Ion Cyclotron Resonance Spectroscopy

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Ion cyclotron resonance spectroscopy is based on the dynamics of charged particles in magnetic and electric fields.[1] In particular, the path of a free charged particle moving in a uniform, static magnetic field, **H**, is constrained to a circular orbit in a plane normal to **H**, but is unrestricted parallel to **H**. Since the force on a charged particle of mass m moving with velocity **v** in **H** is

$$\mathbf{F} = \frac{q}{c}\mathbf{v} \times \mathbf{H} \tag{1}$$

and since this force is always normal to the instantaneous velocity, the particle will move in a circle in a plane normal to **H** such that

$$mv^2/r = \frac{q}{c}vH \tag{2}$$

where q is the charge on the particle, c is the speed of light,[2] r is the radius of the orbit, and v is the component of **v** normal to **H**. It follows from (2) that

$$\omega_c = v/r = qH/mc \tag{3}$$

where ω_c is the angular frequency or *cyclotron frequency* of the orbital motion. The cyclotron frequency is independent of the velocity of the particle, whereas the radius of the orbit is directly proportional to v. These equations of motion are of course familiar as the basis for the cyclotron particle accelerator, and it seems quite natural to refer to the principle of Lawrence's cyclotron[3] as *cyclotron resonance*.

A swarm of ions of a given mass produced, for example, by electron impact will have a distribution of velocities but a sharp cyclotron frequency, ω_c, which depends only on m, q, and **H**. If ions are generated between a pair of parallel plates placed in a magnetic field (Figure 1), and an alternating electric field, **E**(t), is applied normal to **H** at frequency ω, when $\omega = \omega_c$ the ions absorb energy from the alternating electric field and are accelerated to larger velocities and orbital radii. An absorption of energy from **E**(t) is reflected as a change in the power required from the source of **E**(t). The absorption of energy from **E**(t) at $\omega = \omega_c$ by a swarm of ions can thus be detected if an oscillator which is extremely sensitive to changes in load is used as the source of **E**(t).

A commercial ion cyclotron resonance spectrometer based on these principles is currently available.[4] For usual laboratory fields from 0 to 15,000 G, oscillator frequencies, $\omega/2\pi$, from 100 to 800 kHz are necessary to make accessible a mass range of 1 to 230 amu. This is a convenient frequency range for operation of marginal oscillators which have been highly developed for nuclear magnetic resonance.[5,6] The radiofrequency voltage level of a marginal oscillator is extremely sensitive to small impedance changes in the resonant circuit. The parallel plates shown in Figure 1 are incorporated as a capacitive element of the resonance circuit for this oscillator.

A recording of the level of the marginal oscillator as a function of **H** for a fixed oscillator frequency displays the cyclotron resonance spectrum for a mixture of ions of various masses with a scale linear in mass. For sample pressures below 10^{-7} Torr[7] this device is a rather good mass spectrometer quite analogous to the Omegatron[8] with a sensitivity of the order of 1 to 10 ions/cm^3 and a mass resolution as high as 1/30,000. For sample pressures above 10^{-5} Torr, the coherent cyclotron motion of the ions is occasionally interrupted by collisions between ions and neutral molecules, and ion–molecule reaction products may arise.[9,10]

Ion–Molecule Chemistry. Ion–molecule reactions that result in substantial chemical changes have received considerable attention.[11–16] Although the fundamental aspects of ionic collision processes in gases have been studied by a variety of methods,[17–20] most current investigations of ion–molecule reactions involve some type of mass spectrometric method. Current mass spectrometry has acquired considerable versatility

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(1) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).
(2) Gaussian cgs units are assumed.
(3) E. O. Lawrence and M. S. Livingston, *Phys. Rev.*, **40**, 19 (1932).
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(5) R. V. Pound and W. D. Knight, *Rev. Sci. Instrum.*, **21**, 152 (1950).
(6) F. N. H. Robinson, *J. Sci. Instrum.*, **36**, 481 (1959).
(7) A pressure of 1 Torr = 1 mm Hg.
(8) H. Sommer, H. A. Thomas, and J. A. Hipple, *Phys. Rev.*, **82**, 697 (1951).
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(15) P. J. Ausloos, *Advan. Chem. Ser.*, **No. 58** (1966).
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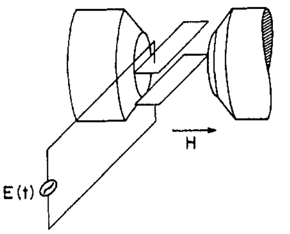

Figure 1. Orientation of magnetic field **H** and parallel plates such that the radiofrequency electric field **E**(t) can be applied normal to **H** at frequency ω.

for the study of ion–molecule reactions through the development of many modifications of basic single-stage instruments of conventional design.[21,22] These modifications include a variety of pulse techniques[23–25] and differential pumping methods which permit operation of ion sources at high pressures.[26–28] However, with single-stage instruments there are usually experimental difficulties involved in identifying the links between reactant and product ions when concurrent ion–molecule reactions occur.

