# THE NON-EXISTENCE OF GASEOUS CYCLOPENTADIENYL CATIONS:  AN OVERDUE CORRECTION TO THE LITERATURE
## USING COLLISION-INDUCED DECOMPOSITIONS AND CHARGE STRIPPING OF NEGATIVE IONS

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*The $C_5H_5^+$ fragment ion bound in many EI spectra is determined not to be cyclopentadienyl cation
by CID-MIKE spectrometry.*

Many unsupported postulations were made in the preceding decade concerning the structures
of gaseous ions which could be highly symmetrical.  Among these was the $C_5H_5^+$ ion, for which the
cyclopentadienyl structure was often written in spite of the anti-aromaticity predicted for that
form.  No evidence was ever offered for the structure, the sole reason for its postulation being
"the prettiness of the resulting ion," to appropriate Biemann's complaint[1] about the liberty
taken in another case.  We have studied the structure of this ion using a new variant of an
established technique for ion structure.

The collision-induced decomposition (CID) or collisional activation technique[2,3] has been
used to study the structures of gaseous negative ions.[4]  One may study either the decomposition
of these negative ions to negative fragment ions (Eq. 1) or to positive fragment ions (Eq. 2,

$$AB^- + N \rightarrow A^- + B + N \qquad (1)$$
$$AB^- + N \rightarrow N + 2e + [AB^+]^* \rightarrow A^+ + B \qquad (2)$$
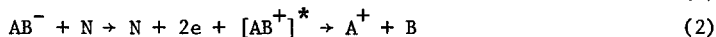
charge stripping).[*]  Either structural method can be empirically related to the organization of
atoms in the ion.  The second also has the advantage that it can correlate the CID spectrum con-
taining peaks due to various $A^+$ to the CID spectra of model isomeric $AB^+$ ions (Eq. 3) to compare

$$AB^+ + N \rightarrow A^+ + B + N \qquad (3)$$

the structures of $AB^-$ and $AB^+$.  It is then possible to find similarities[5] or dissimilarities[6] in
ion structures.  Sometimes the dissimilarities are pronounced and give evidence for new unstable
forms for $AB^+$ ions intermediate in Eq. 2.  In these cases formation by Eq. 2 is a process in
which two electrons are rapidly stripped from $AB^-$ and sufficient internal energy remains in the
new $AB^+$ ions that simple fragmentation is favored over rearrangement, as expected for high-energy
ions according to the quasiequilibrium theory.[6,7]  The $AB^+$ ions from both Eqs. 2 and 3 form a
high-energy population in CA irrespective of their origin, allowing comparison.[4]

Using Scheme 1, we have examined m/z 65 ions, both positive and negative, formed from the
following $C_5H_6$ isomers:  1-penten-4-yne (I), 1-penten-3-yne (II), 3-penten-1-yne (III), 2-methyl-
1-buten-3-yne (IV), and 1,3-cyclopentadiene (V).  This list includes all acyclic isomers but

[*]Confounding of our results by the alternative $AB^- + N \rightarrow A^- + N \rightarrow A^+$ is excluded by the absence
of many critical $A^-$ ions in spectra from Eq. 1.

SCHEME 1

$C_5H_2^{-\cdot}$, m/z 62   $C_5H_6 \longrightarrow C_5H_6^{+\cdot}$, m/z 66   $C_5H_2^{+\cdot}$, m/z 62

$\uparrow$-H                                                    -H $\downarrow$                          $\uparrow$-H

$C_5H_3^{-}$, m/z 63 $\xleftarrow{-H_2}$ $\boxed{C_5H_5^{-} \text{ m/z } 65}$ $\xrightarrow{-2e}$ $\boxed{C_5H_5^{+} \text{, m/z } 65}$ $\xrightarrow{-H_2}$ $C_5H_3^{+}$, m/z 63

-C$_2$H$_2$ $\swarrow$      $\downarrow$-CH$_4$       $\downarrow$-CH$_2$   -C$_2$H$_2$ $\searrow$

$C_3H_3^{-}$, m/z 39   $C_4H^{-}$, m/z 49 / $C_4H_3^{+}$, m/z 51   $C_3H_3^{+}$, m/z 39

$\downarrow$-H                      -CH$_3$ $\swarrow$                           $\downarrow$-H      -H$_2$ $\searrow$

