

# Meetings

## Ionic Intermediates and Energy Transfer in Radiation Chemistry

Radiation chemists are addressing themselves to the following questions: How does a fast charged particle lose energy to the surrounding medium? What are the processes which produce the reactive species after the absorption of energy by a molecule or molecules? And what is the nature and the reactivity of the species? These questions were also being considered 11 years ago when the Faraday Society held its first discussion on radiation chemistry. In attempts to answer these questions at that time there was heavy reliance on information based on chemical analyses, but today additional information is available from the direct observations of identifiable intermediates. Moreover, the radiation chemist now has an advantage over workers of a decade ago with respect to experimental procedures because of the development of gas chromatography and the ready availability of isotopic compounds.

About 250 radiation chemists from 12 different countries attended the recent Faraday Society Discussion on Fundamental Processes in Radiation Chemistry, held from 2 to 4 September at the University of Notre Dame. It was the first time a Discussion had been held in the United States, and it coincided with the dedication of the university's new Radiation Research building. Glenn T. Seaborg made the dedicatory address at the special convocation. James Franck and Samuel C. Lind received honorary degrees.

Among the most important papers presented at the Discussion were those dealing with the role of ionic species in organic liquids and glasses, the transfer of energy in crystals and liquid mixtures, gas phase intermediates, and solvated electrons and related species in polar liquids.

In organic liquids an electron ejected from a molecule upon ionization is believed to be thermalized within the coulomb field of the parent positive ion

if the dielectric constant is low, and it is therefore likely to be recaptured, producing reactive species. But, what is the probability that some electrons escape into the bulk of the solution? To answer this question A. O. Allen (Brookhaven) measured the limiting electrical conductivity at low fields in irradiated hexane and determined that the number of ions escaping recombination per 100 electron volts of absorbed energy was about 0.09—a small percentage ( $\sim 4$ ) of the total number believed to be produced initially. Evidence for a small yield of positive ions in other organic systems was presented by F. Williams (University of Tennessee), who found that the radiation-induced polymerization of cyclopentadiene was strongly retarded by the addition of low concentrations of amines, and that in cyclohexane containing ND<sub>3</sub>, yields of HD in excess of statistical expectation were obtained, a finding which suggests that ND<sub>3</sub>H<sup>+</sup> is an intermediate. Several other speakers presented evidence for a low but finite yield of positive ions in liquid hydrocarbons.

Conclusive evidence for the presence of ionic species in organic glasses was presented by W. Hamill (Notre Dame). Using optical absorption techniques he found that when these glasses were irradiated at 77°K electrons were trapped which showed a visible absorption band with a maximum at 1200 m $\mu$ . In the presence of about 1 percent of a good electron-accepting solute, such as naphthalene, the readily identifiable naphthalenide ion was produced. At lower naphthalene concentrations both the anion and the trapped-electron absorptions were observed. After the electrons had been detached through illumination, they reacted to form more naphthalenide ions. The yield, as reported by Hamill, is three electrons per 100 electron volts.

Whereas Hamill has shown that chemical effects are attributable to electrons, F. Dainton (Leeds) presented convincing evidence for an efficient process of energy transfer in certain

crystalline solutions. This efficiency is apparent from the extremely high yields ( $\sim 25$  molecules per 100 electron volts) obtained for the reduction of FeCl<sub>3</sub> in crystalline benzene (the FeCl<sub>3</sub> concentrations were much too low for electron capture). These yields were not obtained in any nonordered systems such as glasses or supercooled liquids. The interpretation advanced for these results is that excitons are formed in the solvent and that energy transfer is possible if the exciton spectrum is overlapped by the absorption spectrum of the solute.

That energy transfer also occurs in liquid hydrocarbon mixtures was argued by P. J. Dyne (Chalk River), who observed that in hydrocarbon solutions of cyclohexane-d<sub>12</sub> (the "indicator" substance) a much larger hydrogen yield from the "indicator" was obtained than would be expected from its mole fraction, and that the addition of either cyclohexene, carbon tetrachloride, benzene, or *p*-benzoquinone reduced the total hydrogen yield from the solvent. This paper provoked considerable discussion, and evidence was presented by several participants to show that the reduction of the hydrogen yield may be attributed instead to hydrogen-atom scavenging.

A more direct approach to the study of energy transfer was that described by R. H. Schuler (Mellon Institute), in which radicals were detected in irradiated mixtures of liquid ethane and ethylene by an electron-spin-resonance technique. An unexpectedly high yield of vinyl radicals was observed. This result is not explicable as an atom or radical abstraction mechanism but may be interpreted either as transfer of energy to the ethylene from the ethane or as a preferred absorption of energy in the ethylene.

Further support for energy transfer came from a study by R. B. Cundall (Nottingham), who observed an inordinately high yield of *cis-trans* isomerization of 2-butene in benzene solutions. He attributed this result to a triplet state mechanism.

Related to the foregoing papers are the questions raised by M. Burton (Notre Dame): What is the fraction of the energy absorbed nonlocally? and, How does nonlocalized deposition of energy become localized on a molecule or molecules?

No clear answers to these questions were given, but several pertinent experimental results were presented. J. Cunningham (Armour Research Founda-

tion) had found that at low concentrations of silver ions in nitrate crystals the yield of nitrite ions was reduced and silver atoms were obtained. Whether an electron-scavenging process or collective excitation followed by localization on the impurity silver ion site is operative here is not obvious. S. Siegel (Aerospace) reported that D<sub>2</sub>O containing about 0.4 percent HDO irradiated at 4°K produced equal yields of deuterium and hydrogen atoms, as determined by electron-spin resonance; he interprets this finding as illustrating eventual localization of energy at trap sites.

