An Ion Cyclotron Resonance Study of Ion–Molecule Reactions in Methanol

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Abstract: A branching chain mechanism is observed in the methanol ion–molecule system which involves complex formation and collisional stabilization of complex ions. A protonated methanol ion $CH_3OH_2^+$ is the main product of the reactions of primary ions present. Collisions of this ion with methanol lead to complex ions $(CH_3OH)_nH^+$ at high pressure. At lower pressure, in the absence of collisional stabilization, a protonated dimethyl ether ion $(CH_3)_2OH^+$ is produced. The structure of the $(CH_3)_2OH^+$ ion was verified, and the effects of mode of formation and internal excitation on ionic reactivity were observed. The lifetime of the $(CH_3OH)_2H^+$ and $(CH_3)_2OH^+$ ions were estimated to be 2×10^{-6} and 1×10^{-5} sec, respectively. A comparison of ion cyclotron resonance with sector mass spectrometry is made, and the unusual and useful features of cyclotron resonance are discussed. Among the important advantages of ion cyclotron resonance spectrometry are long ion path length and ion lifetimes, and the ease with which path lengths and residence times can be varied. Also important is the ability to study reaction sequences of high-order ions using double-resonance techniques.

A program has been developed in this laboratory using ion cyclotron resonance techniques to study gas-phase ion–molecule reactions. This paper is concerned with the properties of ion cyclotron resonance (icr) as they pertain to such reactions in methanol. Previous reports of ion–molecule reactions in methanol have appeared in the literature and provide an excellent basis for comparing icr with other techniques used in the study of ion–molecule chemistry. Since this is the first report of our work in this field, a discussion of equipment and experimental techniques is included.

An ion traveling perpendicular to a uniform magnetic field will have a circular trajectory. The frequency of revolution is related to the ion mass and the magnetic field strength according to eq I, where ω_c is the natural

$$\omega_c = eB/m \qquad \text{(I)}$$

cyclotron frequency of the ion, e the electronic charge, B the magnetic field strength, and m the mass of the ion. The radius of the circular motion is given in eq II,

$$r = v/\omega_c \qquad \text{(II)}$$

where r is the radius, v the velocity perpendicular to the direction of the magnetic field, and ω_c the natural cyclotron frequency of the ion. It may be seen on inspection of eq I that the cyclotron frequency of an ion is not dependent on its velocity. Two ions of the same charge-to-mass ratio, but traveling with different velocities, will have the same frequency of revolution, but the faster moving ion will describe a larger circle in the plane perpendicular to the magnetic field as indicated by eq II. If a radiofrequency electric field is introduced in the plane of the circular motion, with a frequency of ω_1, equal to the natural cyclotron frequency of the ion (ω_c), the ion will continuously absorb energy from the field. Consequently, the ion velocity will increase and, from eq II, its radius will also increase.

These basic principles were first applied as a method for mass determination of ions by Hipple,[1] in the development of the Omegatron. In this instrument ions were collected at an electrode which they could reach only when in resonance with the radiofrequency field. The equations of motion of electrons and ions undergoing cyclotron resonance have since been treated in detail.[2,3]

The treatment of ion motion in the cyclotron resonance situation when collisions and reactions occur is demonstrably more difficult than when no collisions are allowed. Recent work[4,5] has been directed toward relating collision frequencies and reaction cross sections to the line width and line shape of ions undergoing cyclotron resonance. While approximations to the exact solution to the equation of motions must be used in such situations, Baldeschwieler, *et al.*, have demonstrated that much useful information about ion reactions and reaction sequences can be obtained by the use of single and multiple cyclotron resonance techniques.[6]

Experimental Section

1. Instrumental. The instrument used in this work is a modified version of the Varian Associates ion cyclotron resonance mass spectrometer,[7] developed by Dr. Peter Lewellyn. Figure 1 is a schematic representation of the icr cell. Its over-all dimensions are 2.5 × 2.5 × 13 cm, and it consists of three essentially independent sections (designated in Figure 1 as A, B, and C). In operation the cell is aligned between the faces of a 9-in. magnet with its long axis perpendicular to the magnetic field. The magnetic field is variable from 0 to 15,000 gauss and is uniform over the three sections of the cell to 0.001%. During operation the cell is enclosed in a stainless steel vacuum chamber which is pumped by an 8-l./sec, ion pump. The ion pump is backed by a molecular sieve trap and a 21-l./min mechanical forepump. A base pressure of 10^{-8} mm is easily achieved, and the vacuum assembly is bakeable to 200°.

The ion cell has none of the focusing or repeller electrodes which are required in sector mass spectrometers. Electrons are produced by a heated rhenium filament and accelerated by a variable potential to the ion source. The electrons are unrestricted in their motion parallel to the magnetic field which also serves to collimate the electrons into a narrow beam. The electrons pass through the source and are collected at a trapping electrode which is maintained

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(1) (a) J. Hipple, H. Sommer, and H. Thomas, *Phys. Rev.*, **76**, 1877 (1949); (b) H. Sommer, H. Thomas, and J. Hipple, *ibid.*, **82**, 697 (1951).

(2) C. E. Berry, *J. Appl. Phys.*, **25**, 28 (1954).

(3) D. Kelly, H. Margenau, and S. Brown, *Phys. Rev.*, **108**, 1367 (1957).

(4) D. Wobschall, J. Graham, Jr., and D. Malone, *ibid.*, **131**, 1565 (1963).

(5) J. Beauchamp, *J. Chem. Phys.*, **46**, 1231 (1967).

(6) (a) L. Anders, J. Beauchamp, R. Dunbar, and J. Baldeschwieler, *ibid.*, **45**, 1062 (1966); (b) J. Beauchamp, L. Anders, and J. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967).

(7) Trade name "Syrotron."