$C_3H_2^{-\cdot}$, m/z 38   $C_4H_2^{+\cdot}$, m/z 50   $C_3H_2$, m/z 38   $C_3H^{+}$, m/z 37

omits several unstable cyclic isomers not available to us. Table 1 collects the CA spectra produced according to eqs. 1, 2, and 3 from the $C_5H_5$ ions from these compounds. The positive ions were produced by electron impact ionization; the negative ions, by negative chemical ionization using methane to moderate electron energy. In our methane-enhanced negative chemical ionization experiments the major ion is OH$^-$, produced from adventitious oxygen-containing molecules, and H$^+$ abstraction from $C_5H_6$ to give $C_5H_5^-$ by this ion is likely. This process would be exothermic for removal of either allylic or acetylenic protons, and either type could be removed.

The $C_5H_5^{-}$ Ions Studied by Eq. 1. I and II do not yield a common population of $C_5H_5^-$ ions, which they would if allylic abstraction occurs alone. In at least one of these, then, acetylenic abstraction is significant; it may be in both. On the other hand, evidence for some retention of the acetylenic hydrogen in some $C_5H_5^-$ ions from I and II may be found in the ion intensity ratio R for m/z 39 and 63. In high-energy ions these likely form by removal of H and C≡CH, vs. H and H, from adjacent carbon atoms. As expected, R is 0/0 in $C_5H_5^-$ from IV; if methine H is lost neither $C_2H_2$ nor $H_2$ can be subsequently lost from adjacent carbons. In $C_5H_5^-$ from II, $C_2H_2$ cannot be lost and R = 0. Both losses are seen in ions from the other acyclic isomers (I: R = 0.81; III: R = 0.33); the $C_2H_2$ loss suggests that at least some of the protons lost to form $C_5H_5^-$ were not methine H, for some HC≡C groups remain. Also, $CH_4$ loss to give m/z 49 is important only when $CH_3$ and H may be lost from adjacent carbon atoms in $C_5H_5^-$ (III, IV). $C_2H_2$ loss from cyclopentadienyl anion occurs by ring cleavage. To summarize, even after $10^{-5}$ sec to equilibrate, the $C_5H_5^-$ ions from each source are distinguishable by eq. 1; intensity ratios involving m/z 38, 39, 49, 51, 62, and 63 differ markedly and predictably for each isomer.

The $C_5H_5^{-}$ Ions Studied by Eq. 2. The ions formed by charge stripping of the negative ions are less indicative of the distinctions between structures. This observation was made in spite of the expectation that the positive ions, once formed from the negative ions, contain so much internal energy that they cleave simply before they can isomerize to other more stable forms, by analogy to other systems.[6] However, many isomeric hydrocarbon ions of different structure have very similar CID spectra, and the similarity of these positive ion spectra merely reflects the narrow choice of available reactions. The ions from isomers I, II, and III have similar 39/63 and 62/63 ratios; IV differs from them. The ion from V can be distinguished from all the rest by the 37/39 ratio (0.55 vs. 0.17 ± 0.08) and by other ratios to a lesser extent (39/63 for V

TABLE 1.   Collision-Induced Decompositions of $C_5H_5$ Ions Produced by Equations 1, 2, and 3[a]

