within the micelle would be expected to increase as the temperature is raised toward the Krafft point, the hypothetical melting point of a hydrated solid.[37] A second source of depolarization in labeled micelles and consequently low value for microviscosity is that which results from rotation of the micelle itself.[38] If the rate of micelle rotation is of the same order of magnitude as rotation within the micelle itself, serious error in the microviscosities obtained by this method can be introduced. The degree of depolarization is defined by $r_0/r = 1 + (kT\tau)/(\eta V)$ where k is the Boltzmann constant, T the temperature, η the viscosity, V the effective volume of the fluorescent rotor (micelle and/or the fluorescent label), and τ the average lifetime of the fluorophore.[17] Comparison of the term $1/\eta V$ for both micelle and fluorophore rotation indicates that rotational retardation of the micelle ($V \sim 5000$ Å^3) in water ($\eta = 1.0$ cP) becomes competitive with that of the label in highly viscous micelle interiors.

Other considerations are necessary to account for the discrepancy between microviscosities based on depolarization and those obtained by excimer fluorescence. Additional information regarding structure of anisotropy of the micelle are important. The homogeneous distribution of the label throughout the micelle interior is probably not entirely valid.

The model presented here is based on collision theory which assumes a large number of pyrene molecules for each micelle interior. This assumption implies that the majority of the pyrene collisions are with other pyrene molecules within the micelle. This is not entirely accurate. For example, a microscopic concentration

of 0.16 M pyrene in CTAB corresponds to an average value of six pyrene molecules per micelle if an aggregation of 85 CTAB molecules/micelle is assumed.[39] If a large number of pyrene molecules were present in each micelle, pyrene–pyrene collisions would be far more frequent than pyrene–micelle wall collisions and the Einstein–Schmulochowski equation would be valid. With a small number of pyrene molecules in each micelle, the excimer fluorescence is less than predicted by diffusion theory since the number of pyrene–micelle wall collisions is the same order of magnitude as pyrene–pyrene collisions. Therefore, the intensity of excimer fluorescence is less than predicted and high values of viscosity can be obtained.

We are now in the process of developing expressions to account for both the small number of pyrene molecules per micelle and the population distribution of pyrene molecules in a collection of labeled micelles. The magnitude of the differences introduced by this treatment cannot be estimated at this time. However, it should not greatly affect the relative viscosity values of these surfactants.

Although the variations in I_E/I_M with viscosity do not always follow a linear relationship,[19] I_E/I_M ratios were not affected by other solvent properties other than viscosity. In the calibration curve with structurally similar alcohols and diols, I_E/I_M values were a linear function over a wide range of viscosities. Although absolute microviscosities may not be measurable with a high degree of accuracy, this method is adequate for studying changes in phase or viscosity affected by temperature, pH, ionic strength, and other variables. For these experiments, pyrene excimer fluorescence is suitable as a microviscometric probe system.

(37) K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **66**, 577 (1962).
(38) G. Weber, *Advan. Protein Chem.*, **8**, 415 (1953).
(39) H. V. Tartar, *J. Colloid Sci.*, **14**, 115 (1959).

Mechanism of Ionic Self-Acylation in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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Abstract: A general survey of the ion–molecule reactions of ketones by ion cyclotron resonance spectroscopy shows that self-acylation is a common reactive channel of the molecular ion. Unsymmetrical ketones with no γ hydrogens, RCOR', are shown to yield preferentially the acylated product, RCO$^+$(RCOR'), which results from a cleavage of the molecular ion in an analogous fashion to the preferred fragmentation in mass spectroscopy (RCO$^+$). Pressure studies are used to show that these reactions proceed through a complex intermediate, which is usually stabilized above 10^{-5} Torr as a clustered dimer ion. Acetone is the only case where this cluster is not observed. Ketones with a γ hydrogen undergo an ion–molecule reaction reminiscent of the McLafferty rearrangement rather than self-acylation. The relative ability of acetone, butanone, and 3-pentanone to stabilize an acyl cation (acyl affinity) is shown to follow the increasing polarizability of these compounds.

