A Low-pressure Chemical Ionisation Source: An Application of a Novel Type of Ion Storage Mass Spectrometer

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Summary Results are presented which show that a three-dimensional quadrupole ion storage trap (Quistor), operated at low pressures, may provide a viable alternative to the conventional high-pressure chemical ionisation source normally employed.

THE technique of 'chemical ionisation' mass spectrometry, first described by Munson and Field,[1] has now become an established method[2,3] for the mass spectral characterisation of molecules which, under normal electron impact, form a proliferation of low molecular weight ions. Ionisation of the sample takes place through ion–molecule reactions between reactant ions, held in a relatively high concentration, and substrate molecules, present at a much lower partial pressure.

The most commonly used reactant ions are CH_5^+ and $C_2H_5^+$ formed from methane under conditions where sequential ion–molecule reactions between the primary ions observed in the mass spectrum of methane and methane itself lead to high yields of secondary ions. In a conventional mass spectrometer ion source such conditions are only achieved at high methane pressures, *ca.* 1 Torr, where the most intense ions, CH_5^+ and $C_2H_5^+$, account for 47 and 41% of the total ionisation, respectively.[2] In practice these high-pressure conditions cause experimental difficulties in operating the instrument; in particular the avoidance of high-voltage electrical discharges within the source and reactant gas supply lines and the need for differential pumping to maintain the analyser at an acceptably low pressure.

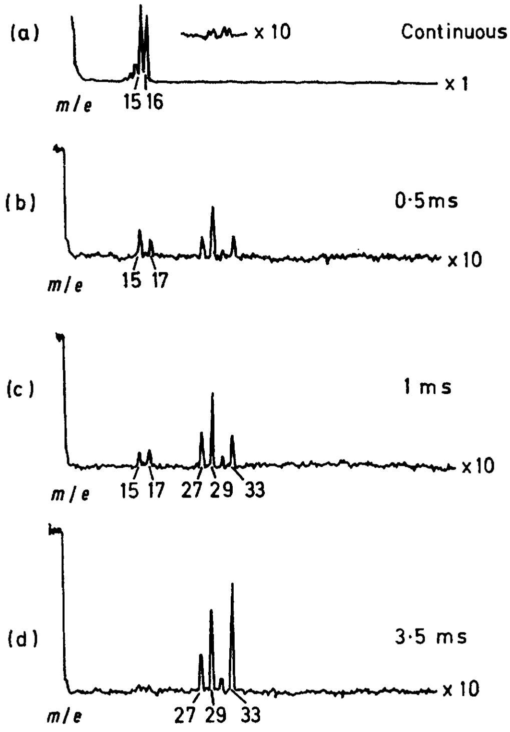

FIGURE. *Chemical-ionisation mass spectra in a methane–methanol* (400:1) *mixture as a function of storage time. Trace* (a) *corresponds to the continuous creation and ejection of ions whilst traces* (b)—(d) *show the effect of ion storage for the times indicated. The peaks at m/e* 27 *and* 29 *arise from the products of ion–molecule reactions of the methane.*

During recent investigations of the characteristics of a novel 'ion-storage' mass spectrometer in our Laboratory it became clear that the pattern of yields of secondary reactions observed for ions formed from methane at *ca.* 2×10^{-4} Torr was such that chemical ionisation should be observable, but at pressures some 10,000 times lower than those normally employed. The experimental system, which is described in detail elsewhere,[4,5] consists of a three-dimensional quadrupole ion storage trap (Quistor)[6] mounted in place of the normal ion source of a Process Analysers Inc. (E.A.I.) QUAD 250A quadrupole mass filter. Ions are created within the Quistor by injecting a pulse of electrons (nominal energy *ca.* 70 eV) and are then stored for a predetermined period before being ejected into the mass filter for analysis. The Quistor was powered with an r.f. supply operating at a zero-to-peak voltage of 600 V, with zero d.c. bias, and a frequency of 2·75 MHz. The duty cycle for ion creation and ejection was maintained at a repetition frequency of 200 Hz.

To test for the expected occurrence of chemical ionisation a small quantity of methanol (partial pressure *ca.* 5×10^{-7} Torr) was added to the methane and the spectra recorded at different storage times. A dramatic growth in the intensity of *m/e* 33 ($CH_3OH_2^+$) was observed as the time available for reaction increased [Figure (a)—(d)]. Figure (a) shows the spectrum taken when ions were continuously created and ejected from the Quistor, in a manner analogous to the behaviour of a conventional ion source, whilst (b)—(d) illustrate the growth of secondary ions and the virtual disappearance of primary species. It is significant that the yield of *m/e* 17 (CH_5^+) at first increases and then decreases, lending strong support to the postulated chemical ionisation reaction:

$$CH_5^+ + CH_3OH \longrightarrow CH_4 + CH_3OH_2^+$$

It is clear, therefore, that ion storage devices of the type described, though not without their own experimental difficulties, offer a viable alternative to the conventionally used technique for inducing chemical ionisation. Present work is in progress on the detailed kinetics of ionic processes occurring within radio-frequency ion traps.

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