

RADIATION CHEMISTRY

Roger E. Rondeau, 1/Lt USAF

Dr. Jack Radell

Directorate of Materials and Processes, ASD

Introduction

The study of radiation-induced reactions, particularly in the field of organic chemistry, has been, until recently, concerned with the transformation of reactants into products. In a typical study of a radiation chemistry system, the first step is usually a qualitative analysis of the ultimately stable products formed. This is followed by the establishment of product yields, usually in terms of G values, the number of molecules produced per 100 electron-volts of energy absorbed. This information is hardly sufficient for a complete understanding of the radiation chemistry of a system. Nevertheless, from such data have emerged various postulations of radiation mechanisms, usually on the basis of free radical paths. Such studies are not without merit. In liquid systems, a free radical mechanism postulation is completely justifiable since free radicals are frequently the most abundant radiation-induced transient species within the system. In gaseous phases, on the other hand, indications are that ion-molecule reactions appear to be a significant or even dominant mechanism of chemical change.

The physically-minded radiation chemist has become more intensely concerned with reaction mechanisms *per se*, realizing that a more fundamental understanding comes only with a detailed consideration of the mechanisms of the various occurring reactions.

This report is a brief summary of the present knowledge of reaction mechanisms in radiation chemistry, especially as they apply to simple organic compounds.

Fundamental Concepts

Types of Ionizing Radiations: in radiation chemistry, the energy range of the ionizing radiation commonly begins at about 100 e.v. but most studies are made with waves and particles in the Mev region (1). These energetic particles are produced by radioactive decay or by artificial means. Table 1 lists typical radiations, their principal physical characteristics, and their sources. For purposes of orientation, it should be noted that the dissociation energy of covalent bonds is in the 3-4 electron volt range.

Initial Events: When electromagnetic radiation passes through a chemical system, we may distinguish three different phenomena which govern the behavior of photons: the photoelectric effect, the Compton effect, and pair production. Figure 1 is a pictorial description of these interactions.

1. At low energies, the most important process is the photoelectric effect. In this process, a photon of energy $h\nu$ ejects a bound electron, (usually from an inner shell) from an atom or molecule and imparts an energy $h\nu - E$, where E is the binding energy of the electron. The quantum of radiation completely disappears in this encounter which is unimportant at energies above 1 Mev.

2. At exceedingly high energies, the photon is again completely absorbed in producing a positive - negative electron pair (pair production) this process is of no significance in radiation chemistry.

3. An important mode of interaction is Compton scattering. In this encounter, the photon transfers only part of its energy to a bound electron (usually an outer shell electron). The gamma rays are thus degraded and deflected. In the energy ranges most commonly used in radiation chemistry studies, and in particular for materials with low atomic numbers such as organic compounds, gamma rays lose most of their energy by the Compton scattering process.

The primary effect of a single gamma ray then may be the production of a highly energetic electron and a positively-charged ion-radical, so called because of its charge and its unpaired electron. At 1 Mev incident energy, essentially all of the electrons may be considered as of the Compton recoil type and the average energy of each electron approaches half that of the incident γ -ray (2).

Such a high energy electron can in turn produce about 20,000 additional ionizations and 30,000 excitations. This leads to the well known phenomenon that the primary events, and often the outcome of many radiation-chemical reactions, are not appreciably affected by the nature of the incident radiation.

Except for the uncharged neutrons, the other principal radiations in radiation chemistry are the alpha particles, the beta particles, and the artificially accelerated charged particles. Therefore, in radiation chemistry our attention should be directed primarily to the effects of charged particles on matter.

Energy Distribution: When a highly energetic electron, proton, alpha or other charged particle passes through a chemical system, it produces excitation and ionization events of the type illustrated in figure 2. The sequence of events is as follows:

Block I. The particle approaches five molecules; the small circles represent electrons.

Block II. The particle disturbs the electrons in some of the molecules.

Block III. The particle has traversed the fifth molecule.

Block IV. The particle has receded, leaving one molecule ionized and two in an excited state. The other molecules have reverted to the original state. The energetic electrons released from the impact process in block IV will continue to induce excitation and ionization processes at an average ratio of 2 to 1, as shown in figure 3. These "hot spots" of ionization and excitation are called clusters or spurs. The volume occupied by these clusters in a liquid has been estimated at an average diameter of 5 \AA ($5 \times 10^{-8} \text{ cm}$) (1). The distance between spurs can vary anywhere between 4600 \AA for 450 Kev electrons to approximately 9 \AA for 6 Mev alpha particles in water.

Geometrical factors are also important. Heavy particles such as alpha particles, protons, deuterons, etc., have the greatest probability of interaction with matter. However, the amount of energy is very limited. Classically, the maximum energy transferable is given by

$$E_{\text{MAX}} = E_{\text{INITIAL}} \frac{4m}{M} \quad (1)$$

where m is the mass of an electron and M is the mass of the charged particle. Thus, for alpha particles, the maximum energy transferable per collision is, classically, only $\frac{1}{1836}$ (from table 1: $\frac{4(m)}{2M}$) of the heavy particle energy. As a result of this combination of high interaction probability and low energy transfer, heavy charged particles form a very dense track of ionized and excited molecules and low energy electrons.

The probability of interaction of electrons with matter is approximately 1,000 times lower than the probability for alpha particles of the same energy. On the other hand an electron can, though relatively rarely, lose up to one half of its energy to a secondary electron. When such a large energy transfer occurs, the path of the electron will be abruptly deflected. As a result, electrons form a much less dense and zig-zagged track. Electromagnetic radiations, X and γ rays, penetrate matter for great distances before they interact with a target molecule or atom to lose all or a large part of their energy in a single event. The interaction results in the ejection of a highly energetic Compton or photo electron which traces its own characteristic trail. Hence, depending on the type of radiation used and the state of the absorbing medium, various tracks are formed which can lead to different chemical results.

