L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, 1960, Chapter 4.

(26) Even if there is no primary isotope effect (i.e., $k_{-1} = k_{-2}$) expression 3 reduces to

$$\frac{-d[\mathbf{9a}]}{dt} = \frac{d[\mathbf{9b}]}{dt} = \frac{k_1[\mathbf{9a}][\mathrm{EtOD}]}{2} = k_{\mathrm{obsd}}[\mathbf{9a}]$$

(27) For β-methoxyacrolein (7) the formyl and hydroxyvinyl protons appear at δ 9.43 and 7.45, respectively (vide supra).

(28) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, Chapter 7.

(29) We find that this exchange process is not strictly first order in malonaldehyde, since, as the concentration of MA is reduced, the coalescence temperature is increased, so that very dilute solutions show considerable broadening of the terminal C–H signals even at 25 °C. Small quantities of acid, Hünigs base, and even solid Na_2CO_3 added to the NMR solution reduce the coalescence temperature and thus the exchange process must be very sensitive to trace catalysis by both acid and base.

Characterization of the Chemical Ionization Condensation Products for the Benzyl Acetate System Using Mass-Analyzed Ion Kinetic Energy Spectrometry

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Abstract: The condensation products resulting from chemical ionization (isobutane reagent gas) of benzyl acetate were characterized using mass-analyzed ion kinetic energy spectrometry (MIKES). These spectra, which provide structural information often lacking in studies on ion-molecule reactions, were obtained by subjecting selected ions to collision-induced dissociation. The benzyl acetate condensation product $C_{14}H_{11}^+$ (179^+) was shown to have the protonated anthracene structure by the identity of its MIKE spectrum with that of the authentic ion, while the $C_{14}H_{13}^+$ (181^+) ion was shown to have a MIKE spectrum identical with that of the 2-benzylbenzyl cation generated from the substituted benzyl alcohol. Other ions in the series $(C_7H_7 \cdot (C_7H_6)_n\text{-}H_2)^+$ as well as in the $(C_7H_7 \cdot (C_7H_6)_n)^+$ series gave spectra which were consistent in detail with the disubstituted phenyl and fused-ring ion structures proposed by Meot-Ner, Hunter, and Field. Both of these classes of ions show characteristic modes of fragmentation, particularly phenyl-methylene bond cleavages with hydrogen transfer. The protonated dimer of benzyl acetate sampled here is, at least in part, a covalent polyether rather than the proton-bound dimer previously proposed. The ion is formed by nucleophilic addition to the protonated acetate and dissociates by simple cleavages with successive losses of acetic acid to yield 241^+ ($C_{16}H_{17}O_2^+$) and 181^+ ($C_{14}H_{13}^+$). The latter is a key intermediate in the formation of the higher condensation products. The observed formation of $C_{14}H_{13}^+$ from the protonated dimer represents a parallel pathway to its formation from the benzyl ion and neutral benzyl acetate as observed in a time-resolved CI study. The key results uncovered by application of MIKES to this system are (1) ion structures have been clarified and (2) the kinetic scheme has been extended.

Chemical ionization mass spectrometry (CIMS) has become a widespread technique both in chemical analysis and in the study of ion-molecule reactions, although much of the complex chemistry in the chemical ionization source is still not well understood.[1-4] One area of ion-molecule chemistry of current concern is that of condensation or polymerization type reactions.[1,5-7] These investigations, in which both positive and negative ion reactions have been studied, are complicated by the paucity of structural information about the product ions.

Using mass-analyzed ion kinetic energy spectrometry (MIKES)[3,8,9] in conjunction with collision-induced dissociation (CID),[9,10] it is possible to probe the structure of these polymeric ions. The MIKES technique has been used extensively in ion structural analysis under several names[3,9-15] and determinations as detailed as the site of protonation have been made.[16] A unique feature of the present study is the interpretation of the chemistry of a system using results from conventional low-energy ion-molecule reactions in conjunction with high-energy MIKES data. The benzyl acetate system was chosen because (1) the system has been the subject of a detailed time-resolved CIMS study,[1] (2) a large number of product ions are generated, (3) an intriguing unassigned metastable peak has been reported.[1]

Experimental Section

All the data reported here were obtained using the MIKES instrument,[8] a reverse-geometry mass spectrometer fitted with a chemical ionization (CI) source. Benzyl acetate, contained in a capillary tube, was introduced via the solid probe into the CI source. Isobutane was used as the reagent gas at a source pressure of approximately 0.5 Torr and a source temperature of 425 K. N_2 was used as the collision gas at an indicated pressure on a Bayard-Alpert gage of 3×10^{-5} Torr. The ion accelerating voltage was 6 kV.

MIKE spectra were obtained by mass selecting ions of interest, having these ions undergo a high-energy collision with the target gas, and then measuring the kinetic energies of the fragment ions by scanning the potential applied to the electrostatic analyzer. An energy resolving slit width of 0.75 mm was used. Spectra are calibrated in terms of ion kinetic energy as a fraction of E, the kinetic energy of the main ion beam, and in terms of fragment ion masses. A typical spectrum was recorded in 7 min, while selected areas of the spectrum were rescanned more slowly to check individual mass assignments.

2-Benzylbenzyl alcohol was prepared by reducing α-phenyl-o-toluic acid with lithium aluminum hydride in anhydrous diethyl ether.[17] The isobutane mass spectrum of the alcohol revealed very little protonated molecular ion, the major ions being 181^+ $[(M + H)^+ - H_2O]$ and 179^+ $[(M + H)^+ - H_2O - H_2]$.

Benzyl-d_3 acetate was prepared from acetyl-d_3 chloride and benzyl alcohol.[18] It had an isotopic purity of d_3 (97%), d_2 (2.9%), d_1 (0.44%) as determined by electron impact mass spectrometry.

