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# SOME RECENT DEVELOPMENTS IN THE STUDY OF UNSTABLE SPECIES*

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## *Introduction*

The papers in this monograph reveal the considerable advances made during the past decade in the direct observation of free radicals, excited molecules, ions, and other reactive particles. These developments have followed the introduction of new techniques for producing large concentrations of these reactive species and have been facilitated by the use of relatively recent analytical devices and by the adaptation of older ones. However, to a large extent these developments are a direct consequence of the extensive studies, carried out during the past 30 years, in which the chemical properties of free radicals have been inferred primarily from an analysis of their chemical reaction products. These older methods are more indirect, but both approaches are required for a detailed understanding of unstable species and their reactions.

Interest in the study of these species has been manifested in various fields. There are, for example, many fundamental problems the solutions of which depend on a more accurate knowledge of the mode of formation and of the behavior of unstable species: typical problems involve dissociation energies of chemical bonds, atomic configuration of stable and unstable molecules, excitation energies, and energy exchange among the bonds of a molecule and between two colliding molecules. Unstable species also play a role in industrial problems, such as corrosion, polymerization, detonation, cracking of petroleum, combustion, flames, and in high-temperature processes of metallurgical interest. Other fields in which these reactive particles are of importance include biology (radiation damage), astronomy (spectra of planets, comets, and the sky), and geochemistry (origin of the earth's composition).

This paper summarizes some of the results described at the conference on which this publication is based, and several related investigations are mentioned. The discussion is classified into the following topics: methods of producing unstable species; methods of observing them; methods of investigating their molecular structure and other physical properties; methods of studying their chemical reactions; and related theoretical problems.

## *Methods of Producing Unstable Species*

Unstable species can be produced[1] by thermal means, by photochemical methods (including, here, the use of X rays), by electrical discharges, and by bombardment with material particles such as electrons and $\alpha$-particles.

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They are also produced in flames (initiated either thermally or by a spark or by atoms).[2]

Major recent developments have occurred in the photochemical and "thermal" methods. The introduction of flash photolysis[3] has permitted the production of large concentrations of free radicals. In the present publication, Ramsay[4] has discussed the absorption spectra of a number of polyatomic free radicals formed in this way. Other applications have been described in a recent review.[5] Depending upon the apparatus, the time of the intense light flash is in the range of 10 to 1000 $\mu$sec.

Shock waves have provided an invaluable extension of the thermal method for producing free radicals, excited molecules, and ions. The application of the shock tube to various problems of chemical interest has been outlined by Hornig[6] in this monograph. In a few microseconds a gas can be heated by the shock to a definite temperature of the order of several thousand degrees centigrade. After an initial equilibration period, the temperature of the shocked gas remains constant until the wave is reflected from the end of the shock tube. Data on the reaction rates and dissociation energies have been obtained from measurements of absorption spectra and of the velocity of the incident and reflected waves.[6] There has recently been described a modified shock tube in which the shocked gas maintains a fixed thermal profile during the time it is at a high temperature.[7] This tube has been used for shock-tube studies that are based on chemical analysis of the reaction products.[7]

The increased interest to photochemists of one of the less-studied spectral regions, the far ultraviolet below 2000 Å. wave length, has been noted by Taylor[8] in the present publication. The usefulness of this less accessible photochemical region lies partly in the fact that many simple molecules do not absorb light of higher wave lengths and can be studied photochemically only in this short wave length region. The light sources employed for such investigations include mercury resonance lamps emitting light at 1850 Å., and resonance lamps utilizing xenon (1470 and 1295 Å.) and krypton (1235 and 1165 Å.). Suitable reaction-cell windows, transparent in various parts of this spectral range, have been fabricated from lithium fluoride, sapphire, and thin quartz. Nelson and Ramsay have recently described a flash-photolysis lamp constructed from a sapphire tube.[9]

Margrave[10] notes that resistance-wound, induction, and solar furnaces are currently employed to produce high temperatures. He observes that an electric discharge still represents the best method of obtaining very high temperatures, of the order of 50,000° K. Broida and his co-workers[11, 12] have employed a microwave oscillator as a modified form of an electrodeless discharge. This apparatus was found to be considerably more efficient and cleaner than an electrode system.

### *Methods of Observing Unstable Species*

Much information about unstable species has been obtained indirectly from an examination of their chemical reaction products. Absorption and emission spectroscopy, mass spectroscopy, and paramagnetic resonance may be included among the more direct methods used to observe these species.

Absorption spectra of several excited molecules in gases, solutions, and rigid solvent media have been examined.[5, 13-15] The number of absorption spectra of gaseous free radicals has increased considerably since the advent of flash photolysis as a tool for producing large concentrations of these species.[4, 5] It seems that no infrared absorption spectra of these unstable free radicals have been observed. While some rapid-scan infrared spectrometers[16] are now available, the slowness of response and the relative insensitivity of present infrared detectors have presumably prevented observations on short-lived free radicals.