Effect of Phase: The distribution of the radiation induced transient species formed along the track of a charged particle will be determined by the linear energy transfer ($-dE/dx$) appropriate to the radiation and the electron density of the medium. The life span and ultimate fate of a molecule activated by radiation may depend on whether it is in a gas, a liquid, or a solid.

1. **Gas Phase:** In the gaseous state, the parent cation is often not neutralized by recombination with its daughter electron because the low density of the medium and the absence of a solvent "cage" allows the electron to maneuver away from the parent ion's sphere of influence (Coulomb attraction). Also, both the mean free path and the average "between-collision" time are relatively large; therefore, excited molecules and ions may exist long enough to react with other transient species or to undergo unimolecular decomposition. Two radicals or ions formed by dissociation of a molecule, have a negligible chance of undergoing primary recombination and usually diffuse apart to react with other fragments. In the gas phase, there is little doubt that ion-molecule reactions are important since in many cases they appear to be a significant, and many times the dominant mechanism of chemical change.

2. **Liquid Phase:** Molecules in a condensed system are intensely influenced by neighboring molecules. Consequently the modes of energy transfer and dissociation are different. In the liquid phase, the Compton electron very often returns to its companion ion within 10^{-13} seconds, before any gross movement of molecules can occur. The attendant charge neutralization process results in the deposition of a large excess of energy within the molecule. If reionization does not occur, the highly excited molecule will usually decompose to form electrically neutral fragments or free radicals. Evidence exists that upon excitation and dissociation, the weakest bond is likely to break, with the excess energy distributed as kinetic energy between the recoil species. The free radicals thus formed are usually surrounded by a "cage" of solvent molecules which hinders their diffusion outside the cage. The result is that the radicals lose their energy by colliding with the cage "walls" and immediately recombine. The probability of such deactivation and recombination decreases if one of the radicals is small. This effect, usually called the Franck-Rabinowitch Cage Effect, operates to decrease yield in liquids when the decomposition proceeds via free radical decomposition.

3. **Solid Phase:** In the solid state, diffusion is an extremely slow process which gives rise to product localization for measurable periods of time. Also, as the result of the systematic arrangement of molecules in crystals, radicals may preferentially attack certain portions of adjacent molecules rather than attack randomly as in the liquid or gas phase. Most organic solids are covalent and localized damage is often subsidiary to the formation of free radicals and molecular products, both of which would be trapped. Fusion of the solid allows the trapped volatile molecular products to escape thereby releasing the free radicals from their position within the lattice and enabling them to react or undergo mutual destruction.

These differences in the state of aggregation of the absorbing or "target" medium often create differences in the nature and yields of radiolytic products. At present, neither the phase effect nor the theory of radiation induced reaction mechanisms are established well enough to allow reliable predictions of the extent the phase will influence the products of a given radiation chemical reaction.

Molecule Activation In a Radiation Field

We have seen that when a charged particle traverses matter, it produces a number of active species of greater-than-average energy. These ephemeral species may revert to their original inactive form or, they may react with neighboring molecules before deactivation. The time it takes for the activated species to become deactivated usually determines their chemical reactivity. If they were completely isolated in space, many ions and radicals would be stable indefinitely. Actually, these "unstable" entities have a fleeting existence only because a more stable situation can be established by interaction with an adjacent molecule or ion.

Excited Species: It has already been stated that in radiation chemistry, there are 1.5 to 2 excited molecules formed per ion pair. For most gases the energy required to form an ion pair, W , is about 30 electron-volts (ev). W is not known for liquids however. Since the ionization potential, I , for most gases is about 10-15 ev, then 15 to 20 ev of absorbed energy must go into electronic excitations. Moreover, many ion-pairs formed in a radiation-chemical process recombine to generate highly excited molecules. This means that the total number of excited species produced by high energy radiation is even greater than expected from ion-pair estimates.

Molecules with excited electrons are usually unstable even if isolated in space. They may be produced directly in an initial event or as a result of an ion recombination reaction. Direct excitation usually results in elevation to low excited states. Since the ground state of most molecules is singlet (no unpaired electrons), the more easily excitable states will also be singlets i.e., ones in which the electrons are still paired although the excited electron is now in a more distant spatial orbit. However, in radiation-chemical reactions triplet states often play an important role. A triplet state can be defined as bond excitation where one of the bonded electrons is excited into a higher energy level with reverse spin. Generally, low triplet states do not possess enough energy to break a covalent bond. Since most upper excited states internally convert in a very short time to the lowest excited states of the same multiplicity, and since internal conversion to the ground state is much slower, most of the chemical changes occur from either one of the two low excited states (3).

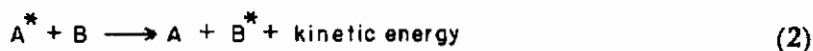
Figure 4 is a schematic diagram of the lowest important electronic energy levels of a molecule. The diagram depicts two systems of levels, the singlet system (S_0, S_1, S_2) and the triplet system (T_1, T_2). Excitation of the molecule occurs by absorption of radiation

which raises the molecule from the ground state (S_0) to elevated singlet or triplet stages. The transition $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ are usually photochemically forbidden and the photochemical absorption processes are usually inefficient and therefore ignored. In radiation chemistry, however, triplets can be formed directly and by ion neutralization as well as by $S \rightarrow T$ transitions; therefore, the relative triplet/singlet yield ratio would be expected to be much higher in radiation chemistry. After excitation to S_1 , the molecule can be deactivated in three ways: 1. by fluorescence, a radiative decay to the ground state (F); 2. by quenching a radiationless decay whereby the excitation energy is converted to thermal energy (Q); 3. by a radiationless internal conversion to a triplet state (C_i). Once the molecule occupies the T_1 level it can either phosphoresce (P) to the ground state or it can be quenched (Q) nonradiatively. If the molecule is initially excited to a higher singlet level (S_n) it usually becomes "degraded" via two alternative paths: a) by an internal conversion (C_i) to a lower-lying singlet level ($S_n \rightarrow S_1$); b) by an internal conversion (C_i) to a triplet level.

