Table VII. Intensity of DBA Fluorescence Sensitized by Triplet Valerophenone in the Solution Containing Phenyl *n*-Butyl α-Peroxylactone[a, b]

intensity (arbitrary units)	[DBA], M	intensity (arbitrary units)	[DBA], M
3.00×10^5	6.27×10^{-4}	1.36×10^5	2.82×10^{-4}
2.40×10^5	5.01×10^{-4}	1.04×10^5	2.04×10^{-4}
1.88×10^5	3.76×10^{-4}		

[a] The concentration of phenyl *n*-butyl α-peroxylactone was estimated by iodometric titration to be 2.5×10^{-3} M. [b] Measurement was performed in nitrogen-saturated Freon-11 solution at room temperature.

mated to be 2.8×10^{-2} M, and resulted in no effect on the decay rate of chemiluminescence.

The quantum yield of triplet valerophenone formation was estimated by the type II reaction of valerophenone. In the presence of 0.15 M triphenyl phosphate, the quantum yield of type II reaction in air-saturated Freon-11 was measured as 0.44 by comparing with the yield of acetophenone in degassed benzene solution, in which the quantum yield was reported as 0.4.[8] A solution of 1.72 mmol of **3** in 21 mL of $CFCl_3$ containing 0.15 M triphenyl phosphate was left at room temperature overnight. The products were analyzed by quantitative VPC with 4% QF-1 mixed with 1% Carbowax 20M on Chromosorb Q column. (The triphenyl phosphate was removed by passing the solution through a silica gel column before injecting into the VPC.) The ratio of acetophenone (0.047 mmol) to valerophenone (1.16 mmol) was 0.048; therefore, the lower limit for the quantum yield of excited valerophenone was 11%. (The other isolated product of the reaction of **2** and triphenyl phosphite ozonide is a polyester, ca. 0.2 mmol.)

Direct Measurement of E_d for Excited Acetone and Benzophenone. The intensity of acetone fluorescence was measured as a function of temperature with a Perkin-Elmer MPF-2A spectrophotometer. In the temperature range from −20 to 50 °C, the intensity of acetone fluorescence does not change if an appropriate correction for concentration variation resulting from the solvent expansion and constriction is made. An air-saturated Freon-11 solution containing 0.05 M acetone was used for these measurements.

The lifetime of acetone phosphorescence was measured as a function of temperature by the single-photon-counting method. In the temperature range from 2.9 to 23 °C, the measurement provided a value of E_d equal to 6.0 ± 0.4 kcal/mol for a nitrogen-saturated Freon-11 solution containing 0.5 M acetone.

The lifetime of benzophenone phosphorescence was measured as a function of temperature by the single-photon-counting method. In the temperature range from −20 to 22 °C the lifetime is about 35 ± 3 μs and is essentially temperature independent. For these experiments the concentration of benzophenone was 1×10^{-3} M in nitrogen-saturated Freon-11 solution.

Measurement of the Lifetime of Valerophenone Generated from 2. It has been reported that 9,10-dibromoanthracene (DBA) can quench triplet acetophenone with rate constant 3.8×10^8 M^{-1} s^{-1} at 40 °C in benzene solution.[7] Assuming that DBA is capable of quenching valerophenone as well as acetophenone, the rate constant in Freon-11 at 25 °C is estimated to be 4.4×10^8 M^{-1} s^{-1} after the correction for the viscosity difference between Freon-11 at 25 °C and benzene at 40 °C. Phenyl *n*-butyl α-peroxylactone was synthesized by reaction of 0.57 mmol of phenyl-*n*-butylketene and 1.6 mmol of triphenyl phosphite in 20 mL of Freon-11 solution. The intensities of DBA fluorescence as a function of DBA concentration are summarized in Table VII.

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Methylketene. Ion Chemistry and Proton Affinity

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Abstract: The gas-phase ion chemistry of methylketene has been investigated using a quadrupole ion store (quistor) as an ion/molecule reaction chamber. The reaction sequences have been elucidated by the new technique quistor resonance ejection (QRE), which closely resembles ion cyclotron double resonance (ICDR). The ion chemistry of methylketene is analogous to that of ketene, and the nonreactive species *m/z* 57 ($C_3H_5O^+$) is the major product at long storage times. The equilibrium for proton transfer between methyl acetate and methylketene ($(CH_3COOCH_3)H^+ + CH_3CHCO \rightleftharpoons CH_3CH_2CO^+ + CH_3COOCH_3$) has been studied and the proton affinity (PA) of methylketene was found to be 845 ± 3 kJ mol^{-1}, based on a value for PA($CH_3CO_2CH_3$) of 839 kJ mol^{-1} relative to the PA(*i*-C_4H_8) at 828 kJ mol^{-1}.

