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Gas-Phase Ion Chemistry

Paul B. Comita and John I. Brauman

The study of the chemistry of ions in the gas phase has advanced rapidly in the last decade due to developments in ion trapping technology, light source technology, and ion detection methods. As is the case in many areas of chemistry, new technology has opened the door to new experiments and insights.

Summary. Progress has been made in the understanding of potential energy surfaces for unimolecular ion dissociations and ion-molecule reactions. With recent advances in instrumentation, many new techniques have been developed to generate and study ions, ion-molecule complexes, and large ionic clusters. Developments in ion spectroscopy have enabled considerable advances to be made in the determination of ion structures.

Perhaps the single most important motivation for studying ions in the gas phase is that the data obtained from such species will reflect the intrinsic properties of the ion. That is, the structure and reactivity are unperturbed by neighboring molecules or ions in the solid phase or solvent molecules and counterions in the liquid phase. The intrinsic properties of a molecular ion can be analyzed and interpreted in a straightforward manner and perhaps be related to a fundamental property of the ion itself rather than to its surrounding environment. The critical effects of solvation can thus be clarified by an understanding of intrinsic molecular properties. In addition, verification and elucidation of solvation effects has become possible with the ability to generate and study large ionic clusters that are composed of many neutral molecules loosely bound to an ion.

Among the challenging experimental aspects of gas-phase ion chemistry today are the quest for an understanding of geometrical structures and bonding and the quest for a detailed understanding of the intrinsic reactivities and potential energy surfaces for ion-molecule reactions with a view towards evaluating theories of the dynamics of chemical reactions.

Reaction Dynamics

Most early studies of ionic reactions in the gas phase focused on unimolecular fragmentations and rearrangements recorded in electron-impact mass spectra. Through the use of new technology and techniques, particularly ion cyclotron resonance (ICR), flowing afterglow, ion beams, and high-pressure mass spectrometry, significant progress has been made in understanding the dynamics and mechanisms of ionic reactions, not only in unimolecular fragmentations but also in reactions of higher order. With the development of new ion trapping technology and detection devices, such as pulsed (and now Fourier transform) ICR and selected ion flow tubes, it has become possible to examine both negative and positive ions with a wide variety of structural features. The dependence of ionic reactions on both temperature and translational energy has been investigated, and with the use of laser sources, the vibrational energy of the ion can be specifically varied to measure its effect on reaction dynamics.

Unimolecular reactions. Unimolecular fragmentation of gas-phase ions can

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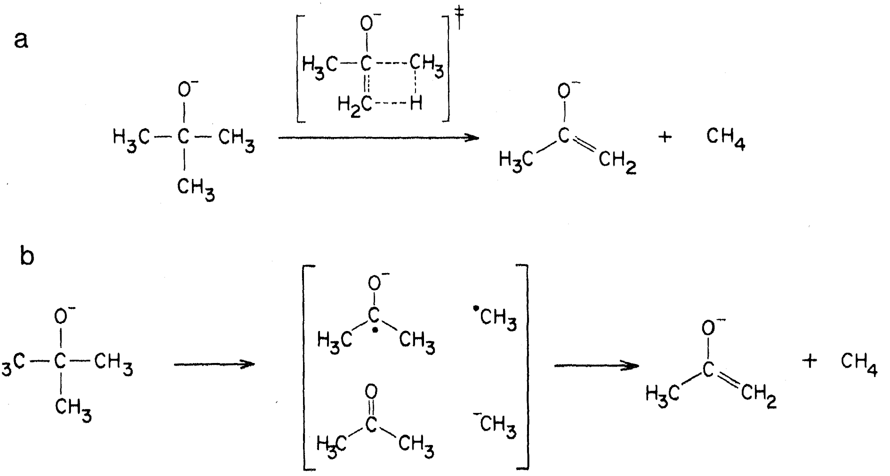


Fig. 1. Two pathways for the IRMP-induced dissociation of *t*-butoxide anion, involving a concerted, four-center elimination (a) and a two-step mechanism with the formation of an ion-molecule complex (b).

be induced with a number of techniques. Electron impact on a neutral molecule can generate ions with excess internal energy, although the internal energy distribution of the ion population is not well defined. Collisional activation is a widely used technique in which ions are accelerated through a neutral gas. Energetic collisions with the neutral molecules result in electronic, vibrational, and rotational energy transfer to the ions, and those ions excited above a threshold for reaction can then undergo dissociation (*1*).