Results and Discussion

1. Protonation and Alkylation of Benzyl Acetate. The reactions of benzyl acetate (BzOAc) in CI using isobutane reagent gas are given in Scheme I. Reaction 1 is an example of the well-known CIMS process, simple protonation of the sample molecule by the reagent ion. The work by Meot-Ner, Hunter, and Field[1] suggests that the formation of $C_7H_7^+$ (reaction 2) occurs in competition with the simple protonation

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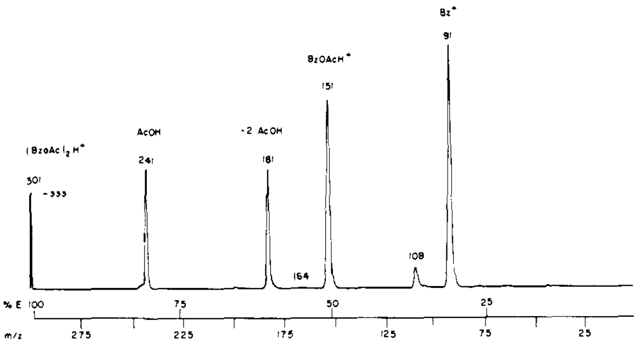


Figure 1. MIKE spectrum of the protonated dimer of benzyl acetate, *m/z* 301. The spectrum records the masses and relative abundances of fragment ions generated from the precursor (301^+) by means of collisions at 6 keV. Elimination of one and two molecules of acetic acid yield the fragments 241^+ and 181^+; these reactions requires the covalently bonded dimer structure (a) rather than a simple proton-bound dimer.

Scheme I. Reactions of Benzyl Acetate in Isobutane CIMS

1) $C_7H_7OAc + t\text{-}C_4H_9^+ \rightarrow C_7H_7OAcH^+ + i\text{-}C_4H_8$

2) $C_7H_7OAc + t\text{-}C_4H_9^+ \rightarrow C_7H_7^+ + (CH_3)_3CO\overset{O}{C}\text{-}CH_3$

3) $C_7H_7OAc + t\text{-}C_4H_9^+ \rightarrow (C_7H_7OAc\cdot t\text{-}C_4H_9)^+$

4) $C_7H_7OAcH^+ + C_7H_7OAc \rightarrow (C_7H_7OAc)_2H^+$

5) $C_7H_7\cdot(C_7H_6)_n^+ + C_7H_7OAc \rightarrow C_7H_7\cdot(C_7H_6)^+_{N+1} + HOAc$ where $n=0\text{-}3$

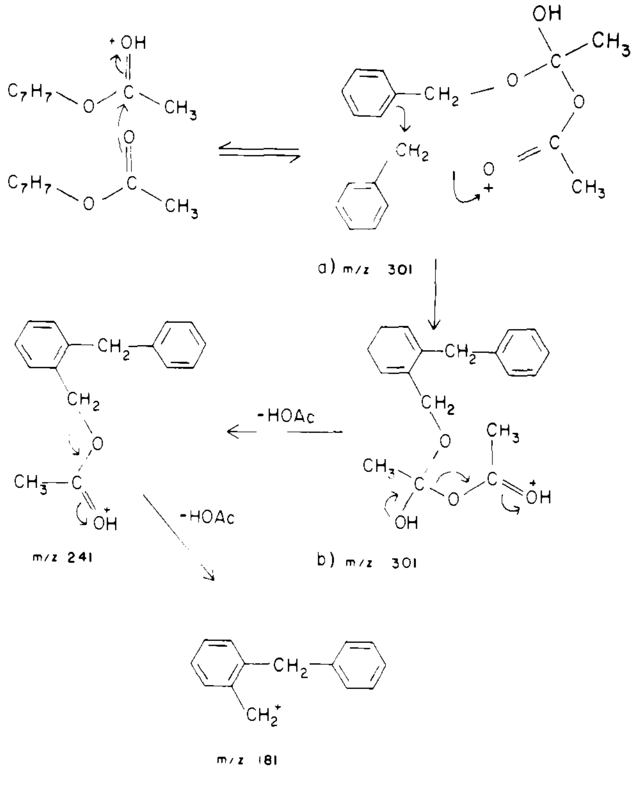
6) $C_7H_7{:}(C_7H_6)_n^+ \rightarrow [C_7H_7\cdot(C_7H_6)_n\text{-}H_2]^+ + H_2$ where $n=1\text{-}3$

of BzOAc.[1] These authors also postulated that the primary ion-molecule encounter results in formation of an addition complex in which the *tert*-butyl cation attaches to the ether oxygen of the acetate group (reaction 3). Fragmentation from this species could lead to either the protonated benzyl acetate, *m/z* 151, or to the benzyl ion, *m/z* 91. The MIKE spectrum of *m/z* 207 corresponding to the proposed (BzOAc-*t*-Bu)$^+$ complex was recorded to check this suggestion. The results tend to support this postulate in that major fragment ions correspond to formation of protonated benzyl acetate (*m/z* 151), the benzyl ion (*m/z* 91), and the *tert*-butyl cation (*m/z* 57). The MIKES data, however, do not exclude the possibility that the $C_7H_7^+$ ion is partly due to fragmentation of protonated benzyl acetate. Moreover, the base peak in the MIKE spectrum of the *tert*-butyl adduct is due to methyl loss, a result which is unexpected if covalent bond formation has not occurred in the adduct.