Introduction

Ketenes and their dimers have been of great interest to researchers because of their frequent appearance as intermediate products in chemical reactions and their great potential as reactants in a number of organic syntheses.[1-3] A corresponding interest in the behavior of such compounds in the gas phase has evolved. A recent communication from this laboratory[4] reported on the ion chemistry of ketene itself, and was in excellent agreement with concurrent work done by Vogt et al.[5] We reported also a value for the proton affinity of ketene which was consistent with recently reported values by other workers.[5-7] The heat of formation of the *tert*-butyl ion, which is taken as a primary standard for that part of the proton-affinity scale relevant to ketene, has been redetermined recently[8] and this necessitates a realignment of the proton-affinity scale. The most recent value for PA(*i*-C_4H_8) is now[9] 828 kJ mol^{-1}.

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(1) Combret, J. C. *C. R. Acad. Sci., Ser. C* **1967**, *264*, 622-624.

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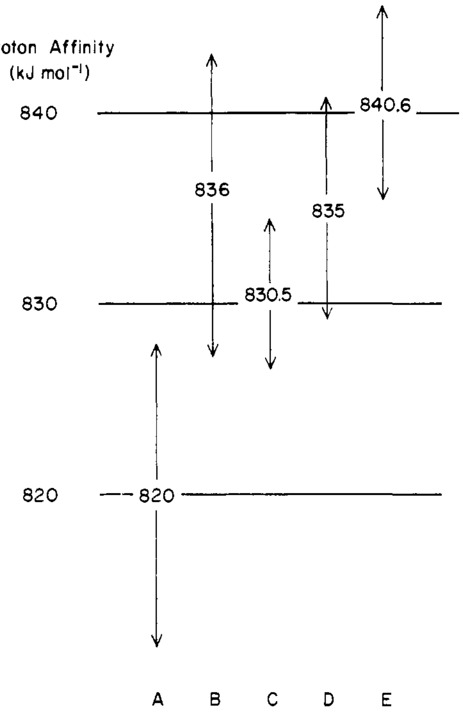

Figure 1. Comparison of reported ketene proton affinities: (A) ref 4; (B) ref 5; (C) ref 6; (D) ref 7; (E) ref 8.

Vogt et al.[5] measured proton-transfer equilibria involving ketene with methyl acetate and tetrahydrofuran and obtained values for $\Delta G°_{298}$ of −1.7 and 5 kJ mol^{-1}, respectively. The proton affinities of methyl acetate and tetrahydrofuran were determined[10] relative to isobutene, and exceeded that of isobutene by 7.9 and 12.1 kJ mol^{-1}, respectively. Thus the PA(ketene) based on methyl acetate is 837.6 kJ mol^{-1}, and based on tetrahydrofuran is 835.1 kJ mol^{-1}, i.e., 836 ± 8 kJ mol^{-1}. Ausloos and Lias[6] had used a value for PA(i-C_4H_8) of 809.6 kJ mol^{-1}; realignment with the new value of PA(i-C_4H_8) of 828 kJ mol^{-1} necessitates the addition of 18.4 kJ mol^{-1} so that their value for PA(ketene) is now 830.5 ± 4 kJ mol^{-1}. Davidson et al.[7] measured four independent proton-transfer equilibria of ketene with diethyl ether, acetone, isobutene, and ethyl formate, at 600 K. As the four determinations of $\Delta G°_{600}$(ketene) were consistent to ~1 kJ mol^{-1}, we need consider only $\Delta G°_{600} = -7.1$ kJ mol^{-1} for the equilibrium between ketene and protonated isobutene; thus the amended value for PA(ketene) is 835 ± 6 kJ mol^{-1}. Lias has recently redetermined[8] the equilibrium constants for the proton-transfer equilibria of ketene with acetone and methyl acetate and found, relative to the PA(i-C_4H_8), that the proton affinities for acetone, methyl acetate, and ketene are 833.9, 838.5, and 840.6 ± 5 kJ mol^{-1}, respectively. Our earlier value for PA(ketene) was 807 ± 8 kJ mol^{-1} based on a value for PA(i-C_4H_8) of 815.9 kJ mol^{-1}. Realignment of the proton-affinity scale (+12.1 kJ mol^{-1} in this case) plus evaluation of symmetry effects (+1 kJ mol^{-1}) lead to an amended value for PA(ketene) of 820 ± 8 kJ mol^{-1}.

