The Nominal Butyl Ester Ion in the Mass Spectra of Long-Chain *n*-Alkyl Esters

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The mass spectra of *n*-alkyl carboxylates in which the alkyl group contains seven or more carbons show a characteristic peak at the mass of the molecular ion of the corresponding butyl ester. Intensity is generally low, of the order of a few hundredths to a few tenths percent of total ion intensity. However, it is comparatively free of interferences and substantially more intense than peaks corresponding to higher and lower homologues. Hence it is a useful feature for qualitative identification. We have explored the origins of this peak in the spectrum of *n*-octadecyl benzoate, employing deuterium labeling, precise-mass measurement, and metastable scanning. The greater part of the intensity appears to arise by a reaction sequence initiated by the familiar γ -hydrogen migration to the carbonyl oxygen, followed by a second hydrogen migration from C-6 to C-2, β cleavage of the bond between C-4 and C-5, and stabilization by a third hydrogen migration probably from C-3 to the carbonyl oxygen. Some 20% of the observed intensity apparently stems from one of a family of reactions giving rise to a homologous series of $(M^+ - C_k H_{2k})$ fragments via nonspecific hydrogen abstraction and β carbon-carbon bond cleavage.

Ryhage and Stenhagen called attention a number of years ago to a low-intensity but characteristic feature of the mass spectra of long-chain n-alkyl esters of carboxylic acids-a peak at the mass (M/z, z = 1) of the molecular ion of the corresponding butyl ester.¹ They observed such a peak in the spectra of docosyl formate, acetate, propanoate, butanoate, and heptanoate at masses 102, 116, 130, 144, and 186, respectively. Intensity at these masses ranged from 0.1 to 0.4%of total ion intensity, greater by factors of 2 to 10 than at masses corresponding to higher and lower homologues of this ion. More recently, in a study of long-range intramolecular interactions,² we noted the corresponding peaks in the mass spectra of several long-chain *n*-alkyl esters of aromatic acids. Thus, benzoates, trimellitic anhydride esters, trimellitimidates, n-alkylmethyl iso- and terephthalates, and 4-n-alkyl 1,2-dimethyl trimellitates show the peak at masses 178, 248, 247, 236, and 294, respectively. Our own files of reference spectra and a literature search³ revealed further examples and demonstrated that the peak is characteristic of n-alkyl esters in which the alkyl group contains seven or more carbons. Although intensity is generally only a few hundredths to a few tenths percent of total ion intensity, the absence of interferences and, except in special cases,² the much lower intensity of homologous ions make this feature easy to detect and useful for qualitative identification.

Hydrogen migration from C-6 to the carbonyl oxygen, rupture of the bond between C-4 and C-5, and formation of a new bond between C-4 and the carbonyl carbon to give 1 (path 1) have been suggested to account for this peak.¹ How-



ever, the implied ten-membered cyclic transition state offers no obvious driving force for so specific a process. The same overall effect might, alternatively, be rationalized in terms of initiation by the ubiquitous γ -hydrogen migration to the carbonyl oxygen,⁴⁻⁶ followed by hydrogen migration from C-6 to C-2, as in 2, β cleavage with respect to the radical center on C-6 and, presumably, some further step such as ring closure to 1 to yield a configuration that is better stabilized than a primary free radical (path 2). The intermediate hydrogen



migration involves a six-membered cyclic transition state, and resembles the series of 1,5 migrations that have been proposed to account for the 4-carbon periodicity of intensity maxima in the $CH_3OCO(CH_2)_m^+$ peak series in the spectra of longchain methyl *n*-alkanoates.⁷

Our spectrum of *n*-octadecyl-6,7- d_2 benzoate^{2b} (isotopic composition: 7% d_0 , 18% d_1 , 63% d_2 , 6% d_3 , 4% d_4 , 1% d_5 , 1% d_6 ; see Experimental Section) shows retention of one deuterium atom in about 32% of the nominal butyl benzoate ions; the spectra of *n*-octadecyl-9,10- d_2 and -9,10,12,13- d_4 benzoates show no retention in these ions. These data are in accord with retention of one hydrogen from C-6, as required by either of the postulated reaction paths. A substantial fraction of the fragment ions of mass 14 u greater, presumably the next higher homologue, also retains one deuterium atom in the spectrum of the 6,7- d_2 benzoate but not in those of the 9,10- d_2 and 9,10,12,13- d_4 benzoates. We infer that the label retained in this case comes most likely from C-7; we have not, however, pursued the question.

