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Ion–Molecule Reactions of Simple Aliphatic Ketones by Continuous and Trapped ICR

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Abstract: It is shown that the ion–molecule chemistry of ketones is much more complicated than was assumed in previous papers. Double resonance acceleration of molecular ions even with rather low rf amplitudes leads to collision-induced dissociation. For ketones larger than acetone the molecular ion appears to isomerize. In addition to the well-known self-acylation reaction of molecular ions, solvated fragment ions are also formed by direct clustering of fragment ions with a neutral molecule. This leads to pressure-dependent double-resonance effects.

One of the well-known reactions in the ion–molecule chemistry of ketones is the formation of acylated product ions according to

$$RCOR^{\cdot+} + RCOR \rightarrow (RCOR)RCO^+ + R\cdot \qquad (1)$$

This reaction appears to be characteristic of the keto form of the molecular ion and has been used in the structure elucidation of $C_3H_6O^+$ ions.[1] Bursey studied the acylation of a large number of molecules by the corresponding reaction of the molecular ion of diones and showed that the rate constant can be strongly dependent on stereochemical factors (see, e.g., ref 2 and 4). The rate constant of (1) for acetone has been reported by MacNeil and Futrell in an extensive study of the ion–molecule chemistry of this molecule.[5]

According to Tiedemann and Riveros[6] reaction 1 proceeds via an activated collision complex which for simple aliphatic ketones except acetone can be stabilized at pressures above 10^{-5} Torr:

$$RCOR^{\cdot+} + RCOR \rightleftharpoons (RCOR)_2^{\cdot+*} \longrightarrow (RCOR)RCO^+ + R\cdot$$
$$\downarrow M \qquad\qquad\qquad (2)$$
$$(RCOR)_2^{\cdot+}$$

These authors also studied the relative proton affinities of a large number of carbonyl compounds.[7]

In cooperation with Dr. J. van Thuijl of this laboratory and Professor A. Maquestiau of the University of Mons (Belgium) we have tried to use (1) in the structure determination of thioketone ions. The keto and enol forms of diisopropyl thioketone have different mass spectra and one should expect the molecular ions to have different structures.[8] With ICR we nevertheless found the $M = 217$ ion $(C_3H_7CSC_3H_7)C_3H_7CS^+$ in both cases. Subsequent double resonance experiments showed that the $M = 217$ ion was not formed from the molecular ion but by direct clustering of the $C_3H_7CS^+$ fragment ion with a neutral molecule. A comparable clustering of CH_3CO^+ with several neutrals has been reported by Bursey and co-workers (see, e.g., 3 and 4). We concluded that for a

general case, reaction scheme 2 should at least be extended to:

$$RCOR^{\cdot+} + RCOR \rightleftharpoons (RCOR)_2^{\cdot+*} \longrightarrow (RCOR)RCO^+$$
$$\downarrow M \qquad\qquad\qquad \uparrow M$$
$$(RCOR)_2^{\cdot+} \qquad (RCOR)RCO^{+*} \qquad (3)$$
$$\updownarrow$$
$$RCO^+ + RCOR$$

It follows that the ion–molecule chemistry of aliphatic ketones is much more complicated than was assumed in previous papers. We therefore studied the reactions of ketone ions in more detail both with normal continuous and trapped ICR. As will be shown even reaction scheme 3 is too simple to account for all observations.

Experimental Section

All ICR results in this paper were obtained with a home-built instrument which includes a Varian 12-in. magnet and a diffusion-pumped vacuum system and dual inlet system constructed by VG Micromass. The solid-state marginal oscillator, built by Mr. J. D. van Gelder of this laboratory, was connected to either the reaction or the analyzer section of a flat four-section cell equipped with a four-grid electron gun. For normal ICR spectra, usually measured with grid modulation, the electronic detection system further consists of a PAR 122 lock-in amplifier, Keithley 610 CR electrometer, and Bryans 2-pens x–y recorder monitoring both the total ion current and the ICR signal intensity. Double resonance experiments were performed with either a Wavetek Model 112 or a Hewlett-Packard 4204A oscillator. The time evolution of ion intensities was measured with trapped ICR according to the method proposed by MacMahon and Beauchamp[9] using Tektronix 160 series pulse generators and a PAR 160 boxcar integrator. Frequencies and time delays were obtained from a Hewlett-Packard 6326A timer-counter. Pressures were read from a Vacuum Generators VIG-21 ion gauge located just outside the vacuum chamber.

