25 October 1968, Volume 162, Number 3852 **SCIENCE**

Ion-Molecule Reactions

Reactions of ions with neutral molecules—possibly the fastest known elementary reactions—are reviewed.

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A succession of breakthroughs in the development of sophisticated instrumentation for the investigation of chemical reactions has radically altered the nature and scope of problems which can be pursued both technologically and in the laboratory. Furthermore, substantive improvement in existing processes and development of new synthetic pathways are dependent upon knowledge of reactive intermediates and upon detailed information about reaction mechanisms. Consequently, the field of reaction kinetics is being pursued with renewed vigor in an attempt to answer detailed questions of reaction mode and molecular dynamics which were scarcely posed a few years ago.

Because many of the intermediates are so reactive and their lifetimes are so short in practical systems, it is difficult to investigate their properties and reactions directly in complex reaction mixtures. It is desirable to isolate the elementary reaction of interest in the closely coupled system so that it may be studied on a molecular basis. Thus it is frequently necessary to carry out these experiments under conditions that are very different from those in the system whose fundamental chemistry is in question. Nevertheless, if the molecular description is sufficiently precise, the properties of the intermediates should accurately characterize the process. Mass spectrometric techniques, which have been used to study ion-molecule reactions, have been devised mainly to elucidate and describe the elementary reactions involved. However, the rate parameters which are deduced provide an explanation of the ion chemistry of complex systems—flames, plasmas, the upper atmosphere, radiation chemistry, and the like—rather than an interpretation of mass spectral data. The very large reaction rates commonly observed for ion-molecule reactions (which exceed by several orders of magnitude the rates of typical "fast" neutral reactions such as free radical reactions) require that they be considered in any system in which ions are formed.

It is perhaps appropriate also to allude briefly to the history of the field. Although it is a relatively new discipline for systematic studies, the investigation of ion-molecule reactions now spans more than five decades. The archetype ion-mole product ion, H_3^+, was known by 1916 (*1*), and the mechanism for its production from the hydrogen molecule-ion

$$\underset{(m/e\ 2)}{H_2^+} + H_2 \rightarrow \underset{(m/e\ 3)}{H_3^+} + H \qquad (1)$$

was deduced by 1925 (*2*). By 1936 a theoretical rate constant had been deduced (*3*) for this reaction which was in excellent agreement with modern experimental measurements. The chemically interesting species I_3^+ and I_3^- were detected in the mass spectrum of iodine vapor by Hogness and Harkness (*4*), who further showed that the intensity of these secondary ions was substantially enhanced by increasing the physical dimensions of the ion source (thereby increasing the path length of the ion in the chamber). They also observed tertiary ions in these experiments, a feat not repeated until fairly recently.

In these measurements the obvious parameter which distinguishes bimolecular from higher-order reactions in the ion source of the mass spectrometer is the pressure-dependence of ion intensities. Under the low pressure conditions customarily employed, direct ionization is a unimolecular process and is first-order with respect to the pressure of the ion source. Therefore, the ratio of the intensity of the secondary ion to that of the primary ion is directly proportional to pressure, the proportionality constant being equal to the product of the rate constant and the ion residence time. This is demonstrated for the interesting hydrocarbon ion-molecule reaction

$$\underset{(m/e\ 16)}{CH_4^+} + CH_4 \rightarrow \underset{(m/e\ 17)}{CH_5^+} + CH_3 \qquad (2)$$

shown in Fig. 1. The finite intercept in the ratio of ion intensities, $I(m/e\ 17)/I(m/e\ 16)$, results from the small, naturally occurring abundances of carbon-13 (present as CH_4^+ in which C is C^{13}) and deuterium (present as CH_3D^+ in which C is C^{12}) in ordinary methane. Bleakney showed (*5*) that a similar curve of relative intensities $I(m/e\ 3)/I(m/e\ 2)$ plotted as a function of the pressure for hydrogen gave an intercept which indicates the presence of about one part of HD^+ per 2500 parts of H_2^+ in ordinary hydrogen. This report confirmed Urey's discovery of deuterium by the method of optical spectroscopy. This most important isotope of hydrogen remained undiscovered for several years because Eq. 1 was so well understood by mass spectroscopists!

In the years between 1930 and 1950, improvements in instrumentation and technique, and particularly improvements in vacuum technology, made it possible for mass spectroscopists to

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concentrate on the basic physics of ionization and dissociation. The nuisance of secondary processes was largely eliminated, and great strides were made in elucidating the properties of isolated gaseous ions. Chemists fortunate enough to have access to mass spectrometers during this period were mainly interested in analytical applications, and it remained for Tal'rose and Lyubimova in the Soviet Union (*6*) and for Stevenson and Schissler in the United States (*7*) independently to rediscover this important class of reactions. Their work provided the first quantitative estimation of reaction rates and emphasized the probable importance of ion-molecule reactions in any system in which ions are formed. This field of research has developed rapidly since then, particularly in the refinement of experimental techniques. A few of these developments will be cited along with selected experimental results.

A number of reviews of ion-molecule reactions are available (*8–12*); each reflects to some degree the particular bias, chemical or physical, theoretical or experimental, spectroscopic or kinetic, of the respective authors. Our approach in the present work emphasizes certain analogies with more conventional chemical systems and points out some systematic features recently discovered which may be of general chemical interest.

Theory

If one considers the general ion-molecule reaction of primary ions, P^+, with neutral molecules, M

$$P^+ + M \rightarrow [PM^+] \rightarrow S^+ + N \quad (3)$$

to produce secondary ions, S^+, it is convenient to divide the theoretical description of the reaction into two parts—the formation of the collision complex PM^+ and its subsequent dissociation into various secondary ions. Only the first part has been considered in any detail thus far.

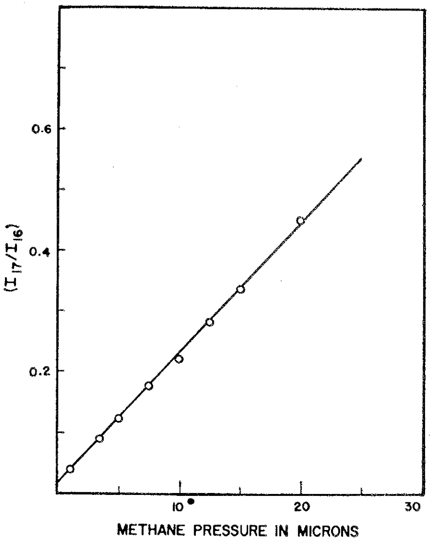


Fig. 1. Ratio of secondary to primary ion intensities $I(m/e17)/I(m/e16)$ in methane as a function of the pressure of the ion source. The linearity of this curve suggests a simple second-order reaction since the molecular ion intensity, m/e 16, is first-order with respect to methane pressure.