The reported value ranges for PA(ketene) are shown in Figure 1 and are in fairly good agreement when one considers the variety of experimental techniques employed, i.e., quadrupole ion storage mass spectrometry in this laboratory,[4,11] ion cyclotron resonance spectroscopy,[5,6] and high-pressure mass spectrometry.[7]

The ion chemistry of methylketene is described in this communication and the coupling of reactant and product ions has been elucidated by the application of a technique entitled quistor resonance ejection (QRE).[12,13] This technique involves the resonant ejection of an ion species from a quadrupole ion store (quistor) and subsequent external mass analysis of the remaining ions by means of a quadrupole mass filter. QRE is very similar to ion cyclotron double resonance (ICDR) except that in ICDR the remaining ion species are detected in situ. The PA(methylketene) has been determined as 845 ± 3 kJ mol^{-1} by a study of the proton-transfer equilibrium between methylketene and methyl acetate where PA($CH_3CO_2CH_3$) is 839 kJ mol^{-1},[8] relative to a PA(i-C_4H_8) of 828 kJ mol^{-1}.

Theory

As has been described in detail,[14] the equations of motion for ions in a three-dimensional quadrupole field take the general form of the Mathieu equation:

$$\mathrm{d}^2u/\mathrm{d}\xi^2 + (a_u - 2q_u \cos 2\xi)u = 0 \qquad (1)$$

where

$u = r$ or z (the cylindrical coordinates of the device) (2)

$$q_z = -2q_r = -4eV/mr_0^2\Omega^2 \qquad (3)$$

$$a_z = -2a_r = -8eU/mr_0^2\Omega^2 \qquad (4)$$

$$\xi = \Omega t/2 \qquad (5)$$

and U is the dc voltage, V is the zero-to-peak (0–p) rf voltage, m/e is the mass-to-unit electronic charge ratio, r_0 is the radius of the ring electrode, z_0 is one-half the spacing between the end-cap electrodes ($r_0^2 = 2z_0^2$), and Ω is the radial frequency of the rf voltage. The general solution to the Mathieu equation is

$$u = \alpha' e^{i\beta\xi} \sum_{n=-\infty}^{\infty} C_{2n} e^{2ni\xi} + \alpha'' e^{-i\beta\xi} \sum_{n=-\infty}^{\infty} C_{2n} e^{-2ni\xi} \qquad (6)$$

where the β value in the above expression is related to the frequency of the ion motion within the quistor and, more specifically, to the dominant secular frequency, ω_u:

$$\omega_u = \beta_u\Omega/2 \qquad (7)$$

The oscillation frequency is dependent upon mass as seen by the approximate expression for β_u,[15] which is good for $q_z < 0.4$:

$$\beta_u = [a_u + q_u^2/2]^{1/2} \qquad (8)$$

Thus, with $a_z = 0$ (no dc component), the ions are oscillating in the z direction with a distinct secular frequency

$$\omega_z = \left[\frac{q_z^2}{2}\right]^{1/2} \frac{\Omega}{2} = \frac{\sqrt{2}eV}{mr_0^2\Omega} \qquad (9)$$

The imposition of a low-level sinusoidal potential of frequency ω_z will cause ions oscillating at this frequency to absorb energy and, in the limit, to be lost from the trapping field. Thus ions of a given m/z ratio can be selectively resonant ejected with no perturbations to trajectories of other stored ions in the device. This resonant ejection technique can be applied to the study of a chemical system within the quistor where resonant perturbation of a precursor ion will be transmitted through chemical interactions and change the relative abundance of product ions.

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(9) A recent value for PA(i-C_4H_8) is 828 kJ mol^{-1} based on unpublished data of Houle and Beauchamp, $\Delta H_f(t\text{-}C_4H_9^+)$ = 681.6 kJ mol^{-1} (based on a redetermination of the ionization potential of the *tert*-butyl radical, and taking a value of 35.1 kJ mol^{-1} for $H_f(t\text{-}C_4H_9\cdot)$). Lias and Ausloos $\Delta H_f(t\text{-}C_4H_9^+)$ = 687.0 kJ mol^{-1} (based on equilibrium measurements involving *tert*-butyl halides and the benzyl ion, taking a value of 891 kJ mol^{-1} for the heat of formation of the benzyl ion). Lau and Kebarle $\Delta H_f(t\text{-}C_4H_9^+)$ = 684 kJ mol^{-1} (based on the Houle-Beauchamp result, and taking $H_f(t\text{-}C_4H_9\cdot)$ = 37.6 kJ mol^{-1}).