Results and Discussion

Acetone. A continuous ICR spectrum of acetone at 1.2×10^{-5} Torr and the time evolution of ion intensities at 3×10^{-6}

Table I. Total Reaction Rate Constants (in 10^{-9} cm^3 mol^{-1} s^{-1}) of Ketone Ions (for Butanone R$_1$ = CH$_3$, R$_2$ = C$_2$H$_5$)

| | Acetone | | | | Diisopropyl |
	This work	MacNeil–Futrell	Butanone	Pentanone	ketone
R$_1$CO	0.2	0.54	0.7	0.08	0.11
R$_2$CO			0.06		
R$_1$COR$_2$	0.6	0.43	0.09	0.08	0.02
(R$_1$COR$_2$)H	0.04	0.43	0.09	0.05	0.02
(R$_1$COR$_2$)R$_1$CO	0.08	<0.54	0.09	0.03	0.02

Figure 1. ICR spectrum of acetone at 1.2 × 10^{-5} Torr.

Figure 2. Time dependence of ion intensities in acetone at 3 × 10^{-6} Torr (ion intensities of the different ions are not comparable).

Figure 3. ICR spectrum of butanone at 2 × 10^{-5} Torr.

Torr measured with trapped ICR are shown in Figures 1 and 2. Values for the total reaction rate constants of the major ions obtained from a number of trapped ICR experiments are collected in the table together with part of MacNeil and Futrell's results.

For the primary ions which react according to

$$CH_3COCH_3\cdot^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)H^+ \quad (4)$$

$$CH_3COCH_3\cdot^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)CH_3CO^+ \quad (5)$$

and

$$CH_3CO^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)H^+ \quad (6)$$
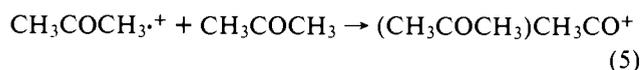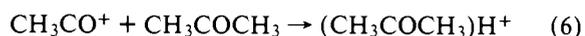
the total reaction rate constants are in reasonable agreement with MacNeil and Futrell's results.

For the secondary ions there seems to be a rather large discrepancy. On closer inspection, however, this difference gives valuable information about the reaction mechanism. (CH$_3$COCH$_3$)H$^+$ reacts by clustering with neutral molecules to form (CH$_3$COCH$_3$)$_2$H$^+$. For (CH$_3$COCH$_3$)CH$_3$CO$^+$ clustering is presumably also the major reaction. In both cases we thus have the reaction sequence

$$A^+ + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (AB)^{+*} \overset{B}{\underset{k_3}{\longrightarrow}} AB^+$$
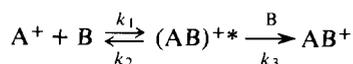
in which an activated collision complex is stabilized by collisions with neutrals. Now, suppose k_1 is 10^{-9} cm^3 mol^{-1} s^{-1}, k_3 is 10^{-10} cm^3 mol^{-1} s^{-1}, and the lifetime of the activated collision complex $1/k_2$ is 5 ms. Then, the decay rate constant of A$^+$ at large trapping times is 0.6 × 10^{-10} at 10^{-5} Torr in agreement with our experimental value whereas from the intensity of A$^+$ after 10 ms one should obtain a rate constant of

4 × 10^{-10} cm^3 mol^{-1} which is close to MacNeil and Futrell's value. This interpretation agrees with the fact that MacNeil and Futrell's high pressure ion source experiments show that at higher pressures the formation of (CH$_3$COCH$_3$)$_2$H$^+$ is a fast reaction. Contrary to the proposed mechanism we found the decay rate constant to be independent of pressure but this result is presumably misleading because at least at the lower pressures the decay by reaction becomes of the same order of magnitude as the loss of ions to the walls. We therefore conclude that both our and MacNeil and Futrell's values are apparent rate constants and that the lifetime of the activated collision complex is a few milliseconds.

In reaction 3 we have included the direct clustering of fragment ions to acylated product ions. In the case of acetone this should be the reaction 43$^+$ + 58 → 101$^+$. From a large number of double resonance experiments w could only conclude that at higher pressures this reaction possibly occurs. The contribution to the M = 101 ion intensity is relatively unimportant at all pressures and a determination of the rate constant, if being nonzero at all, will be very difficult.

According to MacNeil and Futrell, complex interconversion reactions occur between the primary ions. We have observed an interesting reaction not mentioned in previous papers.

