# Meetings

## Physical and Chemical Aspects of Ionization and Excitation Processes

Progress in basic studies of radiation effects on molecular systems is reflected by the extent to which the contributing physical and chemical processes can be clearly recognized and characterized. This was the underlying theme of a United States–Japan Conference on radiation chemistry held in Hakone, Japan, 10 to 13 November 1969. Eight U.S. and 30 Japanese scientists discussed the consequences of ionization and excitation events that are induced in gases, liquids, and solids by radiation. Reports of experimental work emphasized the study of intermediate species as revealed by spectroscopic methods with appropriate time resolution.

In the opening session, T. Watanabe (University of Tokyo) discussed the cross sections for charge-exchange processes that take place with the medium when heavy ions ($Li^{3+}$ to $Ne^{10+}$) in the energy range up to 10 Mev per nucleon are slowed down by passage through matter. Electron attachment to the heavy ion results in ionization of the target molecule whereas the subsequent process of electron detachment from the heavy ion is accompanied by the formation of molecular excited states. The ion pair distribution of the track is then determined by the velocity dependence of the cross sections for these two processes.

The properties and reactions of the excited states of rare gases were discussed by a number of participants. C. E. Klots (Oak Ridge National Laboratory) compared the ionization efficiency of molecules activated by energy transfer from excited argon atoms to the corresponding photo-ionization efficiency. He concluded that the two efficiencies tend to be the same for polyatomic molecules, even though photo-ionization proceeds directly without the intermediate formation of discrete auto-ionization states. T. Sugiura (Takasaki Research Establishment) reviewed the information derived from mass spectrometry about the processes of negative ion formation. He reported that, whereas acetonitrile does not capture electrons of thermal energy, the negative acetonitrile ion can be formed without dissociation in a collision with an excited rare gas species which itself becomes ionized in the process. This finding suggests that a change of molecular geometry may be needed for negative ion formation in this case, and that this is accomplished in the charge-transfer compound state of the reactants.

R. F. Firestone (Ohio State University) described spectroscopic studies aimed at identifying transient atomic and molecular species in the pulse radiolysis of the rare gases. The multiline spectra of excited atomic species having lifetimes of $\sim 1$ μsec are observed in several of the rare gases; in argon a broad absorption band centered at 990 nm is tentatively attributed to an attractive state of a neutral diatomic molecule. This band shows structure under high resolution, and its kinetic characteristics are incompatible with an assignment to ionic species such as $Ar_2^+$. The band fails to appear when 1 percent krypton is present in argon, and no evidence has been obtained for diatomic species made up of different rare gas atoms. Although diatomic states of helium could not be detected in these experiments, such species are known from work carried out on the electron irradiation of liquid helium (*1*).

A. O. Allen (Brookhaven National Laboratory) reviewed some developments in the ionization of liquids by radiation. He outlined a new method which he has developed with W. F. Schmidt for the determination of free ion yields in liquids. Essentially a clearing electrostatic field is applied immediately after a pulse of radiation to measure the ions that have escaped the very fast process of initial (geminate) recombination in the field of the parent ion. The results show that this free ion yield does not depend solely on the dielectric constant of the liquid. For instance, the *G* yields (the number of free ions produced per 100 ev of energy absorbed by the system) for hydrocarbons show considerable variation ranging from less than 0.1 for benzene and unsaturated compounds to 0.9 for neopentane. The yields for several *n*-alkanes lie between 0.1 and 0.2, and are generally lower than yields for the corresponding branched alkanes. High yields, similar to the value for neopentane, are found for other symmetrical compounds such as tetramethylsilane and tetramethyltin. Careful measurements of true electron mobilities in hydrocarbons give values that are much higher than those reported in the past, and the results appear to parallel the ion yield determinations. It is thought that for saturated hydrocarbons and analogous compounds in the liquid state the interaction of free electrons with symmetrical molecules is less than for molecules of lower symmetry; this would explain why in the former case there is a higher mobility and also a larger probability of escape from initial recombination as measured by the enhanced ion yield. The ion yield for neopentane is depressed by the addition of a low concentration of an electron scavenger such as carbon tetrachloride, and this is consistent with the much lower mobility of negative ions relative to that of free electrons. It was stressed that these results on electron mobility in liquids do not coincide or even correlate with suitable extrapolations from gas-phase measurements, and that the interaction of free electrons with molecules in a liquid system should be viewed as a property of the condensed state. The possibility of rapid migration of positive holes in liquids was raised but it appears that positive ion mobilities are normal in these systems.