Unimolecular reactions of ions can in some cases be induced by ultraviolet, visible, or infrared radiation. Ion photodissociation with visible light has been well studied and has become a useful spectroscopic technique that will be discussed further in the section on determination of ion structure.

Infrared multiple-photon (IRMP) activation using a CO_2 laser is an attractive method for activating ions at low pressure, and it has many features that are advantageous for some experiments (*2*). For example, collisional effects on the activation and reaction process are avoided since the low pressures ($\sim 10^{-6}$ torr) used result in a time between collisions that is long compared with the time for multiple photon absorption and dissociation. Also, photoproducts can be detected after a single, moderate intensity (unfocused) laser pulse, so primary reactions can be studied unambiguously.

Since the energy required to break covalent bonds is much greater than the energy of infrared photons from a CO_2 laser (approximately 3 kcal per mole), many photons must be absorbed before dissociation can occur. Much theoretical and experimental work has concentrated on the infrared multiple-photon absorption process (*3*). In general, the absorption of energy into the molecules appears to be a largely incoherent process, and unimolecular reactions induced by this method can be described by statistical reaction-rate theory.

A number of IRMP-induced reactions of negative ions have been investigated with pulsed ICR techniques. One deceptively simple elimination reaction illustrates some of the considerations involved in an investigation of a unimolecular ion reaction. The dissociation of the *t*-butoxide anion upon irradiation with a CO_2 laser gives rise to the acetone enolate ion by elimination of methane (Fig. 1). Two of the simplest pathways by which this fragmentation could occur are a concerted, four-center elimination of methane and a two-step mechanism involving the formation of an intermediate ion-molecule complex. The operative mechanism was revealed by a study of intramolecular kinetic isotope effects (*4*). Measurement of both primary and secondary isotope effects was made possible by dissociating specifically deuterated *t*-butoxide anions and detecting partially deuterated enolate ions. The small, intensity-independent primary effect and the large, intensity-dependent secondary effect were consistent only with a stepwise mechanism in which a rate determining cleavage precedes the proton (or hydrogen atom) transfer.

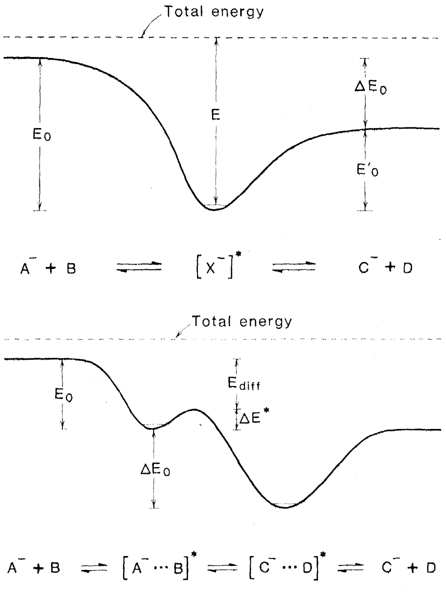
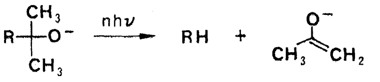


Fig. 2. (Top) Single-minimum potential energy surface for an ion-molecule reaction. (Bottom) Double-minimum potential energy surface for an ion-molecule reaction.

The nature of the initial cleavage was addressed by further studies of IRMP-induced dissociations of alkoxide anions with various alkyl groups. Specifically, experiments were designed to test whether the first step involved homolytic or heterolytic bond cleavage. Alkoxide (1), with R = CF_3, C_6H_5, and H,



$$R-C(CH_3)_2-O^- \xrightarrow{nh\nu} RH + CH_3C(O^-){=}CH_2 \qquad (1)$$

1

eliminates RH exclusively to form acetone enolate and CF_3H, benzene, and hydrogen, respectively (*5*). These results are consistent with initial heterolytic cleavage to form the more stable anion R^- in preference to CH_3^-. For R = *t*-butyl, ethyl, and *i*-propyl, the leaving group ability was found to be *t*-butyl- > methyl > *i*-propyl > ethyl. This order of leaving group ability appears inconsistent with a heterolytic bond cleavage, in contrast to the previous set. It has been explained by a stepwise mechanism involving an intermediate anionic cluster in which an electron is bound nonspecifically by the radical-molecule complex (*5*). An identical order of leaving groups was also discovered in a completely different ion-molecule reaction but has been attributed by DePuy *et al.* to the relative stabilities of alkyl anions (*6*).