2. Protonated Dimer of Benzyl Acetate. Attention was next turned to the structure of the protonated dimer of benzyl acetate, the suggested origin[1] of which is given in eq 4 of Scheme I. This species is of particular interest with regard to studies on the use of protonated dimers for the determinations of relative proton affinities[19] and because of the report of a metastable peak which apparently arises from the protonated dimer but which could not be further assigned.[1]

A proton-bound structure is proposed by Meot-Ner et al. for the protonated benzyl acetate dimer, *m/z* 301. From previous studies on unsymmetrical protonated dimers,[19] we have found that the major collision-induced fragmentation process is cleavage at the hydrogen bond(s) to give the protonated base. This was also found to be the case for an amine-diamine protonated dimer which was shown to have bidentate bonding, and where the only peak in the MIKE spectrum was that of the protonated diamine.[20] With this background information, it was predicted that *m/z* 301 should give rise to only one major fragment ion, that being protonated benzyl acetate, *m/z* 151. Figure 1 shows the MIKE spectrum of the protonated dimer of benzyl acetate. The presence of masses 241 and 181, due to successive losses of CH_3COOH, suggests that an alternative or at least an additional structure exists for this dimeric species. The *m/z* 151 ion could be due to the cleavage of the protonated dimer, *m/z* 301, to re-form protonated benzyl acetate. However, 108^+ is not formed as a result of further fragmentation of the 151^+ ion as shown by the absence of a $151^+ \rightarrow 108^+$ transition in the MIKE spectrum of *m/z* 151. Thus three fragment ions (*m/z* 241, 181, and 108) are not easily accommodated by a proton-bound structure. An alternate structure (a) for the *m/z* 301 ion and a proposed mechanism which explains the observed fragment ions are given in Scheme II. The nucleophilic attack at a carbonyl carbon to form an addition product is well-known in solution and has precedent in mass spectrometry.[21] The reaction corresponds simply to acid-catalyzed addition of the carbonyl oxygen of benzyl acetate to the carbonyl carbon of protonated benzyl acetate. This may proceed through a proton-bound intermediate.[22] It is interesting to note that Kumakura et al.[21e] have proposed an analogous reaction mechanism for the dimerization of *n*-propyl acetate and protonated *n*-propyl acetate. By the reversal of this process *m/z* 151 would again be formed so that this fragment species is not diagnostic of the structure of the dimer. The *m/z* 91 ion also is not structurally diagnostic since it arises by further fragmentation of *m/z* 151 and, as will be seen later, it is also formed in other reactions.

Scheme II. Formation, Rearrangement, and Fragmentation of the Protonated Dimer of Benzyl Acetate



The diagnostic ions in Figure 1, *m/z* 241, 181, and 108, can arise from the condensation product (a) or after a simple isomerization to give (b). A three-dimensional model of (a) shows that the two aromatic rings can be brought into close proximity to one another, such that an electrophilic addition of the methylene carbon of one benzyl group to the ring of the other benzyl group is feasible (Scheme II). This also appears reasonable in light of the proposed charge localization, which increases the electrophilicity of the benzyl group. It should also be noted that a substituted diphenylmethane species is proposed both from the time-resolved CIMS studies and the MIKES experiments. The proposed skeletal rearrangement

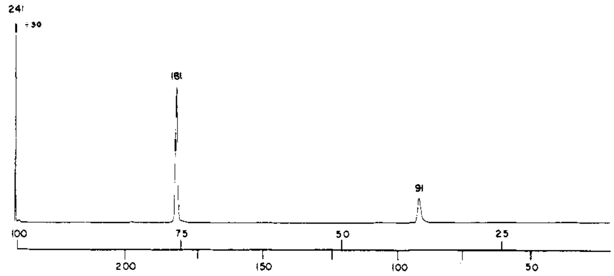


Figure 2. MIKE spectrum of *m/z* 241, a fragment ion of the benzyl acetate dimer.

product (b) can undergo the observed loss of one and two acetic acid groups to give the 241^+ and 181^+ ions, respectively.[23] The MIKE spectrum of the protonated dimer of benzyl-d_3 acetate is entirely consistent with this model, specific loss of two molecules of acetic-d_3 acid being observed. The formation of the low-intensity 108^+ ion can be explained as a simple hydrogen rearrangement with C–O bond cleavage occurring in the protonated dimer (a) as an alternative pathway to the skeletal rearrangement. This four-centered reaction is analogous to those seen for protonated esters;[27b] furthermore, d_3-labeled benzyl acetate resulted in the incorporation of one deuterium atom into this fragment as the formation of ionized benzyl alcohol requires.

The MIKE spectrum of *m/z* 301, the protonated dimer of benzyl acetate, does not disprove a contribution from the structure proposed by Meot-Ner et al., but it does suggest that other structures are present. It is noteworthy that the structure proposed here accounts not only for the MIKE spectrum of the benzyl acetate dimer, but it also shares the ortho-substituted hydrocarbon unit which has been shown to occur in the hydrocarbon ions generated from benzyl acetate both by the time-resolved CI study and by the work discussed below.

A final point which the MIKES observations clarify concerns the much greater abundance of 241^+ observed in the time-resolved study when methane is substituted for isobutane as reagent gas.[1] This follows from the MIKES result which shows the occurrence of the reaction $301^+ \rightarrow 241^+$ and from the fact that the protonated dimer (301^+) formed by methane CI would have more internal energy, therefore, more fragmentation.

3. The Unassigned Metastable Peak from the Protonated Benzyl Acetate Dimer. In the previous work on the benzyl acetate system,[1] a metastable peak was reported at *m/z* 89.7. From time-resolved spectra and from pressure studies, it was determined that this metastable peak arose from *m/z* 301, $(BzOAc)_2H^+$. Further studies revealed that the position of the maximum of the peak could be varied from *m/z* 89.5 to 90.5 and that the peak broadened as the field strength between the ion exit slit and the focusing electrodes was increased. It was concluded that this peak was in fact due to collision-induced dissociation of the *m/z* 301 ion, with the collisions occurring in the high-pressure region just outside the ion source. No further identification of the product ion was made.

