

Is the Methylenemethonium Radical Cation ($\dot{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H}_4$) a Stable Species?

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Theoretical and experimental evidence is presented which casts doubt on the recently reported observation of a $\text{C}_2\text{H}_6^{+\cdot}$ isomer having a methylenemethonium ($\dot{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H}_4$) structure.

It has recently been found, both theoretically and experimentally, that simple ylidions[†] are often more stable than their classical isomers.¹ For example, the ylidions $\dot{\text{C}}\text{H}_2\overset{+}{\text{F}}\text{H}$,

[†] The term ylidion has been introduced (B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5805) to describe the class of radical cations which may be formally regarded as ionized ylides. The ylidions, in turn, are part of a wider class of *distonic* radical cations in which the charge and radical centres are separated.

$\dot{\text{C}}\text{H}_2\overset{+}{\text{O}}\text{H}_2$, and $\dot{\text{C}}\text{H}_2\overset{+}{\text{N}}\text{H}_3$ are all found²⁻⁵ to be more stable than their respective isomers $\text{CH}_3\text{F}^{+\cdot}$, $\text{CH}_3\text{OH}^{+\cdot}$, and $\text{CH}_3\text{NH}_2^{+\cdot}$. A logical question to ask is: what about the next member of the series? Is the methylenemethonium radical cation $\dot{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H}_4$ a stable isomer of the ethane radical cation?

Experimental support for this contention has recently been reported by Rabrenovic and Beynon⁶ using the mass spectrometric techniques of charge stripping and collision-induced

dissociation. From a high pressure ion source containing methane gas, ions (m/z 30) corresponding to the empirical formula $C_2H_6^{+}$ and produced in ion-molecule reactions were isolated by the magnetic sector. On collision with nitrogen gas in the second field-free region of a ZAB-2F mass spectrometer,⁷ an ion kinetic energy spectrum very different from that of ethane molecular ions⁸ was obtained. Of particular prominence were a peak assigned as CH_4^{+} and another peak assigned as $C_2H_6^{2+}$. These results led Rabrenovic and Beynon to claim that the major fraction of the $C_2H_6^{+}$ ions emanating from the high pressure ion source were of the methylene-methonium structure ($\dot{C}H_2\overset{+}{C}H_4$). Theoretical and experimental evidence leading to a reinterpretation of the data is presented here.

Our theoretical approach to the problem utilizes *ab initio* molecular orbital calculations, carried out with a modified version⁹ of the Gaussian 82 program,¹⁰ on a variety of possible candidates for the $\dot{C}H_2\overset{+}{C}H_4$ isomer, including those shown in Figure 1. Geometry optimizations were performed with the 6-31G* basis set¹¹ (in some cases refined at the 6-31G** and MP2/6-31G* levels¹²). The stationary points obtained in this manner were characterized, through the calculation of harmonic vibrational frequencies at the 6-31G**/6-31G* level, as minima (all real frequencies), first-order saddle points (one imaginary frequency), or higher-order saddle points (more than one imaginary frequency).

Only one of the structures (2) which we have examined is located at a minimum on the 6-31G* potential surface. This structure (2) is, however, only a weak complex of the (planar) ethylene radical cation with H_2 .[‡] The C...H bonds are very long (3.4 Å) and the binding energy very small (1.0 kJ mol⁻¹). The binding energy and geometry, unlike those for the closely

