Experimental Section

The esr spectrometer employed, the apparatus used to generate elevated temperatures and to measure the sample temperature, and the sample preparation technique have been described elsewhere.[6c,d]

Purification of the bitropenyl used in this work was accomplished by column chromatography (Merck alumina) using *n*-pentane as eluent, followed by recrystallization from *n*-pentane and then sublimation.

An approximate measurement of the density of bitropenyl as a function of temperature was required for the analysis leading to $\Delta H°$ and was therefore made. A known weight of bitropenyl was added to a section of a graduated 1-ml pipet which was sealed at one end. The volume of the bitropenyl was measured at various temperatures in the range 80–140°.

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Chemical Ionization Mass Spectrometry. IX. Temperature and Pressure Studies with Benzyl Acetate and *t*-Amyl Acetate

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Abstract: The chemical ionization mass spectra of benzyl acetate and *t*-amyl acetate have been determined as a function of the mass spectrometer ionization chamber temperature and the pressure in the ionization chamber of the esters. Most of the runs were made using $i\text{-}C_4H_{10}$ as reactant, but some measurements were made using CH_4 as reactant. The results obtained in the study are the following. (A) As a check on the apparatus and method, measurements were made of the $H(H_2O)_2^+\text{-}H(H_2O)_3^+$, $H(H_2O)_3^+\text{-}H(H_2O)_4^+$, and $H(H_2O)_4^+\text{-}H(H_2O)_5^+$ equilibria in the gaseous water ionic system. Thermodynamic values in good agreement with the results of Kebarle, *et al.*,[9] were obtained for 3,4 and 4,5 equilibria. (B) Ion intensities in $i\text{-}C_4H_{10}$ are presented for pressures of $i\text{-}C_4H_{10}$ between 0 and 1.0 Torr. At pressures above about 0.6 Torr, $t\text{-}C_4H_9^+$ comprises about 95% of the total ionization of the compound. (C) Mass spectra of the two esters with $i\text{-}C_4H_{10}$ as reactant are given at low, intermediate, and high source temperatures. The spectra of benzyl acetate using CH_4 as reactant is given at two temperatures. Extensive changes in the spectra occur as the temperature is changed when $i\text{-}C_4H_{10}$ is reactant. Several equilibria are observed at lower temperatures, and extensive amounts of dissociation occurs at high temperatures. With CH_4 as reactant extensive dissociation is observed at both temperatures studied. (D) Residence times under chemical ionization conditions (reactant = $i\text{-}C_4H_{10}$, $P_s = 0.70$ Torr) are calculated and tabulated for the several ions investigated. An equation for calculating rate constants for unimolecular ionic decompositions occurring under chemical ionization conditions is given. (E) Rate constants for the formation of benzyl ion and *t*-amyl ion from protonated benzyl acetate and protonated *t*-amyl acetate determined at various temperatures. The activation energies and log *A* values for benzyl ion production are 12.3 kcal/mole and 11.2, and for production of *t*-amyl ion the values are 12.4 kcal/mole and 12.4. The relative magnitudes of the activation energies are tentatively identified with the relative energies of the charged centers in the carbonium ions, and it is suggested that the technique may comprise a useful new method for obtaining relative energies of gaseous ions. The lower *A* factor for the formation of benzyl ion is rationalized in terms of the postulate of the formation of a torsional vibration in the $C_6H_5\text{–}CH_2$ bond in the transition state of the reaction. (F) Equilibrium reactions are observed in the formation of the following ions: the protonated dimers of the two esters, the association complexes between the protonated ester molecules and residual water in the mass spectrometer, and the association complex between benzyl acetate and $C_3H_3^+$. The usual thermodynamic quantities are calculated from the equilibria. The entropies obtained for all these reactions are much higher than would be expected for association reactions, and the entropy change for the formation of the protonated dimer of benzyl acetate has the astonishingly high value of +14 eu. (G) The effect of repeller voltage on the chemical ionization spectrum of benzyl acetate was investigated. Dissociation processes increase with increasing repeller voltage, but one finds that a tenfold increase in repeller voltage has about the same effect in increasing the benzyl ion intensity as a 10% increase in temperature. (H) The pressure of benzyl acetate in the ionization chamber was varied, and a rate constant for the over-all reaction of ions from $i\text{-}C_4H_{10}$ with benzyl acetate was determined. Investigations were made at two temperatures (99 and 178°). The values obtained are 5.1×10^{-9} (99°) and 3.2×10^{-9} cc/(mol sec) (178°). These values are in reasonable agreement with theoretical values which can be calculated for ion–permanent dipole reactions. (I) Rate constants for the total reaction of ions from $i\text{-}C_4H_{10}$ and CH_4 with the two esters at various temperatures have been determined. A strong negative temperature coefficient for the rate constant obtained in the $i\text{-}C_4H_{10}$–benzyl acetate system is observed, and extraordinarily large values of the rate constants are observed for all the systems.

We have observed that the temperature of the ion source can have a profound effect upon the chemical ionization mass spectra of substances, and this paper is a report of a study of the phenomenon. We also include the results of pressure studies which were carried out in conjunction with the temperature studies. The compounds investigated were benzyl acetate and *t*-amyl acetate, and the reactant gases were isobutane and methane.

The effect of temperature upon electron impact mass spectra is well known and reasonably well understood.[1,2] With one outstanding exception, very little work has been done to investigate the effect of temperature on ion–molecule reactions. Schissler and Stevenson[3] mention that for ion–molecule reactions of small hydrocarbon ions with small hydrocarbon molecules a small (but real) negative temperature coefficient is to be observed. In another paper Stevenson and Schissler[4] report that there is no systematic variation in the reaction cross sections for the formation of several hydrides (ArH^+, KrH^+, and D_3^+) in the temperature range 380–600°K. Cassuto[5] reports that the rate constant for the formation of CH_5^+ from methane is independent of temperature and that the reaction has a zero activation energy to within 0.2 kcal/mole. It might be mentioned in passing that many contemporary papers reporting studies of ion–molecule reactions do not contain a statement of the temperature at which the experiments are made; that is to say, temperature is obviously not considered to be a significant variable.

The one exception to the neglect of temperature effects in gaseous ionic chemistry is the important and interesting investigation by Kebarle and coworkers[6–10] of ion–solvent molecule interactions in the gas phase. Using high-pressure (0.1–6 Torr) mass spectrometric techniques, these workers determine the equilibrium constants for various gas-phase ion clustering reactions such as

$$H^+(H_2O)_m + H_2O \rightleftarrows H^+(H_2O)_{m+1} \qquad (1)$$

The equilibrium determinations are made over a range of temperatures from 15 to 600°, and from the equilibrium constants and the temperature coefficients of the equilibrium constants, enthalpies, free energies, and entropies for the various reactions are calculated.

Chemical ionization mass spectrometry is a form of mass spectrometry wherein the ionization of the substance under investigation is affected by reactions between the molecules of the substance and a set of ions which serve as ionizing reactants. The reactant ions are formed from the reactant substance by a combination of electron impact ionization and ion–molecule reactions. A short review paper describing the techniques and containing references of previous work has recently been published.[11]

Experimental Section

The apparatus used for these studies was the Esso chemical physics mass spectrometer described previously.[12,13] The ion source consisted of a volume cut out of a rather massive block of metal, and the temperature of the block was measured by means of a chromel-alumel thermocouple attached to the block approximately 0.25-in. from the ionization chamber volume. Since this thermocouple operates in normal use at the ion accelerating voltage (3000 V), its output was measured by a microammeter which was appropriately insulated from ground. This system was calibrated by measuring the voltage developed by the thermocouple with a millivolt meter and converting to temperature by means of a standard voltage–temperature table. For these calibration determinations, the ion accelerating voltage was not applied. The accuracy of the temperature measurements is estimated to be approximately 1°.

The ionization chamber block was heated by means of electrical heaters and also by heat from the electron-emitting filament. The temperature range which could be covered by the equipment was about 40–275°. When the electron-emitting filament was operated at its usual level, the source temperature rose to approximately 100° with all the other heaters off. Measurements at lower temperatures were made by allowing the machine to cool to room temperature with all power off; the filament was then turned on and measurements were made on the fly as the source warmed up.

We have made experiments which lead us to believe that the temperature of the gas in the ionization chamber corresponded satisfactorily to the block temperature as measured by the thermocouple. Space limitation prevents a discussion of these considerations. It perhaps suffices to mention that with the experimental conditions obtaining the average residence time of a gas molecule in the ionization chamber was 35 msec, and the average number of wall collisions experienced by a molecule before passing out of the ion chamber was 2000.

In these experiments the initial ionization is effected by electron impact, and the ions are pushed out of the ionization chamber by the ion-repeller potential. Normally the repeller was maintained 5.0 V positive with respect to the ionization chamber, which corresponds to a repeller field strength of 12.5 V/cm. The electron current passing through the ionization chamber was not continuously monitored, but it was of the order of 10^{-8} A. The mass spectrometer was equipped with a probe electrode which intercepted part of the total ion current emerging from the ion gun, and the electron current was adjusted to maintain this probe current constant at some predetermined value, usually 5.0×10^{-13} A.

The ion exit slit from the ionization chamber was 0.050 mm wide and 3 mm long. Most of the experiments were carried out using isobutane at a pressure of 0.70 Torr as reactant gas, and if one assumes a cross section of 50×10^{-16} cm^2 for ion–molecule reactions in this gas, one calculates an ionic mean free path of approximately 0.3 mm. This is appreciably larger than the ion exit slit width, and thus the flow of ions and gas molecules out of the ionization chamber is approximately effusive. Kebarle and coworkers[8,9] suggest that under these circumstances one will not encounter ion clustering processes outside the ionization chamber due to cooling by adiabatic expansion.

Some aberrant and initially puzzling behavior of the equipment was observed. We found that the peaks in the spectra corresponding to ions formed from the additive substance by fragmentation processes had accompanying them at low temperatures broad satellite peaks located at slightly lower *m/e* values. Various experiments and considerations which will not be described lead us to conclude that the satellite peaks result from collision-induced decompositions occurring in the ion gun just outside the ionization chamber. We believe that the existence of these peaks does not affect the accuracy of the results.