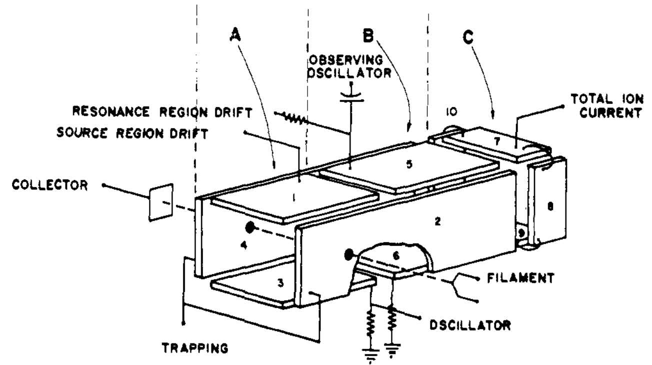

Figure 1. Ion cyclotron resonance cell schematic: (A) ion source region, (B) detector region, (C) total ion collector.

at 20 v positive with respect to the source. The current to this electrode is used to regulate the filament emission.

Ions produced in the source have a circular trajectory perpendicular to the magnetic field, but like the electrons they are free to move parallel to the field. In order to prevent the ions from drifting to the side walls of the cell, a small trapping potential is applied to plates 2 and 4 which creates a potential minimum near the center of the cell. A positive potential traps positive ions and removes scattered electrons and negative ions. When negative ions are being studied, the sign of this trapping potential is reversed and negative ions are trapped in the cell.

An ion in crossed electric and magnetic fields will drift in a direction perpendicular to both fields with a velocity given by

$$v_d = E_s/B \qquad \text{(III)}$$

Here v_d is the drift velocity, E_s is the magnitude of the static electric field, and B is the magnetic field strength. In Figure 1 a static electric field (usually about 0.2 v/cm) is applied to plate 1 which causes the ions to drift down the long axis of the cell into the detector region (Figure 1, B). Under such conditions the ion trajectory is a cycloid, and the drift velocity can be adjusted by varying E_s or B.

In section B, plates 5 and 6 are part of a tuned circuit of an amplitude limited oscillator.[8] The circuit has a high Q value and a high impedance. The oscillator introduces a radiofrequency electric field between plates 5 and 6 and, as previously explained, energy will be absorbed from this field if its frequency (ω_1) is equal to the natural cyclotron frequency of an ion present in the cell. If energy absorption occurs, the Q factor of the marginal oscillator circuit will be changed, and this change is amplified and recorded. In addition, a static drift potential is also applied to plate 5, independent of the drift potential in the source region. Ions not in resonance continue to drift down the long axis of the cell and reach the total ion collector (Figure 1, C, plates 7–10).

2. Simple Mass Spectra. A mass spectrum is obtained by modulating one of the variables affecting the ion density in the detector region, sweeping the magnetic field and phase detecting the level of the marginal oscillator at the modulation frequency. Spectra have been obtained by modulating the source drift potential, the electron energy, the magnetic field, and the trapping potential. Magnetic field modulation provides derivative spectra similar to those obtained in standard esr experiments.[9] The other methods provide absorption spectra. Figure 2 is a simple mass spectrum obtained from methanol by modulating the magnetic field. The pressure was 1×10^{-6} mm, and the electron energy was 70 ev.

Figure 3 schematically diagrams the apparatus as used to obtain simple field modulated mass spectra. In addition to the basic spectrometer, a number of auxiliary pieces of equipment were added. A Princeton Applied Research lock-in amplifier provided a variable reference frequency which was used to modulate the level of the marginal oscillator; 28 cps was the modulation frequency used most often. The signal from the oscillator was then phase detected by the lock-in amplifier, and the output was recorded on the Y axis of a Mosely dual-channel X–Y recorder. The X axis of the recorder was driven by the Varian Fieldial unit supplied with the icr spectrometer. This provided a linear mass spectrum with the signal plotted as a function of magnetic field.

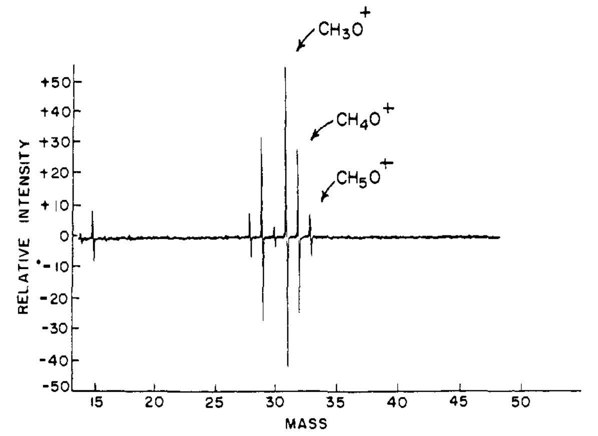

Figure 2. Single resonance spectrum of methanol using magnetic field modulation: pressure = 1×10^{-6} mm, electron energy = 70 ev, ion path length = ∽7 m.

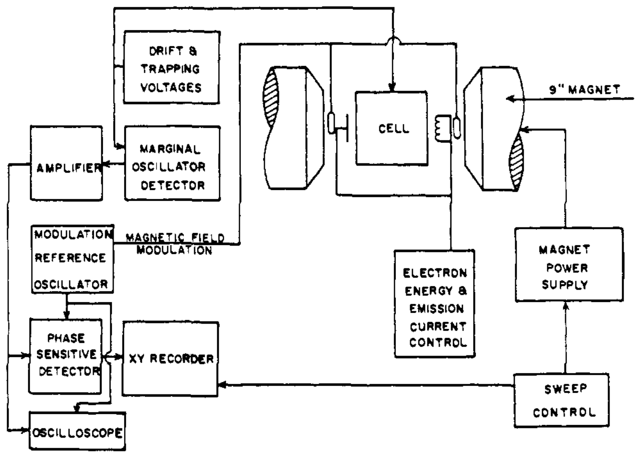

Figure 3. Block diagram of apparatus used for single resonance mass spectra.

Spectra were obtained under steady-state pressure conditions. The pressure was monitored by following the ion pump current, but absolute pressure readings obtained this way were probably good only to an order of magnitude. Pressure changes, however, could be determined with more accuracy.