The ion chemistry of acetone at low pressures ($\sim 10^{-5}$ Torr) reveals a condensation–elimination reaction leading to an acetylated product

$$CH_3CO^+CH_3 + CH_3COCH_3 \longrightarrow$$
$$CH_3CO^+(CH_3COCH_3) + \cdot CH_3 \quad (1)$$
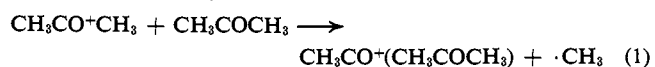
The rate constant for this reaction has been recently reported by Futrell[1] in a comprehensive study of the ion–molecule processes in acetone using ion cyclotron

(1) K. A. G. McNeil and J. H. Futrell, *J. Phys. Chem.*, **76**, 409 (1972).

resonance spectroscopy (icr) and high-pressure mass spectrometry. Reaction 1 had been previously detected by icr and used in a mechanistic study concerning the structure elucidation of the single and double McLafferty rearrangements.[2] Likewise, a variety of related acetylating reactions, and their potential use as an analytical tool, have been shown to occur with butanedione as the ionic reagent.[3-5]

Icr techniques are used in the present study to establish self-acylation as a common ion–molecule reaction for ketones, esters, and carboxylic acids. These reactions are shown to proceed via an excited dimer ion intermediate for the simplest cases. This intermediate can be collisionally stabilized and detected at pressures above 10^{-5} Torr. Gas-phase acylating reactions provide, in principle, a useful starting point for comparisons with well-known acylating processes in organic chemistry.[6]

The question of the product distribution in ketones capable of undergoing several possible self-acylating reactions has also been investigated in connection with the dynamics of the collision complex. The results appear to be systematic and allow for correlations to be made with the mass spectral fragmentation of these compounds.

Experimental Section

Spectra were obtained in a Varian V-5900 icr spectrometer provided with a plug-in unit for the marginal oscillator that allows for operation anywhere between 75 and 155 kHz. This unit extends the maximum mass range of the spectrometer to m/e 286. The loss of resolution and sensitivity at the lower operating frequencies did not affect the results. Spectra were recorded by sweeping the magnetic field while maintaining the frequency fixed at a convenient value for the desired mass range. The electron energy was kept at 15 eV for the present study. Double resonance experiments were conducted in the conventional manner,[7] maintaining low ion currents and irradiating fields no larger than 0.012 V/cm.

Pressures were read from the ion pump control and were thus subject to a large absolute error. The linearity of the VacIon current indicator with pressure was, however, checked against a Veeco ion gauge in the 1×10^{-6} to 5×10^{-5} Torr range.

Elastic collision frequencies were determined by the method outlined by Buttrill[8] using electron energy modulation.

The following compounds showed no appreciable impurities in their mass spectra and were used without further purification: acetone (Fisher), acetone-d_6 (Merck), butanone (Fisher), acetophenone (BDH), 2-pentanone (Eastman), 3-pentanone (Eastman), 2-hexanone (Light), 3-heptanone (Eastman), and 3,3-dimethylbutanone (Eastman). The compound 2,2,4,4-tetramethyl-3-pentanone was prepared and purified by a method analogous to that recently outlined for synthesis of branched ketones.[9]
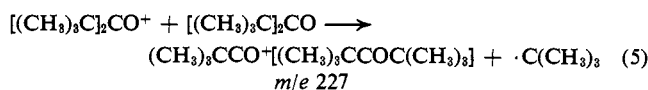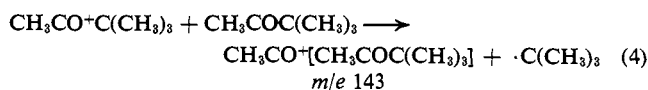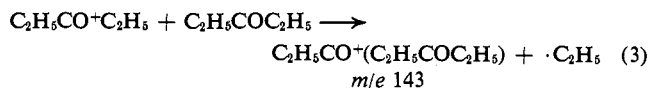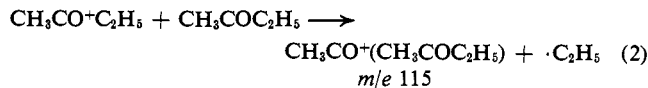
Results and Discussion