Tandem mass spectrometry[29] is a considerably more complex method for studying ion–molecule reactions. This technique involves coupling two mass spectrometers. The first produces ions of known identity and mass which are introduced into a reaction chamber which serves as the ion source of the second instrument. The second spectrometer then analyzes the product ions formed. The tandem method eliminates the difficulties in identifying the relationships between reactant and product ions. However, this technique is complex instrumentally, and most tandem experiments are carried out with reactant ion energies in excess of 1 eV because of problems in controlling low-energy ion beams. On the other hand, the ion cyclotron resonance technique is in fact best suited for experiments involving ion energies from thermal (0.025 eV) to several electron volts. In addition, the double-resonance method allows the relationships between reactant ions and their corresponding product ions to be readily established in complex ion–molecule reaction sequences.[30]

Ion–molecule reaction rate constants are usually dependent on the relative ion–neutral velocities. Thus, if the velocity of reactant ion A^+ is increased by application of a strong radiofrequency electric field, $\mathbf{E}_a(t)$, oscillating at frequency ω_a, where $\omega_a = qH/m_ac$, then a substantial change can occur in the concentration of ion C^+ if A^+ and C^+ are coupled by reaction 4. The consequent changes in cyclotron resonance intensity and line shape of C^+ can be observed with a weak radiofrequency field, $\mathbf{E}(t)$, oscillating at ω_c, where $\omega_c = qH/m_cc$.

$$A^+ + B \longrightarrow C^+ + D \tag{4}$$

The double-resonance experiment also provides some immediate information on the thermochemistry of ion–molecule reactions. The intensity of a product ion signal can increase or decrease with irradiation of a reactant ion. All of the reactions studied by icr for which ΔH is known are consistent with the general observations that the intensity of the product ion signal decreases for exothermic proton-transfer reactions and increases for exothermic charge-transfer reactions.[31] Therefore, the sign of the double-resonance effect allows reactions to be readily ordered in thermochemical series and limits to be placed on various thermodynamic quantities.

It is also possible to eliminate completely reactant ions of a specific mass from the cell using a variety of irradiation and modulation options.[32] The effect which removal of a specific reactant has on the product distribution allows the reaction pathways to be identified and rates to be determined.

Instrumentation

A block diagram of a basic spectrometer is shown in Figure 2. The resonance cell, shown in more detail in Figure 3, is situated between the pole faces of a 9-in. electromagnet. The cell is contained in a bakable stainless steel vacuum chamber which can be evacuated to a pressure of 10^{-8} Torr by means of a getter-ion pump. A gas is introduced into the chamber through a variable leak valve from a sample foreline. Most variations of inlet systems used with conventional mass spectrometers can also be used with the icr spectrometer.

The cell is divided into separate ion source, analyzer, and collector sections. This design eliminates variation of the resonance frequency with space charge effects caused by the electron beam.[33] Ions are produced in the source region by an electron beam which is accelerated from the filament in a direction parallel to the magnetic field. Static voltages applied across the top and bottom plates of the cell then cause the ions to drift in a cycloidal manner through the source region into the analyzer region. Trapping voltages are applied to the side plates in both the analyzer and source regions to prevent escape of ions from the cell because of their velocity components parallel to the direction of the magnetic field.

The top and bottom plates of the cell in the analyzer region form the capacitive element of the resonance circuit of a marginal oscillator detector. Power absorption in the capacitive element results in a change in the

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(28) W. Wexler and N. Jesse, *J. Amer. Chem. Soc.*, **84,** 3425 (1962).