For negative ions, loss of an electron is generally the lowest energy unimolecular reaction. Electron detachment can be effected with both ultraviolet and visible light as well as infrared radiation. IRMP studies of electron detachment have provided information concerning the intramolecular transfer of vibrational energy to electronic energy in molecules (*7*). Because electron detachment is slow, bond cleavage frequently is competitive with it, even if the threshold energy of the cleavage is higher.

Generally, IRMP-induced reactions result in the formation of a single product from the lowest energy reaction. In some cases, however, it is possible to activate ions to more than one reaction threshold, and then multiple products are observed. In these multiple-product reactions, the branching ratio depends on the light intensity, offering the possibility of controlling the chemical reaction by varying the laser parameters, including fluence, intensity, and wavelength.

Multiple products in IRMP-induced reactions arise not only from the reactant acquiring internal energy in excess of more than one reaction threshold (true photochemical branching) but also from IRMP excitation of a primary product. In addition, an IRMP-induced reaction may give rise to an intermediate for which several possible reaction channels exist.

In the case of photochemical branching, products resulting from activation above several thresholds can be expected when the thresholds are very close in energy. The dissociation of isotopically labeled alkoxides constitutes an example of such branching. An example of an IRMP-induced reaction that gives rise to an intermediate that subsequently branches is the dissociation of 1,1,1-trifluoroacetone enolate (*8*). The reaction products are deprotonated ketene (HC_2O^-) and trifluoromethyl anion (CF_3^-), and the ratio of these products depends on the light intensity. True photochemical branching would result from competition between a four-center concerted elimination of CF_3H and a heterolytic cleavage resulting in CF_3^-. Branching from an intermediate ion-molecule complex that is photochemically generated appears to be reasonable since the activation barriers for four-center elimination are large. Branching would then arise from competition between separation of the complex, giving rise to CF_3^-, and proton transfer, yielding ketene enolate.

Ion-molecule reactions. Ions and neutral molecules have long-range attractive interactions arising from ion-dipole and ion–induced dipole forces. Potential surfaces for ion-molecule reactions have energy minima due to these interactions. Two examples of such potential surfaces are depicted in Fig. 2, one with a single minimum in free energy and the other with a double minimum. At the low pressures typical of ion-molecule experiments (10^{-7} to 1 torr), the intermediate complexes frequently cannot be stabilized by collision prior to dissociation and, therefore, still contain the energy of the attractive stabilization. These intermediates (for example, $[A^- \cdots B]^*$ in Fig. 2) are vibrationally excited. The intermediate dissociates either back to the reactants or to the products, through the entrance or exit channel, at a rate governed by this excitation energy; and, as is the case for many unimolecular reactions, this rate can be modeled accurately by statistical reaction-rate theory.

Table 1. Intrinsic nucleophilicities of selected anions.

X^-	ΔE^*_0 ($X^- + CH_3X$) (kcal/mol)
Cl^-	10.2
Br^-	11.2
F^-	26.2
CH_3O^-	26.6
t-BuO^-	28.8

From such a theoretical modeling of ion-molecule reactions with single-minimum surfaces, an exothermic reaction of A^- and B to form products would be expected from each collision of A^- and B. In other words, the efficiency of the reaction, the ratio of reaction rate constant to the collision rate constant ($k_{observed}/k_{collision}$), would be equal to one.

Not all ion-molecule reactions have unit efficiencies, and the double-minimum potential surface has been suggested to account for some reactions with low efficiencies (*9*). For these potential surfaces, the reaction is slow because passage over the central barrier has an unfavorable entropy relative to dissociation back to reactants. The entropy is lower for the forward reaction because its transition state involves the formation of chemical bonds in which rotations have been converted to vibrations with a consequent decrease in the available number of quantum states. The relative energies of the entrance channel and the central potential energy maximum, E_{diff}, in this model determines the efficiency of the reaction. This model also predicts that reactions that are slow for this reason will become slower as the energy (or temperature) increases (*10*).

Gas-phase proton transfers are a set of ion-molecule reactions that have been extensively studied to probe their potential energy surfaces. Proton transfers between ions with localized charge (that is, with the charge centered primarily on one atom in the ion) have been shown to have an efficiency ratio equal to one (*11*). Proton transfers involving ions with delocalized charge, such as enolates, phenoxides, and the benzyl anion, do not have unit efficiencies and can be modeled with a double-minimum potential energy surface with a central barrier (*9*). These reactions may be slow due to small stabilization energies, presumably from poor hydrogen bonding in the ion-molecule complex. The central barriers may be somewhat higher than those for ions with localized charge due to the structural reorganization or charge localization that are required for the reactions to occur. The dynamics of endothermic proton transfers have been studied using a hydrogen-deuterium exchange technique (*12*).