3. Double Resonance. In addition to obtaining simple mass spectra, icr double-resonance experiments were carried out in which information about reaction sequences was obtained. The magnetic field and observing oscillator frequency were constant in this experiment and one ion was continuously recorded. A radiofrequency sweep generator was coupled to plate 3 in the source region. The frequency (ω_2) of this latter oscillator (referred to as the irradiating frequency) was swept while a particular ion was monitored at ω_1. As ω_2 was swept, each of the ions present in the cell passed through resonance and absorbed energy. If the ion being continuously observed as coupled to any of these ions by reaction, a change in its concentration occurred and resulted in a corresponding change in the signal at ω_1. The implications of double resonance are covered in the Discussion section.

4. Ion Path Length and Residence Time. The residence time of any ion in the icr spectrometer is determined by its drift velocity and the cell dimensions. Typical residence times vary from 0.5 to 5 msec depending upon the values chosen for B and E_s in eq IV. The path length of an ion is given in eq IV where v is the velocity of the ion when it is formed and t_r is its residence time. A methanol

$$L = vt_r \qquad \text{(IV)}$$

parent ion CH_3OH^+ (m/e 32), produced with approximately thermal energy, will have a path length ranging from 2 to 75 m. The exact value will depend upon the drift potential applied and the ion

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(8) F. Robinson, *J. Sci. Instr.*, **36**, 481 (1959).

(9) "NMR and EPR Spectroscopy," Permagon Press, New York, N. Y., 1964, Chapter 14.

Table I

Pressure mm,	Ion path length, m	Electron energy, ν	% total ionization							
			CHO^+ (*m/e* 29)	CH_3O^+ (*m/e* 31)	CH_4O^+ (*m/e* 32)	CH_5O^+ (*m/e* 33)	$C_2H_7O^+$ (*m/e* 47)	$C_2H_9O_2^+$ (*m/e* 65)	$C_3H_{11}O_2^+$ (*m/e* 79)	$C_3H_{13}O_3^+$ (*m/e* 97)
10^{-7}	7	70	25	40	26	0.5	...	...	...	...
10^{-6}	7	70	22	37	20	5	...	...	...	...
10^{-6}	20	70	18	34	18.5	16	...	...	...	...
10^{-6}	500	70	5	13	4.5	66	7.5	...	...	...
10^{-5}	500	70	1	8	1	56	33	...	...	...
10^{-5}	50	70	..	..	...	5	45.5	5.5	39	5

kinetic energy on formation. It has also been found possible to trap ions with appropriate combinations of electric fields in the cell. The residence times of ions trapped in this manner can be longer than 1 sec, and their path lengths can approach 1000 m.

Results

Under low pressure (1×10^{-7} mm) and relatively short path length (7 m) conditions, the observed mass spectrum of methanol corresponds closely to that obtained with standard sector spectrometers.

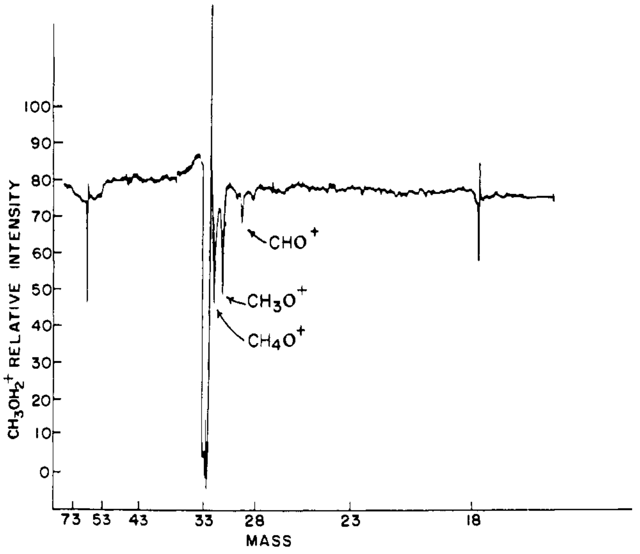

Figure 4. Double-resonance spectrum of CH_5O^+ (*m/e* 33): pressure = 1×10^{-6} mm, electron energy = 70 ev, ion path length = ∽500 m.

Table I summarizes the change in ion intensity caused by changing the pressure and ion path length. In row 2 at 10^{-6} mm, $CH_3OH_2^+$ is observed as the major product ion at *m/e* 33, while in row 3, at the same pressure, the ion path length is longer and more reaction is evident. A comparison of product ion intensities in rows 2 and 3 shows the effect of changing drift velocity on the extent of reaction. Slower drift velocities increase the ion residence time and ion path length, thus increasing the number of collisions suffered by the primary ions. This accounts for the observed increase in $CH_2OH_2^+$ product ion intensity in row 3. Row 4 demonstrates the significant increase in reaction caused by electric field trapping of ions in the icr cell. The extent of primary ion reaction in row 4 is greater than 70% while it is less than 5% in row 2; however, the pressure used in both experiments was the same. In row 5, at 10^{-5} mm pressure, the only major ions present are $CH_2OH_2^+$ (*m/e* 33) and $C_2H_2O^+$ (*m/e* 47), while in row 6, at 10^{-3} mm pressure, major products are detected at *m/e* 33, 47, 65, 79, and 97.

In Figures 4 and 5, double-resonance experiments on the product ions at *m/e* 33 and 47 are shown at 10^{-6} mm. The experiments shown in Figures 4 and 5 were carried out with the irradiating frequency applied in the source region as previously explained. It is estimated that irradiated ions could acquire no more than 2 ev of kinetic energy before leaving the source region under the experimental conditions used. In Figure 4 the effect of accelerating the ions, CH_2OH^+ and CH_3OH^+, is to decrease the intensity of $CH_3OH_2^+$ by about 30% in each case. Figure 5 shows the effect on the intensity of $C_2H_7O^+$ when these ions are accelerated by the same amount. The effect on $C_2H_7O^+$ caused by accelerating CH_3OH^+ is significantly smaller than the effect caused by accelerating CH_2OH^+. The effect of accelerating $CH_3OH_2^+$ is to decrease $C_2H_7O^+$ by 80%.

