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Dear Sir

Alkylation of α-Ethylenic Aldehydes in the Gas Phase

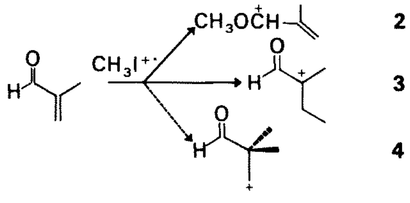
The reactions of carbocations of alkyl iodides with bifunctional compounds in the gas phase have been investigated by Maquestiau and co-workers,[1] Gross and co-workers,[2] Harrison,[3] Cooks and co-workers,[4] and ourselves.[5]

The protonation site of α-ethylenic carbonyl compounds has been determined by ICR.[6] In this work, the reaction of ICH_3 on 2-methyl propenal has been studied under chemical ionization conditions.

The reaction of CH_3I with α-ethylenic aldehydes leads to *O*-alkylation and *C*-alkylation products.

(a) In the ion source equimolar amounts of CH_3I and 2-methyl-2-propenal lead to the adduct ion **1** $[C_4H_6O, CH_3]^+$. This ion reacts in the 2nd FFR to give *m/z* 43 (17%), *m/z* 55 (15%), *m/z* 57 (10%) and *m/z* 67 (58%) (Table 1).

Ion **1** corresponds (Scheme 1) either to the structure **2** if *O*-alkylation occurs and/or to the structure **3** if *C*-alkylation is observed (structure **4**, corresponding to a primary carbocation, is not probable).



Scheme 1

(b) Ion **2** has been generated in the source by α-cleavage of the corresponding ether under electron impact. This ion eliminates CH_2O in the 2nd FFR leading to the *m/z* 55 fragment ion. Furthermore, ions **2a** $[CD_3OC_4H_7]^+$ and **1a** (generated by reaction with CD_3I) lose CD_2O and the kinetic energy releases are similar for **1** and **2**. Hence, it can be concluded that *O*-alkylation occurs.

(c) The metastable adduct ion **1** leads additionally to the abundant fragment ion at *m/z* 43 $[CH_3CO]^+$, *m/z* 57 $[\mathbf{1} - CO]^+$ and *m/z* 67 $[\mathbf{1} - H_2O]^+$. The corresponding peaks are very weak in the MIKE spectrum of ion **2** (Table 1). On the other hand, these peaks are observed with identical kinetic energy releases in the MIKE spectrum of ion **3** (generated in the ion source by protonation of the corresponding α-bromo aldehyde followed by HBr elimination).

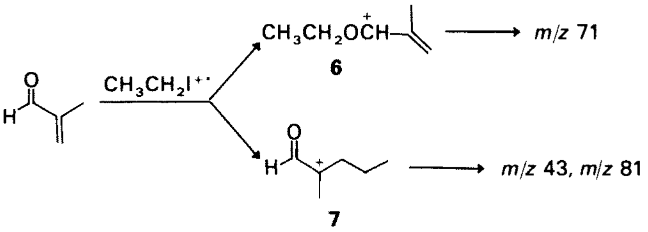
Table 1. MIKE spectra of ions 1 to 3 (VG.ZAB.2F)

	m/z 43	*m/z* 55	*m/z* 57	*m/z* 67
1	17	15	10	58
2	2.5	92	3	2.5
3	39	–	16	45

These data show that *C*-methylation is also observed even if $\Delta H\ [\mathbf{3}] - \Delta H\ [\mathbf{2}] = 79.5\ \mathrm{kJ\ mol^{-1}}$ (MNDO calculation). Similar conclusions have been obtained with different α-ethylenic carbonyl compounds.

The ethyl cation is not implied in the alkylation process

The adduct ion **5** $[C_4H_6O, C_2H_5]^+$, formed in the ion source by reaction of the 2-methyl-2-propenal with C_2H_5I leads in the 2nd FFR to the fragment ions (Scheme 2) *m/z* 43 $[CH_3CO]^+$ (10%), *m/z* 71 $[\mathbf{5} - CO]^+$ (1%), and *m/z* 81 $[\mathbf{5} - H_2O]^+$ (44%) probably by the fragmentation of the *C*-alkylated ion **7**, and to fragment ion *m/z* 71 $[\mathbf{5} - C_2H_4]^+$ (45%) by elimination of the ethyl chain in the *O*-alkylated isomer **6**. Ion **6** generated in the source by α-cleavage of the corresponding ethers eliminates only C_2H_4 in the 2nd FFR.



Scheme 2

Reaction of CD_3CH_2I gives the labelled adduct ion **5a** which eliminates in the 2nd FFR, $C_2H_2D_2$ (86%) and C_2HD_3 (only 14%). So the *O*-alkylated form corresponds to the structure $[CD_3{-}CH_2{-}O{-}CH^+{-}C(CH_3){=}CH_2]$ and any H/D exchanges before alkylation are not important.

A statistical H/D permutation has been observed before in $[CD_3CH_2]^+$ and $[CH_3CD_2]^+$ preceding further reactions.[7] Hence the ethyl cation cannot be the reactant in the *O*-alkylation process.

Ion **5a** leads also to $[C(H,D)_3CO]^+$ ions at *m/z* 43 (57.5%), *m/z* 44 (8.5%), *m/z* 45 (6.9%) and *m/z* 46 (27.1%). Again a reaction of the ethyl cation would lead to H/D excessive exchange in $[CD_3CH_2]^+$ before alkylation and cannot explain the abundance of $[CD_3CO]^+$, *m/z* 46, in **5a**.

In conclusion therefore, the ethyl cation is neither the reactant leading to the *O*-ethylated form nor the reactant giving the *C*-ethylated adduct ion.

Ion–molecule complexes $[C_4H_6O, \text{alkyl iodide}]^{+\cdot}$ are intermediates in the alkylation mechanism.

Ion–molecule complexes formed in the ion source have been characterized by their fragmentations in the 2nd FFR. For instance, the complex $[C_4H_6O, CH_3I]^{+\cdot}$ gives $[CH_3I]^{+\cdot}$ and eliminates $I^\cdot$ under collisions leading to the adduct ion **1**.

The same result is obtained with C_2H_5I. As the reactions with $[CD_3CH_2I]^{+\cdot}$ are not preceded by H/D exchange,[7] the formation of such complexes gives specific alkylation reactions.

Even if secondary mechanisms, such as the reaction of $[C_2H_5IC_2H_5]^+$ cannot be discarded by these experimental data, this work proves that the formation of [α-ethylenic aldehyde, alkyl iodide]$^{+\cdot}$ complexes is the dominant process leading to the alkylation reactions under chemical ionization conditions.

Yours

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