Upon acceleration of the molecular ion M = 58 by double resonance irradiation with rf amplitudes of 100 or 200 mV peak to peak, a rather strong enhancement of the fragment ion M = 43 intensity is obtained. This positive double resonance signal was also obtained for other ketones (see butanone). Even with very high rf amplitudes leading to practically complete ejection of the molecular ion this double resonance effect remains positive. The formation of fragment ions therefore only occurs with accelerated and not with thermal molecular ions. We conclude that this formation of fragment ions from the molecular ion is not a normal ion–molecule reaction but rather an example of collision-induced dissociation[10] observed in an ICR cell (see ref 11 for a previous example). This observation is quite remarkable. In usual experiments of this type kinetic energies of a few thousand volts are used. Here we observe a collision-induced dissociation at kinetic energies of a few electron volts. The molecular ions of ketones thus appear to be very unstable toward dissociation.

Butanone. The ICR spectrum of butanone at 2 × 10^{-5} Torr (Figure 3) closely resembles the spectrum of acetone shown in Figure 1. This correspondence is lost, however, when we compare the trapped ICR curves (Figure 4) and the total rate constants (see the table) with the results for acetone. At first sight one should conclude that all ions except CH$_3$CO$^+$ react
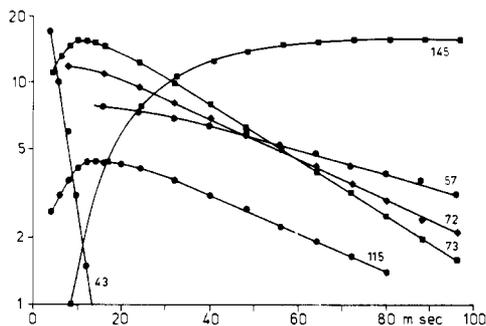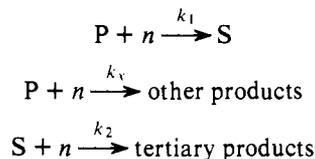
Figure 4. Time dependence of ion intensities in butanone at 6×10^{-6} Torr.

rather slowly. This conclusion, however, is not in agreement with the position of the maximum in the curve for the acetylated product ion $M = 115$ in Figure 4. In normal cases the maximum of the curve for a secondary ion should occur at a time where the intensity of the primary ion is strongly reduced (compare the maximum of $M = 101$ in Figure 2). From a reaction scheme

$$P + n \xrightarrow{k_1} S$$

$$P + n \xrightarrow{k_x} \text{other products}$$

$$S + n \xrightarrow{k_2} \text{tertiary products}$$

the time variation of the intensity of the secondary ion is calculated to be:

$$I_s = \frac{k_1 I_p^0}{k_1 + k_x - k_2} [\exp(-nk_2 t) - \exp\{-n(k_1 + k_x)t\}]$$

By use of this equation $(k_1 + k_x)$ can be calculated from the position of the maximum and the observed value of k_2. In this way we obtained a total rate constant for the primary ion of 0.7×10^{-9} cm^3 mol^{-1} s^{-1} which appeared to be independent of pressure over the range 7×10^{-7} to 1.2×10^{-5} Torr. Both pulsed and continuous double resonance ejection of the $M = 72$ molecular ion in trapped ICR measurements of the $M = 115$ ion furthermore showed that in this pressure range 72 is the sole precursor of 115. The only reasonable explanation of the conflicting rate constants for $M = 72, 0.7 \times 10^{-9}$ from the maximum of 115 and 0.09×10^{-9} from the decay of 72, is a collision-induced isomerization of the molecular ion of butanone resulting in a nonreactive secondary $M = 72$ ion:

$$CH_3COC_2H_5 \cdot^+ + CH_3COC_2H_5 \rightarrow C_4H_8O^+ \quad (7)$$

We have tested this interpretation of our results by an experiment at 1.7×10^{-6} Torr, where the maximum of 115 occurs at about 60 ms, by observing the $M = 115$ ion at 170 ms and ejecting the $M = 72$ ion with a strong rf pulse at different time delays with respect to the electron beam pulse. It appeared that indeed the reactivity of $M = 72$ decays much faster in time than the intensity of the $M = 72$ ion signal. From this experiment we obtained a total rate constant for the primary $M = 72$ ion of 0.8×10^{-9} cm^3 mol^{-1} s^{-1}. In the section on acetone we have mentioned the collision-induced dissociation of the molecular ion. This effect was also observed for the primary butanone molecular ion and thus offered a second possibility to study the isomerization of the molecular ion. By observing the increase of intensity of the rather unreactive $M = 57$ fragment ion at 5×10^{-6} Torr after 100 ms due to pulsed acceleration of the $M = 72$ ion at different times, the total rate constant of the primary $M = 72$ ion appeared to be 1.0×10^{-9} cm^3 mol^{-1} s^{-1}. These two experiments thus confirm the isomerization according to eq 7.[12]