Better to define the chemistry involved and, in particular, to distinguish between the two suggested paths leading to the nominal butyl benzoate ion, we have prepared *n*-octadecyl-2,2- d_2 benzoate and studied the behavior of this compound under electron impact in conjunction with that of the unlabeled and the 6,7- d_2 analogues. Either path 1 or path 2 should yield a product $C_{11}H_{14}O_2$.⁺ containing one hydrogen atom originally from C-6 and both atoms originally from C-2, but in differing positions:



We postulated that 1 might break down further by losing H₂O and that cyclohexanol might serve as a model for the mechanism of the dehydration step. The spectrum shows a peak at the appropriate mass, 160, although it is lower in intensity by a factor of about 10 than the $C_{11}H_{14}O_2$.⁺ peak at 178. Elimination from cyclohexanol under electron impact has been studied extensively.⁸ The preferred process there is 1,4 elimination, which accounts for some 40% of total H_2O loss; 1,3 elimination accounts for most of the remainder. Thus, one might anticipate that structure **1a** containing a deuterium atom from C-6 should lose the label almost quantitatively in eliminating water; the same species containing two deuterium atoms from C-2 should lose one of the two in some 40% of the reacting ions. Structure 1b containing a label from C-6 should lose it in perhaps 20% of the reacting ions; the same species containing two deuterium atoms from C-2 should lose one of them almost quantitatively and both in 20% of the reacting ions

We used precise-mass measurement, at a resolution of 10 000 (10% valley definition), to confirm the elemental compositions of ions under study and to distinguish among isobaric species containing zero, one, and two oxygen atoms. Quantitative separation of isobaric ions containing the same number of oxygen atoms and differing in elemental composition only by virtue of isotopic content—2H vs. D (0.0015 u), 12 CD vs. 13 CH (0.0029 u), 12 CH vs. 13 C (0.0045 u)—would require resolution beyond the capability of our instrument. We therefore measured peak intensities for isotopic analysis of fragment ions of interest also at a resolution of 10 000 and made the necessary corrections for natural heavy-isotopic species with the help of standard abundance tables⁹ as in low-resolution work. Parent–daughter relationships as revealed by decomposition of metastable ions in the first field-

free region of a double-focusing instrument were determined by the usual procedure of focusing on a fragment-ion peak, then holding the magnetic field and the electric-sector voltage constant and scanning the ion-accelerating voltage to increasing values ("metastable scanning").¹⁰ In the spectra obtained when sample was introduced via the heated batch inlet system,² intensities of the peaks with which we were concerned were generally too low to yield the information now sought. These intensities were increased by probe injection of the sample directly into the source and by increasing amplification of the multiplier output by $10 \times$ or $100 \times$ via a Keithley Model 427 current amplifier, replacing the amplifier furnished as original equipment. The probe was not heated directly but was in thermal contact with the source. To make each series of measurements, source temperature was set initially at 180 °C and was increased in small increments as needed to maintain an approximately constant ion-beam current; at about 220 °C, the beam current dropped suddenly to a very low value, signaling depletion of the sample.

These procedures magnified the peaks of interest to a useful level. At the same time, however, they also magnified a great many additional peaks that were so weak as to be easily ignored in the spectra as measured in our earlier work.² In particular, the $C_{11}H_{14}O_{2^{*}}$ and $C_{11}H_{12}O^{*}$ peaks at respective masses 178 and 160 in the spectrum of the unlabeled ester were now clearly seen to be accompanied by peaks at adjacent masses, assuring interferences in the spectra of the labeled esters, and at masses corresponding to higher and lower homologues of $C_{11}H_{14}O_{2^{*}}$, revealing as an illusion, at least in part, the unique role we had attributed initially to this ion in the spectrum.

Results and Discussion

Precise-mass measurement at masses 178 and 160 in the spectrum of unlabeled *n*-octadecyl benzoate confirmed the expected elemental compositions, as shown in Table I. Metastable scanning, as described above, of the ions of masses 160 and 178 identified the respective precursor masses as 178 and 374, as postulated. Thus the reaction sequence is established as:

$$\mathbf{M}^{+} \equiv \mathbf{C}_{25}\mathbf{H}_{42}\mathbf{O}_{2}^{+} \xrightarrow{-\mathbf{C}_{14}\mathbf{H}_{26}} \mathbf{C}_{11}\mathbf{H}_{14}\mathbf{O}_{2}^{+} \xrightarrow{-\mathbf{H}_{2}\mathbf{O}} \mathbf{C}_{11}\mathbf{H}_{12}\mathbf{O}^{+}$$

