between adjacent vibrational and rotational states are approximately 0.1 to 10^{-2} and 10^{-2} to 10^{-4} electron volt, respectively (ref. 11). Molecular rotational levels will therefore be ignored in the following discussion, but vibrational levels are significant for estimation of molecular dissociation accompanying ionizing electron impact.

Potential-Energy Curves for Diatomic Molecules

The important fragmentation process in polyatomic molecular dissociation accompanying impact can occur in a rather complex fashion. However, before discussing ionization and fragmentation in polyatomic molecules, it is well to illustrate the details of such phenomena in the simpler diatomic molecules and then proceed to the more complex systems. A potential-energy curve conveniently describes the binding between two atoms that are brought together to form a diatomic molecule. This curve is a plot of the potential energy of the interacting pair over a range of interatomic distances R. The zero of energy is chosen as that of the dissociated atoms, that is, the atomic pair at infinite separation. Sketch (f) demonstrates the general form of the plot for formation of AB, a molecule with a stable bond. Quantized vibrational levels are denoted by $v = 0$, $v = 1, \ldots$, with the molecule behaving as an anharmonic oscillator. The Born-Oppenheimer approximation assumes that electronic orbital motion is so fast that the electronic states are unaffected by the nuclear motions associated with nuclear vibrations. The nuclear and electronic motions can then be separated in a wave mechanical treatment, and the energy in the curve for E against R becomes essentially the electronic energy plus the repulsive nuclear term (ref. 7). The electronic energy is the sum of the electronic kinetic energy, the attractive nuclear-electron potential energy, and the electron-electron repulsion. The formation of a deep potential-energy well permits effective molecular bonding (ref. 10). The complete energy function E governs the relative motion of the



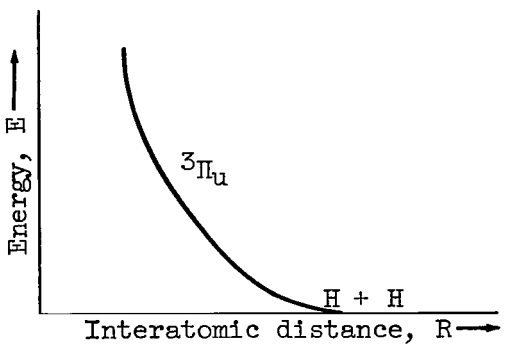
(f) General form of potential-energy curve for a diatomic molecule.

atomic nuclei in the molecule and can be used to calculate the extent of their vibration as an oscillator.

Molecular Binding in Simple Diatomics

With the potential-energy curve introduced, it is possible to discuss qualitatively what happens when two atoms come together to form a molecule. When the atoms are at large separations, there is no interaction; but, as they approach each other, the potential energy of the nuclei and electrons first decreases to a minimum. This minimum of potential for the nuclei is the most stable configuration of the atomic pair. As they come still closer together, the interacting electron clouds repel each other to such a degree that the energy rises steeply.

There may be no binding whatsoever for certain electronic arrangements of a diatomic system. In that case the energy will merely increase monotonically with decreasing R, as shown for the unpaired electronic ground state of $H_2(^3\Pi_u)$ in sketch (g) (ref. 11). Absence of electron pairing, that is, the presence of



(g) Repulsive triplet state for hydrogen molecule.

parallel electron spins, enhances the repulsion of the atomic pair and precludes molecular stability. Wave-mechanical methods of describing bonding lead to more precise interpretations of the chemical bond (ref. 10), but such detailed treatment is not warranted for the purposes of this investigation.

APPENDIX C

MECHANISM OF ELECTRON IMPACT ON MOLECULES

Excitation of Vibration and Rotation by Electron Impact

The nature of the interaction between the free electrons and the bonding electrons determines the consequences of the collision. An incident electron disturbs the potential of the paired electrons in the diatomic bonds, and the extent to which the interatomic bonding is weakened or even destroyed is determined by the extent to which the nuclear positions are perturbed. Purely vibrational and/or rotational transitions, which occur under impact, result in small inelastic energy losses no larger than the order of the average spacings between adjacent levels (i.e., from 10^{-1} to 10^{-4} ev, (ref. 19)) and are not considered important for producing dissociation.