Using the MIKES technique, a systematic study was done to determine the process responsible for this peak. The shift in the peak maximum suggests that with increased field strength more energy is deposited in the *m/z* 301 ion upon collision. Thus an increased percentage of the ions fragment before reaching the field-free region of the mass spectrometer causing a shift in the apparent mass of the metastable toward the actual mass of the fragment ion, i.e., a shift to higher mass. On the basis of this argument it would be expected that *m/z* 89.5 should represent an upper limit on the apparent mass for the process occurring in the field-free region. Using a value of *m/z* 89.5, one calculates an actual mass of the fragment ion of *m/z* 164. This serves as a guide in identifying the metastable peak observed by Meot-Ner et al.

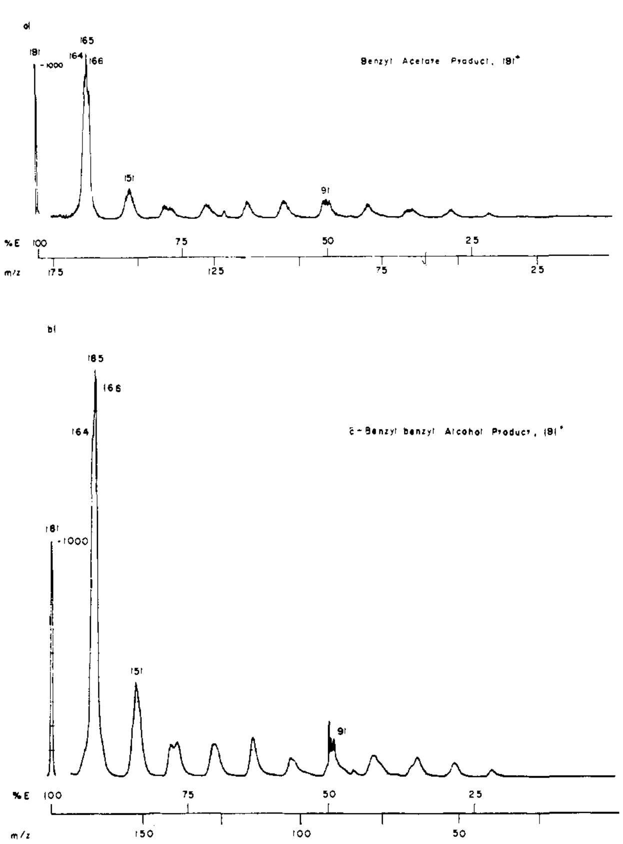


Figure 3. A comparison between the MIKE spectra of *m/z* 181 from (a) a secondary fragment ion of the benzyl acetate dimer and (b) the fragment ion formed by water loss from protonated 2-benzylbenzyl alcohol. The formation of *m/z* 164 accounts for the previously unassigned metastable peak.[1]

The MIKE spectrum of the *m/z* 301 ion (Figure 1) shows a small, diffuse peak in the region of the energy spectrum which would correspond to an ion of mass 164. However, its abundance was too low for an accurate determination of its mass and the low abundance suggests that it may be a secondary fragment ion. Examination of the MIKE spectra of each of the intense fragment ions generated from *m/z* 301 revealed the parentage of *m/z* 164. Figure 2 shows the MIKE spectrum of *m/z* 241. It is evident from this spectrum that formation of the *m/z* 164 ion is not a predominant process, although spectra taken at higher sensitivity reveal small ion currents due to *m/z* 164, 165, and 166. From the absence of 151^+ it is also apparent that the benzyl acetate moiety is not present in this ion; this, together with the fact that loss of AcOH to give 181^+ is the major reaction, makes the spectrum entirely consistent with the proposed covalently bonded structure (Scheme II). Figure 3 is the MIKE spectrum of the *m/z* 181 ion. The major fragmentation here is that sought after, the formation of 164^+, together with 165^+ and 166^+, which may contribute with 164^+ to the previously unassigned metastable peak.

It is clear now why the peak at *m/z* 89.5 follows the same time profile as the *m/z* 301 ion, since it is the product ion of a series of fragmentations of the protonated dimer of benzyl acetate. The low intensity of *m/z* 164 in the MIKE spectrum of *m/z* 301 can be accounted for in terms of a smaller energy transfer in the single-collision conditions of the second field-free region as compared to the milieu in the ion source exit region where multiple collisions leading to extensive fragmentation are more likely. The fact that *m/z* 181^+ loses C_1 fragments to generate the ions *m/z* 164, 165, and 166 is consistent with known electron-impact chemistry. For example,

Table I. MIKE Spectra of $(C_7H_7{\cdot}(C_7H_6)_n{-}H_2)^+$ Ions Arising from the Elimination-Polymerization Reactions of Benzyl Acetate[a]

m/z 359			*m/z* 269			*m/z* 179		
m/z	loss	*I*(rel)[b]	*m/z*	loss	*I*(rel)[b]	*m/z*	loss	*I*(rel)[b]
359	0	100	269	0	100	179	0	100
281	78	1.3×10^{-1}	251	18	3.3×10^{-2}	165	14	8.5×10^{-3}
268	91	3.7×10^{-1}	238	31	1.1×10^{-2}	163	16	5.7×10^{-3}
264	95	1.4×10^{-2}	191	78	3.1×10^{-2}	151	28	1.6×10^{-2}
253	106	3.5×10^{-2}	178	91	4.4×10^{-2}	139	40	5.4×10^{-3}
252	107	5.0×10^{-2}	91	178	3.1×10^{-2}	126	63	3.6×10^{-3}
251	108	4.3×10^{-2}				114	65	1.4×10^{-3}
191	168	6.0×10^{-2}				101	78	1.3×10^{-3}
181	178	2.1×10^{-2}				99	80	1.3×10^{-3}
178	181	1.4×10^{-2}				89.5[c]	0	9.6×10^{-3}
91	268	4.3×10^{-2}				89[c]	1	1.0×10^{-2}
						75	104	3.6×10^{-3}
						63	116	2.9×10^{-3}
						51	128	1.8×10^{-3}
						39	140	7.1×10^{-4}

[a] All data refer to spectra taken in the presence of collision gas. [b] Intensity relative to the primary (reactant) ion as 100%. [c] Doubly charged ions formed by charge stripping.