374 178 160

Table II displays the results of a typical scan through the regions around masses 178 and 160 in the spectrum of unlabeled *n*-octadecyl benzoate under conditions that cleanly separate the components containing zero, one, and two oxygen atoms at each nominal mass. All but 0.4% of total intensity at mass 178 and 100.0% of that at 160 are attributable to the components of interest, the ions containing two and one oxygen atoms, respectively. The $C_{11}H_{14}O_{2^{*}}$ ion at 178 is accompanied by $C_{11}H_{13}O_2^+$ at 177; the intensities attributable to dioxy ions at 179 and 180 are almost entirely accounted for by naturally occurring heavy-isotopic species. The $C_{11}H_{12}O_{1^{*}}$ ion at 160 is accompanied by other monoxy ions at 159, 161, and 162.

The peak intensities assigned to dioxy species in the immediate vicinity of mass 178, as shown in Table II, were corrected for natural heavy-isotopic contributions and normalized to a total intensity of 100 for these peaks alone; those assigned to monoxy species in the vicinity of mass 160 were treated likewise. The resulting intensity distributions are shown in Table III, along with the corresponding distributions

TABLE I: Precise-Mass Measurements at Masses 178 and160 in Mass Spectrum of n-Octadecyl Benzoate

Measured	Assignment		Discrepancy
mass	Formula	Mass	ppm
178.0985 160.0891	$C_{11}H_{14}O_{2}$ ·+ $C_{11}H_{12}O$ ·+	$178.0994 \\ 160.0888$	5 2

TABLE II: Peak Intensities^a in the Regions AroundMasses 178 and 160 in Mass Spectrum of n-OctadecylBenzoate

	No. of oxygen atoms		
Nominal Mass	0	1	2
182	1320	0	2
181	900	0	4
180	500	0	20
179	26	0	172
178	6	0	1360
177	12	6	132
166	800	0	2
165	60	.0	26
164	10	0	194
163	8	8	1030
162	2	36	14
161	10	36	6
160	0	216	0
159	12	38	0

^a Expressed in mm as measured on analog record.

 TABLE III: Normalized^a Isotope-Corrected Intensity

 Distributions in Selected Regions ^b of Mass

 Spectra of n-Octadecyl Benzoates

Mass	Unlabeled	$2,2$ - d_2	$6,7-d_2$
180		54	
179		37	28
178	91	8	65
177	. 9	1	7
163		1	
162	. 11	25	11
161	3	50	21
160	73	19	55
159	13	5	13

 a Normalized to a total of 100 in each of the two mass regions independently. b Only dioxy ions are included in the 177-to-180 mass region, and only monoxy ions in the 159-to-163 mass region.

derived from the spectra of the two labeled n-octadecyl benzoates.

As an aid to estimate and thereby to correct for interferences, we performed metastable scans on the peak at mass 177 and on those at 159, 161, and 162 in the spectrum of the unlabeled benzoate. The scan of the mass 177 peak showed one intense metastable peak, corresponding to the molecular ion, mass 374, as precursor. The ion of mass 159 was found to stem from precursors of masses 177, 374, and 356 ($M^{++} - H_2O$); 161, from 179 (presumably denoting loss of H_2O from the heavyisotopic analogue of $C_{11}H_{14}O_{2^{+}}$); and 162, from 180, 192, and 374. Precise-mass measurement on the peaks at 192, 164, 150, and 136 identified the respective ions as $C_{12}H_{16}O_{2^{+}}$, $C_{10}H_{12}O_{2^{+}}$, $C_{9}H_{10}O_{2^{-}}$, and $C_8H_8O_{2^{+}}$, homologues of

TABLE IV: $C_{11}H_{14}O_{2^{+}}$, $C_{11}H_{13}O_{2}^{+}$, and Their Homologues in the Mass Spectrum of *n*-Octadecyl Benzoate

Mass	Ion	Rel intensity
206	$C_{13}H_{18}O_{2}$.+	0.011
192	$C_{12}H_{16}O_{2}$ +	0.082
178	$C_{11}H_{14}O_{2}$ +	0.47
164	$C_{10}H_{12}O_{2}$.+	0.034
150	$C_9H_{10}O_2$ +	0.11
136	$C_8H_8O_2$ +	0.056
122	$C_7 H_6 O_2 +$	5.31
205	$C_{13}H_{17}O_2^+$	0.005
191	$C_{12}H_{15}O_2^+$	0.033
177	$C_{11}H_{13}O_2^+$	0.039
163	$C_{10}H_{11}O_2^+$	0.30
149	$C_9H_9O_2^+$	0.093
135	$C_8H_7O_2^+$	0.30
123	$\mathbf{C}_{7}\mathbf{H}_{7}\mathbf{O}_{2}^{+}$	100.0

