

OMS Letter

Dear Sir

Ethylation of Ethanol in the Gas Phase

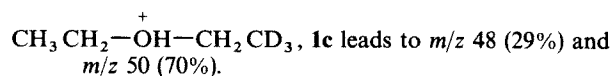
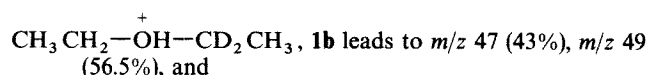
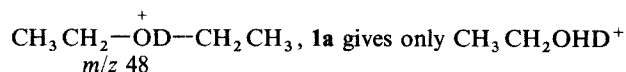
In the gas phase, alkyl halides RX lead either to alkylation¹ or protonation reactions.²

The reagent in these processes (RX^{+} , R^{+} or $R-X^{+}-R$) can often be determined by ion cyclotron resonance but not so easily under chemical ionization conditions. In this work, CH_3CD_2I and CD_3CH_2I have been used to determine the mechanism of the ethylation of ethanol by CH_3CH_2I in the source of a mass spectrometer (VG ZAB 2F).

In the ion source, equimolecular quantities of C_2H_5OH and of ethyl iodide lead to the formation of the symmetrical

protonated ether $CH_3CH_2-OH-CH_2CH_3$. This ion has been selected with the magnetic field and characterized by the fragmentations observed in the 2nd field-free region (2nd FFR).

In Table 1, the spontaneous fragmentations of metastable protonated diethyl ether **1** and its deuterated analogues **1a–1c** have been compared to those of the corresponding ions **2** and **3** generated by ion–molecule reactions. The metastable ion **1** loses ethylene after $H(\beta)$ migration leading to the $CH_3CH_2OH_2$ fragment ion (m/z 47). The results from **1a–1c** show that the $H(\beta)$ migration is selective; a strong primary isotopic effect (**1c**) and a less important secondary isotopic effect (**1b**) are observed:



The same results are obtained for the isomeric ions **2a**, **2b** and **2c** generated by reaction of labelled ethanols with CH_3CH_2I (Table 1).

However, the behaviour of **3a** and **3b** ions, formed by reaction between labelled alkyl iodides and ethanol, shows that two mechanisms are implied in the ethylation reaction. The first one is dominant and selective while, for the second one, hydrogens of the ethyl iodide exchange before alkylation. The non-specific mechanism corresponds, most probably, to the

reaction between the ethyl cation and ethanol. Indeed, spontaneous and collision induced dissociations of $[CD_2CH_3]^+$ and $[CH_2CD_3]^+$ metastable cations show that extensive H/D exchange occurs before the 2nd FFR.

However, the collision-induced dissociations of $[CH_3CD_2I]^{+}$ and $[CD_3CH_2I]^{+}$ metastable ions indicate that in the 2nd FFR these ions still have their initial structures: H/D exchange is not observed. The same conclusion has been obtained by neutralization–reionization mass spectrometry.³

It is possible to conclude from these results that the reaction between $[ICH_2CH_3]^{+}$ and C_2H_5OH corresponds to the dominant and selective mechanism.

The existence of the adduct ion $[CH_3CH_2I/CH_3CH_2OH]^+$ has been proved: this adduct ion has been selected with the magnetic field; in the 2nd FFR this ion leads to

$[CH_3CH_2I]^{+}$ and $CH_3CH_2-OH-CH_2CH_3$. These data confirm that the radical cation $[CH_3CH_2I]^{+}$ is the dominant reagent in the alkylation reaction of the alcohol.

Preliminary results of the study under ICR conditions indicate that $[CH_3CH_2I]^{+}$ reacts easily with C_2H_5-OH while the reactions $[CH_3CH_2]^+ + C_2H_5OH \rightarrow CH_3CH_2-OH-CH_2CH_3$, and $C_2H_5I + [CH_3CH_2OH]^{+} \rightarrow CH_3CH_2-OH-CH_2CH_3$ are very slow.

Yours

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References

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Table 1 MIKE spectra of $CH_3CH_2-OH-C_2(H,D)_2$ ions

		m/z 47	m/z 48	m/z 49	m/z 50
1	$CH_3-CH_2-O-CH_2CH_3/H_3O^+$	100	–	–	–
1a	$CH_3-CH_2-O-CH_2CH_3/D_3O^+$	0.5	99.5	–	–
1b	$CH_3-CH_2-O-CD_2CH_3/H_3O^+$	43	0.5	56.5	–
1c	$CH_3-CH_2-O-CH_2CD_3/H_3O^+$	1	29	–	70
2a	CH_3-CH_2-OD/CH_3CH_2I	4	96	–	–
2b	CH_3-CD_2-OH/CH_3CH_2I	41	0.5	58.5	–
2c	CD_3-CH_2-OH/CH_3CH_2I	–	30	0.5	69.5
3a	CH_3-CH_2-OH/CH_3CD_2I	41.5	3.5	55	–
3b	CH_3-CH_2-OH/CD_3CH_2I	9	26	–	65