The classical orbiting model, derived by Langevin (*13*) and developed in detail by Gioumousis and Stevenson (*14*), considers the ion as a point charge for which the interaction potential with a structureless, polarizable neutral particle is

$$V(r) = -\alpha e^2/2r^4 \quad (4)$$

where α is the polarizability of the molecule, e is the electronic charge, and r represents the internuclear distance. The Heisenberg uncertainty principle requires that the angular momentum at the minimum impact parameter, mvr_c be very much larger than $\hbar$, the quantum of action, if classical mechanics is to be used to describe the collision. This criterion is generally satisfied for the inverse fourth-power potential, provided impact energies are below 1 electron volt.

The classical trajectories for ion scattering in the polarization potential are shown in Fig. 2. There is a critical impact parameter, b_0, which divides the orbits into those which pass through the scattering center for $b < b_0$ and those which approach no closer than $b_0/\sqrt{2}$ for $b > b_0$. In an actual case, repulsive forces would come into play for the first class of closed trajectories. If we now assume that a critical internuclear separation for chemical reaction, r_c, exists and that $r_c \leqslant b_0/\sqrt{2}$, we can deduce a cross section, σ, for the ion-molecule reaction which depends inversely on the relative velocity of the reactants

$$\sigma(v) = \pi b_0^2 = (\pi/v)(4\alpha e^2/\mu)^{1/2} \quad (5)$$

where v is relative velocity and μ is the reduced mass of the reactants; the other quantities have been defined previously.

Table 1. Comparison of experimentally determined rate constants with values derived theoretically on the basis of simple theory.

Reactants	k_{thermal} ($\times 10^9$ cm^3 mole^{-1} sec^{-1})	Calculated value
$CH_4^+ + CH_4$	1.22*	1.36
$NH_3^+ + NH_3$	1.00*	1.23
$H_2S^+ + H_2S$	0.77*	1.12
$D_2^+ + D_2$	1.43†	1.45
$Ar^+ + H_2$	1.68†	1.50
$Ar^+ + D_2$	1.35†	1.09
$CO_2^+ + H_2$	1.15†	1.49

* Values obtained by Gupta *et al.* (*36*). † Values obtained by Stevenson and Schissler (*7, 37*).

For Maxwellian velocity distributions for both ion and neutral reactants, a rate constant, $k = v\sigma(v)$, may be defined, which leads to an energy-independent constant

$$k = 2\pi e(\alpha/\mu)^{1/2} \quad (6)$$

Table 1 compares theoretical rate constants thus calculated with experimental determinations for some simple systems. (These theoretical considerations refer to the rate of formation of the orbiting complex and should be multiplied by a transmission coefficient for comparison with the rate of formation of a particular product.) Table 1 assumes a coefficient of unity for the calculated values.

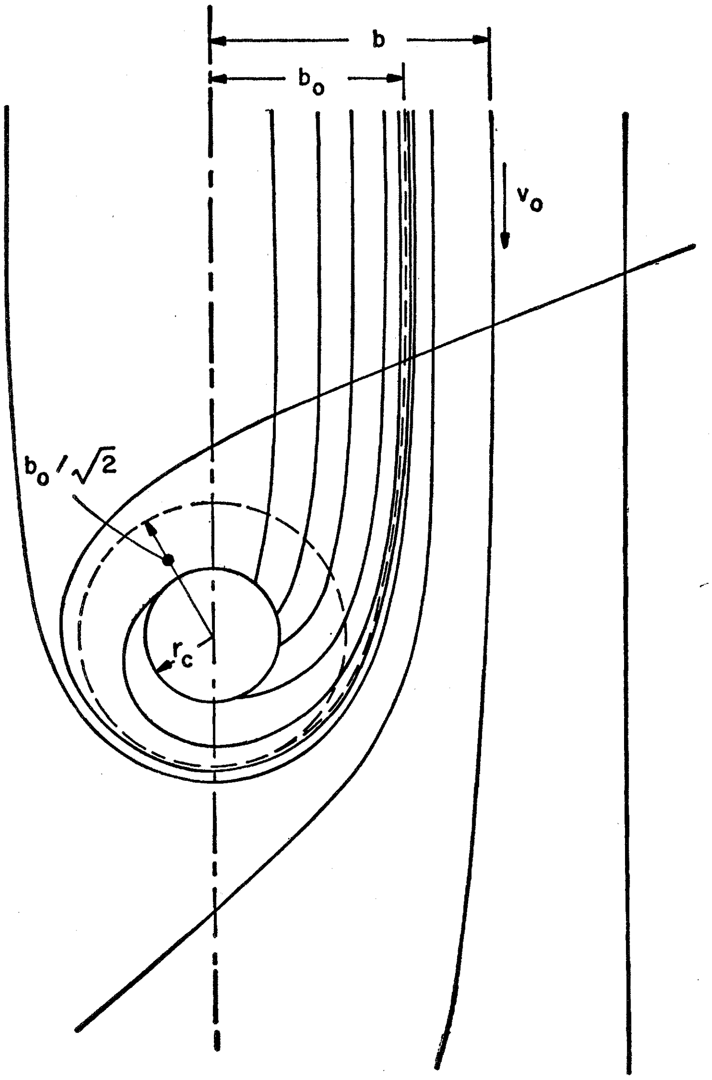
It is rather remarkable that this degree of agreement between theory and experiment is achieved from such simple theoretical considerations. The inverse fourth-power potential is invalid except for a very narrow range of energies. For actual molecules the polarizability is a tensor rather than a scalar field. Polar molecules involve an inverse sixth-power contribution suitably averaged, and for molecular ions the assumption of a point charge certainly breaks down. Quantum effects must be important for many systems, and the range of chemical forces is hardly well described as a δ-function at $r = r_c$. This treatment has also ignored constraints of angular momentum in the decomposition of the complex.