The height of the central barrier, also referred to as the activation energy ΔE^*, for ion-molecule reactions can be determined by a kinetic analysis involving the use of RRKM (Rice-Ramsperger-Kassel-Marcus) theory, a statistical reaction rate theory. The difference in energy (E_{diff}) between the entrance channel transition state and the central barrier in this model is adjusted to give agreement with the experimentally observed efficiency. The activation energy ΔE^* can then be determined if the value of the well depth (the energy minimum between the barriers) is known or can be reliably estimated.

A general class of reactions that can be modeled with a double-minimum potential are methyl transfer reactions, nucleophilic displacement (S_N2) reactions on methyl groups (*13*). Many of these reactions have efficiency ratios of less than one and the central barrier heights can be determined by the above analysis (*14*). The barrier heights calculated by this method can be correlated with the changes in enthalphy of the reaction by means of a rate-equilibrium relationship such as the one embodied in the Marcus theory.

The Marcus theory separates the activation barrier height into two components, one an intrinsic component and the other arising solely from the overall reaction energetics. That is, the height of the energy barrier for an elementary reaction is related to not only the standard energy change for the reaction but also to an intrinsic barrier, the barrier of a hypothetical reaction for which $\Delta E_0 = 0$. For the methyl transfer reactions, the intrinsic activation energies ΔE^*_0 have been compiled for nucleophile-leaving group pairs (*14*). The intrinsic barrier for a cross reaction

$$X^- + CH_3Y \rightleftharpoons CH_3X + Y^- \qquad (2)$$

is the same in the forward or reverse direction, and ΔE^*_0 for the identity reaction ($X = X'$)

$$X'^- + CH_3X \rightleftharpoons CH_3X' + X^- \qquad (3)$$

is obtained directly or by assuming that the ΔE^*_0 for the cross reaction is the mean of the two corresponding identity reactions. Values of ΔE^*_0 (X,X) are listed in Table 1.

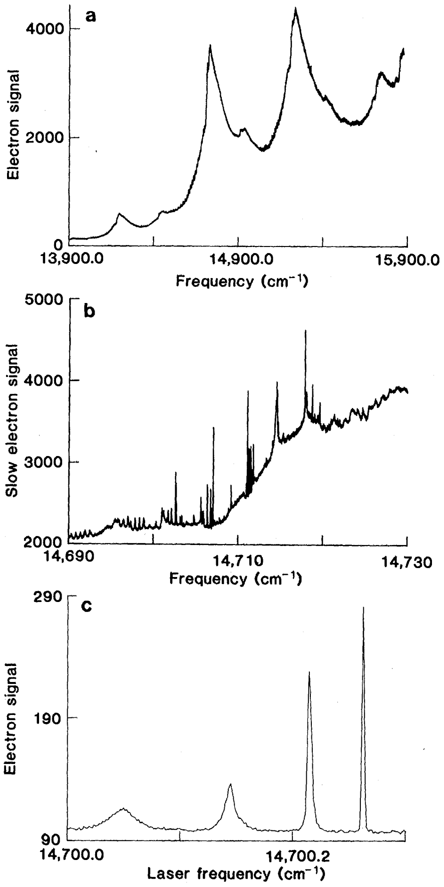


Fig. 3. Electron photodetachment spectra of acetaldehyde enolate: (a) 1 cm^{-1} resolution; (b) data near the 0-0 vibrational transition at 0.03 cm^{-1} resolution; (c) individual rotational transitions fully resolved at a Doppler-limited resolution of 0.0007 cm^{-1}. [Courtesy of the *Journal of Chemical Physics* (*52*)]

Nucleophiles in general appear to have large intrinsic barriers for methyl transfer, especially first row atoms. Strong nucleophiles such as Cl^- and Br^- react rapidly in identity reactions both in the gas phase and in solution. Most of the activation energy for the Cl^- identity reaction in solution is a consequence of solvation effects; F^- and RO^- have high intrinsic barriers in the gas phase as well as additional activation barriers in solution due to solvation. Recent quantum mechanical calculations for the Cl^- identity reactions in the gas phase coupled with statistical mechanical simulations of an aqueous phase potential surface clearly show the influence of solvation: a flattening of the free-energy minima for the ion-molecule complex and a large increase in the free energy of activation (*15*). Albery, Kreevoy, Lewis, and Kukes have applied Marcus theory to solution phase reactions and have found reasonable and consistent intrinsic barriers for methyl transfer (*16*). Further studies of gas-phase methyl transfer reactions have shown that the experimental change in ΔE^* with the ΔE_0 of the reaction (given by the Bronsted coefficient) agrees with that calculated by Marcus theory (*17*).