The icr spectra of carbonyl compounds indicate that the ion–molecule reactions leading to the formation of the protonated species, RCO^+HR', are in general the dominant processes. These reactions, and the subsequent clustering by another neutral molecule,

$[(RR')CO]_2H^+$, have been reported for the case of acetone[1] and discussed in detail elsewhere with regard to the proton affinities of these compounds.[10]

The results analyzed below are restricted to the self-acylation reactions at low electron energies. The product ion intensity for these reactions amounts, in general, to less than 15% of the total ion current.

A. Self-Acylation Reactions in Simple Ketones with No γ Hydrogens.

The following reactions have been observed for simple ketones.

$$CH_3CO^+C_2H_5 + CH_3COC_2H_5 \longrightarrow$$
$$CH_3CO^+(CH_3COC_2H_5) + \cdot C_2H_5 \quad (2)$$
$$m/e \ 115$$

$$C_2H_5CO^+C_2H_5 + C_2H_5COC_2H_5 \longrightarrow$$
$$C_2H_5CO^+(C_2H_5COC_2H_5) + \cdot C_2H_5 \quad (3)$$
$$m/e \ 143$$

$$CH_3CO^+C(CH_3)_3 + CH_3COC(CH_3)_3 \longrightarrow$$
$$CH_3CO^+[CH_3COC(CH_3)_3] + \cdot C(CH_3)_3 \quad (4)$$
$$m/e \ 143$$

$$[(CH_3)_3C]_2CO^+ + [(CH_3)_3C]_2CO \longrightarrow$$
$$(CH_3)_3CCO^+[(CH_3)_3CCOC(CH_3)_3] + \cdot C(CH_3)_3 \quad (5)$$
$$m/e \ 227$$

Similar types of reactions are observed in acetic acid, propanoic acid, and their esters to yield the corresponding acylated ion. Aldehydes and acyl chlorides, compounds for which the neutral product would be an atom, show no tendency to undergo self-acylation under our conditions. However, they may be acylated by other reagent ions.[4]

Reaction 5 shows that the acylation reaction takes place even in a compound that has no α hydrogens and thus is unable to form an enolic molecular ion. Since reactions 1–5 proceed at comparable rates, observation of reaction 5 suggests that these reactions are characteristic of the keto form of the molecular ion, in agreement with previous evidence.[2]

It has been previously shown,[2] and confirmed by our experiments with deuterated acetone, that in the acylating reaction the neutral radical is produced primarily by fragmentation of the molecular ion rather than the neutral.

Reactions 2 and 4 are particularly interesting because two acylated products are possible: in butanone, m/e 115 and 129, and in 3,3-dimethylbutanone, m/e 143 and 185. Expulsion of the higher mass neutral radical is observed exclusively in both cases for pressures less than 9×10^{-5} Torr and for short trapping times. On the other hand, reactions 3 and 5 and reaction 6 in

$$C_2H_5CO^+C_2H_5 + CH_3COC_2H_5 \longrightarrow$$
$$C_2H_5CO^+(C_2H_5COCH_3) + \cdot C_2H_5 \quad (6)$$
$$m/e \ 129$$
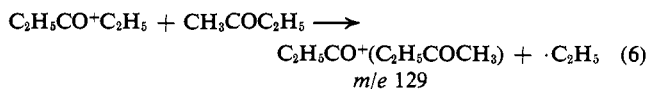
mixtures of ketones show that product ions containing the acyl component not observed in (2) and (4) can be readily obtained in other processes, under similar conditions of pressures and trapping times. Thus, the exclusive appearance of m/e 115 and 143 can only be understood in terms of dynamic factors operating in the collision complex of the reaction.