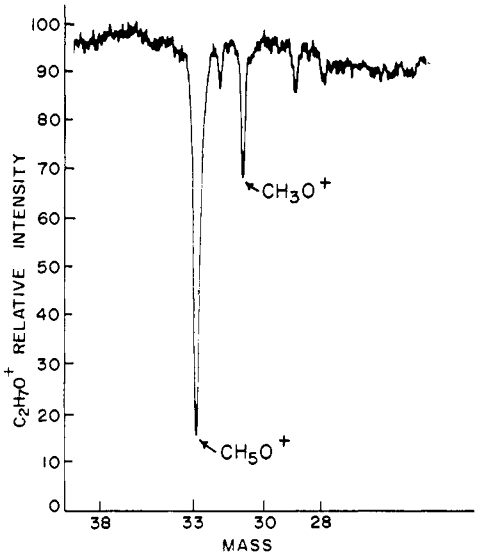

Figure 5. Double-resonance spectrum of $C_2H_7O^+$ (*m/e* 47): pressure = 1×10^{-6} mm, electron energy = 70 ev, ion path length = ∽500 m.

In the same way, double-resonance experiments were carried out on all of the ions present under a variety of pressure and energy conditions. The results of these experiments were used in the confirmation and interpretation of reaction sequences, and the over-all mechanism thus obtained is shown in Figure 6. The proposed or confirmed structures for the ions present are shown in Figure 7.

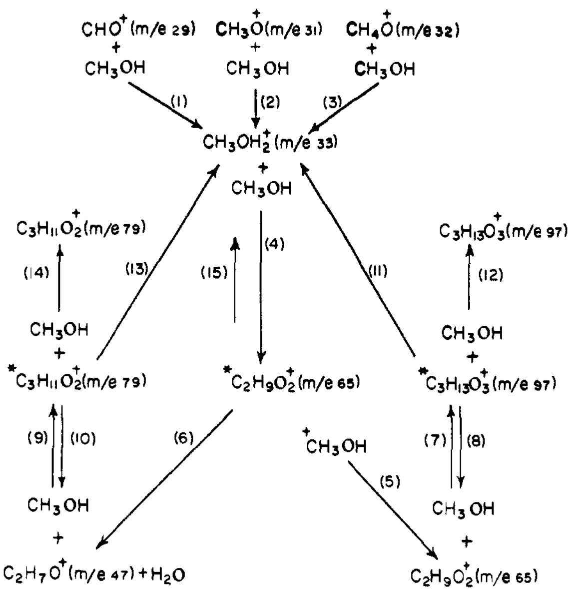

Figure 6. Reaction scheme in methanol.

Discussion

1. Reaction Scheme of Methanol. Proton-transfer reactions leading to a protonated methanol ion, $CH_3OH_2^+$ at *m/e* 33, have been reported in previous studies of methanol.[10-13] Such reactions involving the primary ions CH_3OH^+ and CH_2OH^+ were estimated to be exothermic.[12] In addition, higher order ions $C_2H_9O_2^+$ at *m/e* 65 and $C_3H_{13}O_3^+$ at *m/e* 97 were observed as major reaction products, and product ions $C_2H_7O^+$ at *m/e* 47 and $C_3H_{11}O_2^+$ at *m/e* 79 were reported as a small fraction of the total ionization. One of the significant results of this study is the observation of these latter ions as a major fraction of the total ionization (Table I). This difference with earlier reports results directly from the properties of the icr spectrometer and the low pressures at which ion-molecule reactions are observed in this instrument.

Munson[12] has discussed the reactions occurring in some detail and has suggested a mechanism to explain the observed product ions. This mechanism agrees very well with the one obtained using icr single and double resonance.

In a later paper, Futrell reported similar reactions occurring in ethanol and briefly discussed methanol. Both reports agree on the ions present in methanol, but Futrell[13] reported the $C_2H_7O^+$ and $C_2H_9O_2^+$ ions as third order and the $C_3H_{13}O_3^+$ and $C_3H_{11}O_2^+$ as fourth order, while Munson[11] reported $C_2H_9O_2^+$ as fourth order and $C_2H_7O^+$ as third order, with the $C_3H_{13}O_3^+$ and $C_3H_{11}O_2^+$ being fifth and fourth order, respectively. In these studies the "order" of an ion apparently referred to the number of collisions involved in its production as determined by analyzing the pressure-dependence curves. Our results indicate that at least one more collision is involved in the production of $C_2H_9O_2^+$ (*m/e* 65) than in the production of $C_2H_7O^+$ (*m/e* 47), and similarly one more collision is involved in the production of $C_3H_{13}O_2^+$ (*m/e* 97) than in the production of $C_3H_{11}O_2^+$ (*m/e* 79). If reactions 4–6 (Figure 6) occur as suggested, the observed "order" of the $C_2H_7O^+$ and $C_2H_{11}O_2^+$ ions would depend upon the lifetime of the $C_2H_{11}O_2^+$ complex ion and its residence time in the instrument used.

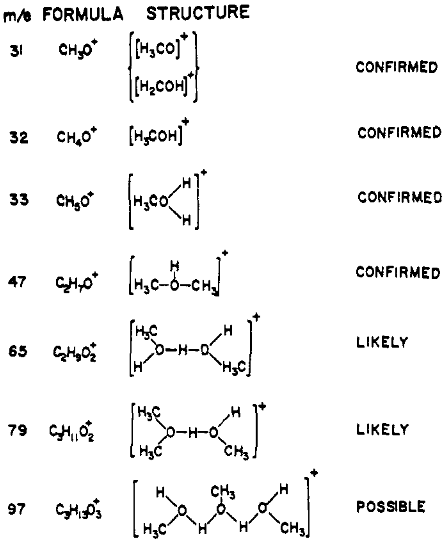

Figure 7. Structures of ions present in methanol.

Since this ion will be excited by at least 20 kcal/mole by such association reactions, it would be expected to fragment unless collisionally stabilized. However, many factors can influence the lifetime of such a complex ion. In addition to the heat of reaction, the internal energy of the reactants, the number of accessible degrees of freedom of the $C_2H_9O_2^+$ complex, and the relative kinetic energy of the reactant ions are all important in this respect. Therefore, while the reported pressure dependences[12,13] do not appear to agree, it is probable that this lack of agreement results from instrumental factors, and that both studies are consistent with the proposed reaction mechanism.