For quantitative determinations of rate constants and equilibrium constants, it is necessary to know the concentration of additive (benzyl acetate or *t*-amyl acetate) in the ionization chamber. Since the concentration of additive was much smaller than that of reactant gas, its determination was not completely straightforward, and the following technique was devised. The additive was introduced into the reservoir of the mass spectrometer gas-handling system through a gallium-covered frit using a capillary dipper. Then a known, constant pressure of isobutane was added to the reservoir to sweep the additive vapor through the gold-foil leak into the ionization chamber of the mass spectrometer. The isobutane which served as sweep gas produced a pressure in the ionization chamber proportional to the amount of sweep gas in the reservoir. For the usual operating conditions this ionization chamber pressure was approximately 0.020 Torr. It was assumed that the relative amounts of additive and sweep gas passing through the ionization chamber were equal to the relative amounts of these substances in the gas-handling reservoir. The pressure of the sweep gas in the

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(1) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, pp 202–204.

(2) M. Spiteller-Friedman and G. Spiteller, *Ann. Chem.*, **712**, 179 (1968). This is a leading reference for recent work on electron-impact temperature effects.

(3) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

(4) D. P. Stevenson and D. O. Schissler, *ibid.*, **29**, 282 (1958).

(5) A. Cassuto, *Advan. Mass Spectry.*, **2**, 296 (1963).

(6) P. Kebarle and A. M. Hogg, *J. Chem. Phys.*, **42**, 789 (1965).

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(8) A. M. Hogg, R. M. Haynes, and P. Kebarle, *J. Am. Chem. Soc.*, **88**, 28 (1966).

(9) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *ibid.*, **89**, 6393 (1967).

(10) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968).

(11) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(12) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

(13) F. H. Field, *ibid.*, **83**, 1523 (1961).

Table I. Experimental Thermodynamic Values for Ionic Equilibria in H_2O ($P_{H_2O} = 0.50$ Torr)
$H(H_2O)_m^+ + H_2O \rightleftarrows H(H_2O)_{m+1}^+$

		ΔH, kcal/mole		$\Delta G°_{300}$, kcal/mole		$-\Delta S$, cal/(deg mole)		$K_{P_{300}}$	
m	$m+1$	F[a]	K[b]	F[a]	K[b]	F[a]	K[b]	F[a]	K[b]
2	3	20	22.3	10	13.6	31	29	2.3×10^7	5.4×10^9
3	4	16.2 ± 1	17	8.2 ± 0.2	8.5	26.7 ± 3	28.3	8.6×10^5	1.4×10^6
4	5	14.8 ± 1.4	15.3	5.2 ± 1	5.5	31.7 ± 4	32.6	8.8×10^3	1.0×10^4

[a] This work. [b] Kebarle and coworkers, ref 9. [c] Standard state = 1 atm.

reservoir was large enough to be measured with a mercury manometer, and the pressure of additive produced by the introduction of a known volume of liquid additive through the gallium-covered frit was calculated from the known volume and temperature of the gas-handling reservoir. We estimate that the accuracy with which the absolute pressure of additive in the ionization chamber is known is on the order of 10%, and the accuracy of relative pressures was probably better than this by a factor of 2 or 3.

The benzyl acetate used in these experiments was obtained from commercial sources. The *t*-amyl acetate was kindly prepared by Dr. W. C. Baird, Jr., of these laboratories by the acetylation of *t*-amyl alcohol in the presence of pyridine. Both esters were purified by preparative-scale gas chromatography, and no detectable impurities were present in the samples on which the mass spectrometric measurements were made.

Results

A. Water Experiments. A partial investigation of the temperature coefficients of the ionic equilibria in water was made as a check on our technique and apparatus. An extensive study of this system has been made by Kebarle and coworkers,[9] and a comparison of our results with theirs is given in Table I. In gaseous ionized water a series of equilibria are set up

$$H(H_2O)_m^+ + H_2O \rightleftarrows H(H_2O)_{m+1}^+ \qquad (2)$$

The equilibrium constant expressions are

$$K_P(m,m+1) = \frac{I_{H(H_2O)_{m+1}^+}}{(I_{H(H_2O)_m^+})(P_{H_2O})} \qquad (3)$$

In this work the water pressures are expressed in atmospheres. Enthalpies, free energies, and entropies are obtained from the equilibrium constants in the usual way, *i.e.*, enthalpies from van't Hoff plots, free energies from

$$\Delta G° = -RT \ln K_P \qquad (4)$$

and entropies from

$$\Delta S = (\Delta H - \Delta G°)/T \qquad (5)$$

Figure 1 gives a van't Hoff plot and a plot of free energy *vs.* temperature for the 3,4 equilibrium, *e.g.*

$$\underset{m/e\ 55}{H(H_2O)_3^+} + H_2O \rightleftarrows \underset{m/e\ 73}{H(H_2O)_4^+} \qquad (6)$$

In the range of temperature and pressure which could be conveniently covered in our apparatus, the dominant equilibrium was that between $H(H_2O)_3^+$ and $H(H_2O)_4^+$ (the 3,4 equilibrium), and the most reliable results were obtained for this equilibrium. At the lowest temperatures attainable, the next higher equilibrium (4,5) occurred to a measurable extent, and it would appear that reliable results were obtained for this equilibrium even though the temperature range over which it was observed was relatively small. At the highest temperatures attainable the 2,3 equilibrium occurred to an appreciable extent, but the van't Hoff plot for the equilibrium constant exhibited a curvature which suggests that collision-induced formation of $H(H_2O)_2^+$ ions occurred. As an approximation, equilibrium constants and thermodynamic quantities were calculated from the experimental points at the four highest temperatures, and these are included in Table I. $H(H_2O)^+$ ion was observed in the spectrum in small amounts, but its intensity was constant over most of the temperature range studied. A small increase commenced at the highest temperatures attainable. It is clear that this ion was formed predominantly by a collision-induced process, and no thermodynamic quantities can be calculated.

Duplicate determinations of the 3,4 and 4,5 equilibria were made, and the average values and the average deviation from average are given in Table I. In view of the approximate nature of the results for the 2,3 equilibrium, only a single determination was made. The agreement of our values for the 3,4 and 4,5 equilibria with those of Kebarle and coworkers[9] is good. The free energies and equilibrium constants given are those for a temperature of 300°K since these are the values tabulated by Kebarle, *et al.* This temperature lies outside the range covered in our work, and the values were obtained by extrapolations of $\Delta G°$ *vs.* T plots such as that given in Figure 1. The Kebarle, *et al.*, equilibrium constants have been converted to a standard state of 1 atm, which is used in this work. The two equilibrium constants for the 2,3 equilibrium disagree significantly, and this is the consequence of the collision-induced production of $H(H_2O)_2^+$. Even with this difficulty, the agreements of the other quantities are not bad, and the correct trends in the quantities are observed.

We conclude from these results that our technique and apparatus are not subject to systematic error other than the possibility of collision-induced dissociation. It appears that this phenomenon can usually be detected and its effect upon the validity of the accuracy of the results adequately evaluated.

B. High-Pressure Spectrum of Isobutane. The use of methane as a reactant in chemical ionization mass spectrometry has been discussed in previous communications from this laboratory,[11] but nothing has been written concerning the use of i-C_4H_{10} as a reactant. Figure 2 shows the variation with pressure of the relative intensities of the several ions formed in i-C_4H_{10}. The source temperature for these measurements was 175°. Several ions of small initial intensity have been omitted from Figure 2 for the sake of clarity. The most important of these are the $C_2H_3^+$ ion (m/e 27) and $C_2H_5^+$ ion (m/e 29). An investigation of the ionic reactions in i-C_4H_{10} has been reported previously,[14] but the highest pressure utilized was only about 0.15 Torr.

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(14) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

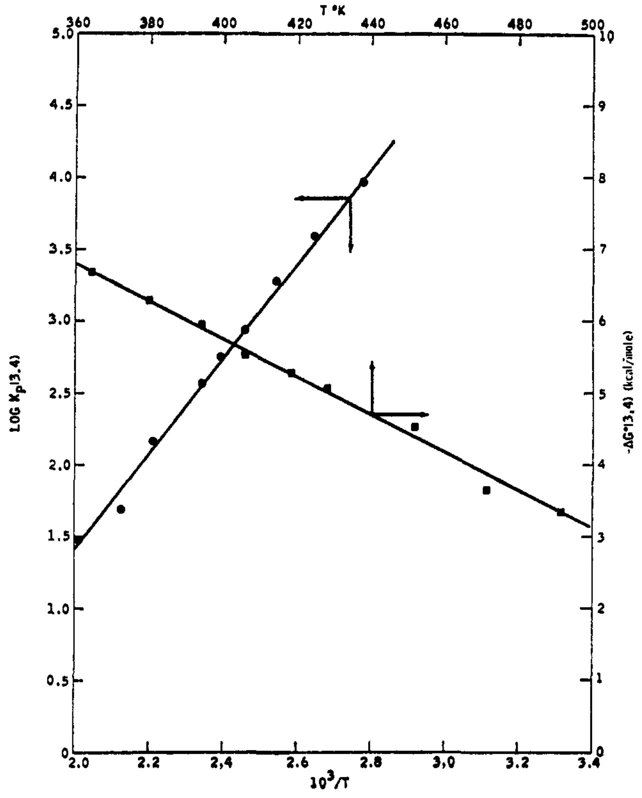

Figure 1. Log $K_P(3,4)$ vs. $1/T$ and $\Delta G°(3,4)$ vs. T. $(H_2O)_3H^+ + H_2O \rightleftharpoons (H_2O)_4H^+$.

The rapid reaction of the various fragment ions to produce the t-butyl ion from i-C_4H_{10} by hydride ion abstraction has been noted previously,[14] and is in keeping with the usual behavior observed in saturated hydrocarbons. A notable exception to this reactivity of the fragment ions is the complete unreactivity of the $C_3H_3^+$ ion (m/e 39) as indicated by its constant relative intensity.