Emission spectra have been observed for numerous excited molecules formed by the absorption of light, and also for those free radicals produced photochemically by light of short wave length.[1] Emission spectra have been recorded for a number of free radicals and excited molecules formed in flames,[2] in electrical discharges,[1] in shock tubes,[17] and by flash photolysis.[5] Energetic free radicals, probably arising from an exothermic collision, have been observed to emit in the infrared region.[18]

The qualitative and quantitative detection of free radicals by mass spectrometry is discussed in this publication by Lossing,[19] who notes that the usual limits of detection are of the order of 1 part in $10^3$ or $10^4$ and that, accordingly, the method is usually practicable only when the free radicals are present in abnormally high concentrations. Such concentrations are obtained by using very high temperatures, electrical discharges, or mercury photosensitization. An increase in sensitivity of detection has been obtained by Foner and Hudson in their study of free radicals produced in flames.[20] These authors withdrew a sample in the form of a molecular beam that they interrupted periodically, and used a phase method of detecting the ion signal. In this way the background arising from dissociation of molecules on the filament was largely eliminated, and the sensitivity was significantly enhanced. Schiff[21] discusses in this monograph the application of mass spectrometry to the study of atomic reactions.

Paramagnetic resonance spectroscopy has proved to be a very sensitive technique for the study of free radicals in liquid and solid states. Its uses and limitations are discussed here by Fraenkel.[22] This technique can be used over a wide temperature range, from zero degrees absolute up to the melting point of the microwave cavity. Because of the relatively long response time of the apparatus, about a minute, to changes of free-radical concentrations, this apparatus can be used to examine only stable free radicals or to investigate unstable free radicals present in steady-state concentration, as in a flow system. Identification of a free radical is made from the number and position of the resonance absorption lines, which give an insight into the interaction of the spin of the electron with the spins of the nuclei. Fraenkel emphasizes the need for caution in the interpretation of the spectra: because dielectric saturation of the sample can readily occur, spurious results can be obtained. Consequently, misinterpretations abound in the literature.

Fraenkel observes that the study of unstable gaseous free radicals by paramagnetic resonance absorption is likely to be very difficult. Because of the coupling of the electron spin and the molecular rotational motions, and because of the onset of free rotation in the gas phase, the spectrum of a paramagnetic gas is very complex, consisting of numerous absorption lines. The intensity of each is correspondingly small. It may be remarked here, however, that no such difficulty applies to the study of gaseous atoms; the paramagnetic resonance absorption spectra of a number of gaseous atoms have been recorded, particularly by R. Beringer and his co-workers, who are quoted by Fraenkel.[22]

Broida[12] discusses the observation of unstable species that have been stabilized either by rapidly freezing them out of a gaseous flow system or by producing them in a solid, for instance, photochemically. The measurements used include ultraviolet, visible, and infrared absorption spectroscopy; emission spectroscopy; paramagnetic resonance; and calorimetry.

In some studies, several independent methods have been used to estimate the concentration of a given unstable species. For example, the concentration of nitrogen atoms produced by an electrical discharge has been determined by mass spectroscopy,[23] by the absorption spectra of atoms frozen out from a flow system,[12] and also by the heat liberated when these trapped atoms are permitted to warm up and recombine.[12] Kistiakowsky and his co-workers[23] have recently compared emission spectra and mass spectra of a gaseous system of nitrogen atoms, while Winkler and his co-workers[24, 25] have studied chemically the reactions of nitrogen atoms with a considerable number of compounds. The paramagnetic resonance spectrum of nitrogen atoms formed in an electrical discharge has also been recorded.[26]

Margrave[10] describes in the present publication many species (generally not free radicals) that disproportionate, polymerize, or condense to solid compounds at low temperatures, but which are stable at high temperatures. Numerous simple molecules containing metal atoms fall into this category. Since these molecules are fairly stable at high temperatures they can be studied by a wide variety of methods under such conditions. The techniques employed have included ultraviolet, visible, and infrared absorption and emission spectroscopy; mass spectroscopy; and measurements of pressure and rate of effusion from the reaction vessel. Many of these species and their reactions are of considerable metallurgical interest.

### *Methods of Studying the Properties of Unstable Species*

Properties of stable and unstable species of particular interest include: the arrangement of the atoms within each molecular or free-radical species; the vibration frequencies of these atoms; the electronic energy levels (and ionization potential) of a species; and the energy required to dissociate it into atomic and other fragments.