In both previous studies the lifetime of the $C_2H_{11}O_2^+$ complex was apparently less than several microseconds, which was the same order of magnitude as its residence time in these instruments. The residence time of the ions in the icr spectrometer is quite long (10^{-3} sec), however, and a complex ion with a lifetime of $\sim 10^{-6}$ sec should fragment completely in this instrument unless it is collisionally stabilized. From Table I, row 5, it is evident that at 10^{-5} mm no collisional stabilization occurs and the ion fragments completely. No $C_2H_9O_2^+$ ion is observed. In Table I, row 6, at a pressure of 10^{-3} mm, the collision time approaches 10^{-6} sec, which is sufficiently short to stabilize some $C_2H_9O_2^+$ before decomposition. However, it has not been determined whether a single collision is sufficient to remove enough energy to produce the stabilized ion we observe. From this experiment a lifetime of $\sim 2 \times 10^{-6}$ sec is assigned to this ion.

The relationship between $C_2H_{11}O_2^+$ and $C_2H_7O^+$ is also confirmed by the double-resonance experiment. At 10^{-3} mm collisionally stabilized $C_2H_{11}O_2^+$ can be accelerated, and a collision-induced dissociation of this ion producing $C_2H_7O^+$ is observed.

Double resonance confirms that in the next step in the reaction sequence (reaction 9, Figure 6), $C_2H_7O^+$ adds

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(10) (a) P. Wilmenius and E. Lindholm, *Arkiv Fysik*, **21**, 97 (1962); (b) E. Lindholm and P. Wilmenius, *Arkiv Kemi*, **20**, 255 (1963).

(11) K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

(12) M. B. S. Munson, *J. Am. Chem. Soc.*, **87**, 5313 (1965).

(13) L. W. Sieck, J. H. Futrell, and F. P. Abramson, *J. Chem. Phys.*, **45**, 2859 (1966).

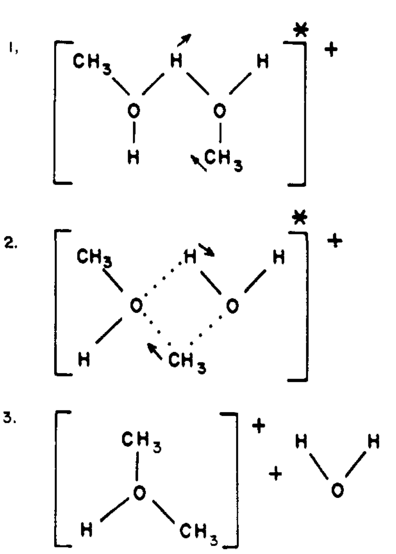

Figure 8. Probable fragmentation mechanism for $C_2H_9O_2^+$.

a neutral methanol to produce another complex ion $C_3H_{11}O_2^+$ (*m/e* 79). This complex ion must also be collisionally stabilized, and thus it is not observed even under moderate pressure conditions (10^{-5} mm) in the icr experiment (Table I). However, its concentration builds up rapidly at pressures above 10^{-4} mm, suggesting that it has a longer lifetime (corresponding perhaps to an increased number of degrees of freedom) than the corresponding $C_2H_9O_2^+$ complex ion. Its lifetime is estimated to be 10^{-5} sec.

Double resonance confirms that $C_2H_9O_2^+$, once stabilized by collision, can then react again *via* a complex formation mechanism to produce a protonated trimer of methanol $C_3H_{13}O_3^+$ (*m/e* 97) (reaction 7, Figure 6). This complex ion must also be collisionally stabilized to be observed.

2. Determination of Ionic Structure. Structure of $C_2H_7O^+$. Ion cyclotron resonance spectrometry may be used to obtain structural information about the species present. Munson[12] suggested that the $C_2H_7O^+$ ion might be a protonated methyl ether ion. Unfortunately, there is no *a priori* method by which such an ion could be distinguished from a protonated ethanol ion since both have the same mass and both are common ions. Either ion could conceivably be formed by an appropriate rearrangement of the excited $C_2H_9O_2^+$ complex ion when H_2O is eliminated (reaction 6, Figure 6). However, since the two ions are structurally very different, their reactions with methanol should also differ, and this effect is readily studied with icr techniques.

A study of mixtures of methanol with methyl ether, and methanol with ethanol, showed that the ion produced by the fragmentation of $C_2H_{11}O_2^+$ in pure methanol is a protonated dimethyl ether ion $(CH_3)_2OH^+$. Confirmation was obtained by comparing the reactions of the $C_2H_7O^+$ ion produced in pure methanol with the reactions of a protonated ethanol ion produced from ethanol, and a protonated methyl ether ion produced from methyl ether. As was expected, the two ions reacted quite differently with methanol.

In pure methanol $C_2H_7O^+$ reacts *via* complex formation (Figure 6) to produce a $C_3H_{11}O_2^+$ ion at *m/e* 79 which must be collisionally stabilized in order to be observed. This product ion does not react further and does not fragment with the loss of a water molecule as does the $C_2H_9O_2^+$ complex at *m/e* 65. In a 1:1 mixture of methanol and ethanol, the following pertinent reactions were observed.

$$CH_3CH_2OH^+ + CH_3OH \longrightarrow CH_3CH_2OH_2^+\ (m/e\ 47) \quad (1)$$

$$CH_3CH_2OH^+ + CH_3CH_2OH \longrightarrow CH_3CH_2OH_2^+\ (m/e\ 47) \quad (2)$$

$$CH_3OH^+ + CH_3CH_2OH \longrightarrow CH_3CH_2O^+H_2\ (m/e\ 47) \quad (3)$$

$$CH_3CH_2OH_2^+ + CH_3OH \longrightarrow C_3H_{11}O_2^+\ (m/e\ 79) \quad (4)$$

$$C_3H_{11}O_2^+ \longrightarrow C_3H_9O^+\ (m/e\ 61) + H_2O \quad (5)$$

A protonated ethanol ion (*m/e* 47) was produced by several different reactions (1–3). At higher pressure in the mixture this ion reacted with ethanol to produce a $C_3H_{11}O_2^+$ at *m/e* 79 (reaction 4) which fragmented with the elimination of water to give a stable ion at *m/e* 61 (reaction 5). At high pressure the ion at *m/e* 79 was collisionally stabilized and could react again with either methanol or ethanol to produce a higher order complex ion.