Most of the chemical ionization runs made in the work reported here were carried out at an i-C_4H_{10} pressure of 0.70 Torr, and thus we give in Table II the spectrum of i-C_4H_{10} at this pressure and a source temperature of 175°. Except for the 3% of $C_3H_3^+$ ions present, the spectrum at this pressure is for practical purposes monoionic, consisting of the t-butyl ion, although this is distributed between m/e 57, 58, and 59 because of C^{13} content.

Table II. Relative Intensities in i-C_4H_{10}[a]

m/e	Ion	Ion
39	$C_3H_3^+$	0.032
43	$C_3H_7^+$	0.003
56	$C_4H_8^+$	0.005
57	t-$C_4H_9^+$	0.918
58	t-$C^{13}C_3{}^{12}H_9^+$	0.041
59	t-$C_2{}^{13}C_2{}^{12}H_9^+$	0.001
69	$C_5H_9^+$	$\sim 3 \times 10^{-4}$
71	$C_5H_{11}^+$	$\sim 3 \times 10^{-4}$

[a] $P_{i\text{-}C_4H_{10}} = 0.70$ Torr, 175°.

Experience accumulated in this laboratory so far is that in chemical ionization reactions the t-butyl ion acts predominantly as a relatively mild Brønsted acid.

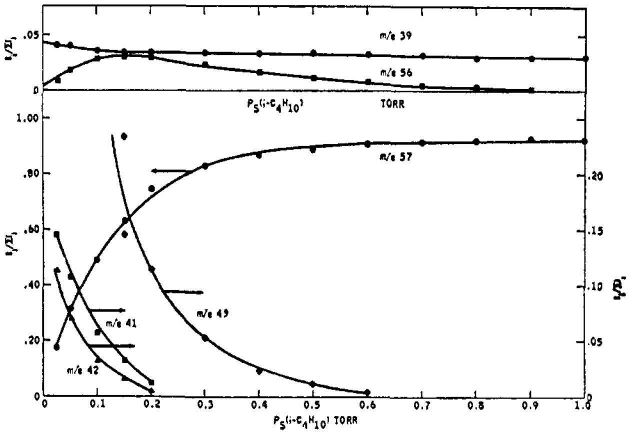

Figure 2. Relative intensities of i-C_4H_{10} ions vs. source pressure (source temperature 175°).

In addition to these, two other chemical ionization reactions can occur with i-C_4H_{10}, and their extent depends upon the identity of the additive substance and the experimental conditions. The t-butyl ion can add to the additive to produce $(MW + 57)^+$ ions, and the $C_3H_3^+$ ions can combine with the additive to produce $(MW + 39)^+$ ions. In our experience so far, the intensities of both of these product ions are invariably small.

C. Mass Spectra of Benzyl Acetate and t-Amyl Acetate. We give in Tables III and IV the chemical ionization mass spectra of benzyl acetate and t-amyl acetate at three ionization chamber temperatures. The reactant gas for these measurements was i-C_4H_{10}. The temperatures chosen lie in the low, intermediate, and high protions of the ranges covered. In Table V we give the chemical ionization mass spectra of benzyl acetate at two temperatures using CH_4 as the reactant gas. From Table III one sees that at the low temperature the dominant ion in the spectrum of benzyl acetate with i-C_4H_{10} reactant is protonated benzyl acetate (m/e 151), and the next most intense ion is the protonated dimer of benzyl acetate (m/e 301). The benzyl[15] ion (m/e 91) is formed by fragmentation of

Table III. Chemical Ionization Mass Spectra of Benzyl Acetate at Three Temperatures[a]

m/e	Ion	Relative intensity at t = 37°	126°	196°
91	$C_7H_7^+$	0.031	0.132	0.773
92	C^{13} isotope	. . .	. . .	0.091
147	?	0.026	0.016	0.055
150	$C_6H_5CH_2OAc^+$ (?)	0.024	0.016	. . .
151	$C_6H_5CH_2OAcH^+$	0.516	0.637	0.082
152	C^{13} isotope	0.061	0.074	. . .
169	$C_6H_5CH_2OAcH \cdot H_2O^+$	0.079	. . .	. . .
189	$C_6H_5CH_2OAc \cdot C_3H_3^+$	0.035	. . .	. . .
301	$(C_6H_5CH_2OAc)_2H^+$	0.175	0.057	. . .
302	C^{13} isotope	0.052	0.016	. . .

[a] Reactant = i-C_4H_{10}, $P_{i\text{-}C_4H_{10}} = 0.70$ Torr, $P_{C_6H_5CH_2OAc} = 4.6 \times 10^{-5}$ Torr, $MW_{C_6H_5CH_2OAc} = 150$.

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[15] In this paper the ion with m/e 91 will be referred to as a benzyl ion. It should not be inferred from this that isomerization to tropylium ion cannot occur. Since the energy of tropylium ion is within 3 kcal/mole of that of benzyl, results and conclusions will not be significantly modified by the occurrence of isomerization.

Table IV. Chemical Ionization Mass Spectra of *t*-Amyl Acetate at Three Temperatures[a]

m/e	Ion	Relative intensity at *t* = 42°	92°	144°
71	t-$C_5H_{11}^+$	0.039	0.541	0.861
72	C^{13} isotope	...	0.030	0.052
79	?	0.029	0.056	0.012
99	?	0.012	...	...
114	?	0.030	...	...
116	?	0.019	...	...
117	?	0.051	0.051	0.017
121	?	...	0.069	0.016
131	t-$C_5H_{11}OAc \cdot H^+$	0.423	0.178	0.032
132	C^{13} isotope	0.037	0.015	0.003
135	?	0.017	...	...
149	t-$C_5H_{11}OAcH \cdot H_2O^+$	0.140	...	...
150	C^{13} isotope	0.012	...	...
191	t-$C_5H_{11}OAcH \cdot HOAc^+$ (?)	0.031	0.018	...
246	?	0.011	...	...
261	t-$C_5H_{11}OAcH \cdot t$-$C_5H_{11}OAc^+$	0.098	...	...
262	C^{13} isotope	0.017	...	...

[a] Reactant = i-C_4H_{10}, $P_{i\text{-}C_4H_{10}} = 0.70$ Torr, $P_{t\text{-}C_5H_{11}OAc} = 5.7 \times 10^{-5}$ Torr, $MW_{t\text{-}C_5H_{11}OAc} = 130$.

Table V. Chemical Ionization Mass Spectra of Benzyl Acetate at Two Temperatures[a]

m/e	Ion	Relative intensity at *t* = 91°	193°
91	$C_7H_7^+$	0.803	0.825
92	C^{13} isotope	0.052	0.066
109	?	0.009	0.015
121	?	0.033	0.043
133	?	0.014	0.013
151	$C_6H_5CH_2OAcH^+$	0.014	0.009

[a] Reactant = CH_4, $P_{CH_4} = 1.00$ Torr, $P_{C_6H_5CH_2OAc} = 4.6 \times 10^{-5}$ Torr, $MW_{C_6H_5CH_2OAc} = 150$.

protonated benzyl acetate. The *m/e* 169 ion is probably the product formed by the reaction of protonated benzyl acetate with the water which is invariably present in small amounts in the mass spectrometer. The *m/e* 189 ion is taken to be the product of the reaction between $C_3H_3^+$ from the i-C_4H_{10} plasma and benzyl acetate. We are unable to write a structure for the ion with *m/e* 147 and a mechanism of formation for the ion with *m/e* 150.

At the intermediate temperature, the protonated benzyl acetate ion still dominates, and in fact its intensity is slightly larger than at the low temperature. The intensities of the ions larger than *m/e* 152 are sharply down, and the intensity of the benzyl ion is up. At the high temperature the benzyl ion dominates the spectrum. We write the following equations for the reactions postulated to be occurring.

$$C_6H_5CH_2OAc + t\text{-}C_4H_9^+ \longrightarrow \underset{m/e\ 151}{C_6H_5CH_2OAcH^+} + C_4H_8 \tag{7}$$

$$C_6H_5CH_2OAcH^+ \longrightarrow \underset{m/e\ 91}{C_6H_5CH_2^+} + CH_3COOH \tag{8}$$

$$C_6H_6CH_2OAcH^+ + C_6H_5CH_2OAc \rightleftarrows \underset{m/e\ 301}{(C_6H_5CH_2OAc)_2H^+} \tag{9}$$

$$C_6H_5CH_2OAcH^+ + H_2O \rightleftarrows \underset{m/e\ 169}{C_6H_5CH_2OAcH \cdot H_2O^+} \tag{10}$$

$$C_6H_5CH_2OAc + C_3H_3^+ \rightleftarrows \underset{m/e\ 189}{C_6H_5CH_2OAc \cdot C_3H_3^+} \tag{11}$$

As the temperature is increased, the rate constant for reaction 8 increases and the intensity of the benzyl ion increases. At the same time the equilibria written in eq 9–11 shift to the left, and in the case of reactions 9 and 10 this gives rise to a higher intensity of protonated benzyl acetate. The intensity of the protonated benzyl acetate thus depends upon the balance between reaction 8, on the one hand, and 9 and 10, on the other.

The spectra of *t*-amyl acetate obtained at three temperatures with i-C_4H_{10} as reactant is given in Table IV. At the low temperature the protonated *t*-amyl acetate ion (*m/e* 131) is the largest in the spectrum, followed by t-$C_5H_{11}OAcH \cdot H_2O^+$ (*m/e* 149) and the protonated dimer (*m/e* 261). The spectrum contains a number of ions for which either the structure or the mode of formation is not apparent. The intensities of these are small. As the temperature is increased the intensity of the *t*-amyl ion grows at the expense of the higher mass ions. Note that the growth of the *t*-amyl ion occurs at appreciably lower temperatures than the growth of benzyl ion (Table III).