 $C_{11}H_{14}O_{2^+}$ at 178. Similar measurements identified the major or sole components at 191, 177, 163, 149, and 135 as $C_{12}H_{15}O_2^+$, $C_{11}H_{13}O_2^+$, $C_{10}H_{11}O_2^+$, $C_9H_9O_2^+$, and $C_8H_7O_2^+$, respectively. Returning to metastable scanning of homologues of $C_{11}H_{14}O_{2^+}$ and $C_{11}H_{13}O_2^+$, we arrived at the molecular ion as the common precursor of all the members examined of both series: the ions of masses 206, 192, 164, 150, 136, and 122; and 205, 191, 163, 149, and 135. The only other metastable peak of substantial intensity so found corresponds to the process:

$$C_{11}H_{14}O_2^{+} \longrightarrow C_9H_{10}O_2^{+} + C_2H_4$$

178 150 28

Weaker metastable peaks pinpointed 163, 177, and 191 as the masses of additional precursors of the ion of mass 135. Our failure to detect contributing reactions of $C_{11}H_{14}O_{2}$.+ homologues may reflect simply their lower abundances than that of $C_{11}H_{14}O_2$.⁺ in the total ion population. Thus, $C_{11}H_{14}O_{2}$ + was now clearly seen to be only one member, although the most abundant one except for the benzoic acid radical cation of mass 122, of a homologous series of ions arising predominantly by loss of olefin molecules from the molecular ion of *n*-octadecyl benzoate. Similarly, $C_{11}H_{13}O_2^+$ of mass 177 was seen to be a member of a second homologous series arising predominantly by loss of alkyl radicals from the molecular ion. Peak intensities corresponding to these two homologous series of ions, corrected for naturally occurring heavy-isotopic species, are shown in Table IV. The intensity scale here is defined by assigning a value of 100.0 to the intensity of $C_7H_7O_2^+$, the most abundant ion in the spectrum of *n*-octadecyl benzoate.

With the help of one further piece of data, the isotopic composition of the *n*-octadecyl-2,2- d_2 ester—9% d_0 , 36% d_1 , and 55% d_2 (see Experimental Section)—we could now proceed to estimate the isotopic composition of the C₁₁H₁₄O₂·+ and C₁₁H₁₂O·+ ions.

If the original tagged atoms in the $2,2-d_2$ ester are retained quantitatively in $C_{11}H_{13}O_2^+$ and no isotope effects intervene, the 9 intensity units assigned to this ion—as shown in Table III at mass 177 in the spectrum of the unlabeled ester—will be distributed in the spectrum of the $2,2-d_2$ ester as 5 units at 179, 3 at 178, and 1 at 177. Removing these contributions from the intensities listed for the $2,2-d_2$ ester and renormalizing gives for the isotopic distribution of $C_{11}H_{14}O_2$.⁺: 2858

No. of		
Mass	D atoms	%
180	2	59
179	1	35
178	0	6

This distribution agrees well with that of the molecular ions and hence indicates quantitative retention of the hydrogen atoms on C-2. Moreover, such internal consistency supports the assumption of quantitative retention of the original C-2 hydrogens in $C_{11}H_{13}O_2^+$. Taking the mass 177 intensity of the $6,7-d_2$ ester at face value and ignoring possible isotope effects, we conclude that 7 units of the $C_{11}H_{13}O_2^+$ ions are unlabeled and assume arbitrarily that the remaining 2 units are singly labeled. Removing these contributions from the intensities listed for the $6,7-d_2$ species and renormalizing yields for the isotopic distribution of $C_{11}H_{14}O_2^{++}$:

Mass	No. of D atoms	%
179	1	31
178	0	69

This distribution agrees with the estimate of 32% deuterium retention arrived at earlier without benefit of high-resolution measurements. Within the limitations imposed by the presence of isotopic impurities in the 6,7- d_2 ester and of a possible small isotope effect, in view of the implied competition between migration of deuterium and protium atoms from C-6, the distribution found is in good accord with the expectation that one hydrogen atom from C-6 is retained in C₁₁H₁₄O₂, as required by either reaction path 1 or 2.