In a 1:1 mixture of methanol with methyl ether, a different set of reactions was observed.

$$(CH_3)_2O^+ + (CH_3)_2O \longrightarrow (CH_3)_2O^+H\ (m/e\ 47) \quad (6)$$

$$(CH_3)_2O^+ + CH_3OH \longrightarrow (CH_3)_2O^+H\ (m/e\ 47) \quad (7)$$

$$CH_3OH^+ + (CH_3)_2O \longrightarrow (CH_3)_2O^+H\ (m/e\ 47) \quad (8)$$

$$(CH_3)_2O^+ + (CH_3)OH \longrightarrow C_3H_{11}O_2^+\ (m/e\ 79) \quad (9)$$

A protonated methyl ether ion was produced by such reactions as 6–8, and this ion then reacted *via* complex formation with methanol to produce a $C_2H_{11}O_2^+$ ion at *m/e* 79. This product ion, however, did not fragment with the loss of water nor did it react further.

Since the reaction of the $C_2H_7O^+$ ion with the methanol in the latter mixture was identical with that of the $C_2H_7O^+$ ion in pure methanol, it was concluded that the rearrangement pictured in Figure 8 is the operative mechanism in pure methanol, and the product ion is a protonated methyl ether ion (Figure 7). Furthermore, if such a mechanism applies generally to the lower alcohols, the production of an ion at *m/e* 61 in the methanol–ethanol mixture is to be expected. Here, an excited, mixed, protonated dimer is produced at *m/e* 79 which rearranges in the same way as the analogous complex in pure methanol does (reaction 6, Figure 6). Thus, the rearrangement product in the methanol–ethanol mixture is a protonated methyl ethyl ether ion. This experiment suggests the possibility of using ion cyclotron resonance spectrometry to determine the effects of functionality and structure on ion reactions.

3. Ion Reactivity as a Function of Internal Energy. Figures 4 and 5 show the results of double-resonance experiments on the protonated methanol ion $CH_3OH_2^+$ and the protonated methyl ether ion $C_2H_7O^+$. An ion subject to irradiation in the source region gains energy until it drifts into the detector region. Since the drift velocity and the distance between the electron beam and the end of the source are both known, the amount of kinetic energy acquired by any given ion may be calculated. However, since collisions also occur during and after acceleration, this calculated energy represents only the maximum ion energy. In the case of the experiments shown in Figures 4 and 5, the ions being irradiated gained not more than 2 ev in the source.

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CH_2OH \qquad (10)$$

$$CH_2OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CHOH \qquad (11)$$

$$CH_3OH_2^+ + CH_3OH \longrightarrow (CH_3OH)_2H^+ \quad \overset{H^+}{} \quad CH_3OCH_3 + H_2O \qquad (12)$$

In Figure 4 a substantial decrease occurs in the intensity of $CH_3OH_2^+$ (about 30%) when the primary ions CH_3OH^+ and CH_2OH^+ are accelerated. This is reasonable since both of these ions are known to react with methanol to produce $CH_3OH_2^+$ (reactions 10 and 11) *via* a complex formation mechanism. However, it is apparent (Figure 5) that the intensity of $C_2H_7O^+$ is reduced by only 8% when CH_3OH^+ is accelerated. The effect of accelerating CH_2OH^+ is to cause a reduction of about 30% in the intensity of $C_2H_7O^+$. The $CH_3OH_2^+$ ion is the immediate precursor to the $C_2H_7O^+$ ion (reaction 5), and in both instances the former ion is reduced by about 30%. It is therefore concluded that $CH_3OH_2^+$ ions produced by reaction 10 must be less effective in reacting to produce $C_2H_7O^+$ than are $C_2H_3OH^+$ ions produced by reaction 11.

There are two possible explanations for this effect. First it is possible that reactions 10 and 11 produce two ions at *m*/*e* 33 with different structures. Two structurally different ions might well exhibit different reactivities toward a neutral methanol molecule. However, it was considered unlikely that there exist two ions with the formula CH_5O^+ in the methanol system.

The possibility of impurity ions was also considered. An oxygen impurity would produce an O_2^+ ion at *m*/*e* 32 which could conceivably pick up a proton by reaction with methanol to give a product ion at *m*/*e* 33. However, the true mass of such an HO_2^+ ion would differ from CH_5O^+ by 0.1%, a mass difference which is easily detectable at *m*/*e* 32. No evidence was found to indicate that such an ion was present. In addition, the reaction is endothermic and therefore unlikely to occur at thermal ion energies.

The second possible explanation is that reactions 10 and 11 produce ions which are structurally identical but are in different states of internal excitation and that the difference in internal energy accounts for the observed difference in reactivities. Of the two alternatives, this one seems to be the more likely and reasonable explanation. This conclusion is based on the following considerations. Reactions 10 and 11 have both been estimated as being exothermic.[12] Reaction 10 is estimated to be 10 kcal/mole more exothermic than reaction 11. A value of 180 kcal/mole is used for the proton affinity of methanol,[14] and the heats of formation are reported by Field and Franklin[15] for the other ions and radicals in these reactions. In addition to thermochemical considerations, the parent CH_3OH^+ ion in reaction 10 may be expected to be more excited than the fragment CH_2OH^+ in reaction 11. Both considerations could lead to $CH_3OH_2^+$ product ions in different states of internal excitation.