We postulate that the following reactions occur in the chemical ionization of *t*-amyl acetate with isobutane as reactant.

$$t\text{-}C_5H_{11}OAc + t\text{-}C_4H_9^+ \longrightarrow \underset{m/e\ 131}{t\text{-}C_5H_{11}OAcH^+} + C_4H_8 \tag{12}$$

$$t\text{-}C_5H_{11}OAcH^+ \longrightarrow \underset{m/e\ 71}{t\text{-}C_5H_{11}^+} + CH_3COOH \tag{13}$$

$$t\text{-}C_5H_{11}OAcH^+ + t\text{-}C_5H_{11}OAc \rightleftarrows \underset{m/e\ 261}{t\text{-}C_5H_{11}OAcH \cdot t\text{-}C_5H_{11}OAc^+} \tag{14}$$

$$t\text{-}C_5H_{11}OAcH^+ + H_2O \rightleftarrows \underset{m/e\ 149}{t\text{-}C_5H_{11}OAcH \cdot H_2O^+} \tag{15}$$

The effect of increasing temperature is analogous to that discussed for benzyl acetate.

As a matter of interest we have run and give in Table V the chemical ionization mass spectra of benzyl acetate obtained using CH_4 as reactant. Measurements were made at two source temperatures. One observes that the benzyl ion has by far the largest intensity at both temperatures, and the intensity of this ion produced by methane at 91° is much greater than the intensity produced by i-C_4H_{10} at 126°. This is the consequence of the fact that the Brønsted acid strength of CH_5^+ is much greater than that of t-$C_4H_9^+$. For the same reason the effect of temperature on the methane spectrum is minimal: so much dissociation is effected by the chemical energy of CH_5^+ that the addition of thermal energy (at least in this range of temperature) has only a minor effect.

D. Rate Constant and Residence Time Calculations. We have postulated that the chemical ionization of benzyl acetate and *t*-amyl acetate by isobutane involves a sequence of reactions which begins with the protonation of the ester. The other ions in the spectra are considered to be produced by subsequent reactions of the protonated ester, which may be decomposition or association reactions. The $(MW + 39)^+$ ions which are sometimes observed in our spectra are not formed from the protonated esters, but the intensities of the $(MW + 39)^+$ ions are always quite small. The reactant ion is taken to be t-$C_4H_9^+$, which is an approximation. One may deduce from Figure 2 that in the near proximity of the electron beam proton-transfer reactions from ions other than t-$C_4H_9^+$ are possible, but in our experience with chemical ionization mass spectrometry we have never had occasion to suspect that such reactions had a detectable effect upon the results. Thus we suggest that in benzyl acetate reaction 7 occurs initially followed by reactions 8, 9, and 10. Reaction 11 occurs concurrently and independently. Analogous reactions occur with *t*-amyl acetate. We undertake to treat the kinetics of these reactions quantitatively.

The *t*-butyl reactant ions are formed in the near vicinity of the electron beam, and they drift to the ion exit slit of the ionization chamber under the influence of the repeller field. Protonated ester molecules are formed along the path of the *t*-butyl ions by proton-transfer reactions, and calculations show that the distribution of the points of formation of the protonated ester ions between the electron beam and the ion exit slit deviates from being uniform by only about 1%; that is, the amount of reaction of the $t\text{-}C_4H_9^+$ ions is small enough that the exponential decay in its concentration deviates from linearity by only a very small amount.

After formation the protonated ester ions drift toward the ion exit slit under the influence of the repeller field, and they also undergo decomposition reactions. These may be looked upon as a set of parallel, competing first-order reactions, that is

$$\text{ROAcH}^+ \xrightarrow{k_i} \begin{cases} P_1^+ + F_1 \\ P_2^+ + F_2 \\ \vdots \\ P_i^+ + F_i \end{cases} \qquad (16)$$

where P_i = *i*th product ion.

The ROAcH^+ ions decay according to the first-order equation

$$(\text{ROAcH}^+)/(\text{ROAcH}^+)_0 = e^{-\sum_i k_i t} \qquad (17)$$

We noted above that as a good approximation the ROAcH^+ ions are initially distributed uniformly over the distance between the electron beam and the ion exit slit. We calculate the average decomposition of ROAcH^+ where the average is taken over the time τ required for an ROAcH^+ ion to drift from the electron beam to the ion exit slit. Thus we write

$$I_{\text{ROAcH}^+}/I^0_{\text{ROAcH}^+} = \overline{(\text{ROAcH}^+)/(\text{ROAcH}^+)_0} = \int_0^\tau e^{-\sum_i k_i t}\text{d}t \Big/ \int_0^\tau \text{d}t \qquad (18)$$

On evaluating the integral in 18 one obtains

$$I_{\text{ROAcH}^+}/I^0_{\text{ROAcH}^+} = (1 - e^{-\sum_i k_i \tau})/\sum_i k_i \tau \qquad (19)$$

We take as $I^0_{\text{ROAcH}^+}$ the sum of the intensities of all the ions formed from ROAc, with the exception of the $(\text{MW} + 39)^+$ ion.

The quantity $\Sigma_i k_i \tau$ is obtained from the experimental values of $I_{\text{ROAcH}^+}/I^0_{\text{ROAcH}^+}$ by solving (19) using an iterative technique. The rate constant is obtained if one knows τ (see below). In turn the rate constants for the formation of the product ions P_i are obtained from

$$k_i = (I_{P_i^+}/\sum_i I_{P_i^+}) \sum_i k_i \qquad (20)$$

Since the pressure in the ionization chamber is 0.70 Torr, the ions undergo many collisions in passing out of the ionization chamber, and ion mobility considerations must be invoked to calculate residence times τ. The monograph by McDaniel[16a] was used as the guide to these considerations, and occasional reference was also made to the monograph of Loeb.[16b] Several different methods can be utilized to calculate ionic mobilities, but it was inferred from the discussion given by McDaniel that the complete Langevin equation is the most suitable (ref 16a, pp 432 ff). Consequently we have used this equation in our work to calculate mobilities. The reader is referred to McDaniel's book for a statement of the equation and its use, and we shall restrict comments here to the aspects of the problem specific to our work. The dielectric constant of $i\text{-}C_4H_{10}$ was taken from the "Handbook of Chemistry and Physics."[17] The term D_{12}, the sum of the radii of the ion and molecule, needed to obtain the Hasse function was approximated by scaling from Dreiding models. Obviously the value used for an unsymmetrical entity such as the protonated benzyl acetate ion constituted much of a guess. Fortunately, this term does not very strongly affect the value of the mobility obtained. The expression for the mobility contains the term $(\rho(K - 1))^{1/2}$ where ρ is the density and K is the dielectric constant of the gas through which the ion travels. Both of these terms are inversely proportional to temperature, and this dependence was taken into account in calculating mobilities at different temperatures.

For purposes of comparison, the residence time of $t\text{-}C_4H_9^+$ in the ionization chamber assuming it to be formed in the electron beam was calculated using several different procedures. The source conditions taken were 423°K, $P_i = C_4H_{10} = 0.70$ Torr, and repeller field strength = 12.5 V/cm. The collision cross section for $t\text{-}C_4H_9^+$ with $i\text{-}C_4H_{10}$ was assumed to be 50×10^{-16} cm^2. The residence times obtained are given in Table VI. The Langevin (complete) and Wannier (high-field) techniques are described in McDaniel[16a] on pp 432 ff and 439, respectively. The Langevin (hard-sphere) calculation was taken from Loeb,[16b] p 42. In the multiple-collision technique the mean free path was calculated from kinetic theory, which in turn gave the number of collisions that $t\text{-}C_4H_9^+$ ion experienced between the electron beam and the ion exit slit. The time between collisions was calculated from the usual free flight expression

$$\tau = (2dm/eE)^{1/2} \qquad (21)$$

and the total residence time was obtained by multiplying this time by the total number of collisions. Finally, as a matter of interest, the free flight residence time (that is, assuming no collisions to occur) was calculated from

Table VI. Calculated Residence Times of $t\text{-}C_4H_9^+$

Method of calculation	τ, sec
Langevin (complete)	1.02×10^{-5}
Langevin (hard sphere)	7.9×10^{-6}
Wannier (high field)	5.6×10^{-6}
Multiple collision	6.2×10^{-6}
Free flight	1.4×10^{-6}

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(16) (a) E. W. McDaniel, "Collision Phenomena in Ionized Gases," John Wiley and Sons, Inc., New York, N. Y., 1964; (b) L. B. Loeb, "Basic Processes of Gaseous Electronics," University of California Press, Los Angeles, Calif., 1961.

(17) "Handbook of Chemistry and Physics," 47th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1966.

eq 21. The agreement between the first four values is such as to lead one to believe that residence times based on any of these methods will have at least a factor of 2 accuracy. Rate constants calculated from the complete Langevin treatment, our method of choice, may probably be looked upon as lower limits to the correct values.

The residence time values used are given in Table VII. These are the times for the ion to drift from the electron beam to the ion exit slit, $d = 0.20$ cm. Temperatures (T) are in °K.

Table VII. Residence Times of Ions

Ion	Gas (pressure, Torr)	τ, sec
$C_7H_7OAcH^+$	i-C_4H_{10} (0.70)	$829 \times 10^{-5}/T$
t-$C_5H_{11}OAcH^+$	i-C_4H_{10} (0.70)	$1040 \times 10^{-5}/T$
t-$C_4H_9^+$	i-C_4H_{10} (0.70)	$433 \times 10^{-5}/T$
$CH_5^+ + C_2H_5^+$ [a]	CH_4 (1.0)	$1860 \times 10^{-5}/T$[b]

[a] Assumed to be present in equal amounts. [b] Average for the two ions.

E. Rate Constants and Activation Energies for the Formation of Benzyl and t-Amyl Ions.

Table VIII contains the activation energies, logarithms of frequency factors, and rate constants at 373°K for the reactions producing the benzyl ion (reaction 8) and the t-amyl ion (reaction 13). Five replicate runs were made for each compound. Rate constants were calculated from eq 19 and 20. Arrhenius plots were made for each compound using the combined data from all of the replicate runs. These plots are given in Figure 3. The lines drawn through the points were obtained from a least-squares treatment of the data, and the values tabulated in Table VIII are obtained from the lines. The uncertainties given for the activation energies correspond to twice the standard errors in the slopes of the least-squares lines.

