

Collision induced dissociation of the retinal protonated Schiff base

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Synopsis Photo-induced dissociation of the n-butylamine retinal protonated Schiff base (RPSB) predominantly leads to a single fragment with $m/z = 248$, suggested to be due to a rather involved sequential bond-rearrangement process. Two earlier experiments with RPSB colliding with atoms at sub-eV energies and at 50 keV both yielded $m/z = 248$ fragments, although other fragments were also present in the latter case. By colliding RPSB at sub-eV to 100 eV energies with N₂ or He, we find that the $m/z = 248$ peak only is present in a very narrow energy window below 1 eV. The fragments that we observe at higher energies (but below 100 eV) may all be explained as due to simple bond-cleavages.

All-*trans*-retinal, also known as Vitamin A aldehyde, is the chromophore of the light-sensitive opsin proteins. It plays an essential role in the biochemistry of the mammalian visual perception. Mainly because of the structural similarities to the chromophore in its natural protein-bound form, the retinal protonated Schiff base (RPSB) with n-butylamine (see Figure 1) has been extensively used as a model compound in many gas-phase studies [1, 2, 3].

Previous studies on the fragmentation of the RPSB have shown a dominating fragmentation channel at $m/z = 248$ both in photo-absorption and low energy (a few eV collision energy with He) collision induced dissociation (CID) [1]. This fragment cannot be explained by simple bond cleavages, but is the result of two consecutive electrocyclization reactions leading to the formation of the n-butylamine Schiff base of β -ionone (see Figure 1) [2, 3].

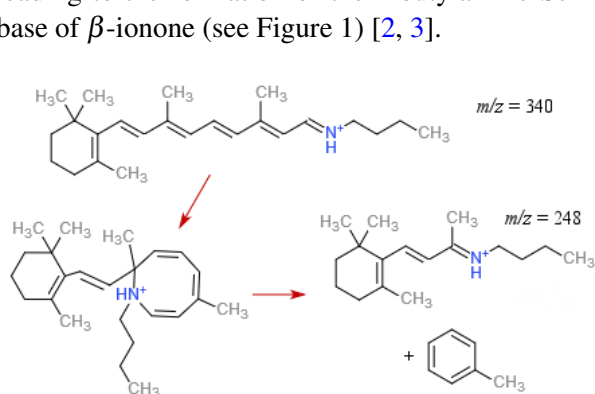


Figure 1. Structure of the retinal protonated Schiff base with n-butylamine (top), and fragmentation mechanism as proposed by Coughlan *et al.* [2] and confirmed by Musbat *et al.* [3]

High energy (50 keV collision energy with atmospheric air) collision mass spectra on the other hand have shown a broad distribution of fragments with the ion at $m/z = 248$ still visible, but not dominating [1].

In this work we present CID mass spectra covering a center of mass collision energy range of below 1 eV up to 100 eV. Low energy mass spectra, recorded with an Orbitrap Elite mass spectrometer at Karolinska Institutet, show that the fragment at $m/z = 248$ is only observed in a small energy range below 1 eV before it completely vanishes, and other, smaller fragments dominate the spectra at higher Orbitrap energies. We have performed single pass experiments of RPSB colliding with He at center of mass energies in the range of 10–100 eV at Stockholm University. Again, no fragment at $m/z = 248$ is visible and then instead all observed peaks can be explained by simple bond cleavages (see Figure 2) [4]. This leaves the question open why this fragment is present [1] at still much higher energies.

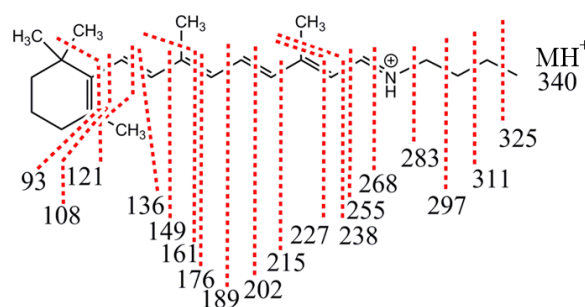


Figure 2. Bond cleavages observed in the present single-pass experiments.

References

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