Phosphorescence usually involves the lowest triplet state while fluorescence usually occurs from the lowest excited singlet state to the ground state which is the lowest singlet state. The reason that only the last step is a radiative one is that the largest energy gap is usually between the ground and the first excited states so that the necessary overlapping of potential energy surfaces required for a radiationless transition is less likely between these two than between closer lying pairs (2).

Excluding collisional deactivation and including the aforementioned processes, the following is a list of the more important processes by which an excited molecule can become deactivated:

- 1) Internal conversion to lower excited levels.
- 2) Internal conversion to the ground state.
- 3) Emission of energy as luminescence (fluorescence and/or phosphorescence).
- 4) Energy transfer, for example



Aromatic and phenylated compounds function very effectively as the molecule B. Such compounds afford protection by absorbing energy from the more sensitive and excited (*) molecule A and dissipate most of it without decomposition. If the additive B protects A by dampening any luminescent effect from A the method of protection is called "quenching"

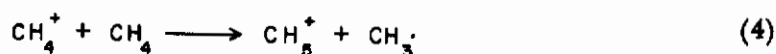
- 5) Stern-Volmer Reactions - complicated reactions involving one or more excited molecules.
- 6) Decomposition reactions leading to molecule or free radical formation.

Free Radicals: The free radicals found in a radiation-chemical process are the products and by-products of the following reactions:

1. Decomposition of excited molecules



2. Ion-molecule reactions; a specific example is



3. Ion-formation (dissociative electron capture)



4. Ion neutralization (dissociative recombination)

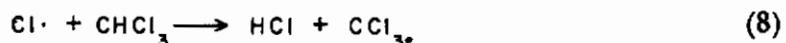


Most of the above reactions will take place in a spur or ion track within 10^{-11} seconds. It is generally agreed that in a radiation-chemical process within a condensed system there exists initially high concentrations of free radicals in spurs or clusters. The number of isolated radicals is believed to be small, even in fast particle tracks. The distribution of radicals in a track will be determined by the Linear Energy Transfer (LET) of the radiation in question and the electron density of the absorbing medium. The concentration will tend to become uniform by diffusion. In liquids this diffusion process is hindered by the Franck-Rabinowitch Cage Effect. According to this principle, a pair of radicals surrounded by a "Cage" of solvent molecules may lose energy and recombine before the moities leave each other's sphere of influence. The "Cage" therefore protects a molecule from dissociation into free radicals. The cage effect therefore operates to decrease the yield in liquid systems when the decomposition is through a free radical process. Once the free radicals diffuse out of the cage their probability of returning and undergoing a secondary recombination is usually very low. Escape therefore allows the radicals the freedom to undergo characteristic free radical reactions such as the following:

1. Radical Displacement



This type of reaction has been used by countless workers to explain radiation induced reactions, e.g., Stein, et. al. (4), explained the formation of HCl in the radiolysis of chloroform with the following reaction.



2. Radical Addition



Free radicals characteristically attack the π electrons of unsaturated compounds to form new radicals such as $\text{AB} \cdot$. Reaction (9) has been shown to be very important in radiation-induced polymerization reactions.

3. Radical Coupling



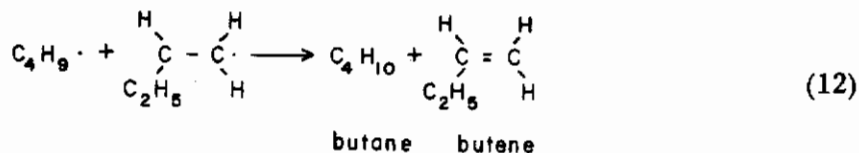
Radical combination or coupling is different from radical recombination to the extent that the latter occurs primarily within the solvent cage. Radical combination is the reverse of the homolytic dissociation of a covalent bond. The activation energy for such

reactions is usually zero while the rapidity is very great. For example, in the gas phase, methyl radicals combine at almost every collision to form ethane. Kerr and Trotman-Dickenson (5) extended their study to the combination of unlike radicals and have found that combination also occurs at every collision in the gas phase. The speed of coupling in the liquid phase is usually slower and the rates of radical coupling reactions usually do not vary far from the velocity of diffusion.

4. Radical Disproportionation



Despite the rapidity of radical combinations, a competing reaction is that of disproportionation into a saturated (AH) and unsaturated (U) molecule. The difference between coupling and disproportionation can be explained in terms of the mode of encounter of the free radicals (6). A head-to-head encounter of radicals A' and B usually results in the formation of one molecule while a head-to-tail encounter sometimes results in the abstraction of hydrogen atom from one radical by the other and the formation of one saturated and one unsaturated molecule; for example:

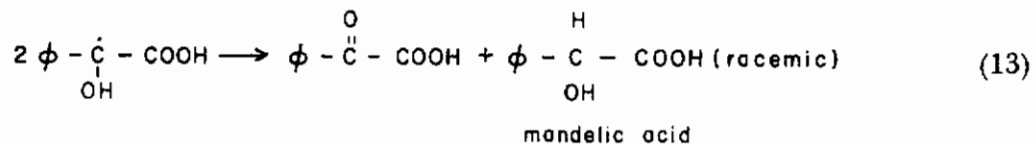


Activation energies for disproportionation are very close to zero and Wagner (7) has observed that such reactions should be important in gas phase radiolyses.

5. Radical Rearrangements or Isomerizations

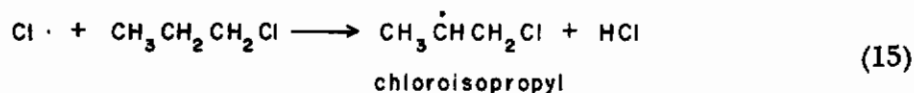
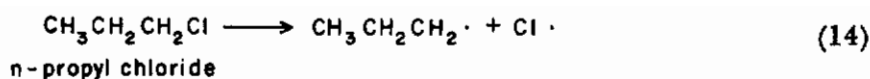
Two types of isomerizations must be considered: the racemization of optically active compounds and the rearrangement of bonds within a radical.