The 159-to-163 mass region involves greater uncertainties. In the spectrum of the 2,2-d₂ ester, the 5 units at 159 are clearly attributable to $C_{11}H_{11}O^+$, 1 unit at 163 to $C_{11}H_{13}DO^{++}$, 10 units at 162 to $C_{11}H_{14}O^{++}$. We arbitrarily assign 3 units at 161 to $C_{11}H_{13}O^+$. In view of the parallel origins of $C_{11}H_{11}O^+$ and $C_{11}H_{12}O^{++}$ by loss of H_2O from $C_{11}H_{13}O_2^+$ and $C_{11}H_{14}O_2^{++}$, respectively, we assume that the ratio of singly to doubly labeled $C_{11}H_{11}O^+$ at 160 and 161, respectively, is identical with the corresponding ratio of $C_{11}H_{12}O^{++}$ species at 161 and 162. Calculation of the isotopic distribution of $C_{11}H_{12}O^{++}$ ions is then straightforward. In the spectrum of the 6,7- d_2 ester, $C_{11}H_{11}O^+$, $C_{11}H_{13}O^+$, and $C_{11}H_{14}O^{++}$ are evidently free of deuterium, and the residual intensities at 160 and 161 define the isotopic distribution of $C_{11}H_{12}O^{++}$ ions. The distributions that result are:

	$2,2$ - d_2 ester	$6,7-d_2$ ester
d_2	20	
d_1	62	25
d_0	18	75

If one assumes that $C_{11}H_{12}O^{+}$ arises solely by dehydration of $C_{11}H_{14}O_{2}^{++}$ and that isotope effects are negligible, these isotopic distributions in conjunction with those of the corresponding $C_{11}H_{14}O_{2}^{++}$ ions lead to the following conclusions: (a) the hydrogen atom originally from C-6 is lost as part of the $H_{2}O$ molecule in (31 - 25)/31 = 19% of the reacting ions; (b) one hydrogen atom originally from C-2 is lost similarly in $(59 - 20)/59 = 66\% \simeq 2(35 - [62 - 39])/35 = 69\%$ of the reacting ions; (c) in none of the reacting ions are both C-2 hydrogen atoms lost.

These conclusions are compatible with neither of the two

suggested reaction paths as written. The small fraction of C-6 hydrogen lost as part of the water molecule rules out a major contribution from path 1. Our failure to find evidence for any appreciable loss of both C-2 hydrogens would seem to rule out structure 1 as an intermediate. If one assumes that hydrogen atoms from C-2 and C-6 are in no case lost together, the data can furnish a basis for a plausible rationale. One of the three hydrogens is incorporated in the water molecule lost from 85 to 88% of reacting $C_{11}H_{14}O_2$.⁺ ions, close enough to 100% that we can take this as an acceptable material balance within the uncertainties associated with unknown, but most likely small,¹¹ isotope effects and the approximations made in estimating isotopic distributions. The data can then be accounted for by assuming that both paths 1 and 2, modified to omit ring closure to 1, contribute, with the second water hydrogen coming from another position, most likely C-3, whence hydrogen migration might be assisted by β activation by the radical center on C-4.

We thus conclude that the 70–80% of reacting $C_{11}H_{14}O_{2^{*}}^{+}$ ions that lose C-2 hydrogen most likely arise by path 2, but with stabilization of the intermediate primary radical via a third hydrogen migration step:



Insofar as one can judge from the product of subsequent dehydration, this appears to be the specific process chiefly responsible for the nominal butyl ester ion that prompted this inquiry. Our data do not, of course, rule out possible contributions from structures isomeric to 3 that do not break down further by loss of water. The minimum chain-length requirement of seven carbons follows directly from the central role of hydrogen migration from C-6. Many systems are known in which otherwise nonspecific migration drops sharply in probability or even vanishes at the terminal carbon.^{2,5,12-14} The source of this effect is presumably the difference between the dissociation energies of primary and secondary carbonhydrogen bonds,¹⁵ which would make the second migration step in path 2 endothermic by some 2–3 kcal/mol in a hexyl ester, whereas it is approximately thermoneutral in a heptyl or longer ester.