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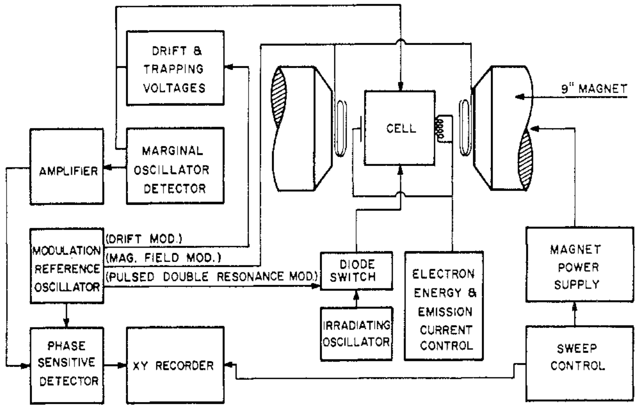

Figure 2. Block diagram of ion cyclotron resonance spectrometer.

resistive impedance of the resonant circuit and is reflected as a change in the radiofrequency voltage level of the marginal oscillator. If the magnetic field or various electrostatic voltages are modulated, the radiofrequency level will vary at the modulation frequency when ω equals the cyclotron frequency of an ion in the cell. The output of the marginal oscillator can then be conveniently detected through the use of a phase-sensitive detector referenced to the modulation frequency. Modulation of the magnetic field is generally satisfactory and has been employed widely. This method gives typical derivative line shapes, as shown in Figure 4.

A pulsed grid modulation scheme involves insertion of a grid into a section milled from the back side of the filament mounting block.[34] By pulsing the bias of this grid the electron beam can be blocked from entering the cell. The major advantage of this method is that it allows, if necessary, production of ions in intervals as short as 100 μsec. During the off portion of the cycle these species can be studied without interference from the electron beam.

The second radiofrequency field required for double-resonance experiments is most conveniently coupled with a small resistance to the bottom plates of the cell in either the analyzer or source region. It is easier to determine the energy of ions if the source region is irradiated. A highly specific double-resonance modulation scheme is illustrated in Figure 2.

A variety of new techniques and modifications of the basic spectrometer greatly expand the dynamic operating capabilities of the icr technique. For example, the potential applied to the trapping plates gives rise to a quadrupole electric field near the center of the resonance cell. The motion of an ion in the cell thus includes a harmonic component at a frequency which depends on the voltage applied to the trapping plates, the spacing of the plates, and the mass of the ion. Beauchamp and Armstrong[32] have shown that if a radiofrequency field oscillating at this frequency is applied to the trapping plates, ions of a given mass can be selectively ejected from the icr cell. Various modulation options then allow presentation of spectra of either the ejected ions or those remaining in the cell. The ion-ejection technique permits the determination of product distributions and their partitioning with ion energy even if complex reaction schemes are operating with competing pathways leading to identical products.

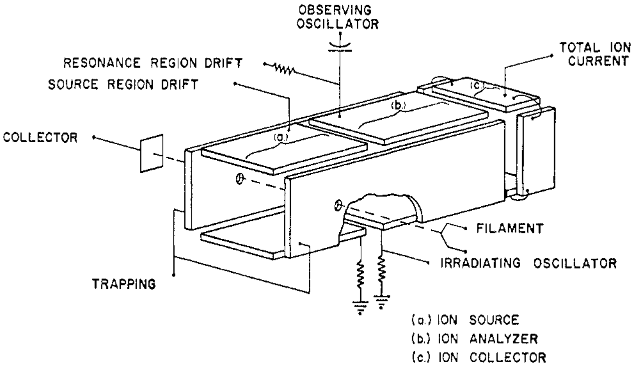

Figure 3. Cutaway view of cyclotron resonance cell. The electron beam is collinear with the magnetic field. (a) Ion source; (b) ion analyzer; (c) ion collector.

McIver[35] has described a trapped ion analyzer cell which can be used in conjunction with pulsed modes of operation to determine ion–molecule reaction rate constants. A very simple trapped-ion cell is shown in Figure 5. This cell employs a single section for ion production and analysis. The end plates are maintained at the same potential as the drift plates with respect to the trapping plates. Ions can be trapped in this structure for times longer than seconds. Another trapping geometry that is convenient for icr is a circular or donut-shaped cell.[36]

A typical pulse sequence is initiated with a 0.1-msec pulse of the electron beam to produce the ions. The ions produced by this pulse of electrons are trapped in the cell for a set interval with the appropriate electrostatic voltages. During this interval, double-resonance experiments can be carried out.[37] Product ions of a given mass can then be observed by pulsing the magnetic field to give resonant conditions for a fixed value of the observing rf field, ω_1. The cyclotron resonance frequency can be changed by applying a radial electric field component. It is therefore also possible to bring an ion of given mass into resonance by applying small voltage pulses to the trapping plates. The detection period can then be terminated by applying a quenching pulse to the upper drift plate. This full pulse sequence can be repeated on a 0.01-sec to several-second time base. McIver[38] has combined these pulse sequences with the ejection technique by applying a radiofrequency field of appropriate frequency to the trapping plates to eject stray electrons. These pulse methods appear to be ideal for the measurement of very slow reaction rates.

