Isomeric Forms of $[C_2H_6]^{+\cdot}$ Ions in the Gas Phase

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Two structural forms of $[C_2H_6]^{+\cdot}$ ions have been identified in the gas phase.

Mass spectra have been used for more than 47 years to deduce the structural formulae of gas-phase ions.[1] The spectrum is typically produced as the result of competitive and consecutive unimolecular fragmentations of molecular ions formed within an ion source from gas-phase molecules, but there are other methods by which different ion species may be formed within the ion source, for example, by allowing ion–molecule reactions to occur within the source before extracting the ions for analysis. This method has been given the name chemical ionization.[2–4] If the sample in such a source is methane, ion–molecule reactions occur, mainly between ions $CH_4^{+\cdot}$ (and CH_3^+ formed by rapid unimolecular fragmentation of $CH_4^{+\cdot}$) and methane molecules. These reactions and further reactions involving the products of the first collisions continue until they result in the formation of stable ions. The major ion species that issue from such a source are CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ [2–7] but there are minor amounts of several other species, including $C_2H_6^{+\cdot}$.[2,6,7] It is the purpose of this paper to compare the structure of these $C_2H_6^{+\cdot}$ ions with that of ethane molecular ions formed by electron impact in a low pressure ionization source.

The primary method of investigating the ion structure was to accelerate the ions through a potential difference of 5 kV, to isolate the $C_2H_6^{+\cdot}$ ions using a magnetic sector field, to pass the mass-selected ions through a low pressure gas-collision cell, and to plot the ion kinetic energy spectrum of the product ions. The instrument used was a modified[8] ZAB-2F mass spectrometer[9] manufactured by VG Analytical Ltd. The method is generally agreed to distinguish gross differences in chemical structure[10] which can give major differences in spectra, although minor differences in relative abundances of peaks may result from differences in internal energy of ions of the same structure.

A second method of gaining information on ion structure is to study peaks formed by charge-stripping reactions, equation (1), where G represents a molecule of collision gas. Both these

$$M^+ + G \rightarrow M^{2+} + G + e^- \qquad (1)$$

methods were used in the present study and the results were as follows.

$C_2H_6^{+\cdot}$ ions formed from both ethane and methane samples were isolated, their empirical formulae checked by accurate mass measurement, and their collision-induced ion kinetic energy spectra obtained. The ions from ethane were formed in a low-pressure electron impact source; those from methane by chemical ionization at a source pressure of *ca.* 1 Torr. The results are shown in Figure 1, (a) and (b) respectively. It can be seen from Figure 1(a) that the major fragmentation peak from ethane corresponds to the formation of CH_3^+, as would be expected from a dimethyl ion, and there are no $CH_4^{+\cdot}$ ions. However, from the methane sample $CH_4^{+\cdot}$ ions give a prominent product ion peak and the relative abundance of $CH_2^{+\cdot}$ ions is also higher than from ethane. This suggests that, when formed from methane, a major fraction of the ions have the $[CH_2CH_4]^{+\cdot}$ structure. The formation of stable complexes of this type by ion–molecule collisions within the source has been postulated by Field[2,5,11] in the case of methane[5] and methane–water mixtures.[11]