The ~20% of reacting $C_{11}H_{14}O_{2}$.⁺ ions that lose C-6 hydrogen most probably arise by hydrogen migration directly from C-6 to the carbonyl oxygen, as in path 1, also modified to incorporate stabilization via 3. This contribution to the $C_{11}H_{14}O_2$ + yield is presumably the counterpart of the observed higher and lower homologues arising by a sequence of nonspecific hydrogen abstraction and β carbon–carbon bond cleavage, with stabilization via a second hydrogen migration step:



Such a sequence requires retention of a hydrogen atom from C-7 in $C_{12}H_{16}O_2$.⁺, the next higher homologue of $C_{11}H_{14}O_2$.⁺, and is therefore supported by our observation that a substantial part of the $C_{12}H_{16}O_{2}$, yield from *n*-octadecyl-6,7- d_2 benzoate contains deuterium. As we suggested in another similar system,² β cleavage on the far side of the radical site would effect loss of an alkyl radical, and may well be the source of the observed $C_{11}H_{13}O_2{}^+$ and its homologues. The relatively high abundance of $C_{10}H_{11}O_2^+$ in this series, as seen in Table IV, is then readily accounted for, because it is the product of the reaction sequence initiated by abstraction from C-2, the most favored position. Low-yield reactions involving such intramolecular nonspecific abstraction from an alkyl chain have been reported as contributors to the mass spectra of aldehydes,^{5b,12} ketones,¹⁶ acids,¹⁷ nitriles,¹⁸ and ethers,¹⁹ as well as esters.^{2,13,14}

The nominal butyl ester ion-at least the bulk of those ions that react further by H₂O loss before departing the ion source and hence contribute to the normal $C_{11}H_{12}O{\boldsymbol{\cdot}}^+$ peak in the mass spectrum-appears to comprise a new member of the growing family of products of reaction sequences initiated by γ -hydrogen abstraction by a carbonyl oxygen atom.^{4-6,20} Cyclization apparently plays an important part in stabilization of fragment ions in some systems,²¹ but it seems to be less frequently preferred by the reacting molecules than by authors trying to rationalize molecular behavior.

Experimental Section

Mass spectra were measured initially on a DuPont Model 21-104 instrument, using electrical scanning, with the inlet system at 250-280° and the source at 250°.² All subsequent measurements, as described above, were made on a CEC Model 21-110b instrument, using probe injection in most cases

n-Octadecyl Benzoates. Preparation of *n*-octadecyl- d_0 and

-6,7- d_2 benzoates has been reported.^{2b} The isotopic analysis of the latter^{2b} was derived from measurements on the $C_{18}H_{36}{\mbox{+}}{\mbox{+}}$ peaks rather than M^+ , because the $C_{18}H_{36}^+$ data agreed well with those on the M·⁺ peaks of the stearic acid-6,7- d_2 from which the ester had been made and with those on both the M·+ and $C_{18}H_{36}$ + peaks of 4-*n*-octadecyl-6,7-d₂ trimellitate anhydride made from the same stearic acid. An estimate of the isotopic distribution based on the M.+ peaks of the labeled benzoate was apparently slightly distorted by contributions from protonated ester arising from a bimolecular process.²²

To prepare *n*-octadecyl- $2,2-d_2$ benzoate, commercial USP grade stearic acid was labeled in the α position by heating for 2 days with 98% D_2SO_4 in a sealed tube at 105–110 °C,²³ and this procedure was then repeated three times. The extent of exchange was monitored by recovering the stearic acid after each treatment and measuring its isotopic composition by mass spectrometry; the fourth treatment had no detectable effect on isotopic composition. Finally, the recovered stearic acid was recrystallized twice from ethanol to remove palmitic and eicosanoic acid impurities. The product melted at 69 °C (lit. mp,²⁴ unlabeled stearic acid, 70 °C). The M·+ peaks in the 70-eV mass spectrum gave the isotopic distribution: 9% d_0 , $36\% d_1$, 55% d_2 . The labeled stearic acid (1.33 g) was added to a stirred refluxing mixture of 0.88 g of lithium aluminum hydride and freshly purified tetrahydrofuran. Refluxing was continued for 10 min, after which the heat was turned off and the mixture stirred for an additional hour. The excess lithium aluminum hydride was decomposed by cautious addition of methanol, followed by aqueous methanol. Solvents were removed by vacuum distillation, and the residue was extracted repeatedly with ether. Removal of the ether from the extract left a solid which was recrystallized from methanol to give octadecanol-2,2-d₂, mp 57 °C (lit. mp,²⁵ unlabeled octadecanol, 58 °C). Equimolar quantities of the labeled octadecanol and benzoyl chloride were dissolved in anhydrous pyridinebenzene mixture and stirred at room temperature for 1 h. The solvent and the volatile pyridine hydrochloride were removed at 0.5 Torr by increasing the temperature to 210 °C, leaving the crude ester as a residue. This was recrystallized from methanol-chloroform to give *n*-octadecyl- $2,2-d_2$ benzoate, mp 42-44 °C (lit. mp,^{2b} unlabeled n-octadecyl benzoate, 42.5-44.0 °C). Isotopic composition estimated from the peaks in the molecular-ion region of the 70-eV spectrum showed slightly higher enrichment than that found for the stearic acid-2,2- d_2 . In our experience, protonated molecules stemming from bimolecular processes occur commonly in the spectra of long-chain alkyl esters,²² and we found clear evidence for such species in the spectra of both the unlabeled and $6,7-d_2$ octadecyl benzoates. We therefore took the isotopic composition found for the stearic acid-2,2- d_2 as our best estimate for the octade cyl-2,2- d_2 benzoate as well. Substantial loss of label in the reaction leading to C₁₈H₃₆⁺ ruled out measurements on this ion for isotopic analysis of the octadecyl-2,2- d_2 ester, in contrast to the corresponding 6,7- d_2 , $9,10-d_2$ and $9,10,12,13-d_4$ esters.^{2b}