Ion-molecule complexes. The techniques described in the previous section dealt with understanding the nature of the barrier in a double-minimum potential energy surface of ion-molecule reactions. The nature and magnitude of the minima are also important, because they are the most energetically stable configurations of the neutral and ionic fragment. Ion-molecule complexes such as these are bound by long-range attractive forces, and they are intermediates in gas-phase ion-molecule reactions such as the proton or methyl transfer reactions. The binding energy of the complex, along with the central barrier height and the overall thermochemistry, completely characterize the double-minimum potential energy surface of a reaction.

The values of the binding energies of ion-molecule complexes are thus of great interest. They have been determined by several experimental techniques. High-pressure mass spectrometry has been used by Kebarle to study the temperature dependence of ion-molecule equilibria, leading directly to binding energies (*18*). Both Bartmess and McMahon have determined energy-well depths using pulsed ICR techniques analogous to those developed for determining gas-phase acidities (*19*). Relative binding energies of ion-molecule complexes are obtained by exchange of the ion between two neutral molecules:

$$\mathrm{R_1H\cdot\cdot Cl^-} + \mathrm{R_2H} \rightleftharpoons \mathrm{R_2H\cdot\cdot Cl^-} + \mathrm{R_1H} \qquad (4)$$

These experiments have elucidated the factors involved in the binding of alkoxide-alcohol complexes, halide-alcohol complexes, and halide-acid complexes. Single molecule binding energies have been shown to be influenced by the size of the ion and the steric requirements of the neutral species.

The binding of gas-phase ions to molecules provides a means of understanding solvation phenomena and also provides a starting point for the investigation of the transition from gas phase to solution phase. The behavior of large clusters of neutral molecules with an ion may approach the behavior of ions in a condensed phase. A key question is at what point do cluster ions have essentially the properties of an ion in solution?

A number of new techniques have been developed specifically for generating ion clusters in the gas phase and studying their stability. Secondary-ion mass spectrometry has been used to generate positively charged ion clusters of nitrogen and nitrogen oxides (*20*). Collision-induced dissociation has given some information on the internal structure of these clusters, which appear to behave, qualitatively, as a central ion with loosely bound solvating molecules. Negatively charged ion clusters have been generated by collisional electron transfer from alkali atoms to neutral clusters formed by expanding a supersonic molecular beam (*21*). Negatively charged ion clusters of hydrogen halides, $(\mathrm{Cl_2})_n$, $(\mathrm{SO_2})_n$, $(\mathrm{NO_2})_n$, $\mathrm{SO_2(CO_2)}_n$, and $(\mathrm{H_2S})_n$ have been formed, and the technique appears to be useful for obtaining electron affinities of clusters only as large as dimers. The influence of the size of the cluster ion on the rate of reaction has been determined for the gas-phase nucleophilic substitution reactions of hydroxide ion in water clusters, but the interpretation of the data is controversial at present (*22*).

Ion Energetics

An understanding of ion energetics is a prerequisite for the formulation and evaluation of dynamical theories of ion-molecule reactions. The thermodynamic parameters that have been shown to be of fundamental importance in this regard are the electron affinities and ionization potentials of molecules and radicals, and the bond strengths of ions and neutral species. Thermochemical cycles can be constructed that connect these quantities to the acidities and basicities of species in the gas phase, properties that have been shown to be substantially different from the corresponding properties of species in condensed phases. New experimental techniques have resulted in extensive tabulations of these thermochemical data, and the understanding of these values has been put on a more solid foundation (*23*).

Systematic evaluation of the gas-phase acidities of neutral molecules and the proton affinities of negative ions continue to provide the basis for any discussion of ionic stabilities (*23*). Comparisons of these data with solution-phase values provide important insights into solvation effects, especially those that are anomalous and specific to certain classes of ions (*24*).