In a study made by Feng and Tobey (8) on the gamma radiolysis of aqueous solutions of mandelic acid, racemization and destruction of the asymmetric center were found to occur. This reaction

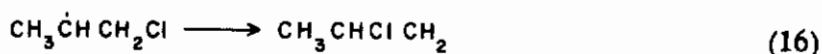


was advanced to explain the observed extent of radiation-induced reaction in optical activity.

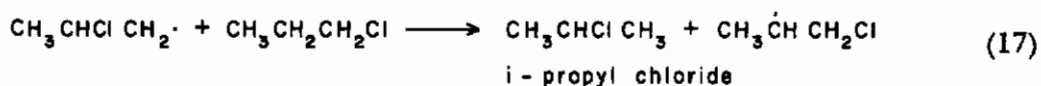
A free radical mechanism has been used also to explain the gamma-radiation induced isomerization of normal-propyl chloride to isopropyl chloride (9). The following sequence of free radical reactions were presented:



It was then suggested that the chlorine atom in the chloroisopropyl radical migrates to the β -position,



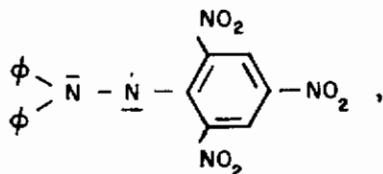
followed by hydrogen abstraction by the chloropropyl radical



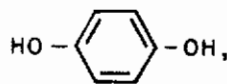
6. Free Radical Scavenging



Reaction (18) represents the closest approach to a basic study of free radicals in radiation chemistry. It entails the use of a radical trap or scavenger, S, which may be a stable free radical such as diphenylpicrylhydrazyl,



a complex molecule such as hydroquinone,



or a simple molecule such as iodine, I_2 . In the ideal case,

reaction (18) must take place before any of the aforementioned free radical reactions. Reaction (10), the coupling of various free radicals to form the original irradiated substance, may be faster than reaction (18), however, this is due primarily to the Franck-Rabinowitch Cage Effect. Scavengers would not be effective in removing radicals until after they had diffused out of this cage (10). Since recombinations within the cage do not enter into the chemical picture and since the object of the scavenger addition is to determine the overall free radical yields, no appreciable error is introduced by disregarding the radicals involved in such a recombination. The possibility exists however, that under different physical conditions the rates of the recombination and scavenging reactions might be sufficiently different and result in different radical yield. For example, a variation in temperature may affect the diffusion rates in such a way that the free radicals within the cage may be separated from each other in a shorter time than it takes for the recombination to occur.

One of the problems which arises when "scavengers" are used to determine the nature of radiation-induced free radicals is that some scavengers appear to react with excited molecules with the formation of products exactly like those formed from free radicals. Therefore, whenever information is given about free radicals yields from scavenger-type reactions, the data should be carefully analyzed before false conclusions are drawn.

Ion-Radicals: In the reaction

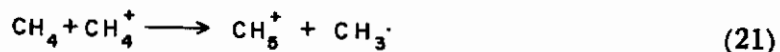


the species AB^+ should not be mistaken for an organic "onium"-type ion because the latter has no unpaired electrons; neither can it be regarded as a free radical since it is positively charged. Because of their charge and the unpaired electron, these bifunctional species have been called ion-radicals. Their existence in the liquid phase is improbable; however, they are produced to some extent in the gas phase and hence, their presence cannot be completely ignored. A mass spectrometer study has called attention to some of the similarities of free radicals and ion-radicals. Three general ion-radical reactions, similar to the general processes known for free radicals were examined.

1. Ion-radical displacement



An analysis of rate constants reveals that ions undergo displacements from 10^3 to 10^5 times faster than free radicals. The reaction is analogous to the well known ion-molecule reaction



2. Ion radical addition



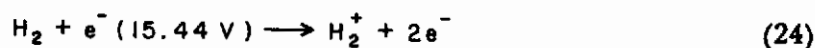
This reaction perpetuates ion radicals in the same way that growing free radical polymer chains are formed.

3. Ion-radical decomposition

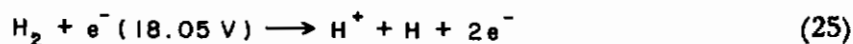


These decompositions result in the formation of many metastable ions observed in mass spectra. Ionic reactions of this type produce free radicals and/or ion radicals. This process is another example of the close relationship between ion-radicals and free radicals.

Ion-Molecule Reactions: Most of the information concerning ion-molecule reactions has been derived from mass spectrometry. Since at 10^{-6} mm pressure in the ionization chamber of the mass spectrometer the mean free path of a molecule is $\sim 10^4$ cm, collisions between molecules and ions are rare and the ions are formed by unimolecular decomposition as a result of direct impact of electrons on the molecular beam. The smallest voltage required to energize the electrons sufficiently to remove an electron from a molecule is its ionizing potential (IP) and is 15.44 V for hydrogen.



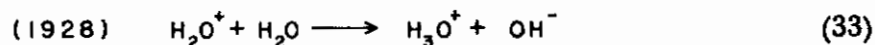
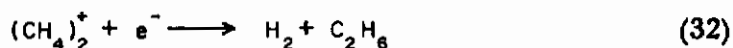
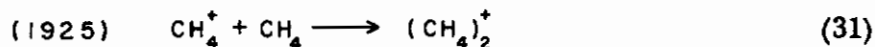
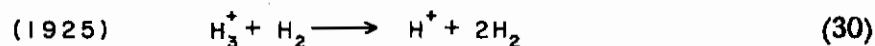
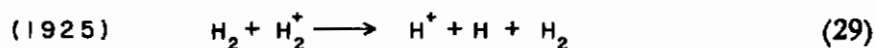
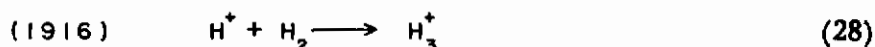
Still more highly energized electrons may cause the molecule to fragment. This necessary voltage is called the appearance potential (AP) and is 18.05V.



