

STRUCTURE OF SMALL FRAGMENT IONS ASSOCIATED WITH CHARGE-REMOTE FRAGMENTATION OF ALKALI-METAL FATTY-ACID ADDUCTS

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Introduction.

Fatty acid anions $(F - H)^-$ react with two alkali metal cations (M^+) in a matrix to form gas-phase singly-charged adducts $(F - H + 2M)^+$ upon fast-atom bombardment (FAB). High-energy collisional activation (CA) of the adducts yields the charge-remote (CR) series of closed-shell fragment ions that correspond to formal, parallel losses of alkanes for saturated fatty acids [1]. A mechanism was proposed that involves the 1,4-elimination of H_2 through a six-membered cyclic transition state with consequent formation of terminally unsaturated products [2]. The mechanism accounts for the fragmentation involving branched and unsaturated precursors and isotopic labeling patterns. The formation of an ω -unsaturated product ion [3] and terminally-unsaturated alkene [4] has been demonstrated.

In addition to the CR series, there are formed a series of radical ions that differ from the CR products by an additional $-H\bullet$. The abundances of the two series appear to be a function of the alkali metal [5]. The radical series has been central to alternate mechanisms that have been proposed for the generation of the CR series, namely by loss of $H\bullet$ from the radical ions [6,7]. The radical mechanisms require the formation of $2H\bullet$ rather than H_2 , the energetic equivalent of the homolytic breaking of the H_2 bond, and initiation by heterolytic cleavage of a C - H or homolytic cleavage of a C - C bond, and are hence energetically less favorable than the 1,4- H_2 elimination mechanism.

In this study, we propose to investigate the abundance and extent of the radical ion series relative to the CR series as a function of the alkali metal ion by high-energy collisionally-activated decomposition (CAD), to probe the structures of the various fragment ions by using high-energy MS/MS/MS (MS^3), to investigate proposed structures of the various precursor and product ions by *ab initio* methods and to determine the origins of the M^+ , M_2^{+} , and M_2O^{+} ions which accompany CAD of the adducts.

Experimental Methods.

Precursor adducts, $(F - H + 2M)^+$, were desorbed by FAB from the precursor fatty acid dissolved in a matrix of the alkali-metal iodide salt and 3-nitrobenzyl alcohol (3-NBA) or triethanolamine (TEA).

All CA was performed at a laboratory energy of 8 keV by using grounded collision cells and an accelerating potential of 8 kV. Helium was the collision gas and beam attenuation was ~60%. High-resolution MS/MS studies were performed on the VG (later Fisons, now Micromass) ZAB-T mass spectrometer, a four-sector instrument of BEBE design which provides for double-focusing MS1 and MS2. MS^3 experiments were performed on the Kratos MS-50TA of EBE design. The precursor adducts were subjected to CA in the first collision cell. The intermediate product ions were mass-selected by B and E_1 such that $B/E_1 = \text{constant}$ relative to the precursor m/z . The intermediate product ions were subjected to CA in the second collision cell, and the resulting fragments were analyzed by employing a MIKES scan with E_2 . This arrangement produces high-resolution mass selection of the intermediate product but low-resolution mass selection of the precursor m/z , and the mass resolution of the second-generation products is degraded by kinetic energy release. The MS^3 studies were performed on this instrument because it affords the greatest throughput for the processes involved. All MS^3 in this study employed adducts derived from n-octanoic acid (caprylic acid) to keep m/z low to accommodate the poor resolution of MIKES spectra.

Ab initio calculations were performed by using the Gaussian 94 suite of programs (Gaussian, Inc.) and Spartan 4 (Wavefunction, Inc.), was employed as a graphical front-end for Gaussian 94. Geometries of candidate structures for adducts and fragments with up to five carbons were optimized initially at the level of HF/6-31G(d), qualified by frequency calculations, and the stationary-point structures were

reoptimized at the level of MP2/6-31G(d). Since the carboxylates have substantial anionic character, diffuse functions in the basis are needed. For that reason and to reduce escalating time and cost, geometries and frequencies are being calculated for the Li adducts by using B3LYP/6-31+G(d) of density functional theory. Finally, geometries are being refined at the level of B3LYP/6-311+G(2d,p).

Results and Discussion.

MS/MS results. In the CAD spectra of the adducts of n-octanoate with two alkali metals, the ratios of relative yields of radical and closed-shell fragment ions at a given number of carbons show dramatic variation with size (number of carbons) and alkali metal. As a function of metal, the radical/closed-shell ratio declines slightly for 3C fragments, but increases substantially for 4C to 7C fragments, most dramatically for the 4C fragment. This indicates some kind of interaction of the alkali metal cations with the rest of the anion beyond the carboxylate. In addition, the relative yields of fragments, M^+ , M_2^{+} , and M_2O^+ , increase greatly with increasing size of the alkali cation. Similar results have been obtained in the CAD spectra of the alkali-metal adducts of palmitate, palmitoleate, phytanate, and 10-oxopalmitate.

MS/MS/MS results. The MIKES spectra of intermediate products, both radical and closed-shell (CR), was obtained for ions having five carbons or less with Li or Na as the alkali metal. All intermediate product ions fragment upon CA to produce the M^+ , M_2^{+} , and M_2O^+ ions, the formation of which must be quite general. In addition, CO_2Li^+ , is formed from the Li-containing intermediates. The fragmentation patterns for the intermediate products form two distinct classes: the radical ions, formula $(CH_2)_{n+2}CO_2M_2^{+}$, which readily lose C_2H_4 units, and the closed-shell products which are much less susceptible to CAD and lose the C_2H_3 , C_3H_5 , etc., series of ions. (The size of intermediate product capable of the next CR round of losses has not been reached). Furthermore, the loss of $H\bullet$ from the radical ions is very weak, which implies that these ions are *not* the precursors for the charge-remote series of ions. In addition, all larger ions produce the two smallest radical ions upon CAD which suggests a rationale for their large abundance in charge-remote spectra.

Ab initio calculation results. Two distinct types of conformations that are candidates for the structure of the intermediate product and precursor ions have been discovered. An 'open' form has both of the metal ions extending away from the carboxylate oxygens. A 'closed' form has one metal ion held between the oxygens. The other metal ion extends away from an oxygen in the smallest ions, but for ions of three or more carbons, there are two possible conformers: one with the other metal ion extending away from an oxygen and the backbone, and the other with the second metal ion located between an oxygen and the backbone and in position to interact with features on the backbone. In addition, the stabilization effected by the second metal ion increases for increasing size (# of C's) of the ions and tends to increase most rapidly for the radical product and least so for the closed-shell unsaturated product, which is in accord with experimental results.

References

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