Despite these serious criticisms, however, the theory of the orbiting complex appears to be a reasonably adequate framework for describing low-energy ion-molecule interactions. Experiments have not yet progressed to a stage that requires a more rigorous description of the basic physics of the reaction complex. Most criticisms of the theory should more properly be addressed to the second part of the general theoretical problem, the decomposition of the complex. Most, if not all, discrepancies between calculated and experimental cross sections can be rationalized by considering the probable multiplicity of reaction channels for the reaction complex. These must include such possibilities as charge exchange, back reaction into the original reactants, and all possible exothermic reaction products in the general case. Very recent theoretical developments provide some guidance regarding this phase of the problem. However, as is also true for other areas of kinetics, for the present we must rely on experiment for detailed information on the actual reaction channels accessible to a given pair of reactants.

Experimental Methods

Beginning in the late 1950's, the first extensive, quantitative investigations of ion-molecule reactions utilized conventional mass spectrometers at slightly elevated pressures. More recent research has been accomplished with specially designed or modified instrumentation capable of more sophisticated experiments. Among the techniques with a particularly chemical orientation have been those for the study of successive reactions which permit many collisions to occur prior to mass analysis. Through construction of tightly enclosed ion sources and incorporation of a high degree of differential pumping (and occasionally by unconventional means for ionizing the gas), it has proved possible to increase source pressures by factors up to 10^5 (*15*). An alternative recent development is the use of ion trap sources (*10, 16*) which extend the source residence time a thousandfold and permit the observation of a complex sequence of ion-molecule reactions at low pressures. Figure 3 shows an electrostatic ion trap designed (*10*) to simulate upper atmosphere conditions in which low gas density leads to long time delays between collisions. Containment by strong magnetic fields (*17*) also gives rise to very long ion-residence times and extensive ion-molecule reactions at low pressure. Both ion trapping and high pressure techniques for the achievement of a controlled, appreciable number of ion-neutral collisions permit a qualitative description of the sequence of ion-molecule reactions in a given system.

Perhaps the most powerful technique developed to date for isolating particular ion-molecule reactions is the use of tandem mass spectrometers (*18*). Figure 4 shows schematically the details of a tandem instrument that we developed; a pictorial view of this machine is given in Fig. 5. Since the ion source and reaction chamber are physically separated, the properties of the ion and neutral reactant may be controlled independently in this apparatus. The temperature and pressure of the neutral molecule and the mass and kinetic energy of the reactant ion are parameters to be specified for a given experiment. In some favorable cases the state of electronic excitation of the ion can also be varied. The second-stage mass spectrometer may be used to identify and measure quantitatively the various products from any given ion-molecule reaction. It is probable that a more ad-



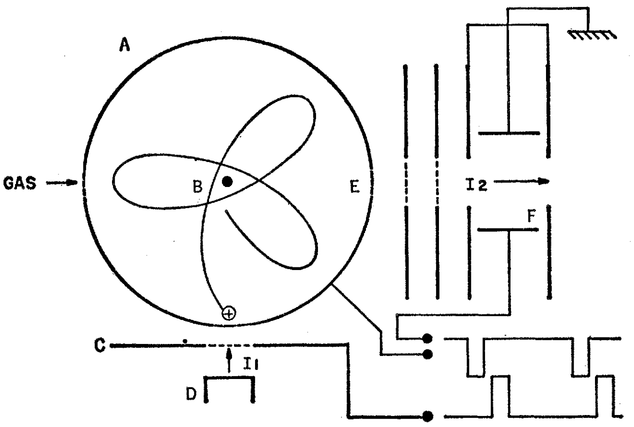


Fig. 2 (left). Classical trajectories for scattering of point charges of velocity, *v*, by a stationary polarizable molecule, for which the interaction potential is $V(r) = -\alpha e^2/2r^4$. For impact parameters, $b > b_o$, the mass points approach no closer than $b_o/\sqrt{2}$, whereas for $b < b_0$ the trajectories pass through the center of mass of the collision partners. For $b = b_o$, orbiting occurs. For clarity in presentation the incoming trajectories are shown, and the figure suggests a chemical cross section for ion-molecule reactions of radius $r_c \leq b_o/\sqrt{2}$. [By permission of John Wiley and Sons, Inc.] Fig. 3 (above). Ion trap source designed by Tal'rose to achieve very long ion-residence times, thereby enhancing the probability of ion-molecule reactions at low pressure. A thin wire electrode, *B*, is held at a negative potential with respect to the chamber walls, *A* (for the study of positive ions). For negative ions the potentials would be reversed. A burst of ions is formed by a pulse of electrons from the cathode, *D*. Because of the small surface area of the central wire, trajectories of the type shown schematically will be described, and ions can be held in the source for a few tenths of a second, compared to typical ion-residence times of microseconds. After a suitable time delay the outer electrode is pulsed negative, and a known fraction of the ions in the cavity at that point in time is extracted through grid *E* and analyzed by a mass spectrometer. [By permission of John Wiley and Sons, Inc.]

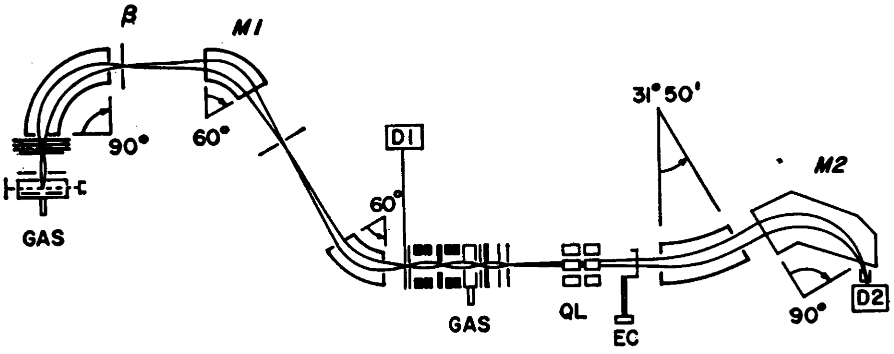


Fig. 4. Schematic representation of a tandem mass spectrometer. Ions are formed by electron impact in the source at the left; their energy is analyzed by a 90° electric sector. The aperture of the energy stop, β, establishes the spread in kinetic energy of the transmitted ion beam. The masses of the ions are analyzed by a 60° magnetic sector, *M1*, and deflected by a 60° electric sector into a deceleration lens which focuses them into a collision chamber and establishes their terminal energy. Unreacted ions and products from ion-molecule reactions of these ions with neutral molecules, supplied to the collision chamber by a separate system for gas handling, are measured by the second mass spectrometer. The ultimate ion detector, *D2*, is a venetian-blind electron multiplier operated in pulse-counting mode which counts individual ions. The in-line configuration of the mass spectrometers was chosen to maximize collection of product ions resulting from momentum transfer collisions since ion-molecule reaction products are expected to forward-scatter.

vanced version of the instrument will be capable of measuring both energy and scattering angle as well as product mass. Pulse counting of product ions approaches the capability to detect single ions.