The energy of fragmenting can be calculated from Hess's law if we make a summation of the processes:

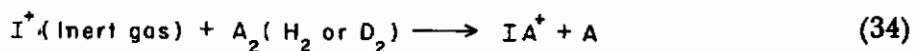


Since most ion-molecules are short-lived, many ions which are formed and disappear in less than 10^{-8} seconds cannot be detected by the mass spectrometer. Some early observed ion molecule reactions (12-15) are:

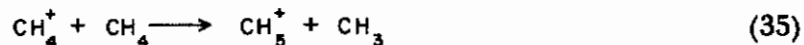


A number of recently discovered ion molecule reactions are tabulated in a review by Lampe and Field (16).

A most interesting positive ion formation for neon, argon, and krypton has also been observed. These positive ions can react with hydrogen or deuterium



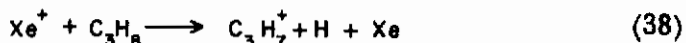
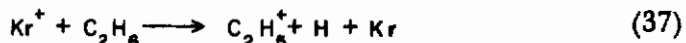
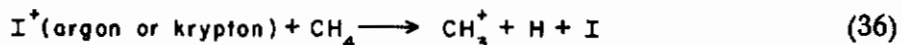
A variety of both organic and inorganic ion molecule reactions have been identified by the mass spectrometer. Perhaps one of the most unusual species was the identification of CH_5^+ from the following:



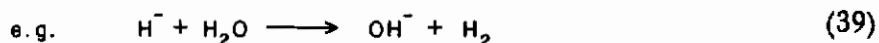
In all these reactions the atom transferred was either positively charged or neutral. The reaction involving the transfer of a proton occurs much more readily than that which involves the transfer of a hydrogen atom.

Although the transfer of a hydride ion had been postulated for many years as one of intermediates in an ion molecule reaction, direct observations were first made in the gas

phase by Lampe and Field in 1958 (17) and are tabulated on page 200 of reference (16). The reaction observed by Meisel et. al. (18) constitutes another example in which the loss of a hydride could account for the changes indicated.

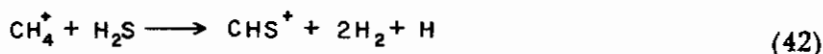


There are two more classes of ion molecule reactions. One is the negative ion reactions about which very little is known:



The above two examples are the only ones we have found.

The second class of ion molecule reactions are of the condensation type. Here a good deal more is involved than the transfer of an atom or atomic ion.



These and a number of other examples are listed on page 202 of reference (16).

The description of ion molecules observed in the mass spectrometer may easily be extrapolated to an environment subjected to ionizing radiation when the electron, just as in the mass spectrometer, is responsible for the overwhelming number of events. Hence, the information presented must be regarded as a potential mechanism of reactions characteristic of molecules in a radiation environment.

Past, Present, And Future Applications

Since a molecule may break in various ways, the complexity of products resulting from these interacting fragments is very great. In addition, the effect of state introduces still another variable. These factors require clarification to understand better the role of ionizing radiation. The problem becomes still more complicated if these studies are conducted in a hard vacuum simulating a space environment. It is in these areas where a variety of basic problems exist and study is necessary. As an example, a very important area for investigation in view of current trends appears to be a study of the effects of ionizing radiation on propellants - both liquid and solid. It is anticipated that chemical propellants may be exposed to the space radiation environment for long periods before being subsequently used for retro, maneuver, or primary propulsion as with a satellite launched missile. Will prolonged exposure bring about chemical changes in the propellant which would impair the operational reliability of the vehicle? For some missions the rocket casing or vehicle shell may be sufficient shield against potentially damaging radiation; for other missions this may not be true. On the other hand, perhaps the effect

of ionizing radiation could be beneficial by using a liquid propellant which would subsequently be changed through exposure to a solid in which form it would be used.

Another concept which might be explored for space applications is the use of a material in a radiation field to serve one function for a limited time and a second function after it has been altered by the ionizing radiation. The potential use of some liquid propellant for shielding and its subsequent use as a solid propellant would be an example of this concept. Or possibly some shielding liquid which would be converted by ionizing radiation to the consistency of a lubricant could be used for such a double duty application.

Radiation chemistry has been disappointing since we have not been able to use it as a catalyst to produce desirable chemical products otherwise not available by conventional means. Although a few such applications are known, a great deal remains to be done in this field - in particular for the development of radiation stable materials. It would be very likely that materials prepared in this way would have passed part of the test for radiation stable materials in their very formation. The preparation of useful ferrocene polymers by irradiating di- and poly-halo ferrocenes appears to be a possible application of this concept. The horizons here are limited only by the imagination of the synthetic chemist. The use of radiation as a catalyst has the unique feature of not requiring the presence of foreign chemicals as is the case with conventional catalysts. Some known examples of chemical changes induced by radiation are the formation of lindane from benzene and chlorine; phenol from water, benzene, and oxygen; ethylene glycol from methanol; aniline from benzene and ammonia; fixation of nitrogen; alkyl sulfonates from hydrocarbons and sulfur trioxide; formation of ascorbic acid and many others.

A great deal of work remains to be done to understand what makes a molecule radiation stable. Many empiric generalizations have appeared in this field, but these fall or are restricted as new cases are discovered. Some work is being done to show the mode of energy transfer from less to more stable molecules. In our laboratory some radiation resistant alkynes have been found to exist although this was not anticipated from the known high reactivity of acetylene itself under ionizing radiation. Rather than accept these results as the fruits of serendipity it is believed a better understanding of radiation stability is required. The ripe possibility exists for obtaining such information as well as useful new materials for a radiation environment if the general area of aromatic compounds are studied in particular, the conjugated cyclic organic compounds having alternating single and double bonds which comply with Huckels rule. Investigations should include studies of stability of molecules ranging from cyclopropene to macrocyclic molecules with 5, 7, 9, and 11 bonds, e.g. the phthalocyanines and porphyrins.

