Intramolecular 1,6-Hydride Transfer in Gaseous Carbonium Ions

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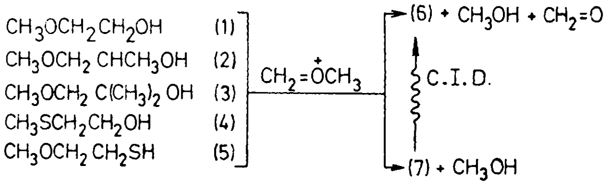
Summary The ion–molecule chemistry of 2-methoxyethanethiol reveals that the major product ion $C_3H_7S^+$ is formed by way of an intramolecular hydride transfer in a precursor ion.

In a study of the gas-phase ion-molecule reactions of 2-methoxyethanol (**1**) and related compounds (**2**—**5**) by i.c.r. (ion cyclotron resonance) techniques we have observed that each reacts with $CH_2{=}\overset{+}{O}CH_3$ *m/e* 45 to give a product ion

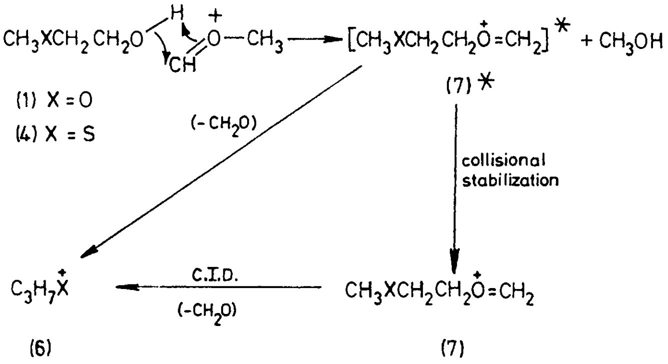
(**6**) *m/e* ($M - 17$) which formally corresponds to the stripping of HO^- from the neutral reactant *M*. Another reaction leads to ion (**7**) *m/e* ($M + 13$). Double resonance experiments indicate that (**6**) can be formed from (**7**) by a collision-induced decomposition (C.I.D.).[1]



The course of these reactions is not obvious, especially in the case of the thiol (**5**) so a detailed investigation was made using labelled substrates. Using a dual-inlet system on a pulsed i.c.r. spectrometer[2] ions at *m/e* 45, 47, and 48, $CH_2{=}\overset{+}{O}CH_3$, $CD_2{=}\overset{+}{O}CH_3$, and $CH_2{=}\overset{+}{O}CD_3$, were generated from labelled 1,2-dimethoxyethane or ethyl methyl ether and treated with the neutral substrates (**1**), (**4**), and (**5**) and their CD_3-labelled analogues.

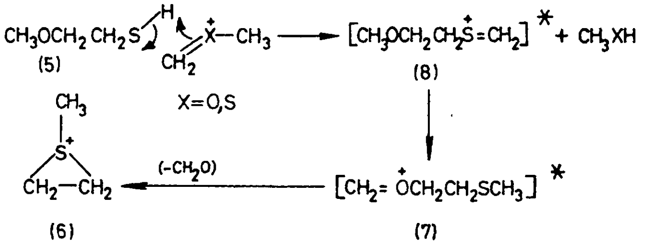
The ion (**6**) from labelled and unlabelled (**1**) and (**4**) had *m/e* ($M - 17$) showing no incorporation of deuterium from the reactant ions *m/e* 47 and 48 and complete retention of deuterium from the neutral substrate. Ion (**7**) showed that the label from $CD_2{=}\overset{+}{O}CH_3$ was retained, while that from $CH_2{=}\overset{+}{O}CD_3$ was lost. Further, (**7**) was formed from $CH_2{=}{}^{18}OCH_3$ with no incorporation of the oxygen label.[3] The results are summarised in Scheme 1 which shows (**7**) to be formed by methylene transfer from the reactant ion to the hydroxy-oxygen of the alcohol accompanied by loss of methanol, and (**6**) to be formed dissociatively from (**7**) by loss of formaldehyde.

The results for the thiol (**5**) are different. The label from *m/e* 47 was retained in (**6**) and only one deuterium in the CD_3 label of (**5**) was retained in (**6**). These results are summarised in Scheme 2. The first step involves transfer of CH_2 from the reactant ion to sulphur with the formation of (**8**) which is isomeric with (**7**). Rearrangement of (**8**) to (**7**) may then occur by way of a 1,6-hydride transfer from the methyl carbon on oxygen to the terminal carbon on sulphur. Subsequent elimination of CH_2O gives (**6**). By this route, CD_2 of *m/e* 47 and one deuterium of CD_3 in (**5**) should be retained in (**6**), as observed. Similar results with (**5**) were observed using $CH_2{=}S^+CH_3$, *m/e* 61, as the reactant ion. The alcohols, however, condensed with the *m/e* 61 ion to give (**7**) but the subsequent dissociation to (**6**) did not occur significantly.



Scheme 1

I.c.r. techniques give no direct proof of ion structure and alternative structures for (**6**)—(**8**) are conceivable. Schemes 1 and 2 are offered as plausible but not proven pathways for the observed reactions. The hydride transfer, which was observed in the direction (**8**) → (**7**) only, is unusual in that high-order hydride shifts are rare in acyclic carbonium ions.[4] It raises some interesting questions as to whether or not the 1,6 shift implicated for the gaseous ions is observable in solution phase, and whether the driving force for the rearrangement is the stability of (**7**) over (**8**) or of the final products [(**6**) and $CH_2{=}O$].



Scheme 2

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