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(14) For leading references see ref 13. See also: Dawson P. H., Ed. "Quadrupole Mass Spectrometry and Its Applications"; Elsevier: Amsterdam, 1976; pp 9–57.

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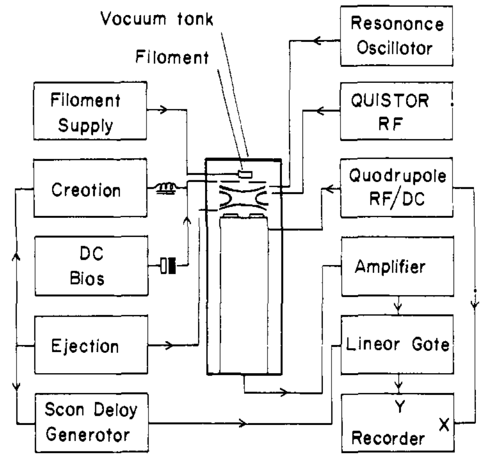


Figure 2. Schematic diagram of apparatus.

Experimental Section

Methylketene was prepared by pyrolysis of propionic anhydride at 480 °C and at a pressure of ca. 25 Pa.[16] The pyrolysis products were passed into a LeRoy still[17] cooled by liquid nitrogen, from which methylketene was distilled at −120 °C and collected as a lime-green solid at −196 °C. Methylketene was identified by the IR absorption (in the gas phase) at 2135 $\mathrm{cm^{-1}}$ and the purity confirmed by the mass spectrum obtained with an AEI MS12 mass spectrometer. In the early preparations the presence of a small amount of volatile white solid with the solid methylketene indicated the presence of less than 5% ketene impurity; this was removed by predistillation before the actual collection of methylketene. Methylketene was stored overnight as a solid at −196 °C. The compound in its liquid state reacts to form a white, crystalline solid on contact with the glass surface of the storage vessel and dimerizes rapidly in the gas phase at pressures as low as 2.0×10^3 Pa.

The apparatus has been described in detail[11] and consists of a quistor mounted in place of the ion source of a conventional quadrupole mass filter (Vacuum Generators Q7B). The ion chemistry of methylketene was studied over the range 0.2–90 ms, with the ion abundances normalized at each storage time to allow for signal variations due to ion losses, migration, etc. In all experiments, the sample gases were admitted to the main vacuum system via an Edwards fine needle valve, Model LB2B, and examined at a total pressure of 1.07×10^{-2} Pa, as measured by an MKS Baratron pressure gauge. The relevant experimental conditions for the methylketene experiments were rf frequency, 1.6 MHz; rf voltage, 260 V (0–p); electron energy, 70 ± 5 eV; ion extraction voltage, −20 V.[18]

The resonant ejection studies were carried out under identical conditions except that a Wavetek Model 134 sweep generator supplied the resonant frequency signal to the repeller end cap (upper end cap electrode), as depicted in Figure 2. These signals were of ca. 1 V (p–p) amplitude and of variable frequency, 60–130 kHz. The entire mass spectrum was recorded after ensuring the complete removal of the precursor ion of interest.

The equilibrium studies involving methylketene and methyl acetate were carried out over a storage time range of 0.2–60 ms. The methyl acetate was obtained from the Fisher Scientific Co. and used without further purification. These studies were carried out with a 5.42:1 mixture of methyl acetate–methylketene which was prepared manometrically, and the relevant experimental conditions were rf frequency, 1.6 MHz; rf voltage, 300 V (0–p); electron energy, 70 ± 5 eV; ion extraction voltage, −20 V.

Results and Discussion

The primary positive ions formed by electron impact on pure methylketene were m/z 14, 26, 27, 28, 54, 55, and 56 under conditions of continuous ionization and zero storage. Under conditions of storage, rapid reaction of m/z 14, 26, 27, and 28 was observed, mainly due to charge transfer to neutral methylketene because of the greater stability of the larger ion. The variation of the logarithm of ion abundances with storage time is depicted in Figure 3. The charge-transfer processes of the smaller ions account for the initial increase in m/z 56.