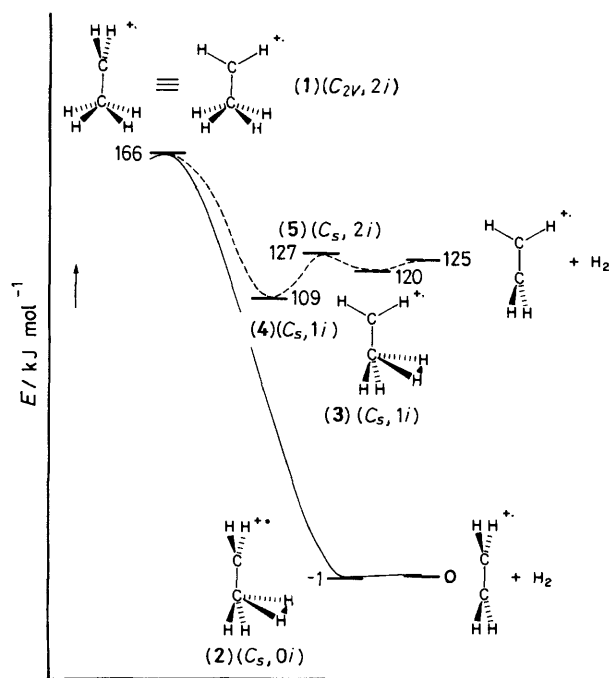


Figure 1. Schematic representation of parts of the $C_2H_6^{+}$ potential energy surface (6-31G**/6-31G*, kJ mol⁻¹) involving $\dot{C}H_2\overset{+}{C}H_4$ structures. The numbers of imaginary frequencies (ni) are shown in parentheses. Points on the dashed line (---) are unstable with respect to methylene rotation. Structures (4) and (5) resemble distorted forms of (3).

[‡] The complex (2) lies 29 kJ mol⁻¹ (6-31G*) above the ethane radical cation (${}^2A_{1g}$ state).

related $C_2H_7^{+}$ isomer,¹³ do not change significantly with optimization at the MP2/6-31G* level. We do not believe that a species as weakly bound as (2) is likely to be observable under the conditions of the Rabrenovic and Beynon experiments.

Vibrational analysis of the other structures displayed in Figure 1 yields one or more imaginary frequencies in each case, *i.e.* none of the structures represents a minimum on the surface, there being respectively one or more pairs of directions in which the energy decreases. Thus, theory predicts that none of the structures of Figure 1 is likely to represent the m/z 30 ion observed by Rabrenovic and Beynon.

Our inability to find a stable $\dot{C}H_2\overset{+}{C}H_4$ structure does not in itself provide conclusive proof that it does not exist. Clearly there is the possibility, however thoroughly a potential surface is searched, for a local energy minimum to be missed. On the other hand, the extent of our search prompted us to believe that a reinterpretation of the experimental results would be desirable.

Such a re-examination was in fact taking place¹⁴ quite independently of the calculations described above. By including a collision cell¹⁵ in the third field-free region of the ZAB-2F mass spectrometer, modified by the addition of a second electric sector,¹⁶ it is possible to select the precursor ion of interest at much higher resolution than that available to Rabrenovic and Beynon.⁶ When this is done, it is observed that the peak at m/z 30 in the mass spectrum of methane from the high pressure source consists not only of $C_2H_6^{+}$ ions, but also of a large contribution of ${}^{13}C^{12}CH_5^{+}$ ions (Figure 2), as might have been expected on the basis of the intense peak at m/z 29 for the normal isotopic species.[§] When each of the components of the doublet is selected in turn by the double-focusing mass spectrometer at a resolution of 6700, it may be seen that the $C_2H_6^{+}$ ions give rise to an ion kinetic energy spectrum (nitrogen collision gas) [Figure 2(b)] very similar to that obtained previously for ethane molecular ions⁸ while the ${}^{13}C^{12}CH_5^{+}$ ions give a spectrum [Figure 2(a)] very similar to the spectrum which had been interpreted⁶ to be that of $\dot{C}H_2\overset{+}{C}H_4$ ions. Further experiments, conducted at a double-focusing resolution of 20 000, produced complete separation of the components at m/z 30 (including a small $C_2DH_4^{+}$ peak which lies between the ${}^{13}C^{12}CH_5^{+}$ and $C_2H_6^{+}$ peaks) and confirmed the results of Figure 2. At this resolution, the small peak at m/z 16 (corresponding to ${}^{13}CH_3^{+}$ and ${}^{12}CDH_2^{+}$ arising from ${}^{13}C^{12}CH_5^{+}$ and $C_2DH_4^{+}$, respectively) in Figure 2(b) disappears. It should also be noted that the measured Q_{min} value (19.4 ± 0.5 eV) for the formation of stable m/z 15 dications, previously assigned⁶ to $CH_2CH_4^{2+}$, is within experimental error of the measured Q_{min} value for formation of $C_2H_5^{2+}$ (19.1 ± 0.5 eV).⁸