Another recent technique for the study of ion-molecule reactions involves the use of radiolysis and short wavelength photolysis to create ions in gases at atmospheric or near atmospheric pressure (*19*). A detailed knowledge of the kinetics of such systems and a judicious application of selected scavengers (reagents which are known from other studies to react in a specific manner with ions suspected of being present in the radiolysis or photolysis system) and of deuterium-labeled compounds has made it possible to obtain relative rate constants and mechanistic data with reliability and precision comparable to careful mass spectrometric measurements.

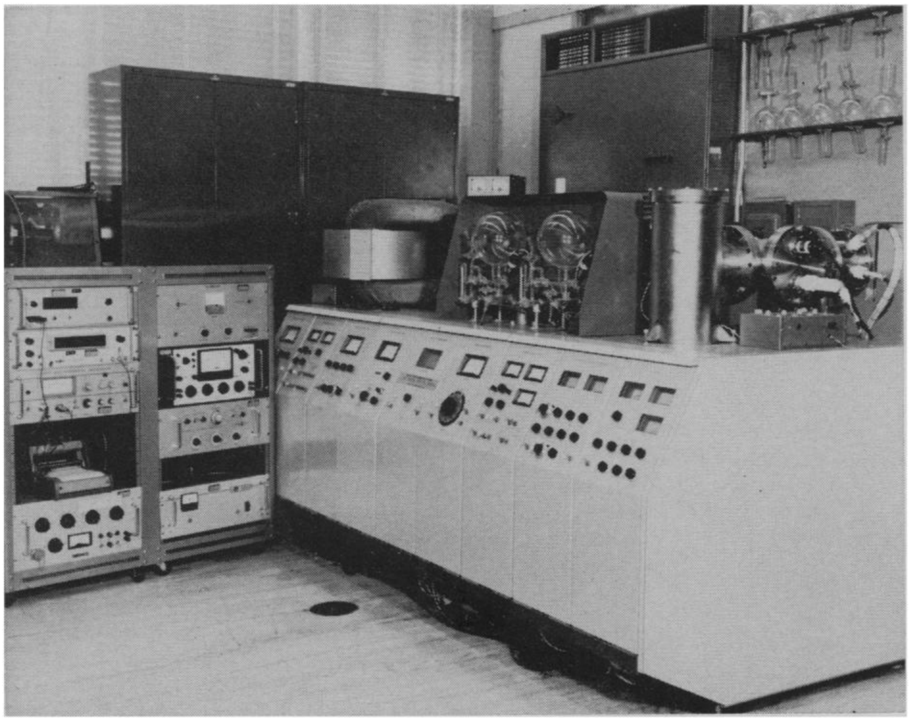


Fig. 5. Front view of the tandem mass spectrometer at Aerospace Research Laboratories.

Solvation Reactions

Mann, Hustrulid, and Tate observed the gas phase reaction

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (7)$$

for the formation of the hydronium ion in 1940 (*20*). The great stability of this product ion plus the small size and large heat of formation of the proton are responsible for the fact that the unsolvated proton cannot exist in solution. In concentrated acid solution it is plausible that the acid species is H_3O^+. However, mass spectrometric studies in the gas phase at high pressures have shown that higher hydrates are readily formed and are quite stable. The reaction sequence (*21*)

$$H_3O^+ + H_2O \rightarrow H_5O_2^+ \quad (8)$$

$$H_5O_2^+ + H_2O \rightarrow H_7O_3^+ \quad (9)$$

$$H_7O_3^+ + H_2O \rightarrow H_9O_4^+ \quad (10)$$

implies that the heat of formation of the hydrates decreases with increasing hydration number.

These experiments further show that there is a very substantial decrease in stability for hydrates higher than $H_9O_4^+$, a deduction also supported by studies in aqueous solution (*22*). This conclusion has been challenged in a recent study by Searles (*22a*). Figure 6 suggests a possible reason for the exceptional stability of the lower hydrates. The implication is that acidic aqueous solutions contain mainly the hydrates H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ in relative amounts which vary with the extent of dilution.

Studies of methanol and ethanol vapor have shown analogous behavior for the mono-, di-, and trisolvated proton, whereas dimethyl ether provided evidence for only mono- and disolvated protons (*23*). Figures 7 and 8 present structures consistent with observation which rationalize these results. The proton in alcoholic solution of acid is therefore most probably present as $(ROH)_nH^+$ (where $n = 1$, 2, 3, depending on dilution); in ether solution the proton is probably present as $(R_1OR_2)_nH^+$ ($n = 1$, 2, depending on dilution).

Intrinsic Acidity or Basicity

Cross reactions between various protonated species are of interest because they establish a scale of acid and base strength. For acids dissolved in the same solvent (for example, water) acid

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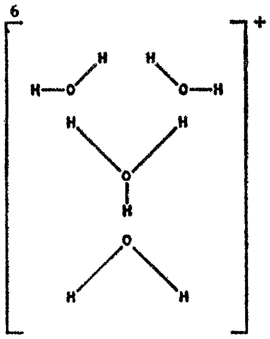

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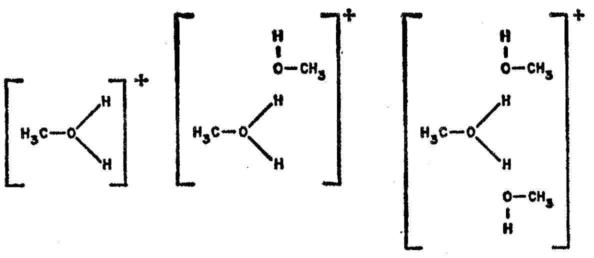

Fig. 6. Possible structure for the solvated proton $H_9O_4^+$, here represented as $H_3O^+(H_2O)_3$. The first solvation sphere in which the three hydrogen bonds of the central ion are saturated is probably a structure of exceptional stability. Fig. 7. Analogous structures for the methanol-solvated proton, here represented as $CH_3OH_2^+(CH_3OH)_n$ with $n = 0, 1, 2$. In this case the solvation sphere is completed when $n = 2$.