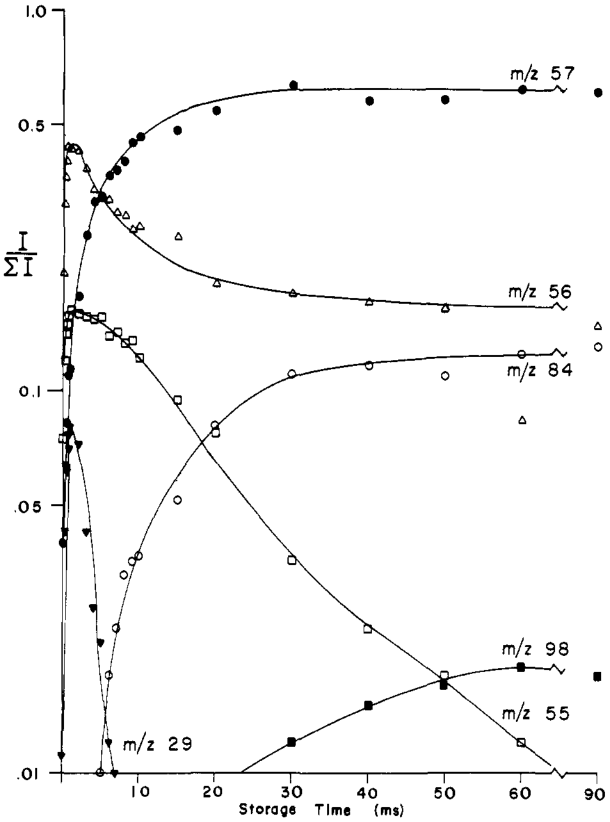
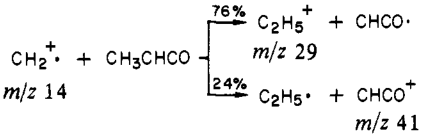


Figure 3. Variation in the logarithm of normalized ion abundances in methylketene: 0–90 ms, 260 V (0–p) at 1.6 MHz, 1.07×10^{-2} Pa.

The m/z 14 ($\mathrm{CH_2^{+}\cdot}$) ion, which reacts mainly in the charge-transfer reaction mentioned above, also reacts with neutral methylketene as in (10) and (11).



$$\underset{m/z\ 14}{\mathrm{CH_2^{+}\cdot}} + \mathrm{CH_3CHCO} \xrightarrow{76\%} \underset{m/z\ 29}{\mathrm{C_2H_5^{+}}} + \mathrm{CHCO\cdot} \quad (10)$$

$$\xrightarrow{24\%} \mathrm{C_2H_5\cdot} + \underset{m/z\ 41}{\mathrm{CHCO^{+}}} \quad (11)$$

m/z 29 peaks rapidly and undergoes proton transfer to methylketene to form the stable protonated parent ion m/z 57.

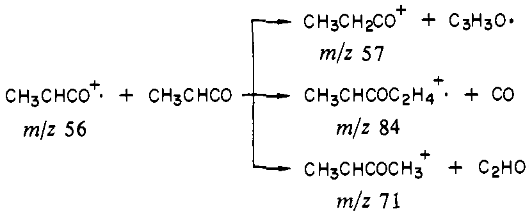
$$\underset{m/z\ 29}{\mathrm{C_2H_5^+}} + \mathrm{CH_3CHCO} \rightarrow \underset{m/z\ 57}{\mathrm{C_3H_5O^+}} + \mathrm{C_2H_4} \quad (12)$$

m/z 41 is formed only in very small quantities (<3% of the total ionization) and forms m/z 69

$$\underset{m/z\ 41}{\mathrm{CHCO^+}} + \mathrm{CH_3CHCO} \rightarrow \underset{m/z\ 69}{\mathrm{C_4H_5O^+}} + \mathrm{CO} \quad (13)$$

a stable ion which accounts for only 1.5% of the total ionization and hence is not shown in Figure 3.

The molecular ion, which accounts for only 20% of the primary ions, is rapidly formed from initial charge-transfer reactions and goes on to react in a number of ways.



$$\underset{m/z\ 56}{\mathrm{CH_3CHCO^{+}\cdot}} + \mathrm{CH_3CHCO} \rightarrow \underset{m/z\ 57}{\mathrm{CH_3CH_2CO^{+}}} + \mathrm{C_3H_3O\cdot} \quad (14)$$

$$\rightarrow \underset{m/z\ 84}{\mathrm{CH_3CHCOC_2H_4^{+}\cdot}} + \mathrm{CO} \quad (15)$$

$$\rightarrow \underset{m/z\ 71}{\mathrm{CH_3CHCOCH_3^{+}}} + \mathrm{C_2HO\cdot} \quad (16)$$

The relative weightings of the above reaction channels are ~70:15:1. Reactions 14–16 are analogous to reactions observed

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[16] Jenkins, A. D. *J. Chem. Soc.* **1952**, 2563.