Methods for determining ion-molecule interaction energies and ionic bond strengths as well as the electron affinities of negatively charged ion clusters are among the recent developments in the acquisition of thermodynamic data for gas-phase ions. The measurement of intrinsic ion properties such as these has been useful in gaining an understanding of structure-reactivity relationships for organic molecules. Analogous data for the bond strengths of transition metal ions and their clusters have not been available until quite recently. Metal-hydrogen and metal-carbon bond strengths of many transition metal cations have been obtained and analyzed by Beauchamp, Armentrout, and co-workers, using ion-beam mass spectrometry (*25*). By adjusting the relative kinetic energies of the transition metal ions, the threshold energies for the formation of a metal-ligand bond can be obtained. Periodic trends in the bond strengths have been analyzed and modeled by simple covalent and electrostatic bonding models. The reactivity and bond energies of transition metal cluster ions, such as Mn_2^+, have been determined (*25*). Both metal-metal bond energies and ionization potentials have been obtained.

Determination of Ion Structure

Spectroscopy of both neutral and ionic molecules in the gas phase encompasses transitions among rotational, vibrational, and electronic energy levels and can give rise to information leading to a specification of molecular structure. The principle spectroscopic methods used to determine ion structure can be grouped into two categories: those which measure light absorption or emission directly (absorption or emission spectroscopy) and those which measure an event, such as photodissociation or electron photodetachment, that follows absorption of light (action spectroscopy). Both types of spectroscopy give rise to detailed structural information about gas-phase ions.

Conventional absorption spectroscopy of gas-phase ions has developed at a much slower pace than that of neutral, closed-shell molecules. This is due to the difficulty in containing ions at such densities that light absorption can be reliably measured and also in devising detection schemes that minimize high background signals from a neutral precursor. In the past 10 years, with the widespread application of laser technology and much clever experimentation and development of new detection methods, considerable progress has been made.

Absorption spectroscopy. The detection of transitions between rotational states by microwave spectroscopy was achieved initially with two- and three-atom molecular ions (*26*). Microwave spectra of HCO^+, NNH^+, and CO^+ were measured with a cell that sustained a direct-current glow discharge. Modulation of the source or magnetic field allowed for highly sensitive detection of microwave absorption. Recent work with improved detector sensitivity has permitted the characterization of HOC^+ and HCS^+.

Transitions between rotational states in simple paramagnetic ions have also been observed by laser magnetic resonance, a technique that makes use of a magnetic field to lift the degeneracy of magnetic sublevels of the ion (*27*). By varying the magnetic field strength, transitions between the sublevels of rotational states can be brought into resonance with an available laser frequency. A number of small ions, such as the positive ions of the hydrogen halides, have been studied with this technique (*28*). The data obtained have been used to derive structural parameters for the ions, such as rotational constants and centrifugal distortion constants, as well as details of electronic structure.

With vibrational spectroscopy, several absorption experiments have produced results for simple positive ions. These include a difference-frequency laser absorption experiment for H_3^+ (*29*) and for HeH^+, NeH^+, and H_3O^+ (*30*) and the measurement of high-resolution spectra of protonated rare gases using Fourier-transform detection methods (*31*).

More recently, a new technique for detecting infrared absorption of ions has been developed (*32*). Ion velocities are modulated by alternating the polarity of a glow discharge, thus shifting the ion absorption frequencies according to the Doppler effect. Phase sensitive detection yields the absorption spectrum of the ion without interference from the spectrum of the neutral precursor, which is in much greater abundance. Vibration-rotation transitions have been observed with this technique for HCO^+ (*33*), HNN^+ (*34*), H_3O^+ (*35*), and NH_4^+ (*36*) as well as other species.

Electronic spectra can be used to study the structures of both the ground and excited states of ions in which the excited states can be reached either by bombarding the corresponding neutral species with electrons or by direct optical excitation. The fluorescence emission spectra consist of vibronic bands that give rise to the determination of vibrational frequencies for ground and excited states and also rotational constants for small ions. Highly precise data have been obtained for moderate size cations by lowering the temperature of the ions. The cooling is accomplished by expanding the sample gas in a supersonic free jet. Recent results from this technique have been reviewed (*37, 38*). In general, open-shell organic cations that are unsaturated, such as substituted acetylene or benzene ions, have been studied by this method because the energy of the emitted photons lies in the visible region of the spectrum, a favorable region for fluorescence detection. Recent work on laser-induced fluorescence of ionic clusters of fluorinated benzenes and inert gases appears to provide information concerning the binding sites of the inert atoms in the ion (*39*).

Action spectroscopy. Three general areas of ion spectroscopy can be grouped into the category of action spectroscopy: photodissociation, electron photodetachment, and photoelectron spectroscopy. These methods are characterized by the detection of an event following the absorption of light by the ion.