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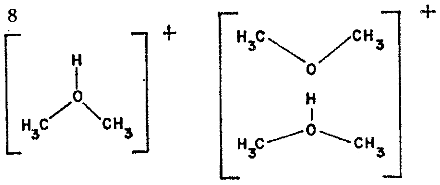

Fig. 8. Analogous structures for protonated dimethyl ether, in which the protonated dimer is the ion of exceptional stability.

strength is defined by the concentration of the solvated proton in equilibrium with the undissociated acid. The familiar unit for characterizing this property is the *p*H of the resulting solution, which establishes the relative strength of weak acids. In order to distinguish the acid strength of strong acids (those completely dissociated in aqueous solution), however, it is necessary to use various nonaqueous solvents. Finally, in order to determine the intrinsic acidity and basicity of species (for comparison between solvents), it is necessary to use the Brønsted-Lowry definition which characterizes an acid as a substance which can transfer protons to a base.

In gaseous ion chemistry, therefore, for mixed solvent systems the stronger acid will transfer protons to the stronger base. For example, the reaction

$$H_3O^+ + C_2H_5OH \rightarrow C_2H_5OH_2^+ + H_2O \qquad (11)$$

which takes place in the mass spectrometer, establishes that H_3O^+ is a stronger acid than $C_2H_5OH_2^+$ and that C_2H_5OH is a stronger base than H_2O. This scheme can be used for systematizing proton transfer reactions in the gas phase.

For the series of compounds NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, such a comparison of competitive proton transfer proved particularly interesting (*24*). Simple organic theory predicts that increasing methyl substitution, which increases the electron density on the adjacent atoms, should increase the base strength of the molecule and decrease the acid strength of the monosolvated proton. Mass spectrometric data revealed that $(CH_3)_3N$ is a stronger base than $(CH_3)_2NH$, whch is stronger than CH_3NH_2, which is a stronger base than NH_3—precisely the order predicted from theory. In aqueous solution a different order is observed, which must be attributed to a differing amount of solvation of the ammonium and substituted ammonium ions. The reaction in solution should therefore be written as

$$NH_4^+ \cdot 4H_2O + (CH_3)_3N \rightarrow (CH_3)_3NH^+ \cdot H_2O + NH_3 + 3H_2O \qquad (12)$$

and the energy required to break up the solvation shell is undoubtedly responsible for the heat absorption of the reaction. In the gas phase the reaction

$$NH_4^+ + (CH_3)_3N \rightarrow (CH_3)_3NH^+ + NH_3 \qquad (13)$$

takes place readily, just as predicted by simple theory for the methyl inductive effect. In such gas-phase studies, therefore, complicating solvation effects are absent, and the intrinsic acidity and basicity of species may be examined.

Chemical Ionization

In addition to reactions of familiar acids and bases, it has been possible to study some rather startling acid-base reactions for species which cannot exist in ordinary solutions. For example, the species CH_5^+ produced in Eq. 2 turns out to be a very strong Brønsted-Lowry acid. The reaction

$$CH_5^+ + H_2O \rightarrow H_3O^+ + CH_4 \qquad (14)$$

is in agreement with our experience that a species such as CH_5^+ cannot exist in aqueous solution. Similarly, the ethyl ion species $C_2H_5^+$ would react in aqueous solution in the same manner

$$C_2H_5^+ + H_2O \rightarrow H_3O^+ + C_2H_4 \qquad (15)$$

but in many common organic solvents would react as follows:

$$C_2H_5^+ + RH \rightarrow R^+ + C_2H_6 \qquad (16)$$

Here the ethyl ion is reacting as a Lewis acid, or electron acceptor, rather than as a proton donor.

These reactions cannot be carried out in solution in a controlled manner but are readily investigated in the gas phase. They form the basis of a new approach to analytical mass spectrometry which has been termed the chemical ionization method by Field and Munson (*25*). The ionization process for the molecules examined takes place by way of the characteristic acid-base reactions cited above rather than directly by electron or photon impact. It is, therefore, a much more selective means of ionizing molecules and can be shown to involve specific functional groups in complex molecules. The specific nature of these ionic reactions is indicated by single-ion experiments in which the tandem mass spectrometer at Aerospace Research Laboratories has been employed. In an investigation of the reactions of propyl and butyl ions with a series of isomeric C_6 alkanes (*26*), a close correlation was observed between the rate of reaction in a particular case and the structure of the neutral reactant. Data for these reactions are presented in Table 2. We infer from these results that secondary and tertiary hydrogens are reactive sites, but that primary hydrogens are much less reactive to these ions.

Carbonium Ion Reactions

Carbonium ion reactions constitute an important mechanism by which chemical change is effected in organic systems. The concept of the carbonium ion intermediate may be traced back to the early works of Walden (*27*) and Gomberg (*28*). In independent investigations these authors demonstrated by conductivity measurements that certain triphenylmethyl systems behave as electrolytes; they thus became the first

Table 2. Relative reaction rates of ions with isometric C_6 alkanes. The numbers in parentheses indicate the number of secondary and tertiary hydrogens in neutral reactant.

Neutral species	Relative rate of reactant ion	
	$C_3H_7^+$	$C_4H_9^+$
n-Hexane (8)	8.0	8.0
2-Methylpentane (5)	5.1	5.0
3-Methylpentane (5)	5.1	5.0
2,2-Dimethylbutane (2)	2.0	1.8
2,3-Dimethylbutane (2)	2.2	2.9

workers to obtain, by physical methods, evidence for stable carbonium ions in solution. It was gradually realized that carbonium ions might be involved as intermediates in many chemical reactions. A broad body of organic reaction theory has evolved over the years through the efforts of such investigators as Meerwein, Ingold, and Whitmore. The experimental evidence which provided the foundations for the development of this theory, however, was derived exclusively from kinetic and stereochemical observations. Until quite recently, the simple alkylcarbonium ion species, which were often postulated as transient reaction intermediates for solution reactions, had not been detected. This resulted largely from the short lifetimes (hence very low steady-state concentration) of these ions in solution and the inadequacy of existing physical methods of detection. In fact, it was not until 1963 that Olah (*29*) and coworkers first observed a stable alkylcarbonium ion complex in a solution of tertiary butyl fluoride dissolved in excess antimony pentafluoride (which acts as a Lewis acid)

$$(CH_3)_3CF + SbF_5 \rightarrow (CH_3)_3C^+SF_6^- \quad (17)$$

by the use of proton magnetic resonance spectroscopy. Prior to the observations of Olah for solutions, however, the formation (*30*) and reactions of carbonium ions produced in the gas phase by electron impact had already been extensively investigated by mass spectrometric techniques. A great deal of information on reactions of simple carbonium ions has already been obtained from such gas-phase studies. In addition to the early work of Stevenson and Tal'rose and colleagues, a substantial body of information on carbonium ion-molecule reactions in hydrocarbons was contributed by Franklin, Field, and Lampe (*8*). Subsequently, many workers have engaged in such studies (*12*).