Further results for butanone include: (a) by far the most important precursor of the $(M + 1)$ ion $M = 73$ is the CH_3CO^+ fragment ion; (b) besides $M = 115$ we found a small signal due to the $M = 129$ ion $(CH_3COC_2H_5)C_2H_5CO^+$. Double resonance experiments showed this ion to be formed by clustering of $CH_3CH_2CO^+$ with a neutral molecule:

$$CH_3CH_2CO^+ + CH_3COC_2H_5$$

$$\rightarrow (CH_3COC_2H_5)C_2H_5CO^+ \quad (8)$$
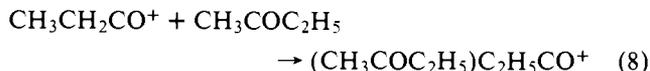
3-Pentanone. According to eq 3 acylated product ions can be formed by two different routes. From acetone and butanone it appeared that acetylation occurs almost exclusively by reaction of the molecular ion. From reaction 8, however, one expects for 3-pentanone both reactions 9 and 10:

$$C_2H_5COC_2H_5 \cdot^+ + C_2H_5COC_2H_5 \rightarrow$$
$$M = 86$$

$$(C_2H_5COC_2H_5)C_2H_5CO^+ + C_2H_5 \cdot \quad (9)$$
$$M = 143$$

$$C_2H_5CO^+ + C_2H_5COC_2H_5 \rightarrow (C_2H_5COC_2H_5)C_2H_5CO^+$$
$$M = 57 \qquad\qquad\qquad M = 143$$

$$(10)$$
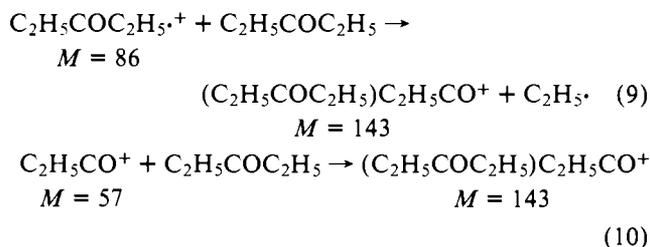
According to reaction 3 the relative importance of (9) and (10) should be pressure dependent. Indeed, at 5×10^{-6} Torr double resonance showed $M = 143$ to be formed from the molecular ion only whereas at 5×10^{-5} Torr reaction 10 is the major source of $M = 143$. At 2×10^{-5} Torr the two double resonance signals for (9) and (10) have about equal magnitude. At high pressures the relatively small double resonance signal for (9) becomes positive in the wings. We ascribed this effect to the collision-induced dissociation of the molecular ion, mentioned before, and subsequent reaction of the resulting $M = 57$ fragment ion according to (10).

The total rate constants for the major ions obtained with trapped ICR are collected in the table. In the present case all ions (except the $M = 29$ fragment not mentioned in the table) seem to react rather slowly. However, we again found the molecular ion to isomerize. From the position of the maximum in the trapped ICR curve for $M = 143$ the total rate constant for the original $M = 86$ primary ion appeared to be 0.5×10^{-9} cm^3 mol^{-1} s^{-1}. Observation of the $M = 143$ ion intensity upon ejection of the $M = 86$ at different times after the electron beam pulse yielded the somewhat larger value of 0.8×10^{-9} cm^3 mol^{-1} s^{-1}.

2,4-Dimethylpentan-3-one. 2,4-Dimethylpentan-3-one (diisopropyl ketone) behaves in much the same way as 3-pentanone, although the rate constants are somewhat different. The formation of the acylated product ion $(C_3H_7COC_3H_7)C_3H_7CO^+$ by clustering of the $C_3H_7CO^+$ fragment with a neutral molecule now occurs at lower pressures than in the case of 3-pentanone. This could possibly account for the somewhat larger rate constant for the $M = 71$ fragment ion (table). For the other major ions the rate constants are somewhat lower than in the case of pentanone. The primary ion again isomerizes. Because in this case the $M = 185$ ion is produced both from $M = 114$ and from the $M = 71$ fragment we have calculated the rate constant of the original primary ion from a curve for $M = 185$ measured with complete ejection of the $M = 71$ fragment ion. This yielded a value of 0.3×10^{-9} cm^3 mol^{-1} s^{-1} which again is lower than in the previous cases.

