Secondary Electron Capture by Hexafluoroacetone

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WHEN a molecule suffers collision with an electron, negative ions may be formed by three different mechanisms, each of which usually operates in different electron-energy regions:

(i) resonance capture, $XY + e \rightarrow XY^-$; $\sim < 2$ ev

(ii) dissociative resonance, $XY + e \rightarrow X^- + Y$; ~ 2—10 ev, and

(iii) ion-pair formation, $XY + e \rightarrow X^- + Y^+ + e$; $\sim > 10$ ev.

We have found the negative molecule-ion, $CF_3{\cdot}CO{\cdot}CF_3^-$ formed in hexafluoroacetone, appearing with quite a sharp onset at an electron energy of 10·5 ev. No parent ion formation was noted below this energy.

Formation of the ion must involve an electron capture process, although 10·5 ev is too high an energy for a mechanism such as (i) to operate. Positive ions begin to be formed in this energy region, ionisation of hexafluoroacetone producing the ion $CF_3{\cdot}CO{\cdot}CF_3^+$ together with two secondary electrons.

$$CF_3{\cdot}CO{\cdot}CF_3 + e \rightarrow CF_3{\cdot}CO{\cdot}CF_3^+ + 2e$$

These secondary electrons will have a range of energies and some of them may well be of sufficiently low energy to be captured by the molecule to form the molecule-ion. If primary and secondary electrons are designated $e(1)$ and $e(2)$ respectively then ion formation by reaction (1) involving primary electrons will have a linear pressure dependence while for reaction (2), involving secondary electron capture, the ion intensity will vary as the square of the pressure of hexafluoroacetone.

$$CF_3{\cdot}CO{\cdot}CF_3 + e(1) \xrightarrow{1} CF_3{\cdot}CO{\cdot}CF_3^-$$

$$CF_3{\cdot}CO{\cdot}CF_3 + e(2) \xrightarrow{2} CF_3{\cdot}CO{\cdot}CF_3^-$$

An investigation of the pressure dependence of the ion current showed the pressure exponent to be

$1{\cdot}92 \pm 0{\cdot}08$, so that clearly secondary electron capture is responsible for the appearance of the parent negative ion at the observed voltage.

It is interesting that formation of the ion by reaction (1) is not observed at electron energies near to zero. Since our primary electrons are emitted from a hot tungsten filament they will have quite large thermal energies. Capture of these electrons produces an unstable molecule-ion which decomposes producing F^-, CF_3^-, $CF_3{\cdot}CO^-$, and $CF_3{\cdot}CO{\cdot}CF_2^-$ ions. From the relative abundances observed for these ions it is apparent that the reaction:

$$(CF_3{\cdot}CO{\cdot}CF_3^-)^* \rightarrow CF_3^- + CO{\cdot}CF_3$$

is the major decomposition mode.

The potential energy curve for the $CF_3{\cdot}CO{\cdot}CF_3^-$ ion must be very shallow for the small difference in the energies of the primary and secondary electrons (probably $< 0{\cdot}4$ ev) to make such a marked difference to the ion formation.

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