Molecular Ionization and Excitation

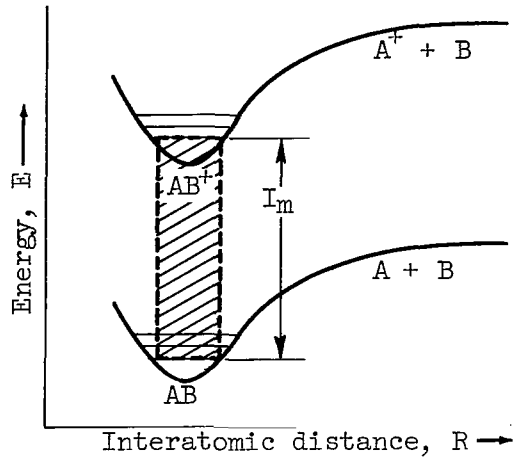
It is clear that transfer of kinetic energy of the free electron to electronic energy of the molecule is the only significant source of molecular fragmentation.

In the single ionization process, one electron receives sufficient energy to be completely removed from the attractive field of a molecule. This event can be accompanied by electronic excitation. Potential-energy curves can be drawn to indicate the position and form of the excited states of molecules and molecular ions. The ground state of the molecular ion is located above the corresponding neutral molecule level by an energy roughly equal to the minimum ionization potential I_m, which is the least amount of energy required to remove an electron from the molecule. A possible arrangement of the two levels is pictured in sketch (h).

Impact Process and Franck-Condon Principle

With the general arrangements of the states of the molecule and ion already outlined, the manner in which transfer between discrete states takes place can be discussed.

The ionizing and/or exciting electron spends a characteristic time in the region of the molecular field. This time, τ_c, is of the order of D/v_e, where D is a representative atomic dimension and v_e is the velocity of the impinging electron. A typical value for D/v_e is 10^{-16} second. Since the interval in which the electronic transition is accomplished is much shorter than the period of nuclear vibration ($>10^{-14}$ sec), a semiclassical argument can be proposed for neglecting nuclear motion during the electron's "quantum jump." The bound electronic motion remains separable from the nuclear motion despite the temporary presence of external forces acting on the entire molecule. This hypothesis is



(h) Franck-Condon region for simple parent molecule ionization with minimum ionization potential indicated.

a logical extension of the previously mentioned Born-Oppenheimer approximation, and, in quantum-mechanical form, it is known as the Franck-Condon principle. In terms of the potential-energy curves, this concept, when validly applied, states that changes in electronic energy are "vertical" transitions that take place with the nuclei at fixed positions (refs. 8 and 19). The Franck-Condon region, here denoted by the vertical dashed lines in sketch (h), defines the limit of electronic and vibrational levels, which are accessible in impact to a molecule in its ground state. This concept can be profitably employed to describe ionization consequences if the details of the curves for V against R are well known for the two states involved. The probability of making certain transitions above the ground state is, of course, a function of the amount of kinetic energy possessed by the incident electron and the "coupling" between the ground state and the state in question. The potential-energy curves for different electronic states can cross each other, and these interstate crossings permit rapid transitions that follow the vertical transitions and may severely complicate any prediction of ultimate impact consequences.