Table II. MIKE Spectra of $(C_7H_7{\cdot}(C_7H_6)_n)^+$ Ions Arising from the Elimination-Polymerization Reactions of Benzyl Acetate

m/z 361			*m/z* 271			*m/z* 181		
m/z	loss	*I* abundance[a]	*m/z*	loss	*I* abundance	*m/z*	loss	*I* abundance
361	0	100	271	0	100	181	0	100
395	2[b]		269	2[b]		179	2[b]	
295	66	7.1×10^{-3}	254	17	1.6×10^{-2}	166	15	8.5×10^{-2}
283	78	9.2×10^{-2}	193	78	3.7×10^{-2}	165	16	9.7×10^{-2}
269	92	3.4×10^{-1}	179	92	2.7×10^{-1}	164	17	7.4×10^{-2}
254	107	1.0×10^{-1}	165	106	1.3×10^{-2}	153	23	1.1×10^{-2}
193	168	9.5×10^{-2}	122	149	6.4×10^{-2}	152	29	1.7×10^{-2}
179	182	1.5×10^{-1}	105	166	1.0×10^{-2}	151	30	1.1×10^{-2}
165	196	7.7×10^{-2}	91	180	5.3×10^{-2}	104	77	9.9×10^{-3}
105	256	1.8×10^{-2}				91	90	9.9×10^{-3}
91	270	4.9×10^{-2}						

[a] Relative to the primary ion as 100%. [b] H_2 loss occurs as a substantial process but its intensity cannot be accurately determined because of interference by a peak due to reflection of the ion beam from the walls of the electric sector.

$CH_3{\cdot}$ elimination from the diphenylmethyl carbonium ion is a prominent process known to involve loss of the bridging carbon.[24]

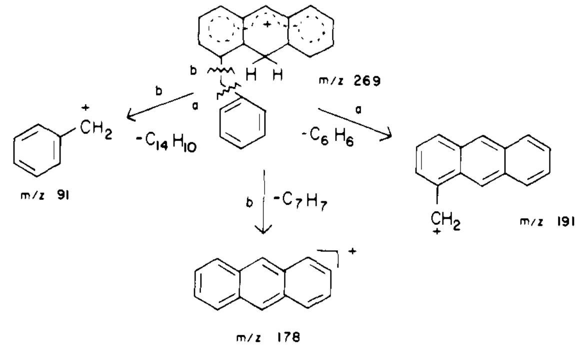
4. Polymeric Reaction Products of the Benzyl Acetate System. From the time-resolved study of the benzyl acetate system, a series of reactions (5 and 6), Scheme I, was observed to give product ions with the general formulas $(C_7H_7{\cdot}(C_7H_6)_n)^+$ and $(C_7H_7{\cdot}(C_7H_6)_n{-}H_2)^+$. Substitution of *p*-fluorobenzyl acetate in the condensation reactions confirmed the stoichiometry of the reaction and supported the postulated ortho-substituted methylene-bridged structures (para-substituted condensation products should have led to loss of fluorine). To further check on these proposed structures, a study of these unique polymeric ions was done using the MIKES technique.

The major fragment ions of the several $(C_7H_7{\cdot}(C_7H_6)_n{-}H_2)^+$ species, as deduced by MIKES, are given in Table I. The corresponding products of the $(C_7H_7{\cdot}(C_7H_6)_n)^+$ series of ions are given in Table II. The general reaction type observed for both sets of ions is a series of methylene-phenyl cleavages accompanied by hydrogen rearrangements. In the remainder of this section, the fragmentations of the polymeric benzyl ions are discussed in relation to their proposed structures. In this discussion, possible structures are shown for the fragment ions. The structure shown for any one fragment ion is only one possibility among many structural isomers, and it is shown only to aid in rationalizing the fragmentation of the precursor. Our objective is to establish the structures of these precursor ions, not those of their dissociation products.

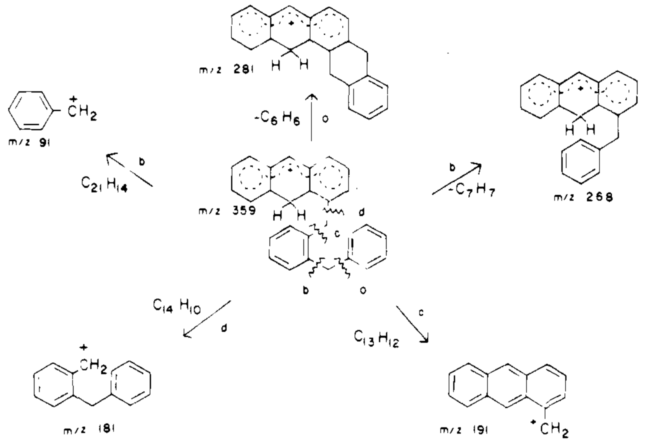
The $(C_7H_7{\cdot}(C_7H_6)_n{-}H_2)^+$ Ion Series. The first ion in the series $(C_6H_7{\cdot}(C_6H_6)_n{-}H_2)^+$ is *m/z* 179. Meot-Ner et al.[1] proposed that this ion had the structure of protonated anthracene and was formed by loss of H_2 from *m/z* 181. This is only possible without skeletal reorganization if the 181^+ precursor is ortho substituted as already suggested (Scheme II). To test the protonated anthracene structure directly, the MIKE spectrum of *m/z* 179 from the benzyl acetate system was compared to that of protonated anthracene, *m/z* 179. The comparison is made in Figure 4, where, except for differences in intensity between the two spectra, an exact correspondence is found.[25] This confirmation of the structure of the *m/z* 179 ion also substantiates the ortho-substituted structure of *m/z* 181 proposed earlier in this paper and in the time-resolved CIMS study.[1]