Table VIII. Kinetic Quantities for Formation of $C_7H_7^+$ and t-$C_5H_{11}^+$

Ion	Activation energy, kcal/mole	Log A	k_{373}, sec^{-1}
$C_7H_7^+$	12.3 ± 0.9	11.2	1.0×10^4
t-$C_5H_{11}^+$	12.4 ± 0.9	12.4	11×10^4

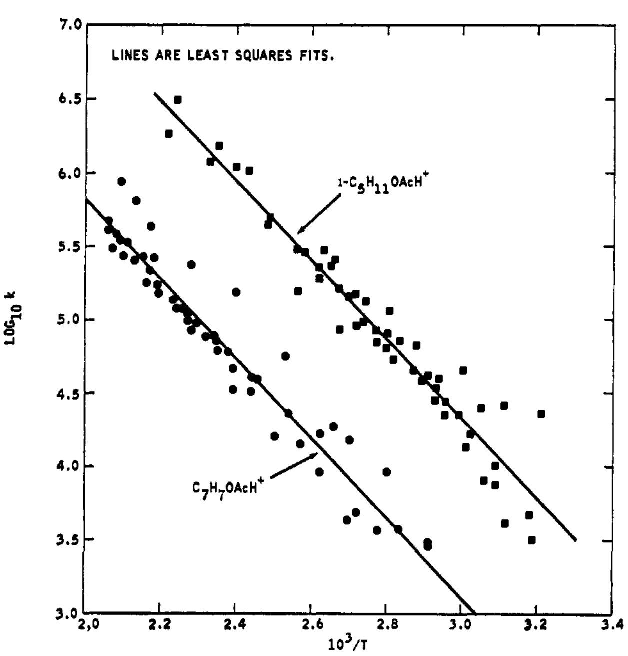

Figure 3. Log k *vs.* $1/T$ for $C_7H_7OAcH^+ \rightarrow C_7H_7^+ + HOAc$ and t-$C_5H_{11}OAcH^+ \rightarrow t$-$C_5H_{11}^+ + HOAc$.

An approximate thermochemical analysis of the reactions can be made as follows. We are not aware of any measurement of the proton affinities of esters, but from the proton affinities of formic, acetic, and propionic acids given by Munson and Franklin,[18] and the proton affinities of water and methanol given by Munson,[19] we estimate the proton affinity of esters to be approximately 195–200 kcal/mole. In this approximation the proton affinity is assumed to be independent of the hydrocarbon groups of the molecule. Then using the published ionic heats of formation[1] we calculate the following energies.

$$RCOOR' + t\text{-}C_4H_9^+ \longrightarrow RCOOR'H^+ + i\text{-}C_4H_8 \qquad \Delta H = -(8 \text{ to } 13) \tag{22}$$

$$C_7H_7OOCCH_3 + t\text{-}C_4H_9^+ \longrightarrow C_7H_7^+ + CH_3COOH + i\text{-}C_4H_8 \qquad \Delta H = +7 \tag{23}$$

$$t\text{-}C_5H_{11}OOCCH_3 + t\text{-}C_4H_9 \longrightarrow t\text{-}C_5H_{11}^+ + CH_3COOH + i\text{-}C_4H_8 \qquad \Delta H = +3 \tag{24}$$

These energies are not very exact, but they indicate that the initial proton transfer from the t-$C_4H_9^+$ ion to produce the protonated ester is exothermic, but the over-all reactions to produce benzyl ion and t-amyl ion are endothermic. This is in accordance with our finding that thermal energy must be added to the system to form the benzyl and t-amyl ions.

We postulate that the activation energies measured in this work correspond to the differences between the energies of the protonated esters and the dissociation asymptotes producing the benzyl or t-amyl ions. According to eq 24 the protonated ester is initially formed with several kilocalories/mole of excess energy, but we suggest that thermal equilibrium is rapidly established. Then the activation energy will be a measure of the energy difference between the equilibrium energy state of the protonated ester and the dissociation asymptote. We think it reasonable to assume that protonation giving rise to fragmentation of the R–O bond in the ester will occur on the carbalkoxy group, and to the extent that the proton affinities of different esters are the same, the activation energies for the reactions producing fragment ions will reflect the energies of the fragment ions. We believe that the proton affinities of esters will not differ significantly, and we tentatively postulate that the differences in the activation energies will be equal to differences in energies associated with the charged centers. It is quite clear that the reactions producing benzyl ion

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[18] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

[19] M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).

and *t*-amyl ion are analogous to $\mathrm{A_{AL}1}$ acid-catalyzed solvolysis reactions in solution, and we suggest that the significance of the activation energy in the gas-phase chemical ionization process is identical with that of the activation energy in the solvolysis. Of course, one expects that the energy relationships in the gas phase will be more straightforward because of the absence of interactions with solvent. To the extent that these assumptions are valid and the expectations are realized, these gas-phase measurements will comprise a valuable addition to the techniques of studying the ionic chemistry of organic systems.

We note from Table VIII that while *t*-amyl ion is produced 11 times more rapidly than benzyl ion, this is completely the result of a larger *A* factor, for within the experimental error the activation energies are equal. This difference in rates is in agreement with the relative rates of solvolysis of compounds containing a tertiary alkyl group and the benzyl group. For example, Streitwieser[20] tabulates the relative rates of solvolysis of $t\text{-}C_4H_9Cl$ and $C_6H_5CH_2Cl$ in a number of different solvents, and the benzyl solvolysis is slower than that of the *t*-butyl by a factor which ranges from 0.082 to 1.7×10^{-4} depending on the identity of the solvent. One infers that the reason for this behavior is generally thought to be that the energy required to form the benzyl carbonium ion is greater than that to form a tertiary alkyl carbonium ion. In view of this, the equality of activation energies found to our gas-phase reactions is surprising, and thus we consider known gas-phase ionic energies, although these are of rather low accuracy. We calculate the group equivalent values for the $(\text{-}CH_2^+)_{Bz}$ and $\geqslant C^+$ groups. In the first of these the group is attached to a phenyl; that is, the group being considered is the benzyl ion group. We obtain the values $\Delta H_F(\text{-}CH_2^+)_{Bz} = 198$ kcal/mole and $\Delta H_f(\geqslant C^+) = 200$ kcal/mole. We conclude that within the accuracy of the values (probably 2–5 kcal/mole) no difference exists between $\Delta H_f(\text{-}CH_2^+)_{Bz}$ and $\Delta H_f(\geqslant C^+)$. The difference in activation energies obtained from our rate study is effectively equal to this difference in ΔH_f values, and thus the two methods for obtaining the energies of the gaseous ions are in good agreement.

These results indicate that the formation of benzyl ions and *t*-amyl ions by heterolytic fission of C_7H_7X and $t\text{-}C_5H_{11}X$ compounds in the gas phase requires equal energies, and the equality probably applies to the formation of other tertiary carbonium ions as well. The difference in rates observed in condensed phase may tentatively be ascribed to other effects such as solvent interactions, entropy effects, etc.

From Table VIII one sees that the preexponential factors for the formation of the two ions in the gas phase differ by about a factor of 10, with the benzyl factor lower. This difference can be accounted for nicely in terms of an explanation taken from Benson.[21] In the ground state of protonated benzyl acetate free rotation of the phenyl group around the $C_6H_5CH_2$ bond can occur, but in the activated state for the formation of $C_6H_5CH_2^+$, overlap of the developing π orbital on the $^-CH_2^+$ group with with phenyl π orbitals will convert this free rotation into a torsional vibration. The resulting decrease in entropy of the activated state reduces the *A* factor for the reaction below that encountered in a system where π overlap of this sort does not occur, *e.g.*, the *t*-amyl acetate system. Benson gives values of $\log A = 14.6$ for

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5CH_2\cdot + CH_3 \tag{25}$$

and $\log A = 14.9$ for

$$C_6H_5CH_2C_2H_5 \longrightarrow C_6H_5CH_2\cdot + C_2H_5 \tag{26}$$

These are to be compared with the average value $\log A = 16$ for neutral bond fission reactions not involving π-overlap restrictions. The difference of 1.1–1.4 in $\log A$ is essentially equal to the difference of 1.2 in the $\log A$ values for the formation of *t*-amyl ion and benzyl ion, and one concludes that the same phenomenon is involved.

The postulate that ionic energies can be identified with the activation energies obtained from the temperature coefficients of chemical ionization mass spectra must be tested by experiments with more compounds before it can be completely accepted. However, the results obtained in this work are encouraging. In prospect, the method appears to be one of some generality and one which has the advantage of providing relative gaseous ion energies with accuracies on the order of tenths of 1 kcal/mole. Such accuracy would permit the use of the gaseous ion energies in condensed-phase chemical problems much more subtle than is presently the case. It is of importance that this method of obtaining ion energies is not an impact method and Franck-Condon restrictions do not apply. Finally, it appears that information about entropy effects in gaseous ionic reactions may be attainable.

F. Equilibrium Reactions in Benzyl Acetate and *t*-Amyl Acetate. In section C it was postulated that the chemical ionization of benzyl acetate and *t*-amyl acetate with $i\text{-}C_4H_{10}$ as reactant involved several gaseous ionic equilibria; namely, the formation of protonated dimers (reactions 9 and 14), the formation of association complexes between the protonated esters and water (reactions 10 and 15), and the formation of an association complex between benzyl acetate and $C_3H_3^+$ (reaction 11). The analog of this reaction does not seem to occur in *t*-amyl acetate. The reason for postulating the existence of these equilibria is that the intensities of the product ions (for example, the protonated dimer ions) exhibit a decrease in intensity as the temperature is increased. This behavior is most easily explained by postulating the existence of an equilibrium. Secondly, a study wherein the pressure of benzyl acetate was varied showed that the intensities of protonated monomer, protonated dimer, and benzyl acetate pressure defined an equilibrium constant. Finally, the temperature variation of the equilibrium constant followed the van't Hoff relationship. The equilibrium constant for the formation of protonated benzyl acetate dimer (reaction 9) may be written as

$$K_P = \frac{760\, I_{H(BzAc)_2^+}}{P_{BzAc}\, I_{HBzAc^+}} \tag{27}$$

where P_{BzAc} = pressure of benzyl acetate in Torr, $I_{H(BzAc)_2^+}$ = intensity of protonated benzyl acetate dimer ions, and I_{HBzAc^+} = intensity of protonated benzyl acetate monomer ions. Plots of this quantity

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[20] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 42.

