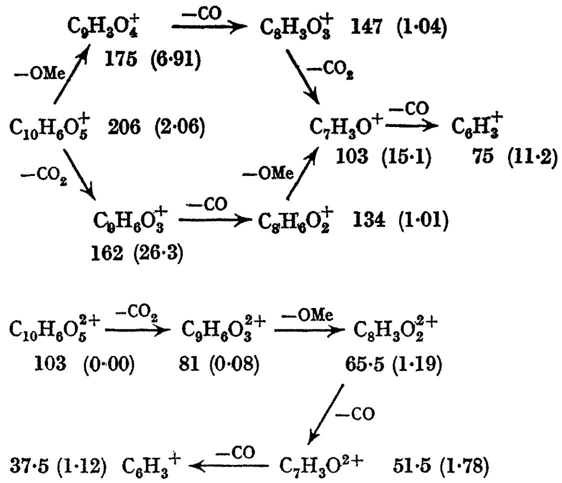
Contrasting Behaviour of Singly and Doubly Ionized Molecules of 4-Methoxycarbonylbenzene-1,2-dicarboxylic Anhydride; Role of the Localized Charges

By SEYMOUR MEYERSON*
(*Research and Development Department, American Oil Company, Whiting, Indiana* 46394)
and IMRE PUSKAS and E. K. FIELDS
(*Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana* 46394)

A LOCALIZED charge may direct the decomposition of ionized molecules produced by electron impact in a mass spectrometer.[1,2a] In the mass spectra of a series of 4-alkoxycarbonylbenzene-1,2-dicarboxylic anhydrides,[3] we found a clear example of the directive role of a localized charge. The methyl ester shows contrasting decomposition sequences of singly and doubly ionized molecules.

Aromatic anhydrides characteristically undergo sequential loss of CO_2 and CO; [2b,4] methyl esters of aromatic acids, similarly, lose OMe and CO.[2c,5] The *m/e* values (given in the Scheme) and the metastable peaks listed in the Table suggest that the dominant reaction sequences for the singly and doubly ionized molecules are (1) and (2) (intensities in parentheses). The high intensity at *m/e* 103, in view of the low intensities at 147 and 134, suggests that the $C_7H_3O^+$ yield may arise in part by loss of CO_2Me from $C_9H_6O_3{}^+$ or of C_2O_3 from $C_9H_3O_4{}^+$ in a single step. However, low intensity does not necessarily rule out an ion as a significant precursor of a further decomposition product occurring in substantially higher intensity.[6] Moreover, the spectrum shows no supporting metastable peak for either of these direct routes. However, the relative contributions of the



Percent of total ion intensity at *m/e* 25 and greater, measured with 70v electrons on a CEC Model 21-103 mass spectrometer with source and inlet system at 250°.

various competing and consecutive reaction steps differ sharply between the singly and doubly ionized molecules.

Metastable peaks in spectrum of 4-*methoxycarbonylbenzene*-1,2-*dicarboxylic anhydride*

Apparent Mass	Transition: Mass number	Transition: Ions
127·4	$206^+ \rightarrow 162^+ + 44$	$C_{10}H_6O_5^+ \rightarrow C_9H_6O_3^+ + CO_2$
123·4	$175^+ \rightarrow 147^+ + 28$	$C_9H_3O_4^+ \rightarrow C_8H_3O_3^+ + CO$
110·8	$162^+ \rightarrow 134^+ + 28$	$C_9H_6O_3^+ \rightarrow C_8H_6O_2^+ + CO$
72·2[a]	$147^+ \rightarrow 103^+ + 44$	$C_8H_3O_3^+ \rightarrow C_7H_3O^+ + CO_2$
54·6	$103^+ \rightarrow 75^+ + 28$	$C_7H_3O^+ \rightarrow C_6H_3^+ + CO$
40·5	$131^{2+} \rightarrow 103^{2+} + 28$	$C_8H_3O_2^{2+} \rightarrow C_7H_3O^{2+} + CO$
27·3	$103^{2+} \rightarrow 75^{2+} + 28$	$C_7H_3O^{2+} \rightarrow C_6H_3^{2+} + CO$

[a] The metastable peak in this region is flat-topped and extends from 72 to 73.

In the former, competing primary reactions are centred in the anhydride and methoxycarbonyl groups. Either primary step is followed by loss of CO, completing the two-step sequence characteristic of the functional group before the first step of the sequence associated with the second group. Relative intensity at *m/e* 131, corresponding to loss of OMe and CO_2, is extremely low (0·03). In the doubly ionized molecule, in contrast, loss of the one neutral product from each of the two functional groups gives rise to a much more prominent peak.

These observations suggest that the centre of reactivity in the singly charged molecule remains localized in one or the other functional group until the appropriate two-step sequence is complete, and only then migrates to the second group. In the doubly charged molecule, however, a reactive centre in the methoxycarbonyl group competes effectively with that in the anhydride group following the primary loss of CO_2. The situation in the doubly charged molecule is most simply visualized by equating the reactive centres with the two charges, largely localized in the functional groups by virtue of coulombic repulsion.

Models similar to that suggested here can account for other known examples in which singly and doubly ionized species of the same molecule show sharply different behaviour.[7]

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