The second ion in the series under discussion is *m/z* 269. This ion along with the remaining ions of this series was proposed to be formed by loss of H_2 from the appropriate precursor in the $C_7H_7{\cdot}(C_7H_6)_n{}^+$ series.[1] By analogy to the 179^+ ion, one would expect an anthracene moiety in the 269^+ ion. The proposed structure for this ion and its major fragmentations are given in Scheme III. The ion has only two methylene-phenyl bonds (a and b), and cleavage at these points is the only simple route to fragment ions. Cleavage of bond (a) occurs with hydrogen transfer and the loss of neutral benzene to form the *m/z* 191 ion. This ion, formulated as an analogue of the benzyl ion, identifies the presence of the protonated anthracene unit in the precursor. As such, it is a particularly useful structural probe and it occurs in both higher members of the $(C_7H_7{\cdot}$

Scheme III. Structure and Main Fragment Ions of *m/z* 269, a Condensation Product of the Benzyl Acetate System



Scheme IV. Structure and Main Fragment Ions of *m/z* 359, a Condensation Product of the Benzyl Acetate System



$(C_7H_6)_n$-$H_2)^+$ series. The second phenyl-methylene bond (b) cleaves both homolytically and heterolytically to form 178^+ and 91^+, respectively. The fragmentation to form 178^+, ionized anthracene itself, involves a transition from an even-electron ion to two odd-electron fragments. While this would seem at first sight to be an energetically unfavorable reaction, it is not uncommon in even-electron ion chemistry, particularly when ionized aromatic systems are generated.[27] The appearance of ions 251^+ and $238^{+\cdot}$, due to loss of one and two carbon moieties, respectively, is not well understood. These processes presumably involve the methylene groups and may be related to the C_1 losses studied by Johnstone and co-workers in both odd- and even-electron ions.[24]

The highest ion in the $(C_7H_7\cdot(C_7H_6)_n$-$H_2)^+$ series reported on here is 359^+. A larger number of methylene-phenyl cleavages are possible and these dominate the MIKE spectrum. This is illustrated in Scheme IV, where the various fragments are shown to be associated with particular bond cleavages (H rearrangements not explicitly shown). The 359^+ ion, like its lower mass counterpart, shows competitive bond cleavages that lead, for example, to ionized anthracene, *m/z* 178^+, and its complement, *m/z* 181^+. All the ions observed, including the odd-electron ions, can be accounted for in terms of primary phenyl-methylene bond cleavages with formation of stable products, both charged and neutral.

The $C_7H_7\cdot(C_7H_6)_n{}^+$ Ion Series. The lowest mass ion of this series is the 181^+ ion. Figure 3a shows the MIKE spectrum of this ion. This data along with that for the other ions of this series is given in Table II. A large loss of H_2 is noted for the *m/z* 181 ion to form the fragment ion 179^+, which substantiates the postulate of Meot-Ner et al.[1] with regard to the origin of the $C_7H_7\cdot(C_7H_6)_n$-$H_2{}^+$ series. As mentioned in the previous subsection, the formation of protonated anthracene (179^+)

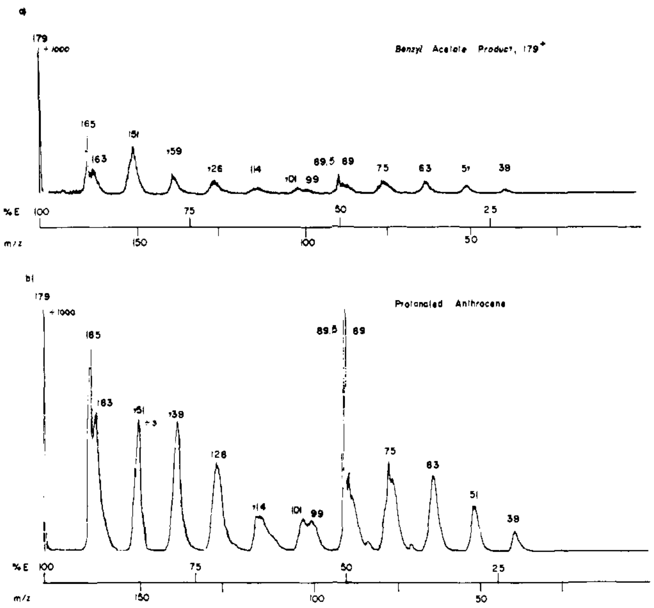
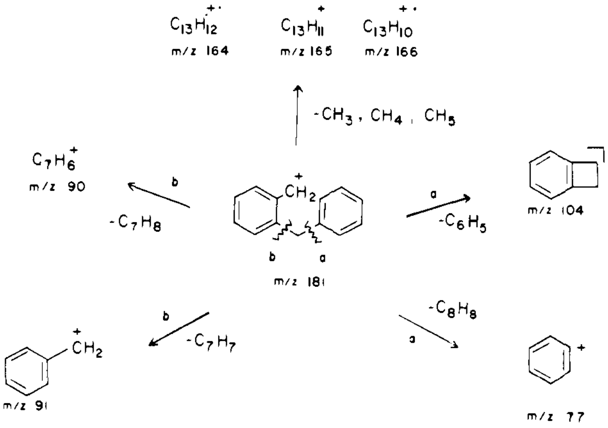


Figure 4. A comparison between the MIKE spectra of *m/z* 179 from (a) the condensation reactions of the benzyl acetate system and (b) protonated anthracene.