[21] S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968, pp 69–72.

Table IX. Experimental Thermodynamic Values for Ionic Equilibria in Benzyl Acetate and *t*-Amyl Acetate

Reaction[a]	$-\Delta H$, kcal/mole	$-\Delta G^\circ_{300}$, kcal/mole	$-\Delta S$, cal/(deg mole)	$K_{P_{300}}$[b]
$HBzAc^+ + BzAc \rightleftarrows H(BzAc)_2^+$	5.4 ± 1.1	9.7	−14 ± 3	1.12×10^7
$HAmAc^+ + AmAc \rightleftarrows H(AmAc)_2^+$	9.1 ± 1.5	9.8	−2 ± 5	1.35×10^7
$HBzAc^+ + H_2O \rightleftarrows HBzAc{\cdot}H_2O^+$	13.7	10	12	3×10^7
$HAmAc^+ + H_2O \rightleftarrows HAmAc{\cdot}H_2O^+$	13.8	10	12	3×10^7
$C_3H_3^+ + BzAc \rightleftarrows BzAc{\cdot}C_3H_3^+$	~10	~10	~−7	$\sim 9 \times 10^6$

[a] BzAc = benzyl acetate, AmAc = *t*-amyl acetate. [b] Standard state = 1 atm.

as a function of the pressure of benzyl acetate in the ionization chamber are given for two temperatures in Figure 4.

Equilibrium constants have been calculated for the several equilibrium reactions using expressions analogous to eq 27. Exact values of the equilibrium constant cannot be calculated for the reactions producing the association complexes between water and the protonated esters (reactions 10 and 15), for the pressure of water in the mass spectrometer is not known. As was mentioned earlier, the water involved in the reaction is residual water in the mass spectrometer. We guess that the water pressure in the instrument is not larger than the pressure of the esters used in the temperature studies, and thus we have calculated equilibrium constants assuming the water pressure to be about 10^{-5} Torr. If the water pressure remains essentially constant, which is a reasonable assumption, reaction enthalpies can be calculated accurately, but free energies and entropies will depend upon the water pressure chosen.

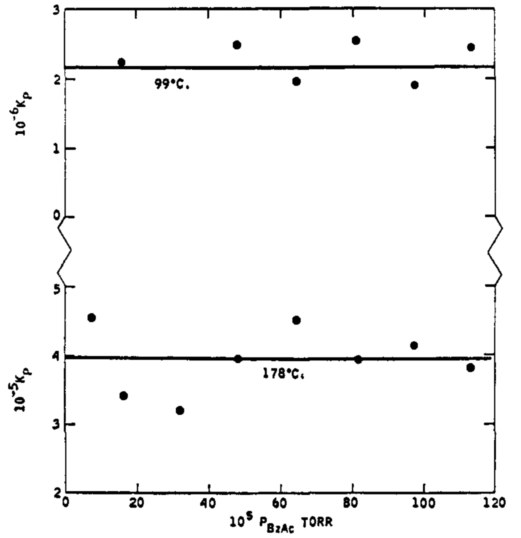

Figure 4. K_P (atm^{-1}) *vs.* P_{BzAc} for $HBzAc^+ + BzAc \rightleftarrows H(BzAc)_2^+$. $P_{i\text{-}C_4H_{10}} = 0.70$ Torr.

For the equilibria producing the protonated dimer ions (reactions 9 and 14), log K_P and $1/T$ values were combined for all the replicate runs (five for each ester), and van't Hoff plots were made for each compound. The lines drawn through the points were obtained from a least-squares treatment of the data, and thermodynamic quantities were calculated from the line. Enthalpies, free energies at 300°K, entropies, and equilibrium constants at 300°K for the five equilibria observed are given in Table IX. The van't Hoff plot for the equilibrium producing protonated *t*-amyl acetate dimer is given for illustration in Figure 5. The uncertainties given for the enthalpies correspond to twice the standard errors in the slopes of the least-squares lines, and the uncertainties in the entropies correspond to the uncertainties in the enthalpies. For the formation of the water association complexes with the protonated ester (reactions 10 and 15), the van't Hoff plot was made from the combined experimental points, but in view of the approximate nature of the value of K_P, the line through the points was decided by eye rather than from a least-squares analysis. The intensities in the formation of the complex between benzyl acetate and $C_3H_3^+$ are small, and the values given for this equilibrium are quite approximate.

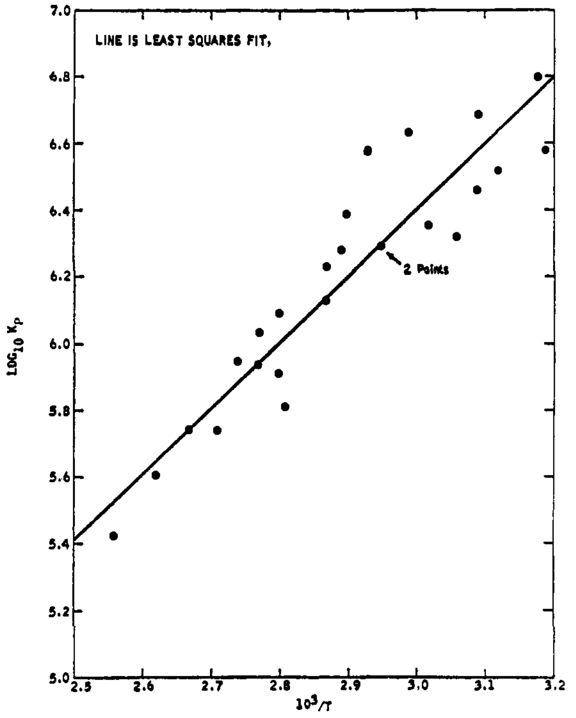

Figure 5. Log K_P *vs.* $1/T$ for $HAmAc^+ + AmAc \rightleftarrows H(AmAc)_2^+$.

The remarkable aspect of these results is the positive ΔS values obtained for the formation of the protonated dimers of benzyl acetate and *t*-amyl acetate and the $BzAc{\cdot}C_3H_3^+$ association complex. As is well known, reaction involving the association of two entities involves the loss of three translational degrees of freedom, which corresponds to an entropy change of −(30–40) eu. Some rotational freedom is also lost. Consequently the over-all entropy change is almost invariably rather strongly negative, and one can observe

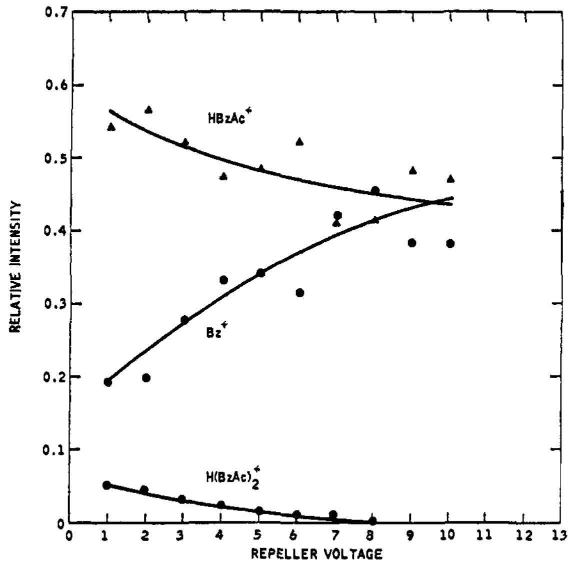

Figure 6. Relative intensities of ions from benzyl acetate *vs.* repeller voltage (source temperature = 153°).

this effect in the entropy values given in Table I for the formation of the several different protonated water complexes. An interesting comparison for neutral species is provided by the dimerization of acidic acid vapor, for which it is reported[22] that K_P at 80° is 27.0, ΔH is -15.3 kcal/mole, and ΔS is -50.0 eu.

In attempting to evaluate the reliability of our results regarding ΔS in the formation of the protonated ester dimers, we should point out that the results are obtained from a number of replicate determinations which exhibited a satisfactory degree of agreement. We think it quite out of the question that the results obtained stem from the occurrence of some kind of random error. It is, of course, harder to decide whether a systematic error is operating, but we think that it is of importance in this regard that with our apparatus and technique some of the equilibria observed have negative entropies. Specifically these are the entropies involved in the protonated water complexes given in Table I and the protonated water–ester complexes given in Table IX. An inspection of these two tables shows that ΔS values ranging over-all from $+14$ to -32 eu have been obtained, and we look upon this as providing some evidence that systematic errors which warp the results strongly in one direction are not in fact present.

We have been unable to discover or conceive of specific errors in these results, and thus we are obliged tentatively to take them as correct. Consequently, we must conclude that an unexpectedly large degree of disorder exists in gaseous protonated benzyl acetate dimer and protonated *t*-amyl acetate dimer. The entropy values given in Table IX suggest that the disorder in the former is slightly greater than that in the latter. By contrast less disorder exists in the protonated water–ester complexes, and from Table I one sees that the least disorder exists in the protonated water complexes. One further sees that as the ΔS values become more negative the ΔH values become more negative. On the surface it would appear that in the formation of these ionic complexes stability can be achieved by trading off entropy effects for enthalpy effects, or conversely.