The technique of using a photodissociation event to study ion structure is made possible by producing an excited state of an ion above a dissociation threshold. The excited state either predissociates by mixing with a repulsive excited state or internally converts to a hot ground state and then dissociates. Spectra are inferred from the wavelength dependence of the dissociation, assuming a constant quantum yield for the process. For example, if all absorption events result in dissociation, then the action spectrum and the absorption spectrum are identical.

Photodissociation experiments have been carried out in ICR spectrometers and have been reviewed (*40*). These experiments generally have low spectral resolution and give rise to electronic spectra that, in some cases, have vibronic structure (*41*). Ions are generated and trapped in an ICR cell, and the photodissociation cross sections are calculated by measuring the fractional decrease in the signal of the ion that is being photodissociated.

Ion beams have been employed by many different research groups to study the photodissociation of small ions (*42*). The technique of photofragment spectroscopy has been used to probe small ions such as O_2^+, Cs_2^+, and SO^+ (*43*). In general, an ion beam interacts coaxially with continuous-wave laser light producing fragment ions that, in turn, are separated according to their mass by an electrostatic quadrupole, selected according to their energy content, and detected. Photofragment spectroscopy experiments in the ultraviolet region are being performed with an ArF excimer laser to study a variety of small ions (*44*) and, in the near-ultraviolet and ultraviolet regions, to study the high-resolution spectroscopy of N_2O^+ (*45*). In the infrared region, photofragment spectroscopy with a continuous-wave CO_2 laser has been used to study vibration-rotation transitions of $H_3{}^+$ and HeH^+ ions (*46*).

A number of advances have been made recently in the area of electron photodetachment of negative ions. In this method, ions are irradiated in an ICR or ion beam; and, depending upon the technique, ion depletion, neutral products, or electron production is measured as a function of light frequency (*47*). For negative ions, photodetachment produces a neutral species in either its ground state or an excited state. If the geometries of the neutral species and the anion are substantially different, then transitions in which vibrational quantum numbers change become important, and vibrational transitions can be observed. These vibrational transitions manifest themselves as onsets in photodetachment cross sections and have provided information on vibronic transitions, rotational fine structure, and spin-orbit splittings in alkoxides, thioalkoxides, and hydrogen sulfide (*48*).

Transitions to electronically excited states of anions can be observed as resonances in photodetachment cross sections. The energy of these excited anion states usually exceeds the thermodynamic threshold for electron detachment. Excitation to the electronically excited state followed by autodetachment provides a pathway for electron loss in addition to direct photodetachment. Broad unstructured resonances have been observed for large delocalized anions that correspond to electronic transitions to excited anion states (*49*). In the threshold region for photodetachment narrow resonances have been observed that have been assigned as dipole-bound states, diffuse excited states of anions that are analogous to Rydberg states of neutral molecules (*50*). Ultrahigh-resolution photodetachment of acetaldehyde enolate and other anions has been carried out using an ion beam and a ring dye-laser operating single-mode (*51*, *52*). Spectra for the electron photodetachment of acetaldehyde enolate are shown in Fig. 3. The data display the remarkable difference in the features of the spectrum with progressively higher resolution. High-resolution spectra show that for high rotational energy levels the line widths become immeasurably broad. These energy levels lie above the threshold for direct photodetachment and have very short lifetimes. The lowest rotational levels were not observed because they lie below the threshold of photodetachment and thus are bound. A complete analysis of the transitions between rotational states of the anion ground state and the excited dipole-bound state has yielded spectroscopic constants and geometries for both states.

Conclusion

The impact of gas-phase ion chemistry on the thinking of chemists has been considerable. Intrinsic thermodynamic and kinetic properties have been determined and evaluated with this technique, leading to a clearer understanding of the relation between structure and reactivity in ionic reactions as well as clarifying the role of solvation in the condensed phase. Measurement of thermodynamic and structural parameters by new spectroscopic methods offers the promise of a better understanding of the properties underlying the structures of ionic molecules.

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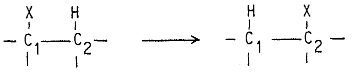
Mechanisms of Coenzyme B_{12}–Dependent Rearrangements

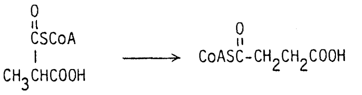
Jack Halpern

Summary. Coenzyme B_{12} serves as a cofactor in various enzymatic reactions in which a hydrogen atom is interchanged with a substituent on an adjacent carbon atom. Measurement of the dissociation energy of the coenzyme's cobalt-carbon bond and studies of the rearrangement of model free radicals related to those derived from methylmalonyl–coenzyme A suggest that these enzymatic reactions occur through homolytic dissociation of the coenzyme's cobalt-carbon bond, abstraction of a hydrogen atom from the substrate by the coenzyme-derived 5′-deoxyadenosyl radical, and rearrangement of the resulting substrate radical. The only role thus far identified for coenzyme B_{12} in these reactions—namely, that of a free radical precursor—reflects the weakness, and facile dissocation, of the cobalt-carbon bond.