S. Sato (Tokyo Institute of Technology) discussed chemical approaches to the study of ionization processes in organic liquids. Electrons and positive ions formed by irradiation can react with scavenger molecules if the latter are present in sufficient concentration to compete with charge recombination. In principle, this method can be used to determine the total ion yield. Sato described the results obtained with nitrous oxide where the amount of liberated nitrogen gas serves as an indicator for the yield of scavenged electrons. A number of semiempirical relations have been proposed to explain the dependence of yield on scavenger concentration. Analysis of the results for saturated hydrocarbons in terms of a simple diffusion model gives estimates for *G* of 2.9 for the total ion yield and of 44 Å as the average of the initial separation distances between positive ions and electrons. Discussion centered on the mathematical difficulties involved in attempting to convert a distribution in time as monitored by the scavenger to the original spatial distribution of ions and electrons laid down by the radiation.

R. H. Schuler (Carnegie-Mellon University) showed how the results of experiments with electron scavengers can be extrapolated to give the free ion yield. The values so obtained are in excellent agreement with the determinations according to the physical method used by Allen and Schmidt. On the other hand, the rate constant of $3 \times 10^{11}$ liter mole$^{-1}$ sec$^{-1}$, estimated from kinetic analysis of the electron scavenging reaction, is about one order of magnitude lower than the value expected on the basis of the highest electron mobilities that have been measured in saturated hydrocarbons. There is still much uncertainty about the distribution of ion recombination times in hydrocarbons. Scavenger studies indicate that, although about half the total number of ions survive less than 30 psec, there is a long tail to the distribution such that a significant fraction of ions ($G \sim 0.5$) persists for times much greater than 1 nsec.

E. J. Hart (Argonne National Laboratory) reviewed the structure and chemical properties of the hydrated electron. Bronskill *et al* (*2*) have shown that the hydration time of the electron is less than 20 psec (*2*). The optical absorption spectrum of the hydrated electron is surprisingly insensitive to the composition of the solution, and even in 1*M* perchloric acid, where the half-life is reduced to 1 nsec, the spectrum is identical to that obtained in dilute solution. There is a shift in the absorption maximum from 1.7 to 1 ev as the temperature is increased from 300° to 650°K, but even at the latter temperature, which is above the critical point, the general shape of the band is unaltered. Similarities exist between the absorption spectra of solvated electrons and *F* centers (the *F* center consists of an electron trapped in the field of a negative ion vacancy in an ionic crystal), and an absorption band located below 200 nm for the hydrated electron may be related to the $\beta$-band of the *F* center in potassium bromide, which appears in the same spectral region.

Theoretical models of the hydrated electron were considered by K. Fueki (Nagoya University). In contrast to the dielectric continuum model proposed by Jortner (*3*), the tetrahedral vacancy description of Natori and Watanabe (*4*) emphasizes a well-defined local structure. The latter model is more in keeping with the observation that the absorption spectrum of the trapped electron in ice resembles that of the hydrated electron, although calculations according to the continuum model are in good agreement with the experimental value for the optical transition energy. Fueki proposed a semicontinuum model that incorporates both long-range and short-range interactions. On the basis of this model, the optical transition energy can be fitted to a cavity radius of 1 Å. Calculations of the spectral broadening that would be anticipated to arise from excess electron-phonon interactions indicate that this effect alone is inadequate to explain the actual width of the spectrum, and transitions to higher excited states are postulated to account for the difference. T. Watanabe also discussed the results of more refined calculations according to the vacancy model for the transition energy and oscillator strength of the optical transition.

