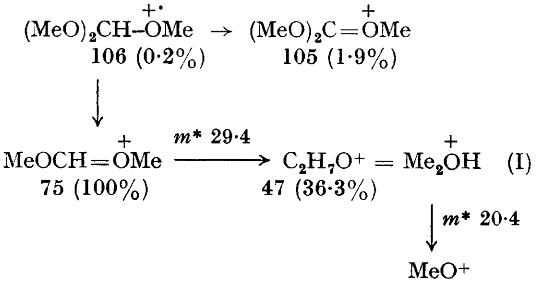
Anomalous Fragments in the Mass Spectra of Trimethyl Orthoformate and Related Compounds

By M. J. RIX, A. J. C. WAKEFIELD, and B. R. WEBSTER
(*Imperial Chemical Industries Limited, Pharmaceutical Division, P.O. Box 25, Alderley Park, Macclesfield, Cheshire*)

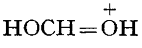
THE mass spectrum of trimethyl orthoformate, as one might expect, exhibits a weak molecular ion and a somewhat stronger peak for the $(M-1)^+$ ion at *m/e* 105. The base peak (*m/e* 75) corresponds to loss of methoxy-radical from the molecular ion and further fragmentation occurs as shown in the scheme, wherein the pathway is supported by the evidence of metastable peaks and accurate mass measurements of the fragments.



$$\begin{tikzcd} \begin{matrix}(MeO)_2CH\text{–}\overset{+\cdot}{O}Me \\ 106\ (0{\cdot}2\%)\end{matrix} \arrow[r] \arrow[d] & \begin{matrix}(MeO)_2C=\overset{+}{O}Me \\ 105\ (1{\cdot}9\%)\end{matrix} \\ \begin{matrix}MeOCH=\overset{+}{O}Me \\ 75\ (100\%)\end{matrix} \arrow[r, "m^*\ 29{\cdot}4"] & \begin{matrix}C_2H_7O^+ = Me_2\overset{+}{O}H\ \ (I) \\ 47\ (36{\cdot}3\%)\end{matrix} \arrow[d, "m^*\ 20{\cdot}4"] \\ & MeO^+ \end{tikzcd}$$

The composition of the peak at *m/e* 47 is most unexpected although the presence of a peak here has been previously reported for this compound by other workers.[1] It is also known[2] that diethyl acetals (II) give rise to a strong peak at *m/e* 47 and this is attributed to a protonated formic acid structure (III) formed by the loss of R together with a molecule of ethylene from each of the ethoxy-groups.

$(EtO)_2CHR$
(II)



$HOCH=\overset{+}{O}H$
(III)

$(R'O)_3CH$
(IV) $R'=Me$
(V) $R'=Et$

It is obvious from the elemental composition of the ion at *m/e* 47 in the spectrum of trimethyl orthoformate (IV) that there is no connection between this ion and the ones observed in the spectra of the diethyl acetals. The composition $C_2H_7O^+$ can only satisfactorily be represented by the protonated dimethyl ether structure (I).

$(MeO)_2CHR$
(VI) $R = H$
(VII) $R = Me$
(VIII) $R = Pr^i$
(IX) $R = Me\cdot[CH_2]_5$

Triethyl orthoformate (V) was also found to show a peak at *m/e* 47, but as was expected this had the elemental composition CH_3O_2 and was therefore of the protonated formic acid type (III). Dimethyl acetals, however, should behave like trimethyl orthoformate; this in fact was confirmed using the dimethyl acetals (VI—IX) whose spectra all showed the presence of the ion $C_2H_7O^+$ together with the metastable peak at *m/e* 29·4 for the transition $75^+ \rightarrow 47^+ + 28$.

Having established that this $C_2H_7O^+$ ion is characteristic of trimethyl orthoformate and related compounds we are continuing our investigations in order to determine the nature of the rearrangements involved.

All spectra were determined using an A.E.I. M.S. 9 double-focussing mass spectrometer.

(*Received, September* 16*th*, **1966**; *Com.* **699**.)

---

[1] "Index of Mass Spectral Data", A.S.T.M. Special Publication No. 356; A.S.T.M., 1916 Race Street, Philadelphia 3, Pennsylvania.

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964, p. 53.