Coenzyme B_{12} (5′-deoxyadenosylcobalamin, abbreviated $AdCH_2$-B_{12}), whose structure is depicted in Fig. 1, serves as a cofactor for various enzymatic reactions (Table 1). [For comprehensive accounts of the chemistry and biochemistry of vitamin B_{12}, see (*1, 2*).] A common feature of these reactions, depicted by Eq. 1, is the 1,2-interchange of a hydrogen atom and another substituent [X = OH, NH_2, C(=O)SCoA, C(=CH_2)COOH or CH(NH_2)COOH] on adjacent carbon atoms of the substrate (*3*). Among these reactions, the methylmalonyl–coenzyme A (CoA) mutase rearrangement (Eq. 2) (*4*), whose mechanism is discussed in this article, is distinctive in that it plays a role in mammalian systems, whereas the other reactions occur only in microorganisms.



$$-\overset{X}{\underset{|}{\overset{|}{C_1}}}-\overset{H}{\underset{|}{\overset{|}{C_2}}}- \longrightarrow -\overset{H}{\underset{|}{\overset{|}{C_1}}}-\overset{X}{\underset{|}{\overset{|}{C_2}}}- \quad (1)$$



$$\underset{CH_3CHCOOH}{\overset{\overset{O}{\|}}{\overset{CSCoA}{|}}} \longrightarrow CoAS\overset{O}{\overset{\|}{C}}-CH_2CH_2COOH \quad (2)$$

Enzymatic studies have provided convincing evidence for the essential features of the mechanistic scheme depicted by Fig. 2 (*5–7*). This mechanism encompasses the following sequence of steps: (i) enzyme-induced homolytic dissociation of the cobalt-carbon bond of coenzyme B_{12} to generate cob(II)alamin (also designated vitamin B_{12_r}) and a 5′-deoxyadenosyl radical (abbreviated $AdCH_2\cdot$), (ii) abstraction of a hydrogen atom (*8*) from the substrate to generate a substrate radical and 5′-deoxyadenosine ($AdCH_3$), (iii) rearrangement of the resulting substrate radical (either directly or through additional intermediate steps) to the corresponding product radical, and (iv) abstraction of a hydrogen atom from $AdCH_3$ by the product radical (*8*) to complete the rearrangement reaction.

The evidence (*5–7*) for this mechanistic scheme includes (i) the demonstration, with the use of deuterium tracers, that the migrating H atom is scrambled with the two methylene H atoms of $AdCH_2$-B_{12}, suggesting that the three H atoms become equivalent during the course of the reaction (consistent with the intermediate formation of $AdCH_3$), (ii) the direct spectroscopic (electronic and electron paramagnetic resonance) observation of the free radical intermediates (B_{12_r} and a carbon-centered free radical) in certain coenzyme B_{12}–dependent rearrangements (notably ethanolamine ammonia lyase and diol dehydrase); and (iii) the demonstration, in at least one case, of the reversible formation of $AdCH_3$ during the course of the enzymatic reaction.

Figure 2 represents the minimal mechanistic scheme that accommodates the above observations. One important feature not specifically depicted by this scheme is that both the coenzyme and the substrate are bound to the enzyme during the course of the reaction. This binding presumably dictates the chemical selectivity and regioselectivity of the H abstraction steps and the stereospecificity of the H-X interchange [for example, retention of the configuration at C-2 for methylmalonyl-CoA mutase (*4*) and inversion for diol dehydrase (*9*)]. The mechanism also may be incomplete in that there may be additional steps and intermediates, such as intermediate hydrogen carriers in the H transfer steps, as well as additional steps and intermediates (for example, carbonium ions, carbanions, or substrate-derived organocobalt complexes) in the rearrangement process itself (that is, the 1,2-migration of X).

In this article, the following themes that relate to the mechanistic scheme of Fig. 2 for coenzyme B_{12}–dependent rearrangements are discussed: (i) the cobalt-carbon bond dissociation energy of coenzyme B_{12}, (ii) the factors that influence cobalt-carbon bond dissociation energies and that may contribute to the enzyme-induced bond weakening and dissocia-

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