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MECHANISM OF ACETYL TRANSFER TO OXYGEN BASES IN ION-MOLECULE REACTIONS OF 2,3-BUTANEDIONE

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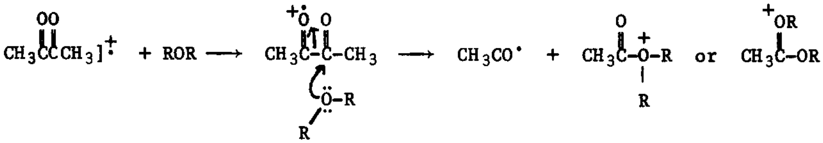
Recent studies using ion cyclotron resonance (icr)[1] have shown great promise for the study of gaseous ion structure through the analysis of ion-molecule reactions.[2,3] The chemistry of the gaseous ions involved may or may not resemble their reactivity in solution chemistry, or even their unimolecular decompositions found in conventional mass spectrometry. A wide range of organic functional groups, whose reactivity in solution and mass spectral chemistry are quite different, have been reported to have been acetylated by 2,3-butanedione using the icr technique.[4]

Elucidation of the reaction pathway by double resonance techniques[5] establishes that the acetylated ions are produced by the reaction of ions of m/e 86 and 129, but not m/e 43, with the appropriate neutral species. While a reasonable reaction pathway may be envisaged for the reaction of m/e 86 with, for example, an alcohol or ether (eq. 1),

(1)



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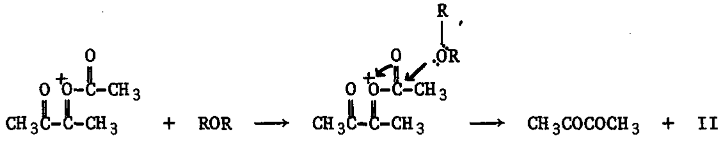
the nature of the m/e 129 species, produced by the reaction of neutral 2,3 butanedione with its molecular ion,[4] in the acetylation reaction is unclear: the structure (III) may transfer any of the three non-equivalent acetyl groups or a specific acetyl group may be transferred. We now report an experiment which distinguishes between these possibilities.

Experiments on mixed systems of butanedione and butanedione-d_6 show that the acetyl group that is added to the neutral molecule to make *m/e* 129 (132, 135, or 138) is the group that is lost when *m/e* 129 reacts to acetylate some other neutral species. That is, 138 and 132 transfer only CD_3CO^+, while 129 and 135 transfer CH_3CO^+ (eq. 2, 3, 4, 5),

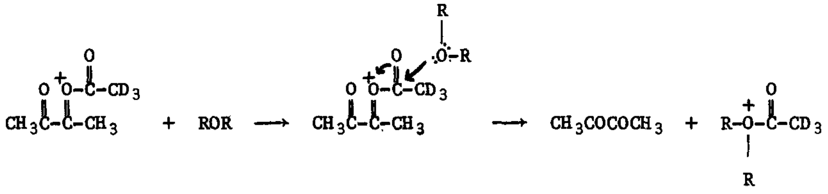
(2)



III

m/e 129

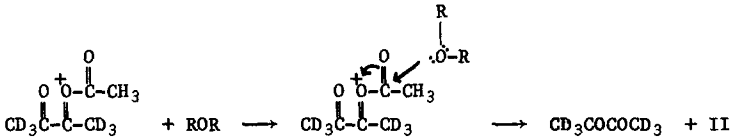
(3)



IV

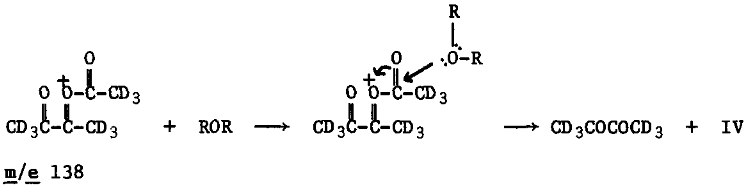
m/e 132

(4)



m/e 135

(5)



when the neutral was either methanol or diethyl ether. (The latter was conveniently used because it is the solvent in the isolation of the fully deuterated butanedione,[6] which was prepared by three exchanges of 5-7 days each in D_2O/DCl.)[7] Thus the added acetyl group in the *m/e* 129 ion is attached to the parent molecule by a bond that is preferentially broken in subsequent reaction; our proposed structure (III) easily meets this criterion.

We note that the *m/e* 129 ion, but not the *m/e* 43 ion, is an active acetylating agent; our reactions do not, therefore, correspond to the $A_{AC}1$ mechanism of esterification[8] in solution chemistry. Nor can the process be accurately described in terms of the typical $A_{AC}2$ acylation mechanism,[9] although the reaction is a bimolecular transfer of acetyl with cleavage at a bond to the acyl group, as the symbol $A_{AC}2$ implies.

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