Structure of Polyatomic Energy States

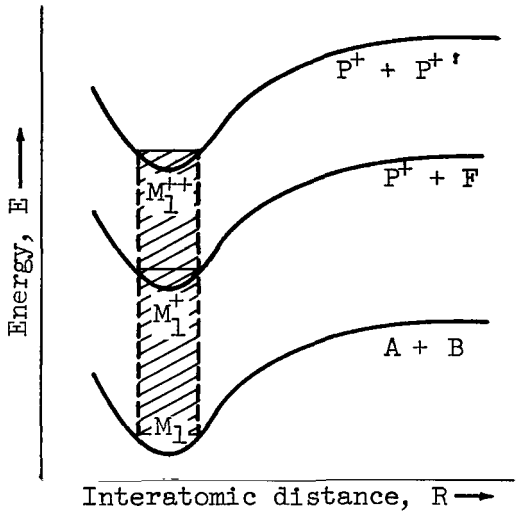
Unfortunately, the behavior of large molecules under impact cannot be discussed in an explicit fashion as can the behavior of diatomic species.

The electronic states of polyatomic molecules are most exactly described by multidimensional potential-energy hypersurfaces rather than the two-dimensional plots of V against R (ref. 11). These surfaces may have many possible minimums, each resembling the potential well of sketch (a), and intertwine in a myriad of intersurface cuts. These surfaces generally cannot be constructed. In fact, their structure can only be reasonably approximated for molecules with not over four or five atoms and with few electrons. Such a calculation must contend with the quantum-mechanical problem of treating a many-electron system. However,

an "effective" potential-energy curve can be handily employed to enumerate qualitatively the possible consequences of the electron bombardment of a polyatomic molecule.

Dissociation of Polyatomic Molecules Under Impact

There are numerous consequences possible upon impact of polyatomic molecules; sketch (i) illustrates the relative positions of two ionic states that can



(i) Franck-Condon region including states of singly and doubly charged molecular ions.

be reached in an inelastic collision.

One class of asymptote in sketch (i) is designated as $P^+ + F$, where P^+ is a primary ion and F is a neutral fragment. Another class is designated $P^+ + P^{+\prime}$ corresponding to dissociation of a doubly charged ion into two singly charged entities, one of which, $P^{+\prime}$, is electronically excited. The probability of any dissociation accompanying or following ionization is naturally dependent on the manner in which complex transitions occur among all electronic states. These transitions are particularly likely in the region of high state density, at least several volts above the ground level of the molecular ion. Such changes of state in a molecular system may take place in a characteristic time of the order of nuclear vibration, that is, $\geq 10^{-14}$ second (ref. 40). Thus, many interstate crossings can be realized before the ion suffers an additional collision with free electrons in the plasma, which may take place in about 10^{-6} to 10^{-2} second. Restrictions on the crossings between electronic states are derived from Wigner's rules for allowed quantum number changes for a change in electronic spin or angular momentum (ref. 40).

APPENDIX D

QUANTUM-MECHANICAL METHOD FOR CALCULATION OF AROMATIC STABILITY

Quantum-mechanical techniques can be readily employed to calculate the stability of particular aromatic molecules and their respective parent ions.

Since π-electrons roam throughout the ring structure, it seems reasonable to construct a molecular wave function for the entire molecule from some arrangement of the electrons on individual atoms. This approach is called the Hückel molecular orbital method, and in one special form it utilizes a total wave function that is a linear combination of atomic orbitals (ref. 41). The so-called resonance integral β_{rs} and familiar coulombic integral α_{rr} (where r and s are atomic orbitals for specific atoms) are the quantities of importance in the energy expression for such a simplified quantum-mechanical solution. The α_{rr} gives the approximate energy of an electron in a 2p atomic orbital, while the β_{rs} represents the interaction energy of two adjacent atomic orbitals. They can be written in the following fashion:

$$\alpha_{rr} = H_{rr} = \int \varphi_r H \varphi_r \, d\tau$$

$$\beta_{rs} = H_{rs} = \int \varphi_r H \varphi_s \, d\tau$$

where r and s specify the atomic orbitals, and $d\tau$ is the volume element for the electrons. The Hamiltonian operator H is esentially a 1-electron operator, and each molecular wave function is of the form

$$\psi_j = \sum_{r=1}^{n} c_{jr} \varphi_r$$

where c_{jr} is the coefficient of the rth atomic orbital in the jth molecular orbital. Solution for energy levels of the system is effected through the use of the quantum-mechanical variational principle, which states:

$$E_j = \frac{\int \psi_j H \psi_j \, d\tau}{\int \psi_j^2 \, d\tau} \geq E_o$$

where E_j is the calculated energy value, E_o is the true energy value, and ψ_j^2 is a normalization factor.