Conclusions

The experiments described above give an illustration of the power of trapped ICR especially when used in combination with double resonance acceleration of the ions. Our results can

be summarized as follows: (a) Molecular ions of ketones are very unstable toward dissociation. Even a slight enhancement of their kinetic energy is sufficient to induce dissociation upon collisions. (b) For ketones having at least one alkyl group larger than methyl thermal collisions induce an isomerization of the molecular ion. It seems rather attractive to describe this reaction as a keto–enol isomerization but at present our experiments do not allow this onclusion. The reverse reaction has previously been observed for activated enol ions obtained by a McLafferty rearrangement.[13,14] (c) Solvated fragment ions are formed both by the well-known self-acylation of the molecular ion and by direct clustering of fragments with neutral molecules. This leads to pressure-dependent double-resonance signals.

The reaction scheme proposed by Tiedemann and Riveros is clearly incomplete. One might even ask whether the formation of dimer ions according to scheme 3 is really true. Since the molecular ions of ketones, other than acetone, both isomerize and give rise to dimer ions, it might be possible that the dimer ion is in fact an enol ion complexed with a keto molecule.

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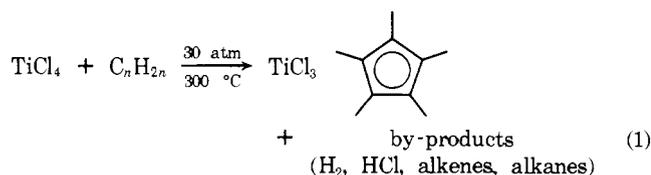(14) J. R. Hass, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *J. Am. Chem. Soc.*, **94**, 5095 (1972).

Ion–Molecule Reactions in Mixtures of TiCl₄ with Olefins in the Gas Phase

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Abstract: Reactions between small olefins and species formed by electron impact on $TiCl_4$ are described. Rate constants determined by an ion cyclotron resonance technique are reported. Ti^+ and $TiCl^+$ complex with the olefins and eliminate hydrogen. $TiCl_2^+$ and $TiCl_3^+$ complex with the olefins and eliminate HCl. In addition, $TiCl^+$, $TiCl_2^+$, and $TiCl_3^+$ also complex with olefins containing a chain of five or more carbons and eliminate smaller olefins. $TiCl_4^+$ is unreactive. General patterns of reactivity and possible reaction mechanisms are discussed.

In solution titanium tetrachloride participates in a variety of interesting reactions with alkenes. In the Ziegler–Natta scheme[1,2] for polymerization of olefins, $TiCl_4$ in combination with aluminum alkyls performs a catalytic function. The process is postulated to occur through ionic- and ion-pair intermediates.[1] Roehl, Lange, Golsal, and Roth[3] report that $TiCl_4$ itself reacts with almost any alkene according to reaction 1.

$$TiCl_4 + C_nH_{2n} \xrightarrow[\text{300 °C}]{\text{30 atm}} TiCl_3$$

$$+ \quad \text{by-products} \qquad (1)$$
$$\text{(H}_2\text{, HCl, alkenes, alkanes)}$$

The gas phase ion chemistry of $TiCl_4$ with olefins includes a number of processes which may be elementary steps in the solution chemistry of $TiCl_4$ with olefins. Ions formed by electron impact on $TiCl_4$ form complexes with olefins. The complexes lose H_2, HCl, and smaller olefins. Properties of the products of these dissociative additions may be deduced from their further reactions. The overall reaction schemes are quite specifically related to the structure of the olefins. Following an account of experimental procedures, we give below the reaction schemes in detail and discuss the relationship between olefin structure and reactivity.

Experimental Section

All experiments were performed on an ion cyclotron resonance[4] instrument of conventional design described elsewhere.[5] Reaction pathways were identified by observing reactant and product ion signal intensities as a function of pressure and by double resonance. Rate constants were determined from single resonance spectra by the method of Comisarow.[6] Reported rate constants represent the average of at least three determinations. The uncertainty in the reported rate constants arises from uncertainty in pressure measurements made with an MKS Baratron Capacitance Manometer and the noise level in the single resonance spectra. Except as noted below, the estimated errors are ±20% or $\pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, whichever is greater.

$TiCl_4$ was obtained from Alfa Products. Impurities were minimized by multiple freeze-pump-thaw cycles using an acetonitrile-CO_2 bath.