Atomic configurations and vibration frequencies, both of the lowest and of excited electronic energy levels, of simple free radicals have been obtained from detailed analyses of their ultraviolet and visible absorption and emission spectra.[27] Dissociation energies have also been determined from some of these studies.[27] Ramsay[4] describes in this monograph the results found for polyatomic free radicals. The data for diatomic free radicals have been reviewed earlier.[5, 27] Analogous results for simple excited molecules have been discussed by Ingold.[28] Infrared emission spectra of hydroxyl radicals of high vibrational energy are available and provide information on structure.[18]

Free-radical sources for these ultraviolet and visible spectra have included flames, electrical discharges, flash photolysis, shock waves, and stellar phenomena. In most of these sources a major problem is to ascertain the emitting or absorbing free radical. Because of the considerable body of chemical information available on photochemical processes and because of the relative simplicity of these systems, flash photolysis appears to be a particularly useful tool for obtaining spectra of free radicals whose identity is not known for certain.

As noted earlier, these spectra also provide a source of data on the electronic energy levels of free radicals. In addition, ionization potentials of free radicals and of atoms, determined mass-spectrometrically, are discussed by Lossing[19] and by Schiff,[21] respectively, elsewhere in these pages. Fraenkel[22] describes inferences that can be drawn about the electronic configuration of free radicals from study of their paramagnetic resonance absorption spectra. For example, data on semiquinones are interpreted in terms of such concepts of electronic structure as hyperconjugation and configuration interaction between $\pi$ and $\sigma$ molecular orbitals.

Among the miscellaneous properties of free radicals that have also been determined may be listed the electron affinity and the heat of formation of the hydroxyl radical, obtained by microwave studies on flames containing alkali metal atoms.[29]

### *Methods of Studying Chemical Reactions of Unstable Species*

Almost all of the information on chemical reactions of unstable species such as free radicals has been obtained from an analysis of the reaction products, which in turn gave some clue as to the free radicals that were present. The data derived in this way from gaseous thermal and photochemical reactions have been summarized by Steacie.[1] In the present publication, Taylor[8] outlines some of the concepts of mechanism used to interpret the photochemical studies.

Much information on these reactions has also become available from studies of organic reaction mechanisms in the liquid phase. Walling[30] describes in this publication some of the generalizations drawn about the types of free-radical intermediates in these processes, their reactions, and the effect of chemical structure on their ease of formation and disappearance. The possible role of these intermediates in biological oxidations, including their function in those induced by radiation damage, is discussed here by Barron.[31]

Among the studies of chemical reactions of free radicals using the newer techniques may be listed measurements of the absorption spectra[5] and of the reaction products[5, 32, 33] of flash photolysis experiments. Another new technique is the measurement of absorption spectra and wave velocity in shock wave experiments. The use of the latter in studying chemical reactions and in determining dissociation energies is discussed by Hornig[6] in this monograph. The advent of the shock tube has extended considerably the upper temperature limit for the convenient study of some reactions. Even the dissociation energy of such stable molecules as nitrogen and carbon monoxide has been estimated by this technique. Hornig[6] also discusses the use of the shock tube in the study of the interchange of vibrational, rotational, and translational energy of molecules.

Lossing[19] describes here the study of homogeneous and heterogeneous free-radical processes using the mass spectrometer, while Schiff[21] discusses its application in investigations of reactions in electrical discharges. Broida[12] considers in detail the uses of the techniques of trapping out atoms from flow systems. The study of free-radical reactions by paramagnetic resonance under steady-state conditions is referred to by Fraenkel.[22] Margrave[10] summarizes some of the studies of the reactions of inorganic molecules at high temperatures. Examples of these include simple vaporization, decomposition of solids (thermally and in arcs), high-temperature reactions between solids, and combustions.

The reactions of gaseous ions have also been the subject of a number of recent investigations.[34] In this publication, Moore and his co-workers[35] describe an ionic-beam apparatus that can be used for the study of the sputtering of metals by fast ions under careful, highly controlled experimental conditions. The angular distribution of the sputtered material is inferred from measurements of radioactivity of the deposits, while the secondary electron emission and reflectivity of the incident ion beam are estimated electrically. Wehner has presented informally the results of a detailed investigation[36] of sputtering of metals by low-velocity ions and has pointed out the important role played by momentum transfer between these colliding gaseous ions and the metal.

A number of techniques recently described in the literature promise to yield much detailed information about the nature of the collision process. These methods include the study of the absorption and emission spectra of the high vibrational energy products of very exothermic reactions of atoms with unstable molecules.[18, 37] These products were observed to possess an abnormal energy distribution. Studies have also been made of the abnormal energy distribution of species in excited electronic states produced in flames,[2] although the unraveling of such processes promises more difficulty than does the elucidation of the former. In addition, the angular distribution of products and reactants of crossed molecular beams has been investigated recently.[38] The primary difficulty in such studies arises from the small number of particles present in a beam, the smaller number of molecules of the reaction products, and the need for very sensitive detection devices. Such a device was available for alkali atoms and their halides.[38] In other experiments, some intensification and enhanced monochromatization of beams has proved possible[39] using a nozzle design of Kantrowitz and his co-workers.[40] Bull and Moon[41] have recently developed a method of energizing mechanically a beam of heavy molecules and have reported a preliminary study of the reaction of gaseous cesium atoms with energetic carbon tetrachloride molecules.