Scheme V. Structure and Main Fragment Ions of *m/z* 181, a Condensation Product of the Benzyl Acetate System



from 181^+ requires the precursor to be ortho substituted. The proposed structure for the *m/z* 181 ion along with its major fragmentations is shown in Scheme V (given in terms of bonds cleaved, without explicit reference to possible associated H migration). The two possible methylene-phenyl cleavages are both observed, indicating the chain-like structure of the ion. Competitive fragmentations led to the odd-electron species 104^+ ion and the even-electron ion 91^+, respectively. The formation of 104^+ from *m/z* 181 is to be contrasted to the even-electron 105^+ ion found in the higher members of this series. This may be due to the lack of readily transferable hydrogens in the first ion of the series. The most intense fragment ions from the 181^+ ion are those corresponding to losses of 15, 16, and 17 mass units. These reactions have been discussed above.

To confirm the structure of the 181^+ ion the authentic ion was generated by water loss from protonated 2-benzylbenzyl alcohol. The MIKE spectrum of this ion is shown in Figure 3b. Except for differences in intensity between the two, the spectra of Figure 3 are essentially identical. This confirms the identity of the 181^+ ions from the two sources, although it does not prove the benzyl as opposed to a tropylium formulation.

Figure 5 shows the MIKE spectrum of *m/z* 271, the second

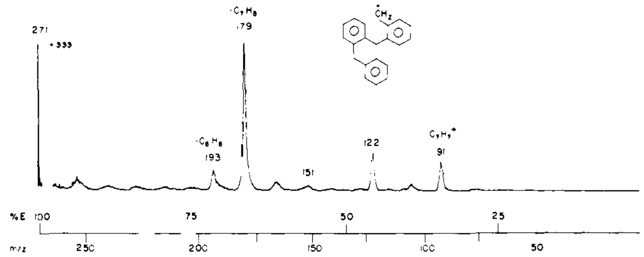
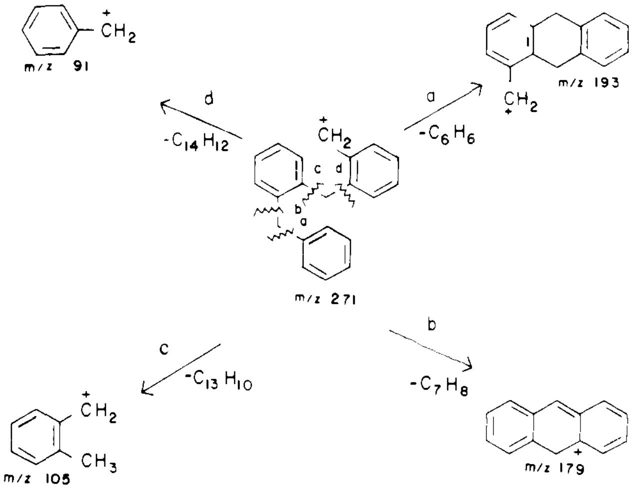


Figure 5. MIKE spectrum of *m/z* 271 $(C_7H_7\cdot(C_7H_6)_2)^+$, a condensation product of the benzyl acetate system.

Scheme VI. Structure and Main Fragment Ions of *m/z* 271, a Condensation Product of the Benzyl Acetate System



ion of the $C_7H_7\cdot(C_7H_6)_n{}^+$ series. The proposed structure of this ion and its fragmentations are given in Scheme VI. The fragmentations are dominated by a series of methylene-phenyl cleavages to form even-electron ions. This is in contrast to the *m/z* 181 ion and the $(C_7H_7\cdot(C_7H_6)_n\text{-}H_2)^+$ series of ions, where there are some important odd-electron ions. This difference may be due to the availability of transferable benzylic hydrogens. The loss of a C_1 unit to form the 254^+ ion is analogous to the behavior of the 181^+ ions. The generation of *m/z* 122 does not correspond to a reasonable fragment ion of a species containing only polymeric ion fragmentations except that it is seen as a minor peak in the spectrum of 181^+. For these reasons and the fact that this ion appears reproducibly on different occasions, it is believed that *m/z* 122 is a fragment ion from an isobaric 271^+ ion from the benzyl acetate system.

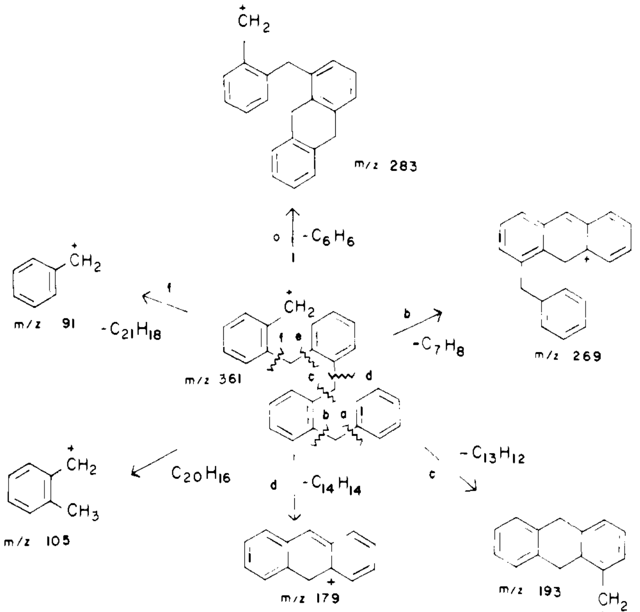
The last ion studied in the $C_7H_7\cdot(C_7H_6)_n{}^+$ series was *m/z* 361^+. The series of methylene-phenyl cleavages, which are indicative of the chain-like structure, are again the predominant fragmentations forming even-electron ions. The structure of the 361^+ ion and its major fragmentations are shown in Scheme VII. In addition to these reactions, that yielding the odd-electron *m/z* 254 ion is quite important in the spectrum of 361^+ suggesting that *m/z* 254 is a very stable species.