The preferential formation of the acetylated ionic products in reactions 2 and 4 is analogous to the fragmentation patterns of these compounds in conventional

(2) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969).

(3) M. K. Hoffman, T. A. Elwood, T. A. Lehman, and M. M. Bursey, *Tetrahedron Lett.*, 4021 (1970).

(4) M. M. Bursey, T. A. Elwood, M. K. Hoffman, T. A. Lehman, and J. M. Tesarek, *Anal. Chem.*, **42**, 1370 (1970).

(5) M. M. Bursey and M. K. Hoffman, *Can. J. Chem.*, **49**, 3395 (1971).

(6) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 257.

(7) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(8) S. E. Buttrill, Jr., *ibid.*, **50**, 4125 (1969).

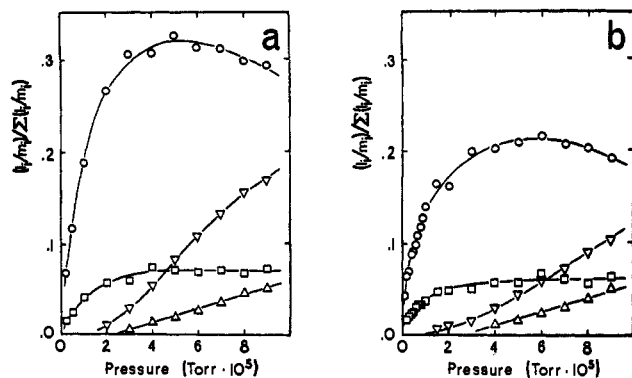(9) J. E. Dubois, M. Boussu, and C. Lion, *Tetrahedron Lett.*, 829 (1971).

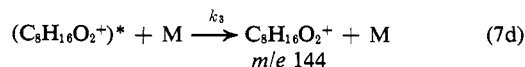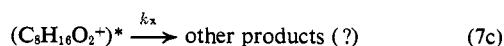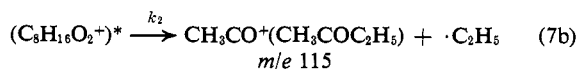(10) P. W. Tiedemann and J. M. Riveros, to be submitted for publication.
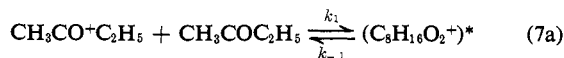
Figure 1. (a) The percentage ion current of product ions in butanone as a function of pressure: (O) $CH_3CO^+HC_2H_5$; ($\triangledown$) $(CH_3COC_2H_5)_2H^+$; ($\square$) $CH_3CO^+(CH_3COC_2H_5)$; ($\triangle$) $(CH_3COC_2H_5)_2^+$. (b) The percentage ion current of product ions in 3-pentanone as a function of pressure: (O) $C_2H_5CO^+HC_2H_5$; ($\triangledown$) $(C_2H_5COC_2H_5)_2H^+$; ($\square$) $C_2H_5CO^+(C_2H_5COC_2H_5)$; ($\triangle$) $(C_2H_5COC_2H_5)_2^+$.

mass spectroscopy.[11] Butanone and 3,3-dimethyl-butanone are cases where, despite the fact that $C_2H_5CO^+$ and $(CH_3)_3CCO^+$ have lower appearance potentials, the species CH_3CO^+ predominates over the other acyl cation at electron energies well above the ionization potential of the molecule. Similarities between ion-molecule reaction products and mass spectral fragmentation might be expected, since the reaction is a cluster-induced cleavage of the molecular ion. That this analogy is indeed remarkable can be further exemplified by the reaction in acetophenone, C_6H_5-$COCH_3$. Although the condensation–elimination process is considerably slower than reactions 1–5, the only product observed, $C_6H_5CO^+(C_6H_5COCH_3)$ (m/e 225), is in agreement with the main fragment observed in the mass spectrum ($C_6H_5CO^+$).