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(35) R. T. McIver, Jr., *ibid.*, **41**, 555 (1970).

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(37) R. C. Dunbar and R. T. McIver, Jr., unpublished results.

(38) R. T. McIver, Jr., unpublished results.

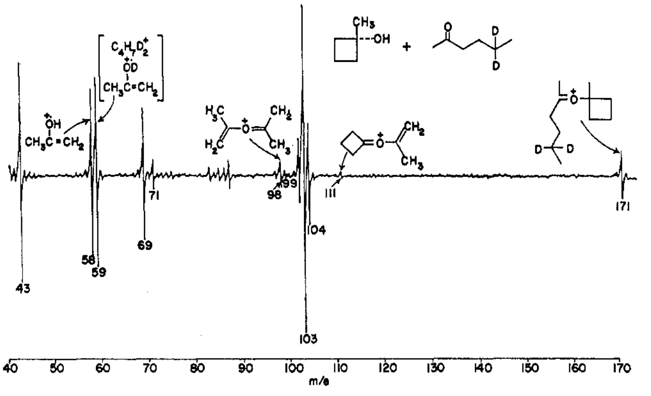

Figure 4. Ion cyclotron resonance spectrum of a mixture of 1-methylcyclobutanol and 2-hexanone-*5,5-d*$_2$, $\omega_1/2\pi$ = 115.0 Hz, 6 × 10^{-6} Torr, 20 eV.

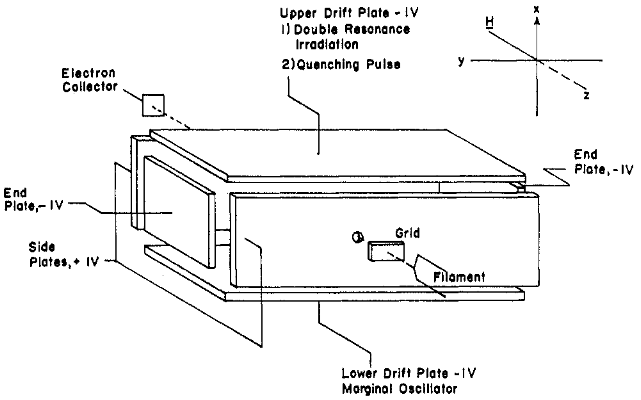

Figure 5. Schematic diagram of the trapped ion analyzer cell. The dc voltages applied to each of the cell plates are suitable for trapping positive ions.

Ion–Molecule Chemistry

Thermodynamic Measurements. Construction of gas-phase acidity and basicity scales is an important application of ion cyclotron resonance spectroscopy. A mixture of the compounds to be tested is simply introduced into the spectrometer with the ionizing voltage set at a value close to the threshold for ionization of a reactant. The thermochemistry of protonation of a specific material by a variety of reactants can then be examined by double resonance and by following the reaction over a wide pressure range. This latter approach reduces the probability that the reactant ion will be excited, since at high pressures the ions are relaxed by many collisions during their residence in the cell.

As an example, demonstration that reactions such as (5) proceed only in the direction indicated resulted in establishment of the acidity series: neopentyl > *tert*-butyl > isopropyl > ethyl > methyl > water and *tert*-butyl ≈ *n*-pentyl ≈ *n*-butyl ≈ *n*-propyl > ethyl.[39]

$$(CH_3)_3CCH_2O^- + CH_3OH \longrightarrow (CH_3)_3CCH_2OH + CH_3O^- \quad (5)$$

This series is consistent with the model which pictures alkyl groups as polarizable and able to stabilize charge by an induced-dipole mechanism.[40] Gas-phase p*K*'s should be a good reflection of intrinsic acidity or basicity, as there are no complicating solvent interactions.[41,42]

By determining the direction of protonation when a reactant is mixed with various species of known proton affinities, absolute proton affinities can be determined to within a few kilocalories per mole. For example, reactions 6 and 7 show that the proton affinity (PA) of phosphine is 185 ± 4 kcal/mole.[43]

$$CH_3CH{=}OH^+ + PH_3 \longrightarrow PH_4^+ + CH_3CHO \quad (6)$$
$$PA(PH_3) \geq 182 \text{ kcal/mole}$$

$$(CH_3)_2CO + PH_4^+ \longrightarrow PH_3 + (CH_3)_2C{=}OH^+ \quad (7)$$
$$PA(PH_3) \leq 189 \text{ kcal/mole}$$