[17] LeRoy, D. J. *Can. J. Res.* **1950**, *28*, 492.

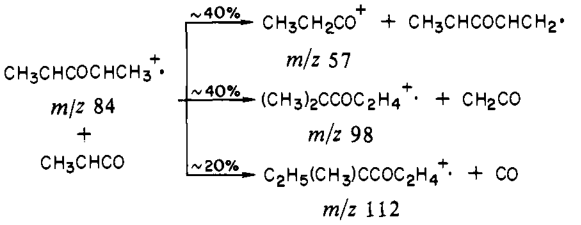
[18] Part 1: Fulford, J. E.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 39–55. Part 2: *Ibid.* **1979**, *30*, 373–378. While the smaller ejection pulse amplitude leads to a diminished ion signal intensity, it is sufficient to empty the trap, leads to enhanced resolution due to a longer transit time through the mass filter, and does not cause mass discrimination after the first millisecond of storage.

in the ketene system.[4,5] A further reaction observed in the ketene system involves the release of two carbon monoxide molecules; the analogous reaction in methylketene is

$$\underset{m/z\ 56}{CH_3CHCO^{+\cdot}} + CH_3CHCO \rightarrow \underset{m/z\ 56}{CH_3CH{=}CHCH_3^{+\cdot}} + 2CO \qquad (17)$$

It is not possible to distinguish between the two ions at *m/z* 56 without labeling experiments. Should the 2-butene ion (*m/z* 56) be produced by reaction 17 it might be expected to react by charge transfer with methylketene as the ionization potential of 2-butene exceeds that of methylketene.[19] The leveling off of the *m/z* 56 ion signal after ~20 ms indicates that this reaction may not, in fact, proceed at a measurable rate. The *m/z* 57 and 71 ions do not react further; the latter does not account for more than 1.5% of the total ionization.

The *m/z* 84 ion reacts further with methylketene to produce *m/z* 57, 98, and 112 slowly. The estimated rate constant for (19)

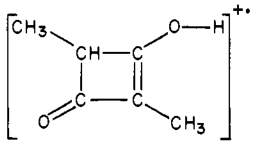


$$\underset{\substack{m/z\ 84\\ +\\ CH_3CHCO}}{CH_3CHCOCHCH_3^{+\cdot}} \begin{cases} \xrightarrow{\sim 40\%} \underset{m/z\ 57}{CH_3CH_2CO^+} + CH_3CHCOCHCH_2\cdot & (18)\\ \xrightarrow{\sim 40\%} \underset{m/z\ 98}{(CH_3)_2CCOC_2H_4^{+\cdot}} + CH_2CO & (19)\\ \xrightarrow{\sim 20\%} \underset{m/z\ 112}{C_2H_5(CH_3)CCOC_2H_4^{+\cdot}} + CO & (20) \end{cases}$$

is 4×10^{-13} cm^3 molecule^{-1} s^{-1} while the rate constant for (20) is of the order of 10^{-13} cm^3 molecule^{-1} s^{-1}.

The reaction sequences (14–16) and (18–20) are supported by resonance ejection. Removal of *m/z* 56 by irradiation at 105 kHz effectively removes almost all ions of higher *m/z* ratio from the spectrum. The sole exception is a small amount (<3%) of *m/z* 96 which may be a fragment of the dimer. Because of diminished resolution of QRE at the irradiation levels necessary for complete removal[13] of *m/z* 56, the contribution of reaction 12 is also lost. Removal of *m/z* 84 by irradiation at 66.5 kHz diminished *m/z* 57 only slightly but completely removed *m/z* 98 and 112. This indicates that reaction 18 accounts for only 3% of the total *m/z* 57 signal. The *m/z* 55 ion, which accounts for ~15% of the total ion abundance after 1 ms of storage, reacts slowly and completely over a period of 70 ms. Because of the proximity of the *m/z* 55 and the more abundant *m/z* 56 ion, it was not possible to identify with confidence the reactive couplings of *m/z* 55 by QRE.

