Doubly charged ions are found in the electron ionization (EI) mass spectra of hydrocarbons, but they are normally relative small in intensity and not very useful in practical applications to chemical analyses. In contrast, we (T. Huret, James Little, Eastman Chemical Co.) noted a very intense doubly charged ion at \( m/z \) 316 in the EI mass spectrum of the following phosphate:
The substructure was confirmed by accurate mass measurements for the doubly charged ion at \( m/z \) 316. This required doubling the \( m/z \) value to search the standard VG OPUS elemental composition program (\( C_{40}H_{57}O_4P, +6.4 \) ppm error, resolution = 4000).

It is interesting to note in the magnetic EI spectrum of the phosphate that no C-13 isotope is observed for the \( m/z \) 316 ion even though the instrument resolution is set at about 1000. This is because the data was processed in the merged mode which summed the ion at \( m/z \) 316.5 with \( m/z \) 316. Many doubly charged ions appear to have no C-13 isotopes in many cases because of the data processing mode or lack of adequate resolution on quadrupole mass spectrometers.

**EI Mass Spectrum of Phosphate Showing Large Doubly Charged Ion at \( m/z \) 316**
The same spectrum processed in the accurate mass mode shows the presence of the C-13 isotope in approximately the expected ratio at \( m/z \) 316.5 in the partial EI mass spectrum below:

**Expanded EI Mass Spectrum Showing Presence of C-13 Isotope for Doubly Charged Ion**
The EI mass spectrum of the phosphite of the above compound also shows a doubly charged ion, but at a much lower intensity (m/z 308.2010, +4.1 ppm error, C-13 at m/z 308.7015). Possibly the change of oxidation state from +3 to +5 significantly alters the EI fragmentation mechanism. The phosphite prefers to be singly charged and lose a di-t-butylphenoxy radical to yield m/z 441 (see spectrum below) and also shows very little loss of a methyl radical from its molecular ion.

**EI Mass Spectrum of Phosphite**

Dr. Fred McLafferty suggested \(^2\) "...you could postulate that you have a double radical ion, with separate ionization on two of the phenyl groups. The ionization energy of one of these should be almost as low as 8eV, and this resulting charge could be far enough away from a second phenyl group to allow its ionization energy to be surprisingly low. Or you could even try to measure this roughly to show why the doubly charged ion is so prevalent... Anyway, the loss of a methyl radical from a t-butyl substituted aromatic ring containing an odd electron of course is totally logical, forming a stable benzyl or tropylium ion, with the second methyl radical loss giving you "bis benzyl ion"... Possibly the much lower probability of this double loss reaction from the phosphite is due to the fact that much more electro-negative phosphate does a better job of screening the two phenyls from each other."

Dr. Kelsey Cook \(^5\) of the Univ. of TN suggested "I'd bet that there is some kind of rearrangement that ends up with a phosphonium or some such structure, rather than a diradical dication." It is set-up for forming a six-membered ring with one of the ortho-t-butyl groups and that might also explain the absence of any triply charged ions.

I found a reference in the literature \(^2\) that sited this unusual doubly charged ion and correctly assigned its structure, but the authors did not find it to be very unusual! The spectrum for the phosphate was not found in either the NIST or Wiley databases. I submitted the spectra in January 2012, so hopefully they will be included in future versions of these commercial databases.

I shared the spectra with Fred McLafferty \(^3\) and he sent me another reference \(^4\) of an unusual doubly charged ion. The structures for the compound and its doubly charged ion are shown below:
Molecular Weight = 652
Molecular Formula = C39H44N2O7

m/z 213

References


5. Dr. Kelsey Cook, E-mail, 3/26/99.