

their possible association with earthquakes. Pomeroy (University of Michigan) presented a study of seismic waves of acoustic frequencies associated with a mine collapse. Stacey (Lamont) discussed a new very sensitive tiltmeter of short length, and Herrin (Southern Methodist), thermoluminescent effects in deformed limestones.

Laboratory studies of rock fracturing as it relates to seismic phenomena were presented by Brace (MIT) and Mogi (Tokyo University).

Kisslinger (St. Louis) discussed spectra of P-waves from Matsuhiro earthquakes, and Aki (MIT) used the

coda to determine the size of the micro-earthquake source, some 10×10 meters for a shock of magnitude zero.

The meetings included several local field trips and an extended trip for the visiting Japanese along the San Andreas fault from San Francisco to Mexico.

This conference was jointly sponsored by the National Science Foundation and the Japan Society for the Promotion of Science. Summaries of all papers are to be published soon.

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Photoionization and Ion-Molecule Reactions

Fifteen years ago, a conference on mass spectrometry which lasted 2 days could encompass the essential elements of the entire field in which the mass spectrometer was applied. It is significant of the rapid growth in the uses of mass spectrometry that a conference of several days duration now can encompass only one or two of the principal fields of mass spectrometry. The growth has been extremely rapid so that today workers in one part of the field are often hard put even to understand work carried out in other parts of it. Thus, a mass spectrometry conference held at Hakone, Japan, was limited in coverage to photoionization and ion-molecule reactions. The conference was jointly sponsored by the National Science Foundation and the Japan Society for the Promotion of Science and was held during the week of 23 September 1968 under the joint chairmanship of Hirohiko Ezoe and the writer.

It is particularly significant that the two topics of the conference are both of relatively recent inception. Although one or two initial papers had been written on each subject in 1955, very little work had been done so that both topics have had essentially their complete development since about that date. Prior to around 1955, ionization was brought about in most instruments by electron impact. However, electron impact has certain disadvantages, especially in obtaining precise data on ionization and appearance potentials. This is a fundamental difficulty resulting from the fact that with electrons the ionization efficiency curve crosses the energy axis at an angle that is often acute. This, combined with the normal spread of

electron energies, makes interpretation difficult and obscures small energy effects resulting from the appearance of higher energy states of the ion. Many of these disadvantages are eliminated if ionization is brought about by ultraviolet light rather than by electrons. This is due to the fact that ionization by radiation is a step function. Thus, excited electronic states can often be observed in normal ionization efficiency curves. In some instances, it has been possible to observe vibrational states as well. Some fine structure is obscured by the peaks corresponding to Rydberg states that occur in the ionization efficiency curves. This can be eliminated if, instead of mass analysis, the energy analysis of admitted electrons is made. With such analysis it has been possible to observe not only electronic and vibrational states but, in some instances, rotational states as well. In the most recent advance, Mark Inghram (University of Chicago), during his lecture on the development of photoionization, described experiments in his laboratory in which both mass analysis of the ions and energy analysis of the electrons are being made. Although this work is in its very early stages, it already offers promise of extremely interesting results.

In describing his work, Itiro Omura (Central Research Laboratory of Hitachi Ltd.) showed excellent data resulting from the coupling of a Quadrupole mass spectrometer to a photoionization source. It might be mentioned that one of the most useful developments in mass spectrometry in recent years has been the widespread application of the Quadrupole mass filter which

is an instrument with many advantages, not the least of which is that it is relatively inexpensive.

In spite of the great advantages of photoionization, it suffers from one obvious disadvantage, namely that it is not capable of generating negative ions by resonance attachment. Thus, there is still a need for a relatively simple, practical source of electrons having a narrow spread in energy. Kogoro Maeda (Electrotechnical Laboratory, Tokyo) described several devices for obtaining beams of progressively narrower energy spread and including a double hemispherical energy selector capable of providing, relatively easily, a beam having a spread of only 0.1 ev.

During the past approximately 15 years, one of the principal topics that has concerned mass spectrometrists has been a theory of the origin of mass spectra. Two principal approaches to the problem have been advanced. The one most generally accepted by Western mass spectrometrists is the absolute rate theory approach developed by Eyring and his students. This treats the formation of fragment ions as a series of rate processes and can be approached by the methods of first-order kinetics. An alternate approach is that of relating the intensities of fragment ions to the distribution of charge in the molecules calculated by a variation of the molecular orbital method. This was originally proposed by Hall and is being applied rather successfully to a number of systems by Kozo Hirota (University of Osaka) and Toshikazu Tsuchiya (Government Chemical Industrial Research Institute, Tokyo). The method requires certain empirical adjustments in order to obtain agreement with experiments, but these are relatively easy to make and result in a satisfactory agreement. Thus, although the absolute rate theory approach appears to be more nearly in accord with the natural phenomena and certainly predicts more of the behavior of ions under decomposition, it is less useful in the actual prediction of mass spectra because of the complexities of the calculation and the large amount of input information required.

In the literature of mass spectrometry, research on positive ions far outweighs the studies of negative ions. The reason for this is that studies of negative ions are generally more difficult. The ion intensities are usually considerably smaller than are those for positive ions and, at least in the resonance region, the negative ion can be observed over a narrow

range of 1 or 2 ev. Nevertheless, the behavior of negative ions offers some rather interesting phenomena and they deserve some studies in spite of the difficulties involved. Toshio Sugiura (Taka-saki Radiation Chemistry Research es-tablishment) reported investigations of negative ions from formic acid, nitro-ethylene, and a number of hydrocarbons in the dissociative resonance capture region. Appearance potentials were measured in a number of instances. Studies of isotope effects were especially interesting. Quite large effects were ob-served with methane, acetylene, and methylacetylene. In all cases the cross section for removal of an H atom from a given position was much greater than that for removing a D atom.