References and Notes

- R. Ryhage and E. Stenhagen, *Ark. Kem.*, **14**, 483 (1959). (a) S. Meyerson, I. Puskas, and E. K. Fields, *Adv. Mass Spectrom.*, **6**, 17 (1974); (b) *J. Am. Chem. Soc.*, **95**, 6056 (1973). See especially A. G. Sharkey, J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **31**, 87 (1959). (2)
- (3)
- J. 67 (1959).
 S. Meyerson, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 309 (1968).
 (a) C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke, and L. C. Leitch, *J. Am. Chem. Soc.*, **91**, 6847 (1969); (b) S. Meyerson, C. Fenselau, J. L. Young, W. R. Landis, E. Selke, and L. C. Leitch, *Org. Mass Spectrom.*, **3**, 689 (1970). (5)

- (6) For a pertinent recent review, see D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74**, 215 (1974).
 (7) G. Spiteller, M. Spiteller-Friedmann, and R. Houriet, *Monatsh. Chem.*, **97**,
- 121 (1966); see also D. H. Hunneman and W. J. Richter, Org. Mass Spectrom., 6, 909 (1972).
- (8) C. G. Macdonald, J. S. Shannon, and G. Sugowdz, Tetrahedron Lett., 807 (1963); H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh. Chem.*, 95, 158 (1964); M. M. Green and J. Schwab, *Tetrahedron Lett.*, 2955 (1968);
 R. S. Ward and D. H. Williams, *J. Org. Chem.*, 34, 3373 (1969); M. M. Green,
 R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Am. Chem. Soc.*, 92, 3076 (1970); J. L. Holmes, D. McGillivray, and R. T. B. Rye, *Org. Mass Spectrom.*, 247 (1972). 7. 347 (1973).
- (9) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry'', Elsevier, New York, N.Y. 1963. (10) J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965);
- K. R. Jennings, *Ibid.*, **43**, 4176 (1965); S. Meyrson, R. W. Vander Haar, and E. K. Fields, *J. Org. Chem.*, **37**, 4114 (1972).
 M. M. Green, J. M. Moldowan, M. W. Armstrong, T. L. Thompson, K. J.
- Sprague, A. J. Hass, and J. J. Artus, *J. Am. Chem. Soc.*, in press.
 R. J. Liedtke and C. Djerassi, *J. Am. Chem. Soc.*, **91**, 6814 (1969); K. Christiansen, V. Mahadevan, C. V. Viswanathan, and R. T. Holman, *Lipids*, 4, 421 (1969); A. G. Harrison, Org. Mass Spectrom., 3, 549 (1970).
 J. Cable and C. Djerassi, J. Am. Chem. Soc., 93, 3905 (1971).
 For a closely analogous photochemical example, see R. Breslow and M.
- A. Winnik, J. Am. Chem. Soc., 91, 3083 (1969); R. Breslow and P. C. Scholl, ibid, 93, 2331 (1971).