B. Mechanism of the Acylation Reactions. The pressure dependence of reactions 2–5 shows the intensity of the acylated ion to increase in the 10^{-6} Torr range and level off around 2×10^{-5} Torr. At the same time, a dimer ion (not present in acetone) is observed to appear above 10^{-5} Torr and to grow steadily with pressure. Such a behavior suggests that these reactions proceed *via* a loosely bound dimer ion which (a) dissociates unimolecularly at low pressures in an analogous kinetic fashion to the fragmentation of an energetic molecular ion, and (b) is stabilized at higher pressures.

For the specific case of butanone, the following mechanism is proposed in accord with the above pressure behavior.

$$CH_3CO^+C_2H_5 + CH_3COC_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_8H_{16}O_2^+)^* \quad (7a)$$

$$(C_8H_{16}O_2^+)^* \overset{k_2}{\longrightarrow} CH_3CO^+(CH_3COC_2H_5) + \cdot C_2H_5 \quad (7b)$$
$$m/e \ 115$$

$$(C_8H_{16}O_2^+)^* \overset{k_x}{\longrightarrow} \text{other products (?)} \quad (7c)$$

$$(C_8H_{16}O_2^+)^* + M \overset{k_3}{\longrightarrow} C_8H_{16}O_2^+ + M \quad (7d)$$
$$m/e \ 144$$

Step 7c includes other possible channels of reaction like hydrogen or proton transfer for the sake of gener-

(11) A. G. Sharkey, Jr., J. L. Schultz, and R. A. Friedel, *Anal. Chem.*, 28, 934 (1956).

ality. This process, as well as any other direct reaction that might deplete the amount of $CH_3CO^+C_2H_5$, will not affect the discussion below.

The above mechanism results in the following expressions (eq 8) for the rate of formation of products (ions/sec) as a function of time, assuming steady-state conditions for the excited dimer ion: $(A^+) =$

$$(A^+) = \frac{k_2(M^+)_0}{k_2 + k_x + k_3(M)} \left\{ 1 - \exp\left[-k_1(M)t\left(1 - \frac{k_{-1}}{k_{-1} + k_2 + k_x + k_3(M)} \right)\right]\right\}$$

$$(8)$$

$$(M_2^+) = \frac{k_3(M^+)_0(M)}{k_2 + k_x + k_3(M)} \left\{ 1 - \exp\left[-k_1(M)t\left(1 - \frac{k_{-1}}{k_{-1} + k_2 + k_x + k_3(M)} \right)\right]\right\}$$

$CH_3CO^+(CH_3COC_2H_5)$ sec^{-1}, $(M_2^+) = C_8H_{16}O_2^+$ sec^{-1}, (M) = concentration of butanone in molecules/cm^3, and $(M^+)_0$ = rate of formation (ions/sec) of molecular ions at the filament ($t = 0$).

The intensity of these peaks in the icr spectrum is obtained by integrating the above expressions over the time spent in the analyzer region of the cell and multiplying them by the characteristic power absorption of the ion. The percentage ion current (J) for these species, after expansion of the exponential to quadratic terms[12] (valid for the present case of low conversion), and correction for the mass dependence of residence times, can be expressed as

$$J_{115} = \frac{(M^+)_0}{T} \frac{A_{115}k_1k_2(M)(\tau'^2 - \tau^2)}{k_{-1} + k_2 + k_x + k_3(M)}$$

$$(9)$$

$$J_{144} = \frac{(M^+)_0}{T} \frac{A_{144}k_1k_3(M)^2(\tau'^2 - \tau^2)}{k_{-1} + k_2 + k_x + k_3(M)}$$

where T is the sum of the power absorptions of all ionic species corrected to equal residence times, $A = q^2E_{rf}^2/4m\xi$, ξ is the frequency of momentum transfer, and τ' and τ are the times at which the ion enters and exits the analyzer region, respectively (mass corrected).