Ionic reactions in solution are complicated by such factors as solvation. Therefore, data relative to the formation and reactions of carbonium ions, which are derived from investigations in the gas phase, are inherently more informative than those obtained from studies of reactions in solution and permit a more realistic assessment of reaction trends.

Several general modes of reaction for carbonium ions with organic compounds have been identified from studies in the gas phase. We have already alluded to some of these in the discussion of acidity and basicity. For example, the earliest major type of ion-molecule reaction to be identified for saturated hydrocarbons was the hydride-ion transfer reaction. Expressed in general form, this reaction is

$$X^+ + C_nH_{2n+2} \rightarrow XH + C_nH_{2n+1}^+ \quad (18)$$

where X^+ represents an alkyl ion. Obviously, this process may also be visualized as an acid-base reaction in which the reacting ion functions as an electron acceptor or Lewis acid. Such reactions were initially established by the mass spectrometric measurements of Field and Lampe (*31*). Ausloos and co-workers (*19, 32*), by employing the radiation chemical techniques already outlined, have obtained a considerable amount of information on the rates of these reactions. They have also drawn some significant conclusions with respect to the structure of the reactant ions and the nature of the intermediates involved. Their studies suggest that for simple alkyl ions the rate of the hydride ion transfer reaction is independent of the source of the reacting ion. This, in turn, implies that the reactant carbonium ion must be capable of readily rearranging, by a shift of H atoms, to the same structure. The investigations of Ausloos (*19, 32*) further indicate that the intermediate complex formed in these reactions (which is somewhat analogous to the activated complex of reaction rate theory) must be quite short-lived, if the term "complex" is at all meaningful for these processes.

The earlier studies of this reaction in conventional mass spectrometers necessarily involved systems in which several ions contributed simultaneously to the hydride-transfer product, which obscured many details of the reaction mechanism. Accordingly, we have reinvestigated these reactions with the tandem mass spectrometer (*33*) which permits an investigation of the reactions of individual ions with selected molecules.

Table 3. Relative rates for hydride ion transfer reactions of propyl ions observed in the tandem mass spectrometer.

Neutral molecule	Relative rates	
	Experimental	Calculated from simple theory
Propane	1.00	1.00
n-Butane	4.44	1.07
n-Pentane	6.04	1.13
n-Hexane	0.58	1.20

The data for the hydride ion transfer reaction obtained with the tandem instrument display some interesting trends. In Table 3 are shown the relative rates for the hydride ion transfer reaction of propyl ions with a series of alkane molecules. Here the reaction rate for propane has been arbitrarily assigned a value of 1 for purposes of this comparison. In agreement with simple collision theory, there is an increase in the reaction rate with increasing molecular size of the neutral molecule. This theory predicts a reaction rate which is proportional to $(\alpha/\mu)^{1/2}$, where α is the polarizability of the neutral molecule. The molar polarizability increases in value with molecular weight in a given series and leads to the quantitative trend indicated in the third column of Table 3.

Hexane appears experimentally to be an exception to these trends, but this deviation can be explained on the basis of competing reactions. Hydride ion transfer is essentially the only mode of reaction for propyl ions with propane, *n*-butane, and *n*-pentane. In the case of hexane, however, ionic reaction products other than the parentless hydrogen are observed. If these additional reaction channels are taken into account, hexane is observed to have the highest reaction rate in this series.

Table 4. Hydride ion transfer reactions: relative reaction rates of $C_4H_9^+$ ions from different sources.

Neutral source	Relative rates		
	n-Pentane	Isopentane	Neopentane
N-Hexane	0.966	0.991	0.0925
2-Methylpentane	.685	.624	.124
3-Methylpentane	.594	.616	.0852
2,3-Dimethylbutane	.412	.364	.143
Cyclobutane	1.21	1.16	0
Cyclopentane	.821	.810	.0681
Cyclohexane	.181	.175	.0210

While the trends in reactivity shown

in Table 3 are consistent with simple theory, the observed rates actually increase at a much faster rate than is predicted. This can be interpreted as indicating that not every ion-neutral collision leads to reaction. The transmission coefficient for the reaction is somewhat less than unity for propane and increases with increasing degrees of freedom for the reaction complex.

It is also informative to compare the relative reaction rates of alkyl ions derived from different source molecules with various neutral species (*26*). Table 4 shows the rates observed for reactions of $C_4H_9^+$ ions derived from three isomeric pentanes. Since the rates for these ions obtained from both *n*-pentane and isopentane are essentially identical, it can be concluded that the reactant ions in both cases have the same structures. Presumably the thermodynamically more stable structure is the one in which the charge is localized on the secondary carbon atom. Since this secondary butyl ion would also be produced from isopentane if the methyl fragment removed were the branched group, the formation of this structure does not necessarily involve rearrangement that requires carbon atom migration.

The $C_4H_9^+$ ions derived from neopentane, in which the ions almost certainly have the tertiary structure, clearly react at a slower rate. This is probably a steric hindrance effect in the interaction. The two types of $C_4H_9^+$ are clearly distinguished in these experiments, and rearrangement to the thermodynamically more stable tertiary butyl structure does not occur when *n*-pentane and isopentane are used as source molecules.

We have already noted that ion-molecule reactions may involve specific functional groups in the neutral reactant. As an example, the specificity of the hydride transfer reaction is readily demonstrated by studies with the tandem mass spectrometer in which isotopically labeled molecules are employed. From the reaction of $C_3H_7^+$ ions with $CD_3CH_2CD_3$, the only observed product ion is $CD_3CHCD_3^+$. Similarly, the reaction of $C_3H_7^+$ with $CD_3CH_2CH_2CD_3$ yields a product ratio of $CD_2CH_2CH_2CD_3^+/CD_3CHCH_2CD_3^+$ equal to 0.08. Thus the preferential point of attack in both cases is at secondary positions of the neutral alkane.