Until further verification of these very unexpected results are obtained, it is not worthwhile to engage in extensive speculation about their significance. However, we point out that the entropy content of the protonated benzyl acetate dimer is on the order of 40 eu higher than might be expected, and accounting for this in terms of the usual concepts of low vibrational frequencies or the generation of new rotations around bonds does not seem possible. It has occurred to us that a possible explanation might lie in a postulate that the proton in the protonated dimer complex has a very large degree of freedom of movement. We have calculated from the Sackur–Tetrode equation the translational entropy of a free proton in a volume of 1000 Å^3 (a cube 10 Å on a side), and it is perhaps of interest that one obtains a value of $\sim+30$ eu. In rather general terms the concept of a very mobile proton could account for the lower entropy found in the protonated *t*-amyl acetate dimer than in the protonated benzyl acetate dimer, in that the phenyl groups in the latter compound would provide additional attractive centers for the proton. A similar rationale can be made for the still lower entropies found in the formation of the protonated ester–water complexes and for the lowest entropies found in the protonated complexes found in pure water.

G. Ion Repeller Studies. The chemical ionization spectra of benzyl acetate with isobutane was obtained at different ion repeller voltages in the range 1–10 V. The pressure of i-C_4H_{10} was 0.71 Torr, and the source temperature was 153°. The results are given in Figure 6, from which it may be seen that fragmentation processes (*i.e.*, the production of benzyl ion from HBzAc$^+$ and HBzAc$^+$ from H(BzAc)$_2^+$) increase with an increase in repeller voltage. This is quite to be expected, but is perhaps of some interest that a 30-fold increase in the average translational energy of the ions at time of collision (corresponding to the tenfold increase in field strength) produces approximately a doubling of the benzyl ion intensity, but the same increase is achieved by increasing the temperature by $\sim$10%. Thus relatively speaking the collision-induced dissociation of ions is not very large, but it probably occurs to a sufficient extent to account for the satellite peaks discussed in the Experimental Section and attributed to collision-induced dissociation in the near vicinity of the ion exit slit of the ion source. One may also conclude from Figure 6 that the absolute values of rate constants and equilibrium constants obtained in studies such as this will have a parametric dependence upon the magnitude of the repeller voltage, and the values given in this work refer to a source strength of 12.5 V/cm.

H. Pressure Studies. The effect of benzyl acetate pressure on the chemical ionization mass spectrum of benzyl acetate obtained with i-C_4H_{10} has been investigated at two temperatures. As was mentioned earlier, we assume that the reactant ion is $C_4H_9^+$, and it reacts with benzyl acetate to produce a variety of ions which for present purposes can be lumped together and designated as ΣBzAc$^+$, that is

$$t\text{-}C_4H_9^+ + \text{BzAc} \xrightarrow{k_t} \Sigma\text{BzAc}^+ + C_4H_8 \cdot \qquad (28)$$

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[22] M. D. Taylor, *J. Am. Chem. Soc.*, 73, 315 (1951).

Applying the usual pseudo-first-order kinetic considerations to this system, we may write

$$\ln\left(1 - \frac{I_{\Sigma \mathrm{BzAc}^+}}{I^0_{t\text{-}\mathrm{C_4H_9}^+}}\right) = -k_t\tau(\mathrm{BzAc}) \qquad (29)$$

where $I_{\Sigma \mathrm{BzAc}^+}$ = sum of intensities of all ions formed from BzAc, $I^0_{t\text{-}\mathrm{C_4H_9}^+} = I_{t\text{-}\mathrm{C_4H_9}^+} + I_{\Sigma \mathrm{BzAc}^+}$, τ = residence time of t-$\mathrm{C_4H_9}^+$ ions in ionization chamber (calculated from Table VII), and (BzAc) = concentration of benzyl acetate. In Figure 7 we give a plot of the left-hand side of eq 29 against the concentration of benzyl acetate, and from the slope of the line and a value of τ calculated from Table VII one obtains the value $k_t = 3.2 \times 10^{-9}$ cc/(mol sec).

As a matter of interest we have calculated a value for the theoretical rate constant for this reaction. We have not been able to find polarizability and dipole moment data for benzyl acetate, but we do find this information for ethyl benzoate which is isomeric with benzyl acetate and contains essentially the same structural features. The molar refraction of this compound is given[17] as 42.6 cc, and the dipole moment is 2.0 D. From the refraction one calculates a polarizability of 1.71×10^{-23} cc. A clear formulation of the theoretical expressions for the rate constants of ion–molecule reactions involving molecules with permanent dipoles is given by Harrison and coworkers,[23] and following them we write

$$k(g) = 2\pi e\left(\frac{2}{\mu}\right)^{1/2} + (2\pi e\mu_D/g\mu) \qquad (30)$$

where g = velocity of ion, $k(g)$ = rate constant (function of velocity), μ = reduced mass of ion and molecule, μ_D = dipole moment, and the other quantities are as usually defined. To obtain the rate constants, appropriate expressions or values for the ion velocity g must be inserted in eq 30. Two possibilities might have a degree of applicability to the conditions obtaining in this work. First, we may use for g the ion drift velocity as calculated from the Langevin mobility theory (section D), and we obtain

$$g = 2.1 \times 10^4 \text{ cm/sec}$$

$$k_t = 1.5 \times 10^{-9} + 4.1 \times 10^{-9} = 5.6 \times 10^{-9} \text{ cc/(mol sec)} \qquad (31)$$

where the two terms in (31) correspond to the ion–induced dipole and ion–permanent dipole interactions, respectively. Alternatively, an average can be taken over thermal velocities of the ion and molecule, and Harrison, *et al.*, give the expression

$$\left(\frac{1}{g}\right)_T = \left(\frac{2\mu}{\pi kT}\right)^{1/2} \qquad (32)$$

and the use of this in (30) gives for the rate constant at 178° the value

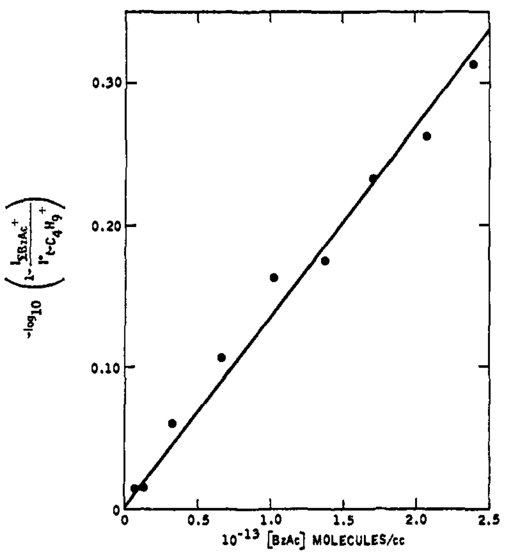

Figure 7. −Log $(1 - I_{\Sigma \mathrm{BzAc}^+}/I^0_{t\text{-}\mathrm{C_4H_9}^+})$ *vs.* benzyl acetate concentration (source temperature 178°).

$$k_t = 1.5 \times 10^{-9} + 2.3 \times 10^{-9} = 3.8 \times 10^{-9} \text{ cc/(mol sec)}$$

The agreement of both calculated values with the experimental value of 3.2×10^{-9} cc/(mol sec) is not bad considering the various uncertainties, and one is tentatively led to think that the rate constant obtained from this pressure study can be accounted for in terms of the usual factors considered to be involved in ion–molecule reactions.

The second temperature at which a pressure study was made was 99°, and from the slope of a plot analogous to Figure 7 and the residence time appropriate to this temperature we calculate a rate constant of $k_t = 5.1 \times 10^{-9}$ cc/(mol sec). Thus the rate constant appears to depend upon temperature, and we shall return to this point later.

As the pressure of benzyl acetate is increased, the spectrum changes. The intensities of ions involved in equilibria change in accordance with the requirements of the equilibrium constant relationships (Figure 4, for example), but in addition to these changes one sees at a source temperature of 178° the growth of the *m/e* 181 ion. This ion grows to approximately 15% of the total benzyl acetate ionization at the highest pressure of benzyl acetate, and its growth is accompanied by corresponding diminution in the intensity of the *m/e* 91 ion. In addition a small amount (about 1% of the total ionization) of the *m/e* 241 ion is formed. In the pressure study at 99° no benzyl ion (*m/e* 91) is formed because of the low temperature, and the spectrum does not contain either the *m/e* 181 or *m/e* 241 ions. From these facts we deduce that the reaction producing the *m/e* 181 ion is

$$\underset{m/e\ 91}{\mathrm{C_7H_7^+}} + \mathrm{C_7H_7OAc} \longrightarrow \underset{m/e\ 241}{\mathrm{C_7H_7 \cdot C_7H_7OAc^+}} \longrightarrow \underset{m/e\ 181}{\mathrm{C_{14}H_{13}^+}} + \mathrm{HOAc} \qquad (33)$$

We suggest the following mechanism for the reaction, which can be looked upon as an analog or example of the well-known thermal pyrolysis reaction of acetate esters.

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[23] S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).