Construction of thermodynamic cycles shows that differences in acidity of negative ions reflect the relative bond strengths and electron affinities of the corresponding radicals. Because of the paucity of reliable electron-affinity data, comparison compounds for determination of gas-phase acidities are not readily available. Brauman and Smyth[44] chose to determine electron affinities by photodetachment using ion cyclotron resonance. This is accomplished by monitoring the change in intensity of the negative ion resonance in reaction 8 as the optical frequency is changed. This method obviates the usual problems associated with determining the concentration of detached electrons. Also, negative ions are easy to generate by icr, and their residence time in the icr cell can be made quite long.

$$A^- + h\nu \longrightarrow A\cdot + e^- \quad (8)$$

Ion–Molecule Reaction Mechanisms. Ion cyclotron resonance can be used to investigate the pathway by which an ion–molecule reaction proceeds and the nature of intermediate species which may be involved. The double-resonance spectra of isotopic mixtures play a central role in these studies. For example, the protonated acetonitrile ion can be produced from acetonitrile by either proton transfer (eq 9) or hydrogen abstraction (eq 10).[45] It is possible to differentiate these pathways by examining the precursor of CD_3CNH^+ and CH_3CND^+ ions produced from a mixture of acetonitrile and acetonitrile-*d*$_3$. Since irradiation of acetonitrile molecular ion (*m/e* 41) causes a change only

$$\begin{tikzcd}
 & CD_3CNH^+ + \cdot C_2H_2N \quad (9) \\[-1em]
 & m/e\ 45 \\
\underset{m/e\ 41}{CH_3CN\cdot^+} + CD_3CN \arrow[uur, "\text{proton}", "\text{transfer}"'] \arrow[dr, "\text{H-atom}", "\text{abstraction}"'] & \\
 & \underset{m/e\ 43}{CH_3CND^+} + \cdot CD_2CN \quad (10)
\end{tikzcd}$$

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(39) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(40) E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York, N. Y., 1957.

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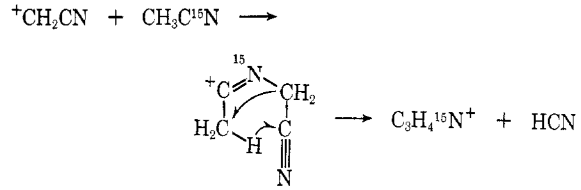
in the m/e 45 ion, proton transfer (eq 9) must be the exclusive pathway.

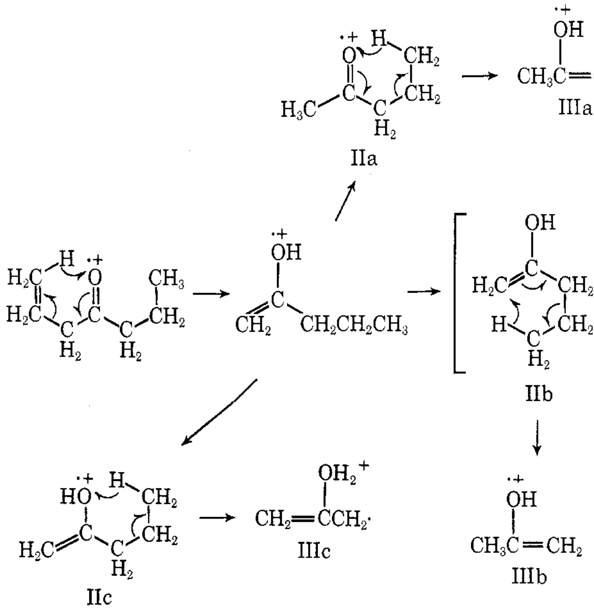
It is also possible in some cases to propose the structure of the collision complex from knowledge of which heteroatoms are retained in the product. For example, the double-resonance spectrum of the m/e 54 species which is produced upon electron impact from a mixture of $CH_3C^{14}N$ and $CH_3C^{15}N$ (eq 11) showed that the nitrogen from the neutral reactant is retained exclusively in the product ion.[46] A collision complex of the general form of I is therefore suggested.