This hypothesis was tested by studying the reaction of CH_2OH^+ and CH_3OH^+ ions with methanol at low impacting electron energies (12 ev). Under these conditions the difference in the reactivity of the $CH_3OH_2^+$ ion produced by reactions 10 and 11 was much smaller. This result is to be expected if, as has been suggested,[6] lower electron energies produce parent ions which are in lower states of internal excitation. It has previously been shown that certain vibrationally excited ions are, in fact, less reactive than similar unexcited species.[16]

It is suggested then that the most reasonable explanation for the observed lack of reactivity of $CH_3OH_2^+$ ions produced by reaction 10 is that they are more excited than those produced by reaction 11, and that the icr double-resonance technique provides a convenient method for studying such phenomena. Alternatively, the same technique proves useful for studying differences in reactivity related to the presence of several ions with the same mass but different structures as demonstrated in the previous section.

Summary of Methanol System

The reaction mechanism presented in Figure 6 branches with the production of the protonated complex ion $C_2H_9O_2^+$ of *m*/*e* 65. At low pressures fragmentation of this complex predominates and the stable methyl ether ion results. This ion can react again by adding a methanol molecule producing $C_3H_9O_2^+$ (*m*/*e* 79) which must be collisionally stabilized. At high pressure $C_2H_9O_2^+$ is collisionally stabilized, and it can react again producing a stable protonated trimer, $C_3H_{13}O_3^+$ at *m*/*e* 97. No further reaction of the $C_3H_{11}O_2^+$ or $C_3H_{13}O_3^+$ ions is observed. Considering the sensitivity of the icr spectrometer and the very high degree of reaction obtained, the probability of further reaction leading to the production of stable higher complex ions must be quite small. However, it should be emphasized that the production of higher complex ions, with short lifetimes (leading to complete fragmentation), cannot be ruled out on the basis of these observations. It is clear that extensive reaction at low pressure results in a different set of product ions than at high pressure.

A number of collision-induced dissociation reactions are also observed. Double resonance confirms the back reactions and fragmentation reaction shown in Figure 6 and provides information about the reactions of these higher order ions. Our results correlate well with previous studies in sector mass spectrometers and confirm Munson's postulated structure for the $C_2H_7O^+$ ion at *m*/*e* 47 as well as his report of no further reaction for the $C_3H_{13}O_3^+$ ion. The effect of internal excitation on the reactivity of $CH_2OH_2^+$ is observed.

Properties and Applications of Ion Cyclotron Resonance

Since ion cyclotron resonance has only recently been applied to the study of ion–molecule reactions in a systematic way,[6] it is useful to summarize the novel features of this technique and compare it to the other types of mass spectrometry which are used in this field. Table II lists the principal features which pertain to the study of ion–molecule reactions.

The long path length and residence time for ions in the icr spectrometer make it possible to study ion–molecule reaction at very low pressures. Extensive reaction can be achieved even at pressures in the 10^{-7}-mm range. It is also possible to vary the path length and the extent of reaction at a given pressure, as demonstrated

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Table II. Relative Intensity of Ions Present in Methanol at 70 ev

	Icr	Field trap icr	Sector	Tandem	TOF[a]
Mass range	0–250	0–250	0–1000	0–1000	0–1000
Differential pumping	Not necessary	Not necessary	Yes	Yes	Yes
Focusing electrodes	No	No	Yes	Yes	Yes
Source repeller field	No	No	Yes	Yes	Yes
Collection efficiency	~100%	~100%	<1%	<1%	<1%
Positive and negative ions	Yes	Yes	Yes	Yes	Yes
Ion path length in reaction zone	2–75 m variable	~1000 m variable	1 cm fixed	1 cm fixed	1 cm fixed
Ion residence time	0.5–5 msec variable	~1 sec variable	$\sim 10^{-6}$ fixed	$\sim 10^{-6}$ fixed	$\sim 10^{-6}$ variable[b]
Pressure range extensive reaction	10^{-6}–10^{-3} mm	10^{-7}–10^{-3} mm	$>10^{-3}$	$>10^{-3}$	$>10^{-3}$
Direct study of reactions of specific primary ions	Yes, double resonance	Yes, double resonance	No	Yes	No
Direct study of reactions of high-order product ions	Yes, double resonance	Yes, double resonance	No	Not easily	No
Energy dependence of specific reactions	Yes, qualitative	Yes, qualitative	No	Yes, quantitative	No

[a] Time of flight. [b] Ions can be extracted from the source using pulsed electric fields, thus varying the ion residence time in the source.

in this work on methanol. These features aid considerably in distinguishing collisional stabilization from true chemical reaction. It was possible to clearly demonstrate that the $C_2H_9O_2^+$ (*m/e* 65) protonated dimer ion results from two collisions involving chemical reaction and at least one inelastic collision resulting in the removal of excess internal energy.

By applying a second radiofrequency field, it is possible to increase the kinetic energy of one ion without affecting any of the other ions present. This experiment is useful in the determination of reaction sequences and in the study of the effects of increased kinetic energy on ion–molecule reactions. The technique is particularly useful at ion kinetic energies in the 0–5-ev range which is difficult to reach by other methods.

Furthermore, while the use of tandem mass spectrometers has made possible the study of specific reactions of primary and, in some cases, secondary ions, there is no method, other than the icr double-resonance experiment, by which the reactions and reaction sequences involving higher order ions may be studied directly. It is possible, of course, to observe high order ions in sector and time-of-flight mass spectrometers, but interpretation of results is often difficult and ambiguous. Double resonance also provides a method of studying collision-induced dissociation processes of high order ions and for simulating the energy conditions existing in various high-energy chemical systems such as discharge and radiolytic systems. The ability to vary the pressure, path length, residence time, and kinetic energy of ions makes it possible to adjust the conditions of an experiment to match the conditions existing in a given system of interest.

Another important use of icr is in obtaining structural information about the species present in a system. Unlike standard-sector mass spectrometry which relies on the interpretation of fragmentation patterns, icr allows a direct experiment to be carried out and permits the effect of structure on reactivity to be studied as in the case of the $C_2H_7O^+$ ion in methanol. Detailed qualitative analysis schemes can be devised to determine the identity and structure of unknown compounds by mixing them with appropriate reagents and studying ion–molecule reaction sequences which occur.