A compound of interest is essentially treated as a set of double bonds, each of which contributes a π-energy of $2\beta_{rs}$ to the calculated total energy E_j. Some idea of predicted stability for the polysubstituted halogenated aromatics can be gotten by solution of a secular expression accounting for the α_{rr} and β_{rs} changes due to all ring substitutions. Solution of the polynomial expression for promising compounds is complicated by the presence of dissimilar terms because of the halogen that provides electrons to the carbon edifice. The halogen atom will effectively act as a potential well at its site on the carbon ring and consequently restrict the mobile electron flow thus changing the delocalization energy.

This approach assumes that throughout there is no π-electron repulsion, a postulate that becomes less of a good approximation as the number of rings in the molecule increases. It is also convenient to consider orbital interaction only between nearest neighbor atoms so that all other β values are zero. In addition, the overlap integrals $S_{rs} = \int \varphi_r \varphi_s \, d\tau$ are ignored. The proven value of the theory in predicting molecular spectra and dipole moments indicates that these approximations may not be too drastic.

The E_j function in the secular expression is minimized with respect to the orbital coefficients $\partial E_j / \partial c_{jr} = 0$ to obtain a value nearest the true energy. Since the minimization is performed with each coefficient, n equations for m atoms are obtained, and this set has a nontrivial solution only if the corresponding secular determinant A_{rs} vanishes (ref. 17):

$$A_{rs} = \begin{vmatrix} \alpha_{11} - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1n} \\ \beta_{21} & \alpha_{22} - E & \beta_{23} & \cdots & \beta_{2n} \\ \beta_{31} & \beta_{32} & \alpha_{33} - E & \cdots & \beta_{3n} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \cdots & \alpha_{nn} - E \end{vmatrix} = 0$$

The resulting polynomial equation has n real roots of the form

$$E_j = F\left[\sum_{j-r} (\alpha_{rr} + m_j \beta_{rs})\right]$$

in terms of the coulombic integral and a fraction m_j of the resonance integral. The quantity β_{rs} is negative, thereby lowering the energy level and increasing stability. Roots of the polynomial equation with values less than those due to α_{rr} represent bound electronic energy levels with lower values than those of the isolated atoms.

In order to account for the presence of halogens on the aromatic rings, the α_{rr} and β_{rs} for the bonds involving the halogen with carbon atoms must be assigned values in terms of the difference between the new atom and carbon. The following formulas can be employed:

$$\beta_1 = k_1\beta_o$$

$$\alpha_1 = \alpha_o + h_1\beta_o$$

where k_1 and h_1 are computed from comparison of the halogen atoms with carbon and α_1 and β_1 are the coulombic and resonance integrals for carbon with the halogen atom of interest (ref. 42). Values of k_1 and h_1 have been suggested for bromine in the literature, but proper values for iodine must be obtained from extrapolation of trends in k and h given for the other members of the halogen family. The k and h values taken for bromine are 0.30 and 1.5; for iodine, they are 0.25 and 1.3 (refs. 17 and 42). With these values known, calculations of the reduction in energy levels and relative stability can be made for these halogenated aromatics.

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TABLE I. - DELOCALIZATION ENERGIES OF SOME AROMATIC HYDROCARBONS

[1 ev = 23.06 kcal/mole.]