- (15) See, for example, F. O. Rice and T. A. Vanderslice, J. Am. Chem. Soc., 80, 29 (1958); A. A. Zavitsas, *ibid.*, 94, 2779 (1972); A. A. Zavitsas and A. A. Melikian, Ibid., 97, 2757 (1975).
- (16) W. Carpenter, A. M. Duffield, and C. Djerassi, J. Am. Chem. Soc., 90, 160 (1968).
- (17) N. C. Rol, *Recl. Trav. Chim. Pays-Bas*, **84**, 413 (1965).
 (18) A. Beugelmans, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 1386 (1964); W. Carpenter, Y. M. Sheikh, A. M. Duffield, Chem. Soc. **186**, 1386 (1964); W. Carpenter, M. Sheikh, A. M. Duffield, Chem. Soc. **186**, 1386 (1964); W. Carpenter, M. Sheikh, A. M. Duffield, Chem. Soc. **186**, 1386 (1964); W. Carpenter, M. Sheikh, A. M. Duffield, Chem. Soc. **186**, 1386 (1964); W. Carpenter, M. Sheikh, A. M. Duffield, Chem. Soc. **186**, 1386 (1964); W. Carpenter, M. Sheikh, A. M. Duffield, M. Sheikh, A. M. Duffield, M. Sheikh, A. M. Duffield, M. Sheikh, M. Sheikh, A. M. Duffield, M. Sheikh, M. Sheikh, A. M. Sheikh, M. Sh and C. Djerassi, *Org. Mass Spectrom.*, **1**, 3 (1968). (19) M. A. Winnik, C. K. Lee, and P. T. Y. Kwong, *J. Am. Chem. Soc.*, **96**, 2901
- (1974).
- (20) Cf. P. J. Derrick, A. M. Falick, A. L. Burlingame, and C. Djerassi, J. Am. Chem. Soc., 96, 1054 (1974); R. P. Morgan and P. J. Derrick, J. Chem. Soc., Chem. Commun., 836 (1974).
- (21) See, for example, W. J. Baumann, A. J. Aasen, J. K. G. Kramer, and R. T.
- See, for example, W.J. Baumann, A.J. Adsen, J. K. G. Kramer, and R. L. Holman, J. Org. Chem., 38, 3767 (1973).
 F. W. McLafferty, Anal. Chem., 29, 1782 (1957); J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry", Elsevier, New York, N.Y., 1960, pp 275 ff; K. Biemann, "Mass Spectrometry. Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1982, p 55. (23) W. E. van Heyningen, D. Rittenberg, and R. Schoenheimer, *J. Biol. Chem.*,
- 125, 495 (1938).
- "Beilstein's Handbuch der Organischen Chemie", Vol. 2, III, Springer-Verlag, West Berlin, 1960, p 991. "Beilstein's Handbuch der Organischen Chemie", Vol. 1, III, Springer-(24)
- (25) Verlag, West Berlin, 1958, p 1834.

The Thermochemistry of $C_2H_4O^+$ lons

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The heat of formation of the molecular ion of vinyl alcohol has been measured by an electron impact method to be 181 kcal/mol. The heat of formation of the transient neutral molecule is estimated to be -26.5 kcal/mol, whence the ionization potential is 9.0 ± 0.15 eV. The significance of these results is discussed with particular regard to some recent metastable ion studies and to the generation of $C_2H_4O^{+}$ ions in the mass spectra of aliphatic aldehydes.

Introduction

In a recent $paper^2$ it was shown that the three isomeric $C_2H_4O^+$ ions (I–III) can unequivocally be identified by the

$$\begin{array}{cccc} CH_2 & --CH_2 & \uparrow^{\ddagger} & CH_3 CHO & \uparrow^{\ddagger} & CH_2 = -CHOH & \uparrow^{\ddagger} \\ O & II & III \\ I & III \end{array}$$

characteristic metastable peaks accompanying their fragmentation by H atom loss:

$$C_{2}H_{4}O^{+} \rightarrow C_{2}H_{3}O^{+} + H^{-}$$

Two further forms of $C_2H_4O^+$ were observed in these experiments but their structures were not confirmed. Although the ionic heats of formation of I and II are well-established, there is no reliable value for III since the parent neutral molecule cannot be isolated. However, the unequivocal participation of III in certain ionic fragmentations² provides a means of deriving its heat of formation as a fragment ion.

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In this paper we report measurements of the heats of formation of $C_2H_4O^+$ ions I and II by direct ionization of parent molecules, and III as a primary fragment ion in decompositions of known mechanism.

Experimental Section

All compounds were of research grade purity or were purified by glc. Metastable peak measurements were performed on a G.E.C.-A.E.I. MS902S mass spectrometer. The electron impact apparatus comprising an electrostatic electron monochromator³ together with a quadrupole mass spectrometer and minicomputer data system⁴ has been described elsewhere.

Results and Discussion

The ionization potentials (IP) of ethylene oxide and acetaldehyde measured in this work are in close agreement with those obtained in photoionization studies.⁵ These IP and the derived heats of formation for structures I and II are given in