# A Mass Spectrometric Method of Locating Double Bonds by the Use of Ion-molecule Reactions

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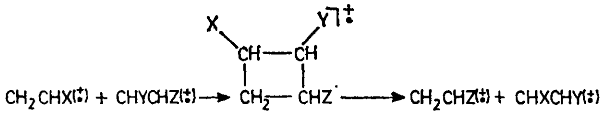
*Summary* A method is described by which the position of a double bond in an unsaturated compound can be inferred from the ionic products given by its reaction with the molecular ion of vinyl methyl ether.

Previous work in this laboratory has shown that in the fluoroethylene[1] and fluoropropene[2] systems, one of the major reactions of molecular ions is to yield new olefinic ions and neutral species. This reaction is thought to proceed *via* a four-centre complex which fragments without rearrangement. The use of deuterium-labelled compounds showed that no H/D atom intra-molecular exchange occurs in this type of reaction. More recently, similar behaviour has been observed in the vinyl methyl ether system[3] and this suggested that reactions of the type shown in equation (1) in which the charge may reside on either of the reactants and products, may be quite general and could possibly be used to locate the position of double bonds in some types of molecule.



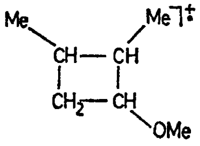
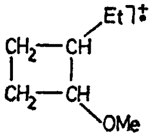
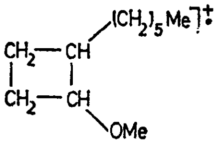
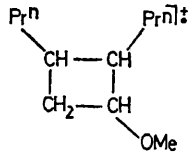
(1)

Reactions of the molecular ion of vinyl methyl ether with a number of unsaturated compounds have therefore been investigated in an ion cyclotron resonance mass spectrometer at pressures of *ca.* $10^{-5}$ Torr and in a high pressure source of an AEI MS50 mass spectrometer at pressures of up to 1 Torr (1 Torr = 133 $Nm^{-2}$). In the latter case, sensitivity was increased by adding $CO_2$ as a charge exchange reagent; this also served to reduce the number of fragment ions formed from vinyl methyl ether. Volatile samples were introduced by premixing them with the vinyl methyl ether (*ca.* 1 : 100) and solids were introduced on a probe.

Several unsaturated hydrocarbons were examined by this technique and the major relevant products are shown in the Table. These products enable one to distinguish the pairs of isomers, but-1-ene and but-2-ene, and oct-1-ene and *trans*-oct-4-ene.

The applicability of the method to the location of double bonds in larger molecules is under investigation. Preliminary results obtained with unsaturated acids, esters and ethers suggest that although reaction (1) becomes much less important as the chain length increases, it is nevertheless possible to infer the position of the double bond. Oleic acid $[Me(CH_2)_7CH{=}CH(CH_2)_7CO_2H]$ was run as an unknown, and was correctly identified from the observation of a peak at $m/q = 200$, given by the ion $MeOCH{=}CH(CH_2)_7CO_2H^{+\cdot}$, and the absence of other peaks that would have been observed if the position of the double bond had been different.

Table

| Reactant | Intermediate | Major product |
|---|---|---|
| $MeCH{=}CHMe$ |  | $MeCH{=}CHOMe^{+\cdot}$ |
| $CH_2{=}CH\text{-}Et$ |  | $EtCH{=}CHOMe^{+\cdot}$ |
| $CH_2{=}CH(CH_2)_5Me$ |  | $Me(CH_2)_5CH{=}CHOMe^{+\cdot}$ |
| $Pr^nCH{=}CHPr^n$ |  | $Pr^nCH{=}CHOMe^{+\cdot}$ |

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[1] A. J. V. Ferrer-Correia and K. R. Jennings, *Internat. J. Mass Spectrometry Ion Phys.*, 1973, **11**, 111.

[2] C. J. Drewery and K. R. Jennings, unpublished work.

[3] C. J. Drewery and K. R. Jennings, *Internat. J. Mass Spectrometry Ion Phys.*, in the press.