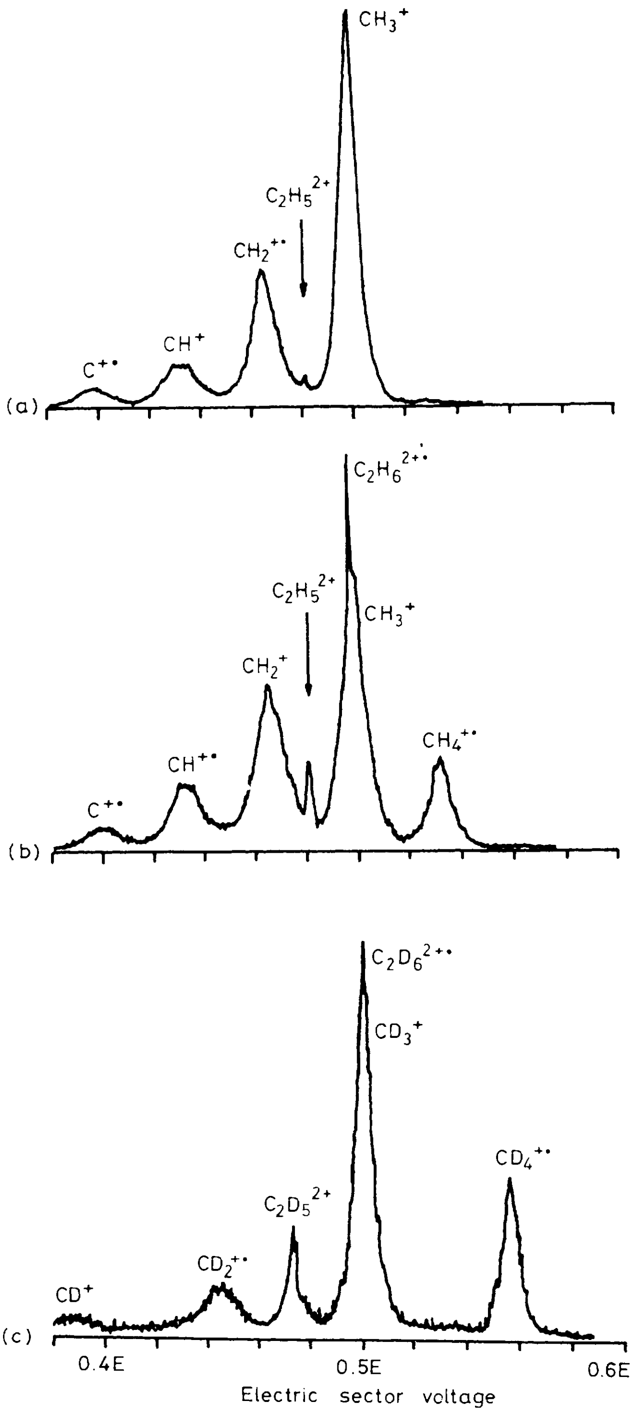

Figure 1. Partial collision-induced ion kinetic energy spectra. (a), (b), and (c) are spectra of $C_2H_6^{+\cdot}$, $C_2H_6^{+\cdot}$, and $C_2D_6^{+\cdot}$ ions from ethane, methane, and tetradeuteriomethane respectively, the latter two using an ion source pressure of 1 Torr. E is the electric sector voltage at which unfragmented ions are transmitted.

Interesting evidence concerning the structures of the $C_2H_6^{+\cdot}$ ions is also obtained from the charge-stripping experiments. The $C_2H_6^{+\cdot}$ ions from ethane do not give a stable $C_2H_6^{+}$ product; those from methane do. The sharp peak due to $C_2H_6^{2+}$, superimposed on the peak due to CH_3^+, is indicated in Figure 1(b). In both cases the reactant $C_2H_6^{+\cdot}$ ions are examined about 10^{-5} s after extraction from the source. Thus, any ions of high internal energy will have fragmented *en route* and only ions having internal energies from the ground state to just above the minimum energy for spontaneous fragmentation remain. The difference in charge-stripping behaviour in the two cases shows that different reactant ion structures are involved. A clue as to the ethane and 'non-ethane' structures is provided by the calculations of Olah and Simonetta.[12] They predicted that for doubly charged ethane, the bridged diborane-like structure, D_{2h}, would be more stable than the D_{3d} geometry or the open-shell configuration[13] and that the dication would be highly unstable towards dissociation into two CH_3^+ ions. This is in agreement with the experimental results for ethane; no stable $C_2H_6^{2+}$ ions are observed. Further calculations by Schleyer[14] predicted that an isomeric form of $C_2H_6^{2+}$, which he calls the 'carbenium–carbonium' structure, would be more stable than the $C_2H_6^{2+}$ of D_{2h} symmetry by about 36 kJ mol^{-1} and might be sufficiently stable to be observed experimentally. We believe that we have observed this ion and that its method of formation, by fast (*ca.* 10^{-15} s) vertical ionization of $C_2H_6^{+\cdot}$ formed by ion–molecule reactions from methane is strong evidence that the singly charged reactant ion does have the composition $[CH_4CH_2]^{+\cdot}$ as suggested by its collision-induced ion kinetic energy spectrum.

The chemical ionization experiments were repeated using CD_4. It was possible in this case, too, to observe stable $C_2D_6^{2+}$ ions. The collision-induced ion kinetic energy spectrum of the $C_2D_6^{+\cdot}$ ions formed showed a prominent peak due to $CD_4^{+\cdot}$ ions as shown in Figure 1(c).

We thank the Royal Society, the S.E.R.C., and the University College of Swansea for support of this work.

Received, 23rd June 1983; Com. 834

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