(11)

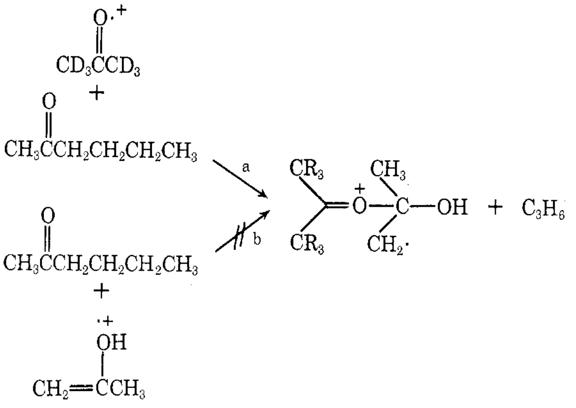
Ion Structure. Establishing the structure of ions resulting from electron-impact-induced fragmentation presents problems which are sometimes not easily soluble using conventional mass spectrometry. Since the reactions of isomeric ions should differ in accord with their structure, ion cyclotron resonance can be a useful tool for ion structure elucidation. Such problems can be approached with a methodology analogous to classical structure studies. Reactions typical of a functionality are first determined using an ion of known structure. The unknown ion can then be tested with established reagents.

For example, photoionization techniques[47] as well as ionization potentials[48] and metastable patterns[49] have been employed to determine the structures of the first (II) and second (III) McLafferty rearrangement ions.



(12)

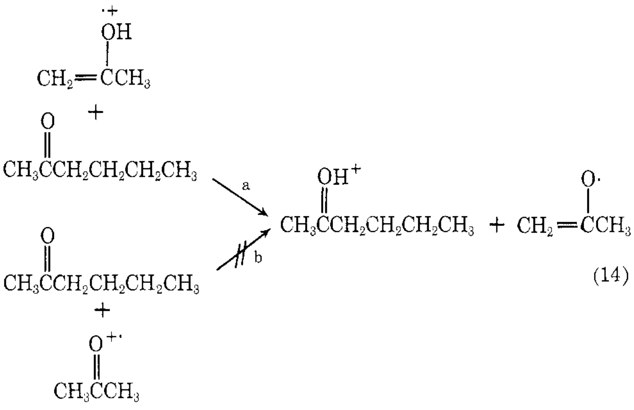
Choosing among the proposed structures for these ions by icr involves establishing whether IIb reketonizes before further decomposition (IIa) and distinguishing between the pathways available for formation of the second McLafferty product.[50,51] The reactivity of keto and enol ions toward various neutrals is in fact different, and therefore these species can easily be differentiated. Thus, although hexadeuterioacetone molecular ion condenses with 2-hexanone with simultaneous expulsion of propene (eq 13a), the unlabeled enol ion[52] does not (eq 13b). However, the reverse is true of proton transfer



(13)

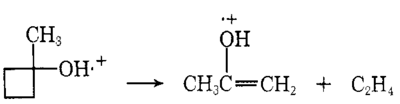
a, R = D; b, R = H

as the enolic species readily donates a proton to 2-hexanone (eq 14a), whereas the keto form does not (eq 14b).



(14)

By these criteria both the single and double McLafferty rearrangement ions have the enol structure. Further support for these choices is provided by establishing the identity of the reactions of these two species with the enol generated by decomposition of 2-methylcyclobutanol (eq 15).



(15)

Inorganic systems are amenable to study by icr as well.[53] It has been recognized that boron hydrides fall

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[46] G. A. Gray, *J. Amer. Chem. Soc.*, **90,** 2177 (1968).

[47] E. Murad and M. G. Inghram, *J. Chem. Phys.*, **40,** 3263 (1964).

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[49] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89,** 5953 (1967).

[50] J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *ibid.*, **91,** 2069 (1969).

[51] G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91,** 3986 (1969).

[52] This ion is available in this reaction mixture as a result of a single McLafferty rearrangement of 2-hexanone.

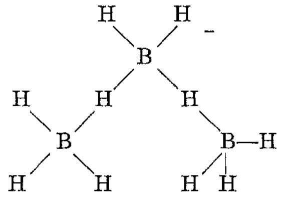
[53] R. C. Dunbar and R. Schaeffer, unpublished observations.

into two series: B_nH_{n+4}, the so-called "stable" hydrides which have a closed, compact framework, and B_nH_{n+6}, the "unstable" hydrides which have exposed terminal BH_2 groups. These classifications provide a useful basis for interpreting the negative ion icr spectra of the boron hydrides. At low electron energies the negative ion spectra of the stable hydrides (B_5H_9 and B_6H_{10}) show only a peak for the M − H ion. Unless this species is formed at high electron energies, it does not decompose further. In contrast, the "unstable" hydrides B_4H_{10} and B_5H_{11} show prominent $M - BH_3$ peaks and a series of product ions $M + n$BH.