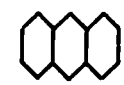
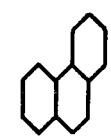
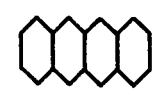
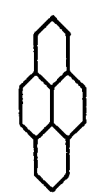
Hydrocarbon	Molecular orbital delocalization energy, β	Empirical resonance energy, kcal/mole	Delocalization energy per π-electron, kcal/electron	Ring structure
Benzene	2.000	36.0	$\frac{36.0}{6} = 6.0$	
Naphthalene	3.683	61.0	$\frac{61.0}{10} = 6.10$	
Anthracene	5.314	83.5	$\frac{83.5}{14} = 5.96$	
Phenanthrene	5.448	91.3	$\frac{91.3}{14} = 6.52$	
Tetracene	6.932	110.0	$\frac{11.0}{16} = 6.87$	
Pyrene	6.506	108.9	$\frac{108.9}{16} = 6.81$	

TABLE II. - MASS SPECTRA OF ANTHRACENE FOR 70-VOLT ELECTRONS

[Total relative abundance of fragments plus ions is 404.0. $P^+ \rightarrow M^+ + F$, where P^+ is the parent ion, M^+ is any secondary ion, and F is the related fragment. $M(P^+)$ for $M/q = 89$ is due to P^{++}.]

Mass to charge ratio, M/q	Relative abundance of ion	Mass to charge ratio M/q	Relative abundance of ion	Mass to charge ratio, M/q	Relative abundance of ion
36	---	74.5	---	102	1.0
37	---	75	4.9	125	.7
37.5	---	75.5	.9	126	1.9
38	0.7	76	13.2	127	.9
38.5	---	76.5	1.5	128	1.2
39	3.9	77	1.6	129	---
49	---	78	.5	139	1.4
50	4.2	79	---	149	1.2
51	3.5	86	1.8	150	4.8
52	.9	87	3.1	151	7.4
61	1.2	87.5	1.1	152	7.6
62	3.3	88	9.4	153	---
63	5.5	88.5	2.0	174	1.4
63.5	---	89	15.6	175	2.6
64	.6	98	1.8	176	14.8
64.5	---	99	1.9	177	6.0
73	---	100	1.8	178	100.0
74	2.8	101	2.5	179	14.5
				180	1.2

Sum of relative abundances of ions = 259.8

TABLE III. - POSSIBLE NEUTRALIZATION PRODUCTS

OF 12 MOST ABUNDANT SPECIES IN PRIMARY

ION SPECTRA OF ANTHRACENE

[Dissociation recombination products are open to speculation.]

Ion $\xrightarrow{e^-}$ Neutralized product	Relative abundance	Fragment (accompanying ion formation)
$C_{14}H_{10}^{+} \xrightarrow{e^-} C_{14}H_{10}$	100.0	None
$C_nH_n^{+} \xrightarrow{e^-} C_nH_n$	15.7	Miscellaneous (Heavy mol. wt. impurity)
$C_{14}H_9^{+} \xrightarrow{e^-} C_{14}H_9$	6.0	H
$C_{14}H_8^{+} \xrightarrow{e^-} C_{14}H_8$	14.8	H_2
$C_{12}H_8^{+} \xrightarrow{e^-} C_{12}H_8$	7.6	C_2H_2
$C_{12}H_7^{+} \xrightarrow{e^-} C_{12}H_7$	7.4	C_2H_3
$C_{12}H_6^{+} \xrightarrow{e^-} C_{12}H_6$	4.8	C_2H_4
$C_{14}H_{10}^{++} \xrightarrow{2e^-} C_{14}H_{10}$	15.6	None
$C_7H_4^{+} \xrightarrow{e^-} C_7H_4$	9.4	C_7H_6
$C_{12}H_8^{++} \xrightarrow{2e^-} C_{12}H_8$	13.2	C_2H_2
$C_5H_3^{+} \xrightarrow{e^-} C_5H_3$	5.5	C_9H_7
$C_6H_3^{+} \xrightarrow{e^-} C_6H_3$	4.9	C_8H_7

NASA-Langley, 1964 E-2030