The ever present requirements of dosimetry exist in both the laboratory and in the field. Although heavy inroads have been made in this area there is ample need for new concepts of dosimetry - physical or chemical. In the liquid phase ceric sulfate, ferrous sulfate, and cyclohexane are commonly used dosimeters, while in the gas phase the most commonly used dosimeter is acetylene. There is some doubt that acetylene is a reliable dosimeter (19). A need exists for the development of an improved gas phase dosimeter. This is especially important since the research in radiation chemistry is heavily dependent upon dosimetry. In the chemical area limited amounts of work has been done on the effect of radiation on optically active molecules. Surely there are a host of other more ingenious approaches to find new concepts and compounds useful in dosimetry. This will no doubt evolve in a better understanding of radiation chemical phenomena. Surely in these and related studies radiation chemistry has found a host of applications.

Some idea of the future of radiation chemistry may be gained from a brief resumé of past accomplishments in the field. A few of the more important examples are: Sterilizing

of heat sensitive products such as, maturing of fruits, wines, liquors, and cheese; production of static free fibers; cross-linking of polymers; vulcanization of rubber without sulfur; syntheses of a new chemicals; grafting of incompatible polymers such as, nylon and cellulose; dying teflon; initiating reactions at low temperatures; and the mutation of plants.

The future application arising from a better understanding of radiation will certainly far exceed these past developments. Foresight on the part of management and the research scientist will be required to anticipate many of these needs by entering the field now and developing the required capability.

V. BIBLIOGRAPHY

1. M. Burton, Record of Chemical Progress, 19, 13 (1958)
2. C. Reid, "Excited States in Chemistry and Biology", Academic Press, (1959)
3. M. Burton, W. Hamill, and J. Magee, Second UN Geneva Conference on Peaceful Uses of Atomic Energy, 29, 391 (1958)
4. G. Stein, M. Ottolenghi, and I. Eliezer, WADD Technical Report 60-668 (1960)
5. J. A. Kerr and A. F. Trotman - Dickenson, Chemistry and Industry 125 (1959)
6. A. F. Trotman-Dickenson, "Free Radicals", John Wiley & Sons, Inc. (1959)
7. C. D. Wagner, Journal of Physical Chemistry, 64, 231 (1960)
8. P.Y. Feng and S. W. Tobey, Journal of Physical Chemistry, 63, 759 (1959)
9. R. H. Wiley, W. Miller, C. Jarboe, J. Harrell and D. Parish, Radiation Research, 13, 479 (1960)
10. R. Britton and I. Zwiebel, WADD Technical Report 60-127 (1960)
11. T. W. Martin and C. E. Melton, Journal of Chemical Physics, 32, 700 (1960)
12. A. J. Dempster, Phil. Mag., 31, 438-43 (1916)
13. H. D. Smyth, Phys. Rev., 25, 455 (1925)
14. S. C. Lind, D. C. Bardwell, Science, 62, 422-24 (1925)
15. H. A. Barton, J. H. Barlett, Jr., Phys. Rev. 31, 822-6 (1928)
16. F. W. Lampe, F. H. Field, Tetrahedron 7, 196 (1959)
17. F. H. Field, F. W. Lampe, J. Am. Chem. Soc. 80, 5587 (1958)
18. G. G. Meisels, W. H. Hamill, R. R. Williams, Jr., J. Chem. Phys. 25, 790 (1956);
ibid. 61, 1456 (1957)
19. H. A. Samuel, private communication

TABLE I
PRINCIPAL FORMS OF IONIZING RADIATION

RADIATION	SYMBOL	RELATIVE MASS	CHARGE	SOURCE
ELECTRON	or e	1	-	NATURAL AND ACTIVATED RADIO - NUCLIDES, PARTICLE ACCELERATORS
PROTON	H^+	1836	+	PARTICLE ACCELERATORS
NEUTRON	n^0	1839	0	REACTOR FISSION PRODUCTS
DEUTERON	D^+	3671	+	PARTICLE ACCELERATOR
HELIUM NUCLEUS	He^{++} or α	7296	++	NATURAL RADIO - NUCLIDES, PARTICLE ACCELERATORS
ELECTRO-MAGNETIC	X and γ	0	0	NATURAL AND ACTIVATED RADIO - NUCLIDES, FISSION PRODUCTS, AND ACCELERATOR TARGETS