Since both ^{10}B and ^{11}B occur in natural abundance, it is possible to use icr double-resonance methods to provide information on the structure of intermediates in boron hydride reactions. An interesting example is reaction 16.[54] All three boron atoms appear with equal

$$BH_4^- + B_2H_6 \longrightarrow B_2H_7^- + BH_3 \qquad (16)$$

probability in the $B_2H_7^-$ product ion, suggesting an intermediate of the form IV.



IV

Kinetic Measurements

Steady-State Methods. In light of the large number of ion–molecule reactions which can be observed by icr, it is useful to be able to obtain reaction rate constants from intensity data. Comisarow[55] and Dunbar[56] have obtained an expression for the instantaneous power absorption of a single ion in terms of the charge on the ion, the electric field, the mass of the ion, its residence time in the cell, and the reduced collision frequency. The equations resulting from this treatment enable computation of the rates of ion–molecule reactions from the single-resonance intensity measurements. Both low- and high-pressure approximate treatments are also available.[57,58]

Pulsed Methods. The development of pulsed methods provides a substantial improvement in the accuracy and versatility with which reaction rate constants may be determined. Using the trapped ion analyzer cell geometry and pulsed excitation, it has been possible to measure with useful accuracy rates as low as 10^{-12} cm^3/(molecule sec).

Preliminary work has been done on a series of gas-phase nucleophilic substitution reactions,[59] as shown in Table I. It is evident that there are significant substituent effects on these rates as the rate for Cl^- displacing Br^- in methyl bromide is about 140 times faster than in *tert*-butyl bromide. The result obtained for R = 1-adamantyl suggests that the reaction mechanism is not simply an SN2 type displacement.

$$Cl^- + RBr \longrightarrow RCl + Br^- \qquad (17)$$

Table I

Rate Constants of the Reactions $Cl^- + RBr \rightarrow Br^- + RCl$ in the Gas Phase

R	k, 10^{+11} cm^3/(molecule sec)	No. of runs
H	~100	5
Allyl	9.4	1
Ethyl	9.2 ± 0.4	4
Methyl	7.7 ± 0.9	4
Cyclopropyl	6.3 ± 1.6	2
Isopropyl	5.6 ± 0.4	2
Benzyl	5.4 ± 0.2	2
1-Adamantyl	3.2 ± 0.4	2
Neopentyl	2.5 ± 0.5	6
Cyclohexyl	2.1	1
tert-Butyl	0.54 ± 0.03	4

Physical Applications

Transient Response Heterodyne Method. An icr transient-response heterodyne technique enables measurement of the total collision rate[56] and ultimately allows separation of this rate into reactive and nonreactive collision rates.

A transient-response experiment is initiated by electron impact producing a packet of ions during a 50-μsec interval. As these ions draft through the analyzer region, they are detected with the marginal oscillator set at a frequency slightly different from the cyclotron resonance frequency of the ion. The response to this pulsed excitation is then a beat signal at the difference frequency. Ion–molecule collisions affect the amplitude of the beat signal by upsetting the coherent motion of the ions.

Experiments measuring the collision rate for $N_2\cdot^+$ in N_2 are a good test for the method since ample data are available on this system. The heterodyne experiments confirm the previously obtained total rate constant of (0.8 ± 0.1) × 10^{-9} cm^3/(molecule sec). This value should be compared with the value of k of 0.43 × 10^{-9} cm^3/(molecule sec) calculated assuming all momentum relaxation is due to an ion–induced-dipole attractive potential. Since the collision rate is considerably larger than the polarization limit value, nonorbiting charge-transfer reactions must be a prominent feature of this system.