F. Williams (University of Tennessee) reported hyperfine structure attributable to interaction with two equivalent nitrogens in the electron spin resonance (ESR) spectrum of an excess electron center in acetonitrile-$d_3$. The optical spectrum of the same center shows vibrational fine structure which is interpreted in terms of a change in molecular geometry on electronic excitation.

Several contributions were concerned with the specific reactions of certain free radical and ionic intermediates in the condensed phase. R. H. Schuler described how the powerful technique that he and Fessenden have developed for the *in situ* radiolysis of organic liquids in the cavity of an ESR spectrometer has been extended to the study of aqueous solutions. Identification of paramagnetic species from the isotropic ESR spectra is usually unambiguous, and, for certain systems, the method can provide more detailed information than is obtainable by optical (pulse radiolysis) and chemical studies.

J. E. Willard (University of Wisconsin) summarized recent progress in studies of trapped intermediates in organic solids, with particular emphasis on trapped electrons and the alkyl radicals formed in dissociative electron capture by alkyl halides. In contrast to many other intermediates whose concentrations reach stationary values on prolonged irradiation of solids, trapped electrons in hydrocarbon glasses reach a maximum concentration which then declines on continued gamma irradiation. The fact that infrared irradiation of trapped electrons enhances absorption in the ultraviolet region whereas subsequent ultraviolet irradiation regenerates trapped electrons suggests that reaction of electrons with free radicals may contribute to this effect. Willard also discussed the question of whether hydrogen atoms result from the radiolysis of hydrocarbon glasses in the range from 4° to 77°K. Except for methane, the results are negative, although parallel studies show that at least in some matrices, hydrogen atoms generated by the photolysis of hydrogen iodide are trapped under the same conditions.

H. Yoshida (Hokkaido University) reported on thermal decay rates of trapped electrons in hydrocarbon glasses. The decay curve could be resolved into two first-order components, and these are attributed to separate decay processes characterized by different kinds of electron traps. However, reservations were expressed in the subsequent discussion about the uniqueness of interpretations based on kinetic analysis of composite decay curves.

M. Dole (Baylor University) presented an account of transformations between alkyl and allyl-free radicals in gamma-irradiated polyethylenes. At room temperature and above, the conversion of alkyl and allyl-free radicals in gamma-irradiation is a first-order process. The reaction is accelerated in the presence of molecular hydrogen, and the activation energy is thereby lowered from 17 to 13.5 kcal mole$^{-1}$. Moreover, the reaction in deuterium gas proceeds with the formation of HD, which suggests that atom abstraction by the alkyl radical from deuterium is followed by the attack of D· on the hydrocarbon chain. This mechanism allows free radical migration by a random walk to the vicinity of the unsaturated groups. H. Kashiwabara (Hokkaido University) described the photoinduced reactions of allylic radicals in gamma-irradiated polyethylene. Alkyl radicals are regenerated by the ultraviolet irradiation of allylic radicals at 77°K, but with light of longer wavelengths scission of the main chain is also reported to occur.

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## Gene Regulation in Mammalian Cells

Problems of differentiation and gene regulation in mammalian cells formed the subject matter of the most recent Basel Colloquium, 31 March to 2 April 1969. This was the fifth in a series of meetings taking place every 2 years and devoted to different topics of genetics.

Based on existing knowledge of relations between DNA and proteins, of cell metabolism, and of subcellular structure details, the discussions were focused on conceptual and experimental aspects of gene regulation in mammalian cells. The realization of a close relationship between mechanisms of gene regulation in mammalian cell differentiation and in immune expression provided a thread of continuity for the various sessions.