As with other techniques, however, icr has limitations. The accessible mass range is more limited than in other types of mass spectrometers. Although many chemical systems can be studied within this mass range, studies on large organic molecules could prove difficult to carry out. The mass range could be increased with the use of higher field magnets and lower operating frequencies for the marginal oscillator. The present range as indicated in Table II is from 0 to 250 amu.

Another point is the qualitative nature of some of the information. Currently, the double-resonance technique provides useful qualitative information about the changes which occur in reactions when the reacting ion is accelerated. For instance, we have observed that the intensity of ions produced in exothermic chemical reactions is always decreased when the reactant ion is irradiated. It would be tempting to consider that this decrease is due to a change in the reaction cross section; however, Beauchamp[5] has pointed out that a detailed quantitative analysis of such situations while possible is quite complicated. When an ion is irradiated in the double-resonance experiment, its path length, collision frequency, and reaction cross section are all changed. Each of these variables is involved in the final determination of product ion intensity, and an observed change cannot be assumed to be a result of a change in reaction cross section only. Tandem mass spectrometers and beam techniques are more quantitative when they can be used to study specific reactions. Unfortunately, the reactions of high order ions cannot be as easily studied using these methods.

Another problem which arises is the current limited nature of the icr spectrometer. At ion currents much in excess of 10^{-11} amp, space charge repulsion prevents the ions from reaching the detector region. It is therefore not possible to carry out a continuous pressure dependence experiment over the entire range of accessible pressures. It is found that the emission current must be decreased as the pressure is increased in order to prevent an unacceptable increase in ion current. This represents somewhat of an inconvenience but does not limit the information which can be obtained.

These early problems do not present insurmountable barriers, and it seems apparent that ion cyclotron resonance spectrometry should complement the existing techniques used to study ion–molecules reactions and should aid in the understanding of reaction mechanisms and intermediate species present in high-energy chemical systems.

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Tracer Studies of Acid-Catalyzed Reactions. VII. Mechanism of Alkylcyclopropane Isomerization over Silica–Alumina

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Abstract: The olefin products from the isomerization of several alkylcyclopropanes over silica–alumina have furnished information regarding the Brønsted or Lewis nature of the active sites. Only normal olefins were formed from methylcyclopropane. The product ratios (~50% *trans*-, ~25% *cis*-2-butene, and ~25% 1-butene) were essentially independent of the extent of conversion and reflected the lower activation energy (~0.8 kcal/mole) for the formation of *trans*-2-butene. The pressure dependence of the isomerization rate was less than first order in methylcyclopropane or in cyclopropane. Tracer experiments with both compounds revealed that one hydrogen (or deuterium) atom was transferred intermolecularly in each isomerization act. A small inverse isotope effect indicated, however, that carbon–hydrogen bond rupture was not rate limiting. Both normal and branched olefins were formed from either *cis*- or *trans*-1,2-dimethylcyclopropane, but no 2-methyl-1-butene was detected. Only branched olefins resulted from *gem*-1,1-dimethylcyclopropane isomerization, but no 3-methyl-1-butene was formed. All of these data were consistent with a Brønsted (c-$C_nH_{2n+1}^+$ intermediate) rather than the bimolecular Lewis acid mechanism (c-$C_nH_{2n-1}^+$ intermediate) which has been suggested for cyclopropane. Microcatalytic deuterium tracer experiments demonstrated that the protonic sites were associated with carbonaceous residue ("coke") formed by reaction of substrate with the catalyst surface.

Although both Lewis and Brønsted acid sites appear to exist on aluminum silicates,[1] there has been considerable uncertainty concerning the function of these sites in chemisorption[2] and in the catalysis of specific hydrocarbon reactions.[3] Recently, we have presented evidence that Brønsted protons, furnished by a carbonaceous residue, serve as sites for the formation of the *sec*-butylcarbonium ion,[4] which in turn acts as a common intermediate in the interconversion of the *n*-butenes over silica–alumina.[5] This model predicted semiquantitatively the selectivities and their temperature dependencies, explained the relative reactivities, and provided reasonable values of certain thermodynamic-state functions between the three isomers. The purpose of the present paper is to present evidence that such Brønsted acid sites are also responsible for the formation of carbonium ion intermediates during alkylcyclopropane isomerization to olefins over a similar catalyst.

Larson, Gerberich, and Hall[3] used deuterium isotopes in microcatalytic experiments to demonstrate that one hydrogen atom was exchanged intermolecularly during cyclopropane isomerization to propylene over silica–alumina. These data could be explained by either a bimolecular hydride transfer (I) or a protonic mechanism (II) and would require either a $C_3H_5^+$ (Lewis site) or a $C_3H_7^+$ (Brønsted site) intermediate surface complex, respectively. Studies[6] of the isomerization of methylcyclopropane (MCP), ethylcyclopropane (ECP), and the three dimethylcyclopropanes (DMCP) have now enabled us to distinguish between these possibilities on the basis of product distributions.

Experimental Section

Catalysts and Pretreatment. Houdry M-46 silica–alumina (12.5% Al_2O_3) was used in all experiments. The catalyst had a surface area of 270 m^2/g and was ground and sieved to 40–60 mesh. Pretreatment included slowly increasing the temperature to 530° during evacuation, treatment with O_2 for 2 hr at 530°, and overnight evacuation at the same temperature to a "sticking" McLeod vacuum. The catalyst was cooled to reaction temperature and contacted with flowing helium (microcatalytic experiments) or cooled to −195° under vacuum where a measured quantity of reactant was frozen into the reaction vessel which was then rapidly warmed to reaction temperature (static experiments).

Gases. All gases were obtained from commercial sources: cyclopropane from Ohio Chemical & Surgical Equipment Co.; methylcyclopropane from API standard samples; and cyclobutane, cyclopropane-d_6, and methyl cyclopropane-d_8 from Merck Sharp and Dohme of Canada, Ltd. The latter compound was purified by semipreparative-scale glpc, and all gases were twice distilled from −78 to −195° and thoroughly outgassed before use. The *trans*-2-butene-d_8 was prepared by exchange with D_2 over a pure

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