Electron-Impact Spectra. When the energy of an incident electron is just equal to the excitation energy of a molecule, an inelastic collision can produce an electronically excited molecule and near-zero-energy electrons. The icr cell geometry is such that these low-energy electrons are trapped in a fashion similar to negative ions, and they can be drifted from the source into the analyzer region.[60] It is possible to detect selec-

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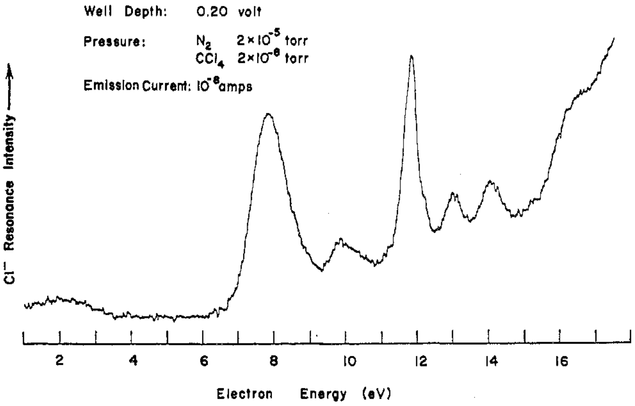

Figure 6. Inelastic excitation spectrum of N_2 obtained by scavenging trapped low-energy electrons with CCl_4 and measuring the resultant Cl^- with ion cyclotron resonance spectroscopy. The prominent features at 7.8 and 11.8 eV correspond, respectively, to excitation of the $B^3\pi_g$ and $E^3\Sigma_g^+$ states of N_2. The peak at 2.0 eV results from temporary negative ion formation.

tively these electrons by taking advantage of the fact that dissociative attachment processes (eq 18) can occur, for example in CCl_4, with a large cross section for low-energy electrons.[61,62] The cross section for this reaction falls very rapidly for electron energies above 0.1 eV.

$$CCl_4 + e^-_{\text{thermal}} \longrightarrow Cl^- + CCl_3\cdot \qquad (18)$$

Thus, by adding a small amount of a scavenger such as carbon tetrachloride to nitrogen and observing the intensity of the chloride resonance as a function of electron energy, Beauchamp and Ridge[60] were able to obtain the electronic spectrum of nitrogen shown in Figure 6. A peak is observed in the intensity of the Cl^- ion for those electron energies which correspond to the spacing of electronic states in nitrogen. The selection rules for inelastic electron-scattering processes are quite different from the familiar optical selection rules, so the collisions exciting triplet states of nitrogen are readily apparent. Electron-impact spectra of this sort using this simple scanning trick can be obtained in a variety of interesting molecules with no modification of the basic spectrometer.

Ion Photodissociation. The feasibility of using icr to study the photodissociation of positive ions has also been demonstrated.[63] To observe a photodissociation process, primary ions are generated by electron bombardment and trapped in the icr spectrometer for times of the order of seconds. Monochromatic light from a continuous source and filters or a monochromator is passed down the length of the icr cell and dissociates a small fraction of the primary ions. The secondary ions produced by photodissociation are observed with the marginal oscillator as a function of the incident optical frequency. Dunbar[63] has observed the processes

$$CH_3Cl\cdot^+ + h\nu \longrightarrow CH_3^+ + Cl\cdot \qquad (19)$$

$$N_2O\cdot^+ + h\nu \longrightarrow NO^+ + N\cdot \qquad (20)$$

The threshold for process 19 lies at about 5500 Å, but the rise of the cross section from threshold is gradual. The cross section (σ) for this process at 3500 Å is estimated as 5.4×10^{-18} cm². For reaction 20, σ (6250 Å) is approximately 0.3×10^{-18} cm².

Summary

Ion cyclotron resonance spectroscopy can yield information on many aspects of ion–molecule chemistry. The method is ideally suited for experiments involving ion energies below several electron volts and hence provides a valuable complement to other techniques. Cyclotron multiple resonance is uniquely suitable for establishing relationships between reactant ions and product ions in complex ion–molecule reaction sequences. The double-resonance experiments with isotopic species yield information on reaction mechanisms and the nature of intermediate species. Ion–molecule reactions which occur at low energies are quite sensitive to the nature of functional groups and the details of molecular structure. Reactions of ions or neutral molecules with specific reagents in the cyclotron spectrometer can thus be used to characterize unknown species. It is reasonable to project that more sophisticated applications of these basic cyclotron resonance methods to problems of chemical interest will follow as the instrumentation becomes more widely available.

Various routes for the development of the basic technique appear to be very promising. Pulsed cyclotron resonance techniques have intriguing analogies to nmr spin–echo experiments and are the technique of choice for making accurate measurement of ion–molecule reaction cross sections as a function of energy for low ion energies. The combination of optical effects with cyclotron resonance appears to have many applications. It is reasonable to anticipate that there will be numerous new developments and improvements which will greatly expand the range of chemical applications of these methods.

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