The previous experiments⁶ had also been carried out with tetradeuteriomethane and the ion kinetic energy spectrum of the m/z 36 ion had similarly been interpreted to be that of $\dot{C}D_2\overset{+}{C}D_4$. This was repeated in the present work using a freshly obtained sample of CD_4 . The m/z 36 peak was found to consist of at least 90% $C_2D_6^{+}$ ions when examined at a mass resolution of 10 000 or higher. The ion kinetic energy spectrum (nitrogen collision gas) of the $C_2D_6^{+}$ ions selected at this resolution, or of all m/z 36 ions selected at low resolution (2000), was clearly a deuterium-labelled version of Figure 2(b). No conditions were found (including, for

[§] Discussions with Professor Beynon confirmed that the previous authors were well aware of the need to separate the $C_2H_6^{+}$ ions from any other species present at m/z 30 and that they were confident that the necessary resolution had been achieved before the published results⁶ were produced.

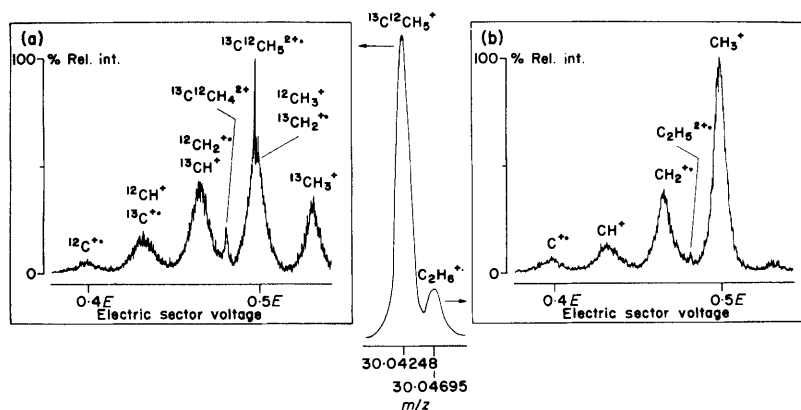


Figure 2. The m/z 30 peak (measured at a mass resolution of 6700) from the high pressure ion source containing methane. Inserts (a) and (b) show the ion kinetic energy spectra of each of these components when subjected to nitrogen collision gas.

example, the addition of trace amounts of water to increase the contribution of CD_3OH_2^+ ions to the m/z 36 peak) under which the previously published spectrum,⁶ particularly the peak assigned as CD_4^{2+} , could be reproduced.

There has also been a report¹⁶ of $\text{C}_2\text{H}_6^{2+}$ dications derived from m/z 30 ions produced from ethane. In the light of the present results, it is possible that the peak assigned in that study to $\text{C}_2\text{H}_6^{2+}$ is in fact again due to $^{13}\text{C}^{12}\text{CH}_5^{2+}$ [*cf.* the $^{13}\text{C}^{12}\text{CH}_5^{2+}$ peak in Figure 2(a)].

We conclude from the experimental part of the present investigation, through use of instrumentation capable of demonstrably higher specificity in precursor ion selection than available previously, that stable methylenemethonium ions are unlikely to have been generated in the original experiments. This supports expectations based on the *ab initio* molecular orbital calculations that $\dot{\text{C}}\text{H}_2\text{CH}_4^+$ ions are unlikely to be observable.

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