I reported results of some studies of ion-molecule reactions involving S^- , SH^- , CN^- , and O^- with several small inorganic molecules. Rate constants were determined in a number of in-stances and were found to be compara-ble to rate constants observed with positive ions.

Within the past 2 or 3 years, sev-eral new and very exciting methods of studying ion-molecule reactions have been developed. Among the most im-portant of these is the application of crossed molecular beams. Richard Wolf-gang (University of Colorado) de-scribed the first studies on reactions occurring at controlled kinetic energies between 0.5 to 25 ev, in which both the angular and velocity dis-tributions of the products were mea-sured. Reactions of the type $Ar^+ + H_2 \rightarrow ArH^+ + H$ had previously been sup-posed to involve a long-lived interme-diate at low energies and spectator strip-ping at high energies. The crossed beam experiments showed, however, that a direct mechanism involving the induced dipole interaction of both reactants and products seems to hold over the entire energy range. Spectator stripping is approached as a limiting case only at the highest energy. On the other hand, the reactions of certain hydrocarbon ions, for instance that of $C_2H_4^+$ with C_2H_4 , can involve an intermediate which has a lifetime of at least several rotations before dissociating into prod-ucts.

One of the oldest methods of study-ing ions in gases has been the use of the drift tube which permits the study of ion mobilities. Unfortunately, with our present knowledge of the almost uni-versal occurrence of ion-molecule re-actions, it is no longer possible to be entirely certain of the nature of the

phenomena studied in drift tubes unless the ions present are subject to mass analysis. Yozaburo Kaneko (Tokyo Metropolitan University) described a very elegant system used in his labora-tory in which mass-analyzed ions are injected into a gas greatly diluted with helium (in order to thermalize the ions) and, after passage through the drift tube, they are again mass analyzed. In this way, not only mobilities but ion-molecule reactions and reaction rates can be obtained.

One of the most exciting develop-ments in mass spectrometry in the past few years has been the advent of ion cyclotron resonance spectroscopy. This technique provides for ion trapping in crossed electric and magnetic fields. This results in a long mean free path for the reactant ions so that pressures in the reaction zone can be maintained at a relatively low level. Ion cyclotron double resonance techniques make it possible to identify all of the reactants contributing to a particular product ion without the necessity for resorting to the measurement of appearance potentials. Thus, reaction mechanisms are readily determined and large amounts of in-formation not previously obtainable by the more conventional methods have already been developed. This instrument is being exploited very effectively in the laboratories of J. L. Beauchamp (Cali-fornia Institute of Technology) who has added the additional refinement of a photoionization source. By studying a series of reactions involving small dif-ferences in energy, it has been possible, with the aid of the double resonance technique, to determine the gas phase proton affinities of organic molecules such as aldehydes and ketones. An in-teresting process observed in the course of this work involves the formation of partially hydrated protonated aldehydes by abstraction of water from secondary alcohols.

Of a quite different nature has been the recent work of F. H. Field (Esso Research and Engineering Company) in the development of a technique that he has named chemical ionization. In Field's laboratory it was observed that with quite pure methane at pressures above a few tenths torr all primary ions had disappeared and essentially the only ions present were CH_5^+ and $C_2H_5^+$, both of which were completely un-reactive with methane and so remained at constant intensity for pressures up to 2 torr, the practical limit of the instru-ment. Other materials were found to behave in a similar fashion. Thus, iso-

butane at a pressure above about 0.5 torr gives the *t*-butyl ion as almost its only peak. However, these systems are capable of reacting as either Brønsted or Lewis acids with certain compounds and, in studying a number of these, Field found that a completely different kind of spectrum was obtained from the products of ion-molecule reactions in the methane plasma than were obtained by electron impact or photoionization. This can be extremely valuable because many compounds, notably long-chain, paraffin hydrocarbons, give only very faint peaks in the mass region near the parent and indeed for any ions above the C_5 to C_6 range. Thus, there are obvious advantages for analytical pur-poses and identification of unknown compounds. Recent studies reported by Field of benzyl acetates showed that certain of the reactions were quite temperature-sensitive with the result that rate constants and activation energies could be obtained by the usual techniques of reaction kinetics. It thus appears that reactions in the plasma existing in the ion source at the high pressure conditions can be treated in a fashion quite similar to that of reactions in ionic solutions.

Somewhat akin to ion-molecule re-actions are the chemi-ionization or Hornbeck-Molnar processes by which ions are formed as a result of bonding between an electronically excited neu-tral and the neutral in its ground state. These processes were first identified by Hornbeck and Molnar and have been studied periodically since then. Studies by F. W. Lampe (Pennsylvania State University) of the rare gases showed that several states are involved in the reactions and that these have different lifetimes. Thus, by measuring ionization efficiency curves at several delay times, both the reaction rate and lifetime of several reactive species could be identi-fied.

Of a somewhat different nature was the study by Ikuzo Tanaka (Tokyo Institute of Technology) who employed a photon beam to bring about excitation of acetylene which then underwent chemi-ionization reaction with the ground state acetylene molecule. This reaction has not been observed under electron impact. The reason for the dif-ference is not apparent. Tanaka also dis-cussed a number of ion-molecule reac-tions that occur in acetylene and diolefin systems, in all of which ionization was brought about by photon impact.

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