The similar types of fragmentations seen in all the members of this series confirm the proposal of a common structure type. In addition, the spectra can be interpreted in detail in terms of the structures advanced by Field and co-workers using quite different mass spectrometric methods.

Conclusion

The MIKES technique can be extremely useful in structural elucidation as shown by this study on the benzyl acetate polymeric ions. It is also useful in fragmentation mapping as demonstrated by the determination of the origin of a previously

Scheme VII. Structure and Main Fragmentations of *m/z* 361, a Condensation Product of the Benzyl Acetate System[a]



[a] The fragment ion structures are shown for clarity of exposition; the structure of 361⁺ follows from the observed reactions as indicated by bond cleavages (a–f).

reported but unassigned metastable peak. The present results largely confirm the structures suggested in a previous time-resolved CIMS study[1] and they provide extra data. The presence of a covalent structure in the protonated dimer (301^+) ion population represents a new finding. The occurrence of isomeric structures for proton-bound dimers has been noted before[17] and may be a widespread phenomenon with carbonyl compounds. It has also been found that the protonated dimer fragments yield 241^+ and 181^+. These species participate in the reactions leading to the polymeric species. This connection between the protonated dimer and 181^+ represents an extension to the set of reactions considered in the earlier kinetic study.

Most significantly, this study demonstrates how high-energy ion-molecule reactions can be used to complement studies on their low-energy counterparts. This is particularly valuable in that structural information is provided by the MIKES methodology which complements the detailed thermochemical and kinetic data available from studies in the low-energy regime.

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Effect of Reaction Energetics on the Hydrogen Chemical Ionization Mass Spectra of Halobenzene Derivatives. Estimates of the Heats of Formation of Substituted Phenyl Cations

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Abstract: The H_2 chemical ionization mass spectra of the halobenzene derivatives XC_6H_4Y (X = F, Cl, Br; Y = NH_2, OCH_3, F, Cl, Br) as well as the isomeric dichloroanilines and *N,N*-dimethylanilines have been determined. The major fragmentation reactions of the protonated molecule, MH^+, produce either $YC_6H_5^{+\cdot} + X\cdot$ or $YC_6H_4^+ + HX$ depending on the identity of the halogen X and the substituent Y. In several cases the $YC_6H_4^+$ ions undergo further reaction with H_2. The formation of the odd-electron products $YC_6H_5^{+\cdot} + X\cdot$, unusual in chemical ionization mass spectrometry, is shown to result from the thermochemical stability of $YC_6H_5^{+\cdot}$ compared to $YC_6H_4^+$. The competition between the two reaction channels depends strongly on the relative stabilities of HX and X·. From this reaction competition estimates are derived for the heats of formation of substituted phenyl cations as follows ($\Delta H_f°$ in kcal mol^{-1}): $H_3CC_6H_4^+$, 253; $H_2NC_6H_4^+$, 253; $CH_3OC_6H_4^+$, 225; $FC_6H_4^+$, 227; $ClC_6H_4^+$, 264; $BrC_6H_4^+$, 275. The estimated uncertainty in these values is ±4 kcal mol^{-1}.

Introduction

Earlier studies[1-3] of the H_2 chemical ionization (CI) mass spectra of the halobenzenes have shown that, in addition to charge transfer to the aromatic system, the mass spectra can be rationalized in terms of the fragmentation reactions 1 and 2 of the protonated molecule. The phenyl cation formed in (2) has been shown[3,4] to react further with H_2 to produce protonated benzene (reaction 3).

$$C_6H_5X\cdot H^+ \rightarrow C_6H_6^{+\cdot} + X\cdot \quad (1)$$

$$\rightarrow C_6H_5^+ + HX \quad (2)$$

$$C_6H_5^+ + H_2 \rightarrow C_6H_7^{+\cdot} \quad (3)$$

It was observed[1,2] that the relative importance of (1) and (2) depended strongly on the identity of the halogen X and this has been rationalized in terms of the relative energetics of the two fragmentation reactions. Table I records the fractional intensities of the $C_6H_6^{+\cdot}$ and $C_6H_5^+ + C_6H_7^+$ products for the halobenzenes and compares these intensities with the standard enthalpy changes for reactions 1 and 2. The latter refer to decomposition of the ground-state protonated halobenzene and have been derived using $\Delta H_f°(C_6H_5X\cdot H^+)$ values derived from the proton affinities $PA(C_6H_5F)$ = 182 kcal mol^{-1},[5] $PA(C_6H_5Cl)$ = 182 kcal mol^{-1},[5] and assuming the same proton affinities for bromo- and iodobenzene. The remaining thermochemical data have been taken from ref 6 with the exception of $\Delta H_f°(C_6H_5^+)$ = 266 kcal mol^{-1}.[7]

As the data in Table I show protonated fluorobenzene and protonated chlorobenzene fragment only by reaction 2 and this is consistent with the energetics data which show this reaction to be strongly favored thermochemically. However, for the bromobenzene system ~23% of the fragmentation of MH^+ proceeds by (1) to give the benzene molecular ion and a bromine atom. This also is consistent with the thermochemistry which shows that (1) and (2) have similar energetics requirements, with (1) having a slightly higher energy requirement, consistent with its lesser importance. For protonated iodobenzene fragmentation by (1) is strongly favored thermically and this is the only fragmentation reaction which is observed.

The observation of the odd-electron products $C_6H_6^{+\cdot} + X\cdot$

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