For experiments carried out at approximately constant residence times, the proposed mechanism leads to (a) a linear dependence on pressure for J_{115} and a quadratic for J_{144} when $(k_{-1} + k_2 + k_x) \gg k_3(M)$, and (b) a zero pressure dependence for J_{115} and a linear dependence for J_{144} when $(k_{-1} + k_2 + k_x) \ll k_3(M)$.

Figure 1a shows the percentage ion current of the product ions in butanone plotted as a function of pressure. The behavior above 4×10^{-5} Torr is in excellent agreement with the predicted high pressure limit (case b above). Figure 1b shows identical behavior for 3-pentanone, where the acylated product corresponds to m/e 143 and the dimer ion to m/e 172. Pressure studies carried out for reactions 4 and 5 are also consistent with the idea of a dimer ion intermediate for the condensation–elimination reaction.

The lifetime of the excited dimer intermediate can be estimated by taking the ratio of the percentage ion current at a low pressure and at the limiting value,

(12) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 72, 3599 (1968).

$J_{115}(low)/J_{115}(high) = k_3(M)/(k_{-1} + k_2 + k_x)$. (The quantity (M) refers to the concentration of butanone at low pressure.) By taking $k_3 = 1 \times 10^{-9}$ cm³/(molecule sec)[13] and by using the uncorrected reading of the VacIon current, an approximate lifetime $(1/(k_{-1} + k_2 + k_x))$ of 2×10^{-3} sec is obtained for the excited intermediate. This value seems to be unreasonably high and is probably due to a rather large error in the absolute value of the pressure.

C. Ketones with γ Hydrogens. Ketones with γ hydrogens undergo condensation–elimination reactions that are considerably more complicated than those discussed in part A. In fact, the main product of this type of reaction is the ion–molecule analog of the McLafferty rearrangement that is observed in the mass spectra. For example, in 2-pentanone

$$CH_3CO^+C_3H_7 + CH_3COC_3H_7 \longrightarrow$$
m/e 86
$$C_3H_6O^+(CH_3COC_3H_7) + C_2H_4 \quad (10)$$
m/e 144
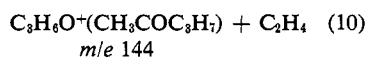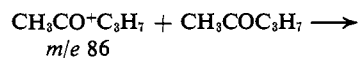
is reminiscent of the mass spectral fragmentation[14]

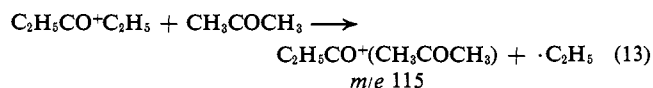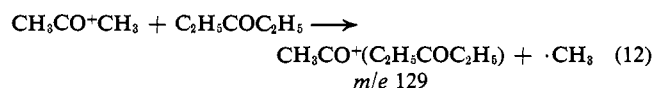$$[CH_3CO^+C_3H_7]^* \longrightarrow CH_3\text{—}\overset{\overset{\displaystyle \parallel}{CH_2}}{C}\text{—}O^+H + C_2H_4 \quad (11)$$
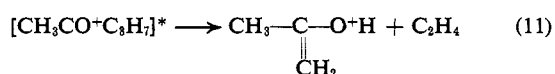
Our experiments do not provide any means to distinguish between the possible enol or keto form of the $C_3H_6O^+$ species in the cluster. Several features distinguish 2-pentanone from the ketones previously discussed: (a) the dimer ion is again observed but at pressures as low as 6×10^{-6} Torr; (b) the product of reaction 10 decreases above 3×10^{-5} Torr; (c) the decrease of m/e 144 is apparently related to the appearance of $C_3H_7CO^+(CH_3COC_3H_7)$.