| m/z | $H_2C=CHCH_2C\equiv CH$, I eq. 1 | eq. 2 | eq. 3 | $H_2C=CHC\equiv CCH_3$, II eq. 1 | eq. 2 | eq. 3 | $HC\equiv CCH=CHCH_3$, III eq. 1 | eq. 2 | eq. 3 | $H_2C=C(CH_3)C\equiv CH$, IV eq. 1 | eq. 2 | eq. 3 | cyclopentadiene, V eq. 1 | eq. 2 | eq. 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 63[b] | 32 | 23 | 22 | 31 | 22 | 30 | 30 | 30 | 27 | – | 37 | 25 | 28 | 33 | 31 |
| 62 | 16 | 10 | 11 | 31 | 10 | 13 | 37 | 12 | 11 | 83 | 7 | 10 | 38 | 7 | 13 |
| 61 | – | 5 | 6 | – | 5 | 5 | – | 4 | 4 | – | 3 | 5 | – | 3 | 6 |
| 60 | – | 1 | 1 | – | 1 | 1 | – | 1 | – | – | – | 1 | – | 1 | 1 |
| 52 | – | – | – | – | – | – | – | – | – | – | – | 1 | – | – | – |
| 51 | 3 | 4 | 2 | 8 | 4 | 1 | – | 3 | 2 | – | 8 | 3 | – | 5 | 2 |
| 50 | – | 7 | 4 | – | 9 | 3 | 8 | 6 | 3 | – | 5 | 5 | – | 5 | 4 |
| 49 | 4 | 2 | 2 | – | 3 | 1 | 16 | 3 | 1 | 17 | 2 | 2 | 2 | 2 | 1 |
| 41 | – | 1 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 39 | 26 | 25 | 28 | – | 26 | 37 | 10 | 24 | 36 | – | 23 | 27 | 29 | 18 | 27 |
| 38 | 19 | 10 | 11 | 31 | 8 | 5 | – | 7 | 6 | – | 7 | 10 | 5 | 9 | 7 |
| 37 | – | 5 | 8 | – | 4 | 3 | – | 6 | 4 | – | 2 | 5 | – | 10 | 3 |
| 36 | – | 2 | – | – | 1 | – | – | – | – | – | – | – | – | – | – |
| 32.5[c] | – | – | – | – | – | – | – | – | – | – | – | 1 | – | – | – |
| 31[c] | – | – | 1 | – | – | – | – | – | – | – | – | – | 1 | – | – |
| 27 | – | 3 | 2 | – | 2 | 1 | – | 2 | 2 | – | 1 | 2 | – | 1 | 1 |
| 26 | – | 2 | 2 | – | 2 | 1 | – | 2 | 2 | – | 4 | 2 | – | 4 | 1 |
| 25 | – | – | – | – | – | – | – | – | – | – | – | – | – | 1 | 1 |

[a] corrected for unimolecular decompositions and multiplier discrimination, and expressed as per cent of total detected decompositions.  These spectra were obtained on a ZAB/2F mass spectrometer, using ions accelerated through 6 kV and $N_2$ collision gas at gauge pressure of $8 \times 10^{-7}$ torr. Reproducibility from day to day = $\pm$ 1.

[b] In the case of positive ions the loss of H to give m/z 64 was found to be a low-energy process, and its intensity was often almost entirely due to unimolecular processes.  Following convention, its intensity is not included in the sum of the ion intensities from which the table was prepared.

[c] doubly charged ions, resulting from charge stripping according to the process

$$AB^{+\cdot} + N \rightarrow AB^{2+} + N + e$$

vs. I, II, III: 0.55 vs. 1.0 ± 0.2).  The first ratio suggests the propargyl structure for $C_3H_3^+$ from V, and another, cyclopropenyl, by other routes.  To summarize, the cyclopentadienyl cation can be distinguished from its isomers easily.

The $C_5H_5^+$ Ions Studied by Eq. 3.  We did not expect to find congruence between the positive ion spectra formed by eq. 2 and those formed by eq. 3.  The hydrogen lost from each isomer of $C_5H_6^{+\cdot}$ to give $C_5H_5^+$ is probably not the same as that lost from the neutral to give $C_5H_5^-$.  Also, isome-

rization of unsaturated hydrocarbon ions of this energy range occurs in a small fraction of the
time available to ions in the source; both $C_5H_6^{+\cdot}$ and $C_5H_5^+$ ions can isomerize, for low-energy
routes are available for electron-deficient species produced by 70-volt electrons, in contrast
to the paucity of such routes available to source $C_5H_5^-$ ions produced by gentler processes. We
compare the known cyclopentadienyl cation (V, eq. 2) with other $C_5H_5^+$ ions (eq. 3). The spectra
have many points of difference: m/z 39/63, R = 0.55 vs. 1.1 ± 0.2; 37/39, 0.55 vs. 0.16 ± 0.13;
62/63, 0.21 vs. 0.43 ± 0.07, to use most of the intense ions. Therefore we may conclude that
the cyclopentadienyl cation is not formed in the electron-impact-induced fragmentation of these
five compounds. Since the CID spectra of $C_5H_5^+$ ions produced from many compounds by electron im-
pact are nearly identical,[8] we may also conclude that the cyclopentadienyl cation is not generally
formed in electron impact mass spectra.

We also conclude that (as an analytical application) eq. 1 is a better discriminant than
eq. 2 for studying structures of $C_5H_5^-$ ions, and thus for distinguishing between the isomeric
structures of their precursors. Since there are almost no methods for distinguishing between
structures of highly unsaturated hydrocarbons by mass spectrometry (charge stripping[9] being a
notable exception), we propose to investigate this approach to structural differentiation
further.

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