X-RAY INTERACTIONS

Atom Or Molecule

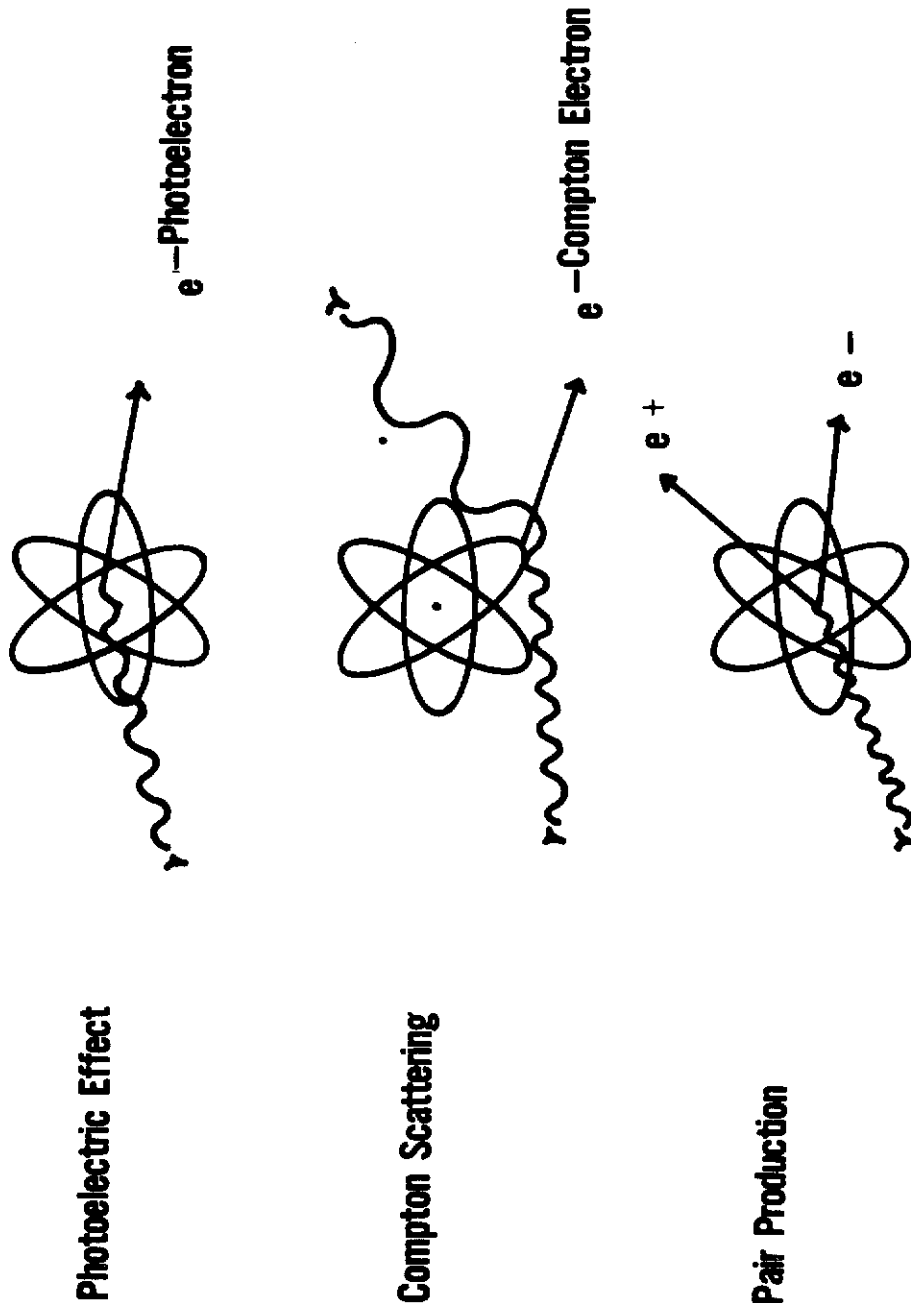


Figure 1.

Contrails

PRIMARY EFFECTS

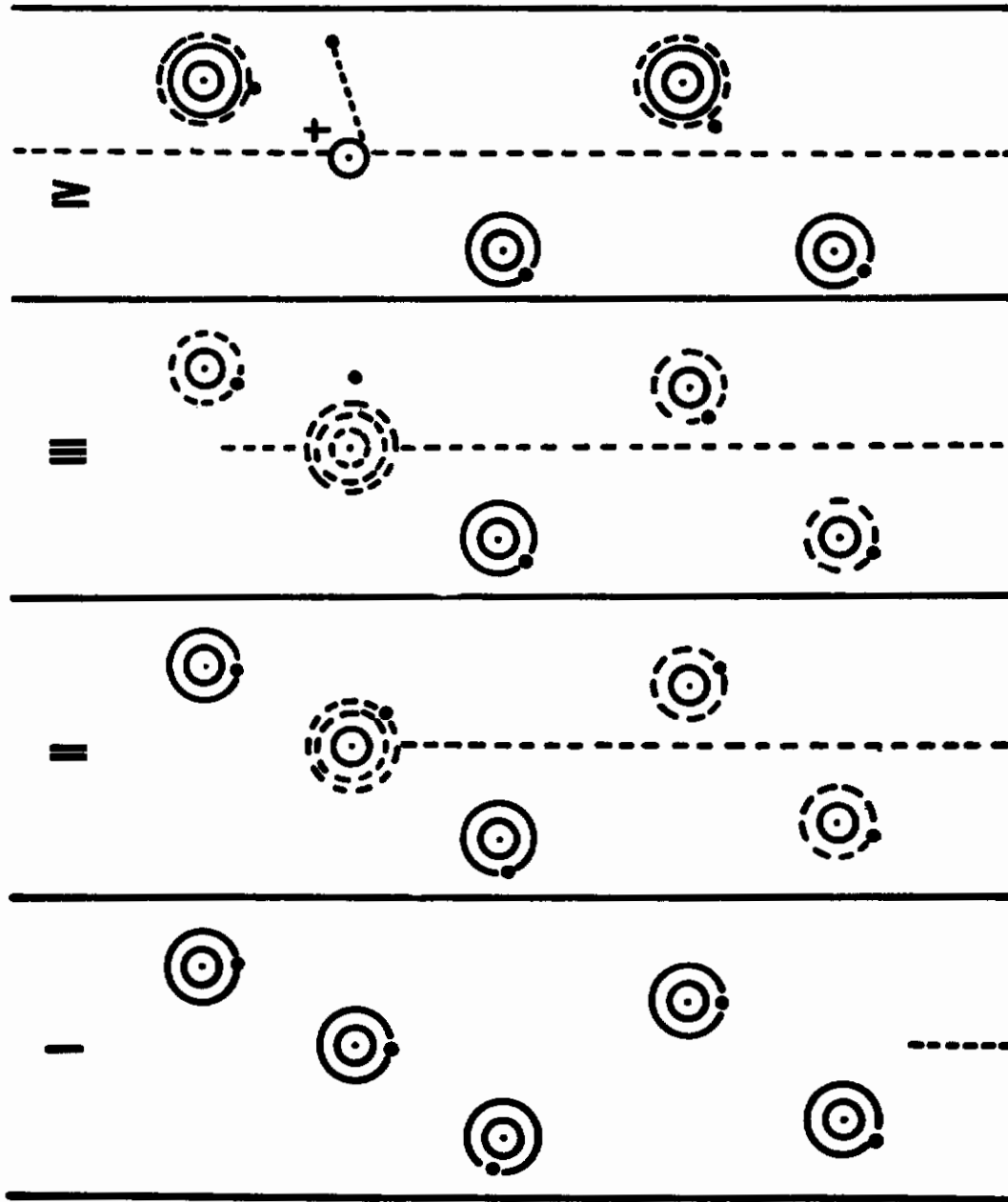


Figure 2.