The preferential formation of a McLafferty type ion clustered by the neutral ketone is also observed in 2-hexanone and 3-heptanone. However, minor quantities of acylated products are also detected.

The condensation–elimination reactions in ketones with γ hydrogens become less important than for the ketones of part A. Thus, the intensities of the product ions are found to be less than 4%. Furthermore, analogies between product distribution and preferred mass spectral fragmentations are no longer straightforward.

D. Acylation Products in Mixtures of Ketones. Acyl Affinities. Mixtures of some of the ketones mentioned in part A give rise to more complicated icr spectra because of the presence of cross acylated products. For example, in a mixture of acetone and 3-pentanone, the following cross ions are observed.
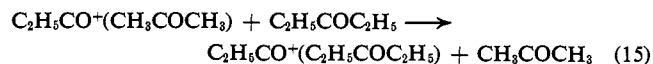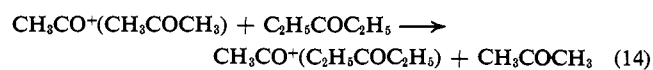
$$CH_3CO^+CH_3 + C_2H_5COC_2H_5 \longrightarrow$$
$$CH_3CO^+(C_2H_5COC_2H_5) + \cdot CH_3 \quad (12)$$
m/e 129

$$C_2H_5CO^+C_2H_5 + CH_3COCH_3 \longrightarrow$$
$$C_2H_5CO^+(CH_3COCH_3) + \cdot C_2H_5 \quad (13)$$
m/e 115

Double resonance was used in these mixtures to determine the relative ability of the neutral to stabilize the clustered acyl ion. The results give relative acyl affinities by methods similar to those used for proton affinities.[15] For example, the reactions 14 and 15 take place above 10^{-5} Torr, whereas the reverse reac-

$$CH_3CO^+(CH_3COCH_3) + C_2H_5COC_2H_5 \longrightarrow$$
$$CH_3CO^+(C_2H_5COC_2H_5) + CH_3COCH_3 \quad (14)$$

$$C_2H_5CO^+(CH_3COCH_3) + C_2H_5COC_2H_5 \longrightarrow$$
$$C_2H_5CO^+(C_2H_5COC_2H_5) + CH_3COCH_3 \quad (15)$$

tions are not detected by double resonance. Experiments carried out with deuterated acetone agree with previous results[3] that these substitutions only take place at the clustering neutral.

The relative acyl affinity determined in these experiments increases in the order $CH_3COCH_3 < CH_3COC_2H_5 < C_2H_5COC_2H_5$. This is analogous to the increasing order of proton affinities.[10]

Conclusions

The present studies show that the ionic self-acylation of ketones in the gas phase occurs by reaction of the molecular ion and proceeds through a complex ion intermediate. The pressure dependence of these reactions in the range of 10^{-6} to 10^{-4} Torr shows that this complex intermediate, a dimer ion, can be stabilized at pressures above 10^{-5} Torr in an icr spectrometer. Acetone is the only case where a dimer ion cluster is not detected at the higher pressures. The decomposition of the unstabilized complex intermediate follows, in general, the dominant fragmentation patterns of ketones in mass spectroscopy. This analogy and the apparent long lifetime of the complex suggest that the quasiequilibrium theory of mass spectra[16] should be applicable to the product distribution of these reactions. Such a theory has been successfully used by Buttrill[17] to account for reactions in ethylene and ethylene–acetylene mixtures which proceed via an "intimate" complex mechanism. It is interesting to note that the decomposition of the excited intermediate into the acylated product and a neutral radical apparently takes place before complete charge randomization occurs in the intermediate. This conclusion is based on the fact that it is the molecular ion which predominantly fragments in the clustering process with the neutral.