Methylketene in the gas phase was stored overnight and allowed to dimerize spontaneously. A number of spectra were recorded the next day and showed the presence of higher mass fragments. The dimer of methylketene at *m/z* 112 was observed under continuous ionization and zero storage conditions. At 50 ms storage, *m/z* 57 was the dominant ion but new ions at *m/z* 113, 121, 140, and 168 were observed. These are all products of reaction of the dimer in an analogous way to the monomer. The dimer, of *m/z* 112, is assumed to have the structure I as the white, crystalline form of the dimer has been shown[20] to possess this structure.



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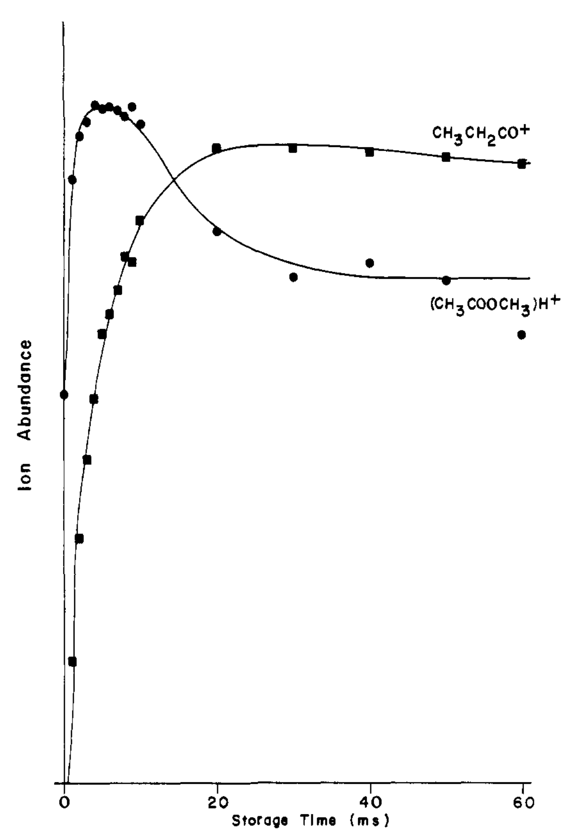

Figure 4. The relative abundances of $(CH_3COOCH_3)H^+$ and $CH_3CH_2CO^+$ observed in a 5.42:1 methyl acetate–methylketene mixture as a function of time.

Proton Affinity of Methylketene

The proton affinity of methylketene can be determined by examining the equilibrium established with some other compound which possesses a very similar proton affinity. The proton affinity of ketene has previously been determined to be 820 ± 8 kJ mol^{-1}[4] and it was expected on the basis of structure that the proton affinity of methylketene should be slightly higher than this. Thus methyl acetate, with a proton affinity of 839 kJ mol^{-1},[8] was chosen as a suitable component for such an equilibrium. The equilibrium observed was

$$\underset{m/z\ 75}{(CH_3COOCH_3)H^+} + CH_3CHCO \rightleftharpoons \underset{m/z\ 57}{CH_3CH_2CO^+} + CH_3COOCH_3 \qquad (21)$$

The relative abundances of $CH_3CH_2CO^+$ and $(CH_3COOCH_3)H^+$ observed as a function of storage time in a 1:5.42 methylketene–methyl acetate mixture are shown in Figure 4. The total pressure was 1.07×10^{-2} Pa.

The equilibrium constant can be calculated from the relative abundances of the two reactant ions at equilibrium and the relative concentrations of methylketene and methyl acetate in the mixture:

$$K_{eq} = [CH_3CH_2CO^+][CH_3COOCH_3]/[(CH_3COOCH_3)H^+][CH_3CHCO] \qquad (22)$$

and was found to be 11.5 ± 0.3 at 320 ± 20 K. The temperature was measured, in a separate experiment, by a thermocouple in contact with an end cap. The value of the equilibrium constant indicates that proton transfer occurs preferentially from the protonated methyl acetate to the methylketene and hence methylketene has the higher proton affinity. The equilibrium constant corresponds to a free-energy change of 6.5 kJ mol^{-1} for the proton-transfer reaction (21) where

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (23)$$

To estimate the enthalpy change associated with reaction 21, it

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is necessary to consider the entropy changes associated with the proton transfer. For *most* ion/molecule equilibria, ΔS may be approximated by ΔS_{rot}, the rotational energy difference due to changes in symmetry numbers.[8,21] It has been assumed for methylketene that protonation occurs on the carbon atom adjacent to the methyl group. If this is indeed the case, reaction 21 is accompanied by no changes in either external or internal symmetry numbers; thus ΔS_{rot} is 0 and the reaction is 6.5 kJ mol^{-1} exothermic. This leads to a proton affinity for methylketene of 845 $\pm$ 3 kJ mol^{-1}, some 25 kJ mol^{-1} higher than the proton affinity of ketene.