### *Related Theoretical Problems*

The articles in this monograph present data of value in the consideration of many theoretical problems such as the detailed electronic structure of molecules and of free radicals, the nature of the collision complex in various chemical reactions, and energy transfer in chemically reactive and nonreactive collisions.

The data on interatomic distances and force constants of free radicals and of excited molecules will be, of course, of considerable value in solving problems of chemical structure. Bond-dissociation energies, ionization potentials, and data on hyperconjugation and configuration interaction that perhaps may be obtained from paramagnetic resonance studies are of similar assistance. The number of simple molecules about which structural information is becoming available has been extended considerably by studies of the type described in this monograph by Margrave.[10] Similarly, the detailed structure of an increasing number of simple free radicals has been ascertained as a result of investigations of the type discussed here by Ramsay.[4]

The theoretical calculation of activation energies of chemical reactions still represents a formidable problem,[42] not in principle but in practice. In this publication Walling[30] discusses some of the qualitative factors (bond strength, and steric, polar, and resonance energy effects) that are used to interpret data on reaction rates and on their activation energies. Further quantitative progress in these theoretical considerations probably must await analogous advances in the study of the simpler problem of the electronic configuration and energy of stable molecules. Intensive and fundamental investigations into the latter problem have been carried out in recent years by such investigators as Mulliken, Lennard-Jones, Coulson, and their co-workers, and these studies have been reviewed in the volumes of the *Annual Review of Physical Chemistry* for 1950 to 1956. It is perhaps of some interest to remember that one of the simplest chemical reactions to treat theoretically is a very common one in free-radical investigations: this is the abstraction of an atom from a molecule by another atom or by a free radical.

Another subject of considerable interest is the mechanism of dissociation of molecules and of recombination of free radicals. Particular problems here concern: first, the detailed nature of the collision complex in the reaction; and, second, the ease of energy transfer between the vibrations of relatively long-lived high-energy molecules that are intermediates in these processes. Several recent theories that are adaptations of earlier ones have been formulated.[43-47] Each theory makes specific assumptions about both problems and has been applied to a few of the numerous data on these reactions that have become available. Further applications will be of interest. In this publication Stevens and Boudart[48] discuss the photochemical dissociation of several molecules, as inferred from their fluorescence spectra. The analysis was made for several wave lengths of the light and for several temperatures. These authors infer from the results that anharmonicity plays an important role in these high-energy molecules in facilitating the ready interchange of energy between the vibrations of such a molecule. Should this be generally established, it would have important consequences for the theory of unimolecular dissociation and bimolecular association reactions. Marcus and Rice,[43, 44] in their theory, assumed anharmonicity to be an important factor in coupling the vibrations of a molecule, while Slater[46, 47] ignored it in his model. Recent data on the dispersion of sound waves in gases show that energy is readily exchanged between the different vibrational modes of gaseous molecules, even for molecules having little vibrational energy.[49a] In this case, however, the transfer is probably intermolecular.[49b]

A related problem of particular theoretical interest is the recombination of atoms in the presence of third bodies. The experimental results obtained by using flash photolysis and shock waves over an extraordinarily wide temperature range are discussed in this monograph by Hornig.[6] Theoretical interpretations of these results have necessarily been approximate and for the sake of simplicity have emphasized one factor or another. A simple interpretation based on statistical considerations of energy exchange between different types of mechanical motion in the collision complex has been suggested.[6, 50] Again, it has been observed[51] that some of the data can be explained in terms of van der Waals' forces in this collision complex. These questions probably will be resolved by further studies.

Stevens and Boudart[48] summarize some recent work on the interchange of vibrational, rotational, and translational energy. The experimental data have been obtained from sound dispersion and absorption in gases and from the effects of gases on the rates of chemical reactions, on fluorescence, and on shock-wave phenomena. Stevens and Boudart[48] also describe the conditions under which the efficiency of a collision may be highly specific. They outline the various theoretical models used to interpret the data. The relaxation of abnormal energy distributions through collision processes is discussed here by Shuler.[52a, 52b] Hirschfelder and Eliason[53] estimate the large collision diameters of electronically excited atoms, and note the use of these calculations in the theory of flame propagation.

Some of the newer techniques mentioned earlier,[18, 37, 38, 41] may be expected to stimulate further the theoretical investigation of collision processes. A qualitative theoretical model for the interpretation and prediction of some processes involving the formation of products with initially abnormal energy distribution has recently been formulated.[54] Indeed, these many new experimental approaches have widened appreciably the scope of theoretical investigation of collision phenomena.

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