Whitehouse, in his discussion of possible mechanisms of regulation in mammalian cells, proposed the application of the concept of the "master-slave" gene organization of chromosomes in the control of immunoglobulins. One single gene (the master) is assumed to control the constant part of the myeloma protein molecule, and five alternating genes (the slaves) would control the variable parts of the molecule. Whitehouse also emphasized the role of the nonhistone, that is, acidic proteins. Their specificity in the unmasking of organ-specific DNA is particularly interesting in view of the acidic protein nature of the specific repressor substance in *Escherichia coli* and bacteriophage. In discussing polytene chromosomes, W. Beerman reported the attachment of acidic proteins as the first event in the puffing phenomenon, preceding RNA synthesis.

Gene amplification and its role in regulation was discussed by several speakers. The DNA body found in oogonia and oocytes of *Acheta*, which is indistinguishable from heterochromatin and appears in electron microscope pictures to resemble synaptonemal complexes, was discussed by Lima-de-Faria in its relation to gene amplification in the nucleolar organizing region. An interesting suggestion of Whitehouse refers to the multiplicity of regulatory functions residing in heterochromatin and the possible absence of crossing over in regulatory genes; if the amplified genome is indeed endowed with regulatory function, crossing over may not be expected to occur in it.

The necessity of distinguishing between the concepts of gene redundancy and gene amplification became apparent in the course of discussions. Redundancy as a constant phenomenon of the genome and defined as the continuous existence of a large number of repeats next to each other must be distinguished from the transitory selective multiplication of genes described as amplification. Giacomoni reported redundancy of ribsomal RNA genes in hamster cells, and Motulsky in his discussion called attention to the interesting findings of Schroeder of multiple hemoglobin $\gamma$-chain genes in man.

Mechanisms of inactivation of the mammalian X chromosomes were discussed, among others, by Klinger, Cattanach, Fraccaro and Gianelli; the last-mentioned reported an interesting distortion of the expected random distribution of inactivation of parental X chromosomes in the mule. In spite of the indisputable evidence for the existence of X inactivation, its mechanism remains unclear. In this connection, the report by Klinger of the effect of cell density on the frequency of cells with sex chromatin bodies appears most significant.

Discussion by B. Ephrussi served to delineate the potentialities as well as the limitations of somatic cell genetic analysis. He dealt with two aspects of such studies, "karyotype" and "epigenotype," the latter encompassing problems of embryonic differentiation. Ephrussi proposed a division into "household" and "luxury" functions subject to different regulatory mechanisms. He referred to the mutual exclusion of luxury functions in differentiation, a principle which was taken up again later in discussions of immune expression. Further questions raised by Ephrussi concerned concepts of repression and of dedifferentiation, and he proposed a scheme of gene regulation which possibly could be tested experimentally. The emphasis on problems and questions rather than on existing data and answers lent special significance to this talk, which ended with an appeal for the isolation of more mutations in the mouse having relevant effects; these would serve as tools for the analysis of regulatory mechanisms in differentiation.

The early activation of ribsomal RNA genes in the mouse was reported by Monesi. Cell hybridization studies formed the subject of several papers, among them one by Siniscalco and Klinger demonstrating intergenic complementation of two X-linked genes. The problem of somatic segregation was discussed by C. E. Ford, G. Martin, and S. Ohno. The close relation between problems of cell differentiation and of immunology became particularly apparent in Cepellini's talk about the regulation of immunoglobulin genes. Concepts of dosage compensation, of allelic and nonallelic exclusion, and of functional haploidy, particularly in plasma cells, were included in this discussion, as well as possible mechanisms of repression and derepression. Finally, Cepellini challenged the one-gene : one-polypeptide dogma, proposing a new definition of the gene in accord with the possible control of one polypeptide by more than one gene.

The regulation of gene expression in single cells formed the subject of the discussion by Pernis who stressed the evidence for allelic exclusion in the case of immune substances produced by plasma cells. Seegmiller and Danes respectively dealt with problems of regulation of metabolic pathways in several uric acid anomalies and in cystic fibrosis of the pancreas. Gartler reported studies in which X-linked glucose-6-phosphate dehydrogenase variants served as tools for developmental analysis of morphological structures such as hair roots in the skin. This