The mechanism reported in this work should provide a useful insight into an ion–molecule process which has a wide range of applications. Thus, recent studies have shown the use of the acylating reaction to detect steric inhibition in ion–molecule reactions,[18] and ketonization of enolic ions.[19]

Finally, the relative stability of the clustered acyl ions, determined in our case by double resonance experiments, correlates with the polarizability mechanism which has been found to account for the order of proton affinities.[20] Such a trend has been also established for

(15) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1738 (1968).
(16) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).
(17) S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 6174 (1970).
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Solid-State Chemistry of Irradiated Choline Chloride[1,2]

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Abstract: Further details have been established concerning the radiolysis of the α form of crystalline choline chloride. Esr studies at $-196°$ indicate the presence of a biradical, $(CH_3)_3N^+\cdot\cdot CH_2CH_2OH$---$Cl^-$, that diffuses apart with rising temperature, and also indicate the presence of an ethanol monoradical. Radical-decay kinetics, radiolysis kinetics, thermoluminescence studies, and experiments with a photoelectron emitting dye all appear to confirm an important role for detrapped electrons in the radiolysis mechanism.

Crystalline choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+\cdot Cl^-$, is the most ionizing-radiation sensitive compound known. Among the most pertinent facts known at the outset of the present study are that (1) the G for radical production (radicals produced/100 eV absorbed) is about 2, while the G for radiolysis (molecules of choline chloride destroyed/100 eV) can be as high as 55,000,[3] (2) a high-temperature polymorph (called the "β" form) is not abnormally radiation sensitive, (3) the main radiolysis products are trimethylamine hydrochloride and acetaldehyde, (4) radiation damage can be deferred indefinitely by irradiating and storing at $-78°$, and (5) electron donors accelerate the radiolysis, and electron acceptors retard it. The known details of the radiolysis have led to proposals for the radiolysis mechanism,[3,4] but we are still unable to establish the unique property of the choline chloride's α form (the polymorph that is so radiation sensitive) that makes possible its remarkably efficient chain decomposition.

The present study was undertaken to determine the effect of certain variables on the radical-decay kinetics and radiolysis kinetics of the γ-irradiated α form. The variables employed were total dose, concentration of free electrons, and the temperature at which the radiolysis is allowed to proceed. Because radiolysis does not proceed at low temperatures, we have the opportunity to study the relationship of the radicals initially created in the α form by the ionizing radiation at low temperature and the radicals subsequently participating (at higher temperatures) in the chain mechanism of radiolysis. Most of the research reported here was designed to test our previously stated hypothesis that detrapped electrons react with radicals to form excited species that participate in self-propagating chains.[4]

Experimental Section

Our sources of choline chloride and Brilliant Green, purification procedures, method to determine extent of radiolysis, source of γ rays, irradiation techniques, and general laboratory procedures were recently described.[4] The electron spin resonance spectra and changes of radical concentrations were determined on a Varian Model E-3 spectrometer equipped with a variable temperature assembly. Thermal emission characteristics were observed with a Harshaw Model 2000A thermoluminescence detector, to which we added an external temperature programmer. All thermoluminescence experiments were done with a temperature rise rate of 20°/min.

Results and Discussion

Esr Spectra. Figure 1 shows the esr spectrum of a polycrystalline sample of choline chloride γ-irradiated at $-196°$ and measured at the same temperature. Figure 2 shows the corresponding spectrum of an identical sample that was also irradiated at $-196°$; it was then warmed to $-20°$, then recooled to $-196°$. It is obvious that some irreversible changes occur during the warming; for instance, the shoulders indicated by the arrows in Figure 1 have completely disappeared. These changes have been observed by Symons[5] who interpreted them as reflecting the disappearance of ClOH$^-$ radicals. However, we believe that they are more likely explained by the diffusing apart of spin-coupled radicals and by a change in the nature of the monoradicals (see below). In addition, the formation of ClOH$^-$ would depend upon the presence of water, and we have found unchanged esr spectra regardless of whether our deliquescent crystals were exposed to air or to conditions of rigorous moisture exclusion.

In Figure 3 we have recorded the esr spectrum (at $-166°$) of a γ-irradiated polycrystalline sample in the

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