Equilibrium measurements have been made in this laboratory on several two-component systems wherein at least one of the components was an aliphatic alcohol; methanol, ethanol, 2-propanol, and 2-butanol together with formic acid, dimethyl ether, and ethyl acetate were investigated. The values of $\Delta G°$ obtained for each two-component system were in good agreement with reported values.[10] In addition to the above studies, quistor resonance ejection has been used to establish the existence of equilibrium in the carbon dioxide–methane system, and is currently being used in the study of equilibria involving negative ions.

The gas temperature is measured by two methods, though in separate experiments. Firstly, the reactant gases are assumed to be in thermal equilibrium with the body of the quistor, and the temperature of the quistor is determined with a thermocouple in contact with an end-cap electrode. Secondly, the temperature of nitrogen in the quistor is calculated from the observed rotational distribution of the nitrogen first negative system emission in the vicinity of 391 nm.[22] There is good agreement between the two methods.

Several attempts have been made to determine ion kinetic energies within the quistor as a knowledge of ion energies is essential to the study of chemical processes by this technique.[23] A distinction must be made between primary ions which are formed initially throughout the effective reactor volume and secondary ions formed in subsequent ion/molecule reactions. Primary ion kinetic energies in collision-free systems[24] and secondary ion kinetic energies pertaining after several collisions[25] have been calculated. There is good agreement among the estimates of mean primary ion energies in collision-free systems. Simulation studies[25] indicate that, although a fraction of secondary ions may possess several electronvolts of kinetic energy, rapid energy dissipation is effected in the first 6–10 collisions so that after 15 collisions the mean ion energy is $\ll$1 eV. Several well-characterized chemical systems have been examined by quadrupole ion storage mass spectrometry[26] and rate constants have been obtained in good agreement with literature values. The observed rotational temperature of the ions obtained in the spectroscopic study of the nitrogen first negative system referred to above should coincide with the temperature of neutrals within the quistor as the number of collisions required to equilibrate rotation with translation is small (approximately five to ten). The rotational temperature is within 20 °C of that obtained with the thermocouple and less than 40 °C above room temperature. Thus it may be concluded that the ion rotational and neutral translational energies are equilibrated and thermal. If the ions were kinetically heated by the rf field, one might expect to see some rotational perturbation in the emission spectrum, even though the lifetime of the (0,0) transition of the nitrogen first negative system ($\sim 8 \times 10^{-8}$ s[27]) is short with respect to the periodicity of the rf potential applied to the quistor. No perturbations were observed in the 21 rotational levels monitored.

The conclusion of these studies is that a rapid diminution of primary ion kinetic energy occurs during the initial $\sim$100 μs of storage at $\sim 10^{-2}$ Pa, and is accompanied by migration of thermalized secondary ions toward the center of the quistor. Thus one may expect to observe some manifestation of translationally "hot" ions initially and, subsequently, reactions of thermalized ions at longer storage times.

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Crystal and Molecular Structure of 1,4,7-Trithiacyclononane

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Abstract: The crystal and molecular structure of 1,4,7-trithiacyclononane has been determined from a single-crystal X-ray study. The compound crystallizes in the rhombohedral space group $R3c$ with six molecules per unit cell of dimensions (hexagonal axes) $a = b = 12.584$ (3), $c = 9.209$ (2) Å. The observed and calculated densities are 1.41 (1) and 1.42 g cm^{-3}, respectively. Full-matrix least-squares refinement using 252 unique reflections having $4° \le 2\theta \le 50°$ and $I \ge 3\sigma(I)$ converged at $R = 0.0217$ and $R_w = 0.0285$. The compound exists, in the crystalline state, in the C_3 conformation with the sulfur atoms endodentate. The transannular S–S distance is 3.45 Å.

The conformation adopted by all of the crown thioethers[1] as yet studied by X-ray crystallographic methods (1,4,7-trithio(12-crown-4),[2] 1,4,8,11-tetrathio(14-crown-4),[3] 1,4-dithio(15-crown-5),[2] and 1,10-dithio(18-crown-6))[2] is one in which all of the sulfur

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