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_2O 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_2^+, CO, and O_2 are produced, but the CO_2^+ reacts with the O_2 by charge transfer and the resulting O_2^+ effects the oxidation of CO to CO_2. This mechanism is proposed to explain the apparent radiation stability of CO_2. 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 calculated 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 $m\mu$ and a molar extinction coefficient of about 10^4 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^{10} 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 *p*H exists as O^-, 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 structures been elucidated. They are characterized by conversion to red pigments on heating with mineral acid. An important place in this class is occupied by the flavan-3,4-diols, which have been implicated in astringency and (in studies by Roux, Hillis, and others) in the biosynthesis of condensed tannins. A new group of leucoanthocyanins is the proanthocyanins, whose aglycones are oligomeric in nature and have monomers joined by various linkages. An example is the dimer composed of cyanidin and (+)-catechin, isolated in 1962 by Freudenberg and Weinges, in which a ketal linkage is involved. Geissman and Dittmar have isolated from the avocado seed a condensation product of flavan-3-ol and flavan-3,4-diol, which appear to be joined by a carbon-carbon linkage.

Other flavonoid compounds which have been known for many decades but whose structures have been elucidated only recently are the glycoflavonoids, or C-glycosylflavonoids. These were reviewed by Margaret K. Seikel (U.S. Forest Products Laboratory, Madison, Wisconsin). Although vitexin, an 8-glycosylapigenin, was discovered in 1898 by Perkin, the structure of the hydroxylated side chain was fully worked out only 6 years ago and is still questioned. During the past decade this field has developed rapidly to the point where almost two dozen compounds, mostly flavones, are now recognized to have widespread distribution among plants. The existence of a carbon-linked sugar chain can be recognized by the great resistance to hydrolysis under conditions in which glycosidic cleavage normally occurs. Although the nature of the flavonoid is readily determined, the major stumbling block thus far in making structural determinations has been to establish the nature and the point of attachment of the side chain, which are known unequivocally only for vitexin and its 5-deoxy derivative. *Vitex lucens*, the classical source of vitexin, has been shown by Seikel to contain additional glycoflavonoids, among which luteolin derivatives possibly containing two side chains are of greatest interest.

Flavonoid glucosides of a North American native skullcap (*Scutellaria epilobifolia*) were discussed by J. E. Watkin (National Research Council of Canada, Saskatoon), whose prime interest has been biosynthetic relationships. In addition to the 7-glucuronide of 5,6,7-trihydroxyflavone (baicalein), a known compound, the 7-glucuronides of the new aglycones, 2′-methoxy-5,7-dihydroxyflavone, (-)-5,6,7-trihydroxyflavone, and 5,7,8-trihydroxyflavone, have been identified in this species. A very active glucuronidase found in this plant has also been partially purified. Watkin's studies at the enzyme level have not yet contributed positive results to answer the puzzling question of what additional intermediates are concerned in the formation of flavonoids from cinnamic acids and acetate.

During the second session, several groups of phenolics other than flavonoids were considered. Although chlorogenic acid has been known since 1837, and other hydroxycinnamoylquinic acids have been known for many years, the analogous shikimic acid esters, which are closely related biosynthetically, were unknown until the recent work of Goldschmid and Hergert on western hemlock. V. P. Maier (U.S. Department of Agriculture, Pasadena) dealt with the occurrence, isolation, structural chemistry, and chemical synthesis of these esters. Three new compounds which he isolated from dates—dactylifric acid, isodactylifric acid, and neodactylifric acid—were considered in detail. Crystalline dactylifric acid was shown, by degradation and synthesis, to be 3-*O*-caffeoylshikimic acid, while iso- and neo-dactylifric acids appear, from their periodate reactivities, to be 4-*O*- and 5-*O*-caffeoylshikimic acids, respectively. All are enzymic browning substrates. Maier emphasized the susceptibility of these compounds to acyl migration and the potential complexities due to the possible presence of multi- or mixed hydroxycinnamoyl residues. Important advances, which may extend to the biochemical field, can be expected in this area.

The fungi were considered during a contribution by T. J. Sproston (University of Vermont, Burlington) on the isolation and characterization of 1,4-naphthoquinones. Although quinonoid compounds are also formed by lichens and green plants, they are most readily recovered from fungal cultures, where they sometimes separate in crystalline form. A detailed report on the isolation and characterization of lambertellin, a new hydroxy-1,4-naphthoquinone from *Lambertella hicoriae* Whet., was presented. Existing evidence points to its identity with 2,3-(2-keto-methyl-α-pyrano)-5 hydroxy-1,4-naphthoquinone, there being still some doubt about the position of the methyl substituent.

W. L. Stanley (U.S. Department of Agriculture, Albany, California) reviewed recent developments in the chemistry of coumarins and discussed methods for recovering, separating, identifying, and synthesizing natural coumarins. He showed representative spectra from a large collection which he has accumulated. He discussed in detail his own work on the identification of coumarins and furanocoumarins from cold-pressed lemon, grapefruit, and lime peel oils. With the aid of column and chromatostrip chromatography, 12 of these compounds have been positively identified and several others have been tentatively identified. In lime oil were found at least five such compounds previously unreported from that source, and in bergamot oil, two. The structure of a new coumarin, auraptenol, from Seville orange oil, has been established to be 7-methoxy-8-(2-hydroxy-3-methyl-3-butenyl) coumarin.

The Plant Phenolics Group of North America plans to publish the proceedings of the symposium.

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