Another important ion-molecule reaction involves transfer of a proton from certain donor ions to the neutral reactant. These reactions occur for certain carbonium ion systems. Additional ion-molecule reactions which have been systematized include the transfer of H_2^-, H_2, and H species. Many such reactions are cataloged in other comprehensive reviews (*12*).

Ion Energetics

It has already been mentioned that heats of solvation can be derived from certain ion-molecule processes. We will now consider briefly other useful thermochemical information which may be obtained. In single-source mass spectrometric studies, one of the principal means of establishing the reaction mechanism involves a comparison of appearance potentials for reactant and product ions. The appearance potential (*A.P.*), is the minimum electron energy at which a given ion appears in the mass spectrum. If the reaction that produces a given ion does not form excited products, the appearance potential is effectively the heat of the reaction. With this assumption, heats of formation of ions can be obtained from such data. Thus for a given reaction induced by electron impact

$$R_1R_2 + e^- \rightarrow R_1^+ + R_2 + 2e^- \qquad (19)$$

Hess's Law of constant heat summation yields the relation

$$A.\,P.(R_1^+) = \Delta H_{\text{reaction}} = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2) \qquad (20)$$

Appearance potentials have been used by many investigators to obtain estimates of bond strengths (*D*) and ionization potentials (*I.P.*) of ions from the relation

$$A.P.(R_1^+) = I.P.(R_1) + D(R_1 - R_2) \qquad (21)$$

If the heats of formation of reactant and product species are known, one can determine the heat of reaction for a given ion-neutral interaction. This quantity is of considerable significance in determining the probable reaction pathway of an ion-molecule reaction, since, to a very good approximation, any reactions observed in conventional mass spectrometers for ions of low velocity must be exothermic or thermoneutral.

In many cases, it is difficult to obtain by direct electron impact particular ions formed in an ion-molecule reaction. In such cases, if it is assumed that for the reaction observed $\Delta H \leqq 0$, and if the other thermochemical data are known, upper limits for heats of formation of these unorthodox ions can be established from Hess's Law. Such thermochemical data are tabulated elsewhere (*8, 12*); a comprehensive tabulation of heats of formation of gaseous ions produced directly by electron impact is available (*29*).

Another useful thermochemical quantity which can be evaluated from ion-molecule reactions is the proton affinity, *P*. In principle, this could be determined directly by carrying out the ion-molecule reaction

$$B + H^+ \rightarrow BH^+ \qquad (22)$$

The proton affinity is the negative heat of this reaction

$$P(B) = -\Delta H_{22} = D(B - H^+) \qquad (23)$$

That is

$$P(B) = \Big[\Delta H_f(BH^+) - \Delta H_f(H^+) - \Delta H_f(B)\Big] \qquad (24)$$

Munson (*34*) has obtained relative proton affinities indirectly for some polar molecules by observing proton exchange reactions between molecules. The order of such proton affinities can be readily determined from such experiments. If the proton transfer reaction

$$BH^+ + C \rightarrow CH^+ + B \qquad (25)$$

occurs, then $P(C) > P(B)$. In this manner, Munson established the order: $P(H_2O) < P(CH_3OH) < P(CH_3OCH_3)$; $P(HCHO) < P(CH_3CHO) < P(CH_3COCH_3)$; $P(CHOOH) < P(CH_3COOH)$; $P(NH_3) < P(CH_3NH_2) < P(CH_3)_2NH < P(CH_3)_3N$.

In addition to data obtained with low velocity ions, one can obtain insight into the energetics of certain reactions by using accelerated ions. Giese and Maier (*35*) have pioneered the study of endothermic dissociative charge transfer reactions for the determination of bond energies. A sharp threshold is observed for such processes in which the translational energy of the impacting ion is used to drive the reaction. The amount of energy E_r which is available for reaction with a neutral particle of mass M_n is related to the laboratory energy of the impacting ion of mass M_i by the expression

$$E_r = E_l[M_n/(M_n + M_i)] \qquad (26)$$

which relates the center-of-mass energy to the measured laboratory energy. At threshold this energy should correspond to just that energy necessary to overcome the heat absorption of the dissociative charge transfer reaction. This is directly related to the appropriate bond energy of the dissociating species. Threshold energies observed by Giese and Maier (*35*) for CO, N_2, and N_2O were in excellent agreement with that predicted from accepted values of bond energy for these systems. Any uncertainty in the kinetic energy of the impacting ion is reduced by the mass ratio in Eq. 26, which considerably reduces any effects of energy spread in the beam. This suggests that the technique may become as valuable as electron or photon impact for the determination of such properties for neutral molecules.

Summary

Although some of the best work in progress explores the fundamental physics of ion-molecule interactions by measurements of microscopic cross sections as a function of energy with crossed-beam studies of inelastic and elastic scattering, we have emphasized instead the chemical implications of ion-molecule reactions. Many of the general reactions can be systematized as acid-base reactions by considering the ionic reactants as either Lewis or Brønsted acids.

Data on the energetics of ion-molecule reactions and on the reactions of specific ions yield significant information relevant to carbonium ion reactions and radiation chemistry. Studies of the elementary reactions of isolated ions with molecules have only recently become possible, and we can anticipate some exciting results in this area. Nearly all studies to date have addressed themselves to positive ions, and techniques have just now evolved which make possible the detailed investigation of reactions of negative ions. Whatever directions these new developments take, the study of ion-molecule reactions will constitute one of the most active areas of chemical kinetics for the next several years.

References and Notes

1. A. J. Dempster, *Phil. Mag.* **31**, 438 (1916).

2. T. R. Hogness and E. G. Lunn, *Phys. Rev.* **26**, 44 (1925); H. D. Smyth, *ibid.* **25**, 452 (1925).

3. H. Eyring, J. O. Hirschfelder, H. S. Taylor, *J. Chem. Phys.* **4**, 479 (1936).

4. T. R. Hogness and R. W. Harkness, *Phys. Rev.* **32**, 784 (1928).

5. W. Bleakney, *ibid.* **41**, 32 (1932).

6. V. L. Tal'rose and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **86**, 909 (1952).

7. D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **23**, 1353 (1955). Stevenson (*9*) credits Eltenton and Nier with the discovery of this reaction in 1940, but the significance of the very large kinetic rate constants for these reactions was first pointed out in the United States in the work cited.