Several excellent papers on gas phase radiolysis were presented, pertaining to ionic species and excited molecules as intermediates and their relative yields. Incidentally, much of our knowledge about the possible reactions between ions and molecules in gases derives from recent mass spectral studies in which both the products and the rates of these reactions have been determined.

The importance of ionic species was stressed by D. Dominey (Harwell). In the radiolysis of carbon dioxide, CO<sub>2</sub><sup>+</sup>, CO, and O<sub>2</sub> are produced, but the CO<sub>2</sub><sup>+</sup> reacts with the O<sub>2</sub> by charge transfer and the resulting O<sub>2</sub><sup>+</sup> effects the oxidation of CO to CO<sub>2</sub>. This mechanism is proposed to explain the apparant radiation stability of CO<sub>2</sub>. Similarly, G. Johnson (Newcastle-upon-Tyne) concluded that in the gamma-ray-induced chain oxidation of CO the chain is initiated and propagated by ionic species, some of which he believes are in excited states.

The importance of neutral species in the gas phase was discussed by D. Beck (Freiburg). He used a novel apparatus which consisted of a mass spectrometer adapted to detect neutral species (radicals and molecules) formed in the electron bombardment of hydrocarbon vapors. His results show that, for aliphatic hydrocarbons, approximately one neutral molecule decomposes for each ion produced. P. Ausloos (National Bureau of Standards) pointed out, however, that extrapolating from mass spectra to gas phase radiolysis is not entirely valid, since pressure has a strong effect on the fate of the parent ion. He concluded from studying deuterated and nondeuterated hydrocarbon mixtures that excited molecules account for a maximum of 20 percent of the products at atmospheric pressures.

If the initial yields of ionic species, radicals, and excited molecules are known, and if all subsequent reactions of these species are considered, the final products of the radiolysis may be cal-

culated a priori. This theoretical approach was taken by J. L. Magee (Notre Dame) for determining the yield of ozone from oxygen. Good agreement with experimental results is obtained if it is assumed that one excited molecule is formed per ion pair produced. An objection to this treatment was raised by A. Henglein (Hahn-Meitner Institute), who pointed out that reactions of excited-molecule ions should also be considered.

Without question, recognition that the solvated electron ( $e_{aq}^-$ ) is an important intermediate in water radiolysis has been a significant development in radiation chemistry. That there were two different reducing species and that the one formed in higher yield possessed a unit negative charge had been established by product analysis methods in recent years. And in 1962 the optical absorption spectrum of the solvated electron was determined by means of the pulse radiolysis technique (the radiation chemistry analog of flash photolysis). The absorption is broad and intense, showing a maximum at about 700 mμ and a molar extinction coefficient of about 10<sup>4</sup> liter per mole per centimeter.

By fast photoelectric recording of this absorption, it is possible to carry out direct kinetic studies. In one such study by J. Keene (Christie Hospital) the half-life of the solvated electron was determined to be 25 microseconds. Similarly, M. Matheson (Argonne) reported on the absolute rate constants for the reactions of the solvated electron with various organic and inorganic reagents. He found that the solvated electron reacted rapidly with reagents of high electron affinity. He also showed that the very important reactions  $e_{aq}^- + e_{aq}^-$ ,  $e_{aq}^- + H_{aq}^+$ ,  $e_{aq}^- + OH$ , and  $e_{aq}^- + H$  all proceeded with rate constants of about 10<sup>10</sup> liter per mole per second.

These precise determinations are of significant value to radiation-chemistry theory. For example, the diffusion-kinetic theory, which is used to explain why a fraction of those species initially formed in the "spurs" recombine whereas the remainder diffuse into the bulk of the solution, requires, among other parameters, a knowledge of absolute rate constants. These experimentally determined values have only recently become available.

Since the solvation of ions requires a medium of high dielectric constant, it was natural to ask if the solvated electron could exist in other polar solvents. The answer was supplied by L.

Dorfman (Argonne), who reported direct observation of the solvated electron in methanol and ethanol. The spectra are similar in all three media, and the reactivities toward various reagents are much the same. Dorfman was also able to show that many of the trapped species that Hamill had observed in the glassy state, which were formed by the reaction of thermalized electrons with dissolved solutes, could also be detected as transients in liquid ethanol. The yield of the solvated electrons in ethanol, however, seems to be lower than in water.

The yield of the solvated electron in water is still the object of active investigation, as are the nature and yields of other species formed concomitantly. G. Scholes (Newcastle-upon-Tyne) presented evidence which supports a yield for the solvated electron of  $G = 3.0$ , and he also demonstrated an independent yield of hydrogen atoms of about 0.7 atom per 100 electron volts. G. Hughes (Liverpool) suggested that the OH radical (the oxidizing species) at high pH exists as O<sup>-</sup>, on the basis of its different reactivity in basic as compared to acidic media.

Although many advances, in both theoretical understanding and factual knowledge, have been made since the first Faraday Society Discussion on radiation chemistry, many unresolved problems remain. Clearly their resolution will require more research with the many new, sophisticated experimental techniques now available.

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## Phenolics of Higher Plants

The growing interest in the chemistry of the numerous phenolic compounds which occur among higher plants was reflected in a recent symposium sponsored by the Plant Phenolics Group of North America. Two sessions of the Group's third annual meeting, held on 6 and 7 September at the University of Toronto, were devoted to the symposium.

The first session was devoted to flavonoid compounds. T. A. Geissman (University of California, Los Angeles) reviewed the leucoanthocyanins. These have been known for many years, but only recently have their