

OMS Letters

Dear Sir

Study of the Ethylation of Ethanol by Using a Dual-cell Fourier Transform Mass Spectrometer

In a recent letter, Audier *et al.*¹ reported mass spectrometric studies of the ethylation of ethanol in the gas phase. In another letter, Thölmann and Grützmacher² discuss the advantages of external ionization for the study of ion-molecule reactions in Fourier transform ion cyclotron resonance spectrometers. The dual trapped-ion cell arrangement³ employed in the Nicolet FTMS-2000 Fourier transform mass spectrometer (FTMS or FT/ICR) offers unique advantages for studies of this nature,^{4,5} and we wish to report its application for ion-molecule reactions in the gas phase by using the ion-molecule reactions of ethyl iodide and ethanol as an example.

In single-cell FTMS instruments, both of the reactants are present in the trapped-ion cell. In this case, both ethanol and iodoethane are introduced into the cell. After the ionization event, both ethanol and iodoethane molecular ions, protonated molecules, and fragment ions are present. However, ejection pulses can be used to remove all ionic species, except the reactant ion of interest. A delay period follows during which the reaction is allowed to occur. Because the ethanol and iodoethane neutral reactants are still present in the single cell, the selected reactant ion can undergo reactions with both compounds. Because of the possibility of charge transfer and protonation reactions, the reaction to form the protonated diethyl ether may not be characterized, even with isotopically labelled compounds. In single-cell FTMS instruments this problem can partially be overcome by the use of pulsed valves for sample introduction, but a more elegant solution is to employ the features of the dual trapped-ion cell arrangement. The neutral gas that is to react with the ions of interest can be kept at constant, known pressures in one cell, and the ions formed from another gas, which is pulsed into the other cell.

By using the dual-cell arrangement, the reaction mechanisms under study can be elucidated without the use of labelled compounds.

The reactant ion (e.g. $[\text{EtI}]^+$) is formed in Cell 1 by using pulsed valve introduction of the reactant gas, followed by electron ionization. A second gas (e.g. EtOH) is present at a constant pressure in Cell 2. Ion ejection events are used to isolate the reactant ion population in Cell 1, and it is transferred to Cell 2 where reactions occur for a selected interval. After the reaction period, the product ions are detected. It should be mentioned that ions can be formed and detected in both cells.

In this manner the reactions of $[\text{C}_2\text{H}_5\text{OH}]^+$ with iodoethane were found to yield the iodoethane molecular ion through charge-transfer reactions. The reactions of $[\text{C}_2\text{H}_5\text{I}]^+$ with ethanol were found to produce the protonated ether ion $[(\text{C}_2\text{H}_5)_2\text{OH}]^+$, whereas the ethyl ion, $[\text{C}_2\text{H}_5]^+$, did not produce the protonated ether ion upon reactions with either reactant.

As pointed out by Audier *et al.*,¹ the protonated ether ion is produced via a transition complex, $[\text{C}_2\text{H}_5\text{I} \cdot \text{C}_2\text{H}_5\text{OH}]^+$ (m/z 202). This intermediate could not be directly observed in the FT mass spectra, and thus, the transition complex must fragment in a shorter time than the spectral acquisition time. However, indirect evidence was found that shows that the initial step in the reaction of the iodoethane molecular ion with ethanol is the production of a complex at m/z 202. Figure 1(a) shows a mass spectrum obtained after reaction of the

iodoethane molecular ion with ethanol for 5 s. The formation of the protonated ether ion at m/z 75 can be observed as explained above. The spectrum shown in Fig. 1(b) was obtained under the same conditions, except using a method⁶ involving the use of an ejection pulse that ejected any ion present at m/z 202 during the entire reaction time. The absence of the product ion at m/z 75 in the spectrum in Fig. 1(b) supports the existence of the intermediate complex.

The dual-cell arrangement adds considerably to the power of FTMS for the study of ion-molecule reactions, and in many cases evidence for the existence of short-lived reaction intermediates can be obtained by ion ejection techniques.

Yours

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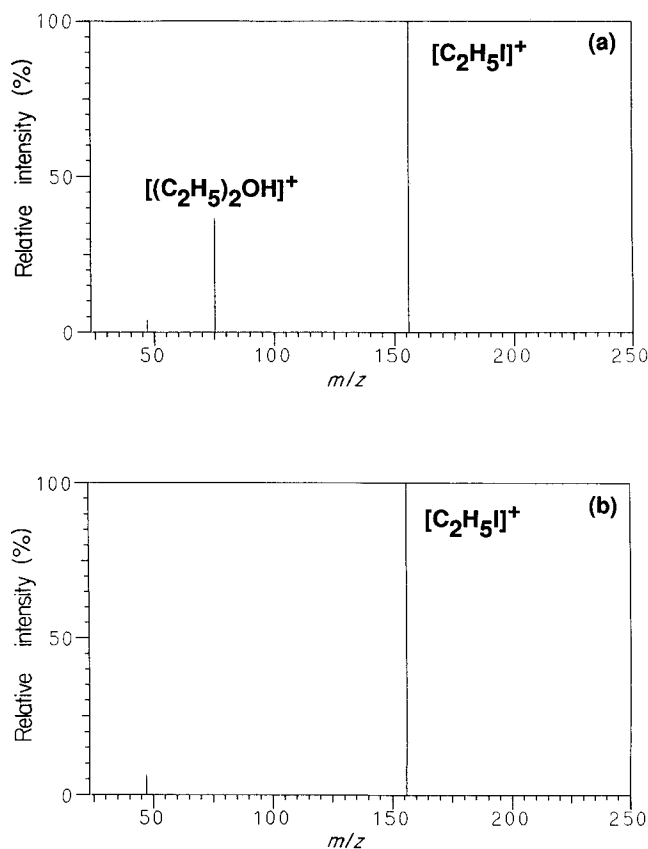


Figure 1. Indirect evidence for the existence of an intermediate complex at m/z 202. (a) Mass spectrum illustrating the formation of the protonated ethyl ether molecule in the reaction of the iodoethane molecular ion with ethanol. (b) Mass spectrum obtained under the same conditions as (a) except with continuous ejection of m/z 202 during the entire reaction period.

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References

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