8. F. W. Lampe, J. L. Franklin, F. H. Field, in *Progress in Reaction Kinetics,* G. Porter, Ed. (Pergamon Press, New York, 1961), p. 61.

9. J. Durup, *Les Réactions entre Ions Positifs et Molecules en Phase Gazeuse*, (Gauthier-Villars, Paris, 1960); M. Pahl, *Ergeb. Exakt. Naturw.* **34**, 182 (1962); C. E. Melton, in *Mass Spectrometry of Organic Ions*, F. W. McLafferty, Ed. (Academic Press, New York, 1963), p. 65; D. P. Stevenson, in *Mass Spectrometry*, C. A. McDowell, Ed. (McGraw-Hill, New York, 1963), p. 589; H. M. Rosenstock, *AEC Report JLI-658-3-T, TID-4500* (1959).

10. V. L. Tal'rose, *Pure Appl. Chem.* **5**, 455 (1962); V. L. Tal'rose and G. V. Karachevtsev, in *Advances in Mass Spectrometry*, W. L. Mead, Ed. (Institute of Petroleum, London, 1966), vol. 3, p. 211.

11. M. J. Henchman, *Ann. Rept. Progr. Chem. Chem. Soc. London* **62**, 39 (1965); J. B. Hasted, *Physics of Atomic Collisions* (Butterworths, London, 1964), chap. 14; P. Ausloos, Ed., "Ion-molecule reactions in the gas phase," *Advan. Chem. Ser.* **58** (1966).

12. J. H. Futrell and T. O. Tiernan, in *Fundamental Processes of Radiation Chemistry*, P. Ausloos, Ed. (Wiley, New York, 1968), chap. 5.

13. M. P. Langevin, *Ann. Chim. Phys.* **5**, 245 (1905).

14. G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.* **29**, 294 (1958).

15. C. E. Melton, *ibid.* **33**, 647 (1960); F. H. Field, *J. Amer. Chem. Soc.* **83**, 1523 (1961); S. Wexler, A. Lifshitz, A. Quattrochi, *Advan. Chem. Ser.* **58**, 193 (1966); G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, G. G. Volpi, *J. Chem. Phys.* **40**, 5 (1964); P. Kebarle and A. M. Hogg, *ibid.* **42**, 668 (1965); J. H. Futrell, T. O. Tiernan, F. P. Abramson, C. D. Miller, *Rev. Sci. Instr.* **39**, 340 (1968).

16. P. A. Redhead, paper No. 132 presented at the 14th annual conference on Mass Spectrometry and Allied Topics, Dallas, Tex., May, 1966; W. G. Monrad, T. Pauly, R. G. Hert, *Rev. Sci. Instr.* **35**, 661 (1964).

17. J. Baldeschwieler, *Science* **159**, 263 (1968).

18. E. Gustaffson and E. Lindholm, *Arkiv Fysik* **18**, 219 (1960); G. V. Lavrovskaya, M. I. Markin, V. L. Tal'rose, *Kinetika i Kataliz* **2**, 21 (1961); G. R. Hertel and W. S. Koski, *J. Amer. Chem. Soc.* **86**, 1683 (1964); C. F. Giese and W. B. Maier, II, *J. Chem. Phys.* **35**, 1913 (1961); J. H. Futrell and C. D. Miller, *Rev. Sci. Instr.* **37**, 1521 (1966).

19. P. Ausloos, S. G. Lias, A. A. Scala, *Advan. Chem. Ser.* **58**, 264 (1966).

20. M. M. Mann, A. Hustrulid, J. T. Tate, *Phys. Rev.* **58**, 340 (1940).

21. P. Kebarle and A. M. Hogg, *J. Phys. Chem.* **42**, 789 (1965).

22. M. Eigen and L. DeMayer, in *The Structure of Electrolyte Solutions*, W. J. Hamer, Ed. (Wiley, New York, 1959), chap. 5.

22a. S. Searles, thesis, University of Alberta (1968). Searles has measured in a high pressure mass spectrometric experiment the enthalpies and entropies of solvation for potassium ion and water hydrates and for ammonia. In contrast to the other two systems, he finds no structure in the plot of these thermodynamic functions versus solvation number for water. He therefore concludes that the solvated proton is better represented as $H^+(H_2O)_n$ rather than $(H_3O^+)(H_2O)_{n-1}$ as presented in Fig. 6.

23. M. S. B. Munson, *J. Amer. Chem. Soc.* **87**, 5313 (1965); L. W. Sieck, J. H. Futrell, F. P. Abramson, *J. Chem. Phys.* **45**, 2859 (1966); J. H. Futrell and T. O. Tiernan, unpublished work.

24. M. S. B. Munson, *J. Amer. Chem. Soc.* **87**, 2332 (1965).

25. ——— and F. H. Field, *ibid.* **88**, 2621 (1966); F. H. Field, *Accounts Chem. Res.* **1**, 42 (1968).

26. T. O. Tiernan, B. M. Hughes, J. H. Futrell, in preparation.

27. P. Walden, *Chem. Ber.* **35**, 2018 (1902).

28. M. Gomberg, *ibid.* **35**, 2403 (1902).

29. G. A. Olah, *Chem. Eng. News*, 27 March 1967.

30. F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press, New York, 1957).

31. F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.* **80**, 5587 (1958).

32. S. G. Lias and P. Ausloos, *J. Chem. Phys.* **37**, 877 (1962); R. P. Borkowski and P. Ausloos, *ibid.* **40**, 1128 (1964); *ibid.* **38**, 36 (1963); P. Ausloos and S. G. Lias, *ibid.* **45**, 524 (1966).

33. T. O. Tiernan, "Hydride ion transfer reactions in hydrocarbon systems," presented at the 155th national meeting of the American Chemical Society, San Francisco, Calif., April 1968; T. O. Tiernan, in preparation.

34. M. S. B. Munson, *J. Amer. Chem. Soc.* **87**, 2332 (1965).

35. W. Maier, II, *J. Chem. Phys.* **41**, 2174 (1964); C. F. Giese and W. B. Maier, II, *ibid.* **39**, 197 (1963); W. B. Maier, II, *ibid.* **42**, 1790 (1965).

36. S. K. Gupta, E. G. Jones, A. G. Harrison, J. J. Myher, *Can. J. Chem.* **45**, 3107 (1967).

37. D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **29**, 282 (1958).