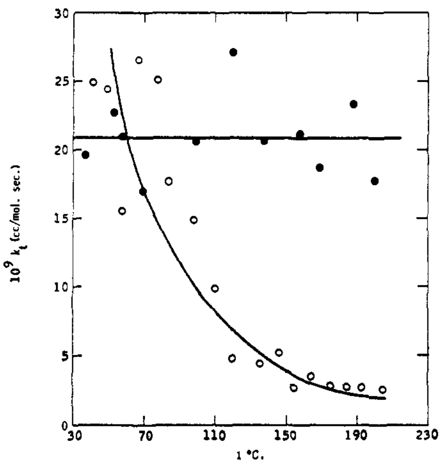
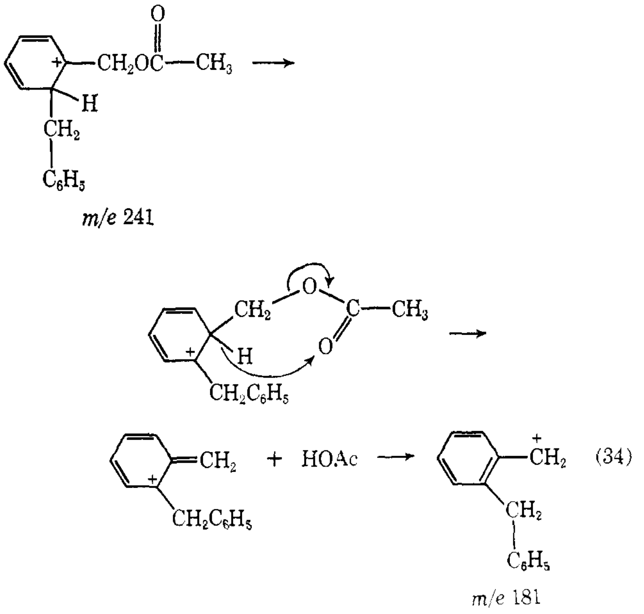


Figure 8. Benzyl acetate total ionization *vs.* temperature. $k_t = -A \log [1 - (\Sigma \mathrm{BzAc}^+/\Sigma \mathrm{total})]$. ○, reactant = $i\text{-}C_4H_{10}$, $A = 1.20 \times 10^{-12}$; ●, reactant = CH_4, $A = 2.78 \times 10^{-12}$.



m/e 241

(34)

m/e 181

We can obtain the rate constant for reaction 33 using equations analogous to eq 18, that is

$$1 - \frac{I_{181}}{I^0_{91}} = (1 - e^{(\mathrm{BzAc})k_{181}\tau_{\mathrm{Bz}^+}})/(\mathrm{BzAc})k_{181}\tau_{\mathrm{Bz}^+} \qquad (35)$$

Equation 35 is solved for $k_{181}\tau(\mathrm{BzAc}^+)$ using the experimental ion intensities by means of an iteration technique. The residence time, τ_{Bz^+}, is calculated from Langevin drift velocity considerations. The values of k_{181} calculated at the several pressures was sensibly constant although random scatter existed. The average value for measurements at nine pressures of benzyl acetate (corresponding to the range of pressures given in Figure 7) is $k_{181} = 3.8 \times 10^{-9}$ cc/(mol sec). The close agreement between this value and the value for k_t, the rate constant for the total ionization of benzyl acetate by $t\text{-}C_4H_9^+$, is to be noted.

Another type of pressure study which was carried out was to vary the pressure of $i\text{-}C_4H_{10}$ while maintaining the pressure of benzyl acetate and the source temperature constant with values of 4.6×10^5 Torr and 172°, respectively. The $i\text{-}C_4H_{10}$ pressure was varied between 0.5 and 1.0 Torr, with measurements being made at 0.1 Torr intervals. The effect of this change in reactant pressure upon the chemical ionization mass spectrum of benzyl acetate was minimal. The insensitivity of the spectrum to the $i\text{-}C_4H_{10}$ pressure is desirable from the point of view of chemical ionization mass spectrometry, for it demonstrates that extreme care concerning the pressure of the reactant gas is not necessary.

I. Effect of Temperature on Total Ionization of Esters. One observes for some systems a very strong effect of temperature upon the total ionization of the ester, that is, for instance, upon $\Sigma\mathrm{BzAc}^+$ as represented in reaction 28. For the $i\text{-}C_4H_{10}$–benzyl acetate system the total ionization of benzyl acetate decreases sharply as the temperature increases, but for the benzyl acetate–CH_4 system the decrease is much smaller. The *t*-amyl acetate-$i\text{-}C_4H_{10}$ system seems to lie between the other two systems and exhibits some variability of results.

The pressure studies discussed in section H lead one to believe that it is reasonable to calculate rate constants for total ionization reactions such as reaction 28, and rate constants have been calculated for the several reactions at different temperatures. The calculations are made using equations such as (29). However, the particle concentration of reactant (benzyl acetate or *t*-amyl acetate) in the ionization chamber will vary with temperature, and because of changes in density the residence time τ will also change with temperature. Thus we have

$$k_t = -AT^2 \log \left(1 - \frac{I_{\Sigma\mathrm{additive}}}{I_{\Sigma\mathrm{total}}}\right) \qquad (36)$$

where the constant A must be evaluated appropriately for each system.

We give in Figure 8 values of the rate constants for the total ionization of benzyl acetate using both $i\text{-}C_4H_{10}$ and CH_4 as reactants. The difference in the variation of the rate constant with temperature in the two systems is remarkable. Equally remarkable is the magnitude of the rate constants obtained with $i\text{-}C_4H_{10}$ at low temperature and with CH_4 at all temperatures. The behavior for *t*-amyl acetate with $i\text{-}C_4H_{10}$ as reactant is not well established. The results scatter much more than do those for benzyl acetate with $i\text{-}C_4H_{10}$, and one cannot decide whether a decrease in the rate constant with the temperature increase is occurring or not. Part of the problem stems from the fact that, because *t*-amyl ions formed more easily than benzyl ion, the runs with *t*-amyl acetate were not carried to temperatures as high as those with benzyl acetate. However, it is established that the rate constant in the *t*-amyl acetate system is on the order of $15\text{–}20 \times 10^{-9}$ cc/(mol sec) at the lower end of the temperature range.

Rate constants with magnitudes on the order of 20×10^{-9} cc/(mol sec) have not previously been reported nor have strong negative temperature coefficients for rate constants. There is no theoretical explanation for either of these observations. From eq 30 and 32 one can expect a $T^{-1/2}$ dependence of rate constant for polar molecules, but this is much weaker than the temperature effect found for benzyl acetate with $i\text{-}C_4H_{10}$. Under these circumstances one must be strongly concerned with the possibility of experimental error. Errors could occur in the pressure determinations and residence time considerations, or result from mass discrimination effects. The calculation of rate constants may not be valid. However, we are unable to think of an error or a combination of errors that is probable enough to warrant suppression of the results. At the same time, prudence dictates that a discussion of their significance be deferred until more experimental results are obtained.

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Effect of Temperature on the Mass Spectra of Benzene at High Pressures

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Abstract: The mass spectra of benzene have been obtained as a function of temperature at pressures of 0.5 and 1.0 Torr. The $C_6H_6^+$ and $(C_6H_6)_2^+$ ions are involved in an equilibrium reaction, and the relative amounts of the two ions present in benzene mass spectra depend on temperature. Equilibrium reactions are also found to occur for several minor ions in the benzene spectrum. Thermodynamic quantities for the equilibria are calculated from the temperature coefficients of the equilibrium constants, and it is found that ΔH and ΔS values for the benzene monomer–dimer equilibrium are -15 kcal/mole and -23 cal/(deg mole), respectively.

Two papers have appeared recently on the ion–molecule reactions occurring in benzene gas at elevated pressures.[2] The two works disagree on one important point, namely, the relative amounts of the monomeric benzene ion ($C_6H_6^+$) and dimeric benzene ion ($(C_6H_6)_2^+$) produced. Field, Hamlet, and Libby[2a] found that only a small amount of dimer ion was formed ($I(C_6H_6^+) = 0.57$ and $I((C_6H_6)_2^+) = 0.021$ at $P_{C_6H_6} = 0.34$ Torr), but Wexler and Clow[2b] observed a much higher production of the dimer ion. Their relative amounts seemed to depend upon the electron energy used, but it appears from their Figure 1 that at 400 V and $P_{C_6H_6} = 0.31$ Torr, $I(C_6H_6^+) \cong 0.20$ and $I((C_6H_6)_2^+) \cong 0.30$. The temperature at which their experiments were made was 122°, whereas ours was 236°. This temperature is mistakenly given as 210° in ref 2a. We show in this paper that the relative amounts of the monomeric and dimeric benzene ions are temperature dependent, and the discrepancy in the results obtained by the two groups of workers is the result of the different temperatures used in the two experiments.

Experimental Section

The Esso chemical physics mass spectrometer[3,4] was used in this work. Its application to the determination of the temperature coefficients of mass spectra, equilibrium constants, and rate constants is described in the accompanying paper.[5] The temperature studies of the benzene spectra were made using several different sets of conditions. For two of the runs the benzene pressure was maintained at 0.50 ± 0.01 Torr. In one of these runs the metastable suppressor electrode of the mass spectrometer was not activated, but for the other run it was maintained at a voltage high enough to suppress most of the ions formed by collision-induced dissociation in the near vicinity of the ion exit slit of the ion source. This collision-induced dissociation phenomenon is discussed extensively in ref 5. In the run without the metastable suppressor applied, the intensities of the *m/e* 78 ions were corrected for the contribution from the collision-induced ions by subtracting the intensities of these ions as determined by a visual inspection. To gain some insight into the possible effect of pressure, a run was made at a benzene pressure of 1.0 ± 0.1 Torr. The metastable suppressor electrode was activated. Finally, a run was made on a mixture of approximately 1.0 Torr of CH_4 and 0.55 ± 0.05 Torr of benzene. The metastable suppressor was also activated for this run.

A run in which the pressure of benzene was varied at a source temperature of 92° was made.

The benzene used was zone-refined material obtained from James Hinton Co., Valparaiso, Fla. Toluene was reagent grade from Baker and Adamson, and methane was research grade from Lif-O-Gen.

Results

The temperature studies consisted of determining the spectra of benzene at a number of ionization chamber temperatures between 60 and 200°. The spectra of benzene at a pressure of 0.50 Torr at three temperatures are given in Table I. Of greatest interest is the fact that the relative magnitudes of the intensities

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(1) (a) Esso Research and Engineering Co.; (b) University of California at Los Angeles; (c) supported in part by the Chemical Directorate of the U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-67-1255A.

(2) (a) F. H. Field, P. Hamlet, and W. F. Libby, *J. Am. Chem. Soc.*, **89**, 6035 (1967); (b) S. Wexler and R. P. Clow, *ibid.*, **90**, 3940 (1968).

(3) F. H. Field, *ibid.*, **83**, 1523 (1961).

(4) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 2621 (1966).

(5) F. H. Field, *ibid.*, **91**, 2827 (1969).