SPUR FORMATION

⊙ + Ionized
⊙ Excited

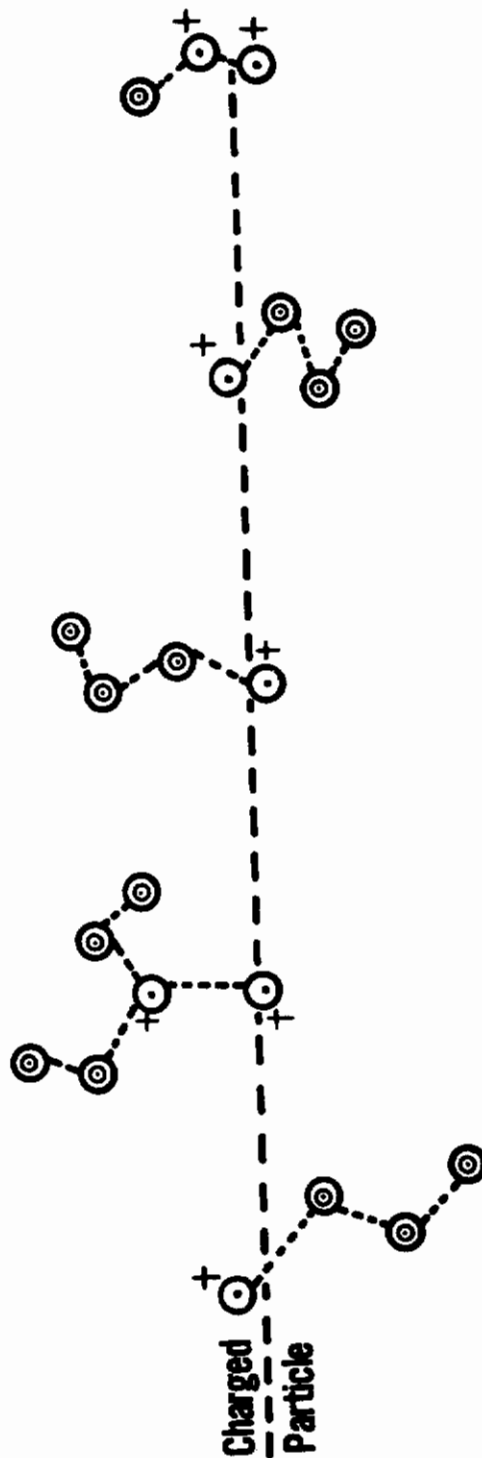


Figure 3.

EXCITED STATE ENERGY DIAGRAM

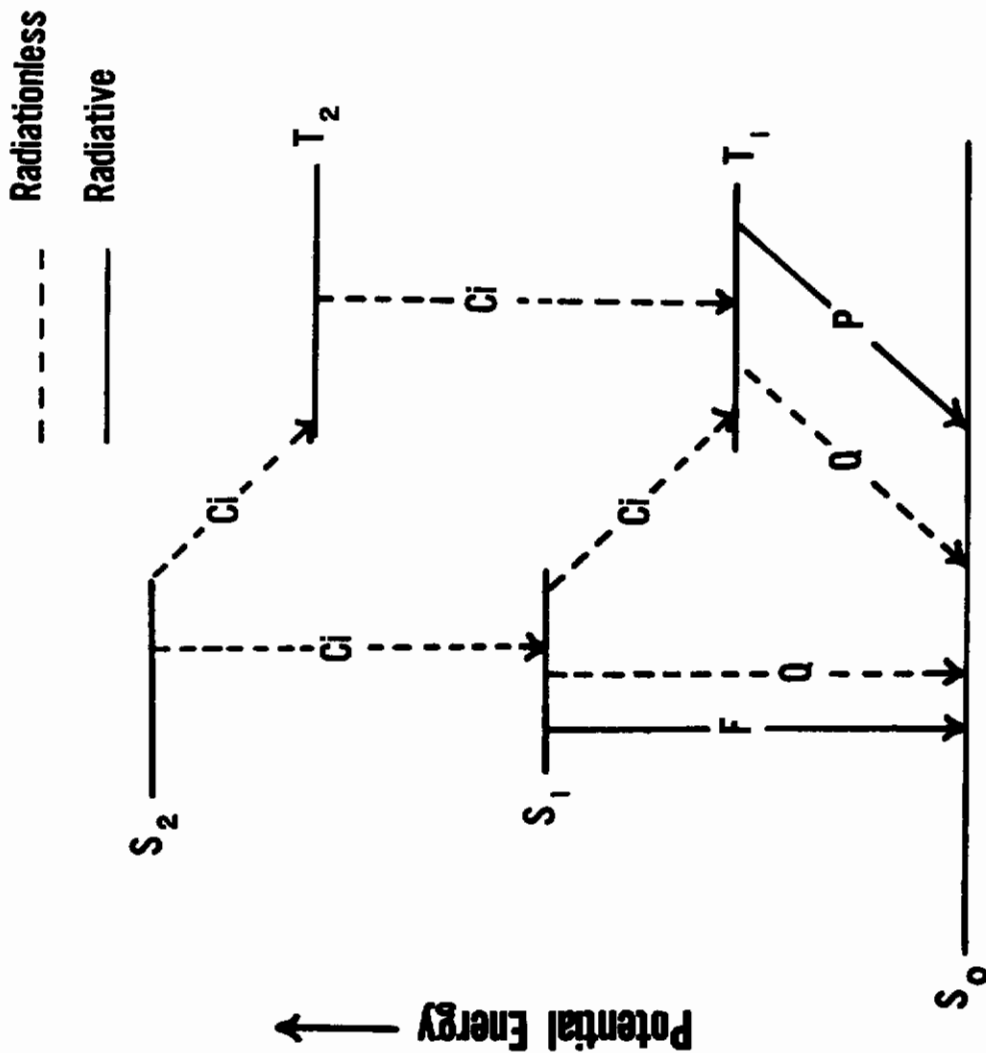


Figure 4.