Ionization and fragmentation of six-membered heterocycles containing oxygen-comparative studies on electron and photon impact on the 3,4-dihydro-2H-pyran molecules

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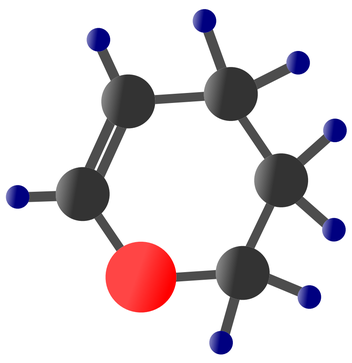
Introduction



3,4-dihydro-2H-pyran molecule

The study aimed to investigate the single ionization and fragmentation of 3,4-dihydro-2H-pyran (DHP) molecules initiated by electron and photon impact. The ionized fragments or excited radicals formed in these processes are chemically reactive species that can interact with surrounding molecules in their vicinity, leading to uncontrolled chemical reactions. Since DHP is one of the building blocks for compounds found in living organisms and is used to synthesize various drugs [1], [2], this type of research may be vital for developing medical diagnostic and therapeutic techniques using ionizing radiation.

Experimental description

The measurements of ionization triggered by electron impact were carried out at GUT using the quadrupole mass spectrometer EPIC 300 (Hiden Analytical). DHP molecules were provided to the mass spectrometer chamber, where they collided with the electron beam. As a result, the molecules were excited, ionized and fragmented. When the ionized fragments were formed, the focusing system directed them into the quadrupole. The ions were selected and then detected by the channel duplicator detector. For comparison, the dissociative photo-ionization of DHP was investigated using a PEPICO technique crossed with synchrotron radiation from the ELETTRA Synchrotron Radiation Facility in Trieste. The photon-induced experiment was discussed elsewhere in detail [3].

Results

Electron and photon-induced mass spectra of 3,4-dihydro-2H-pyran are shown in Figures 1 and 2, respectively. Tables 1 and 2 list the relative intensities of the identified cations and the neutral products, which most likely occured during the reactions. Figure 3 presents branching ratios of the most intensive fragments. Their threshold energies are shown in Table 3.
The results reveal that exposure to photons causes more severe fragmentation of DHP than collisions with electrons of the same energy. Indeed, under photon irradiation, the parent ion intensity decreases by two, and the low mass fragments become intensive. The electrons do not transfer all their translational energy to the target but carry part of it as internal kinetic energy. Therefore, the parent ion is more vulnerable to photon collisions than electron ones.

Electron impact ionization

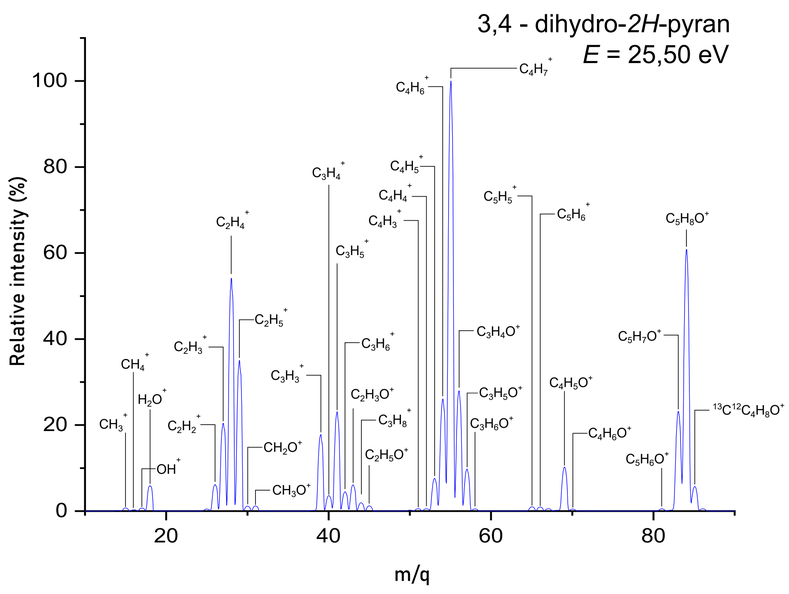


Figure 1. The mass spectrum of 3,4 - dihydro-2H-pyran.

Table 1. Relative intensities of the cations, their assignments, and the most probable neutral fragments.

M (u)	Cation assignment	I_{Rel} at E = 25.50 eV	Possible neutral products
85	$^{13}C^{12}C_4H_8O^+$	5.74	
84	$C_5H_8O^+$	60.88	
83	$C_5H_7O^+$	22.82	H
70	$C_4H_6O^+$	0.48	CH_2
69	$C_4H_5O^+$	10.27	$CH_2 + H$
66	$C_5H_6^+$	0.96	$O + H_2$
65	$C_5H_5^+$	0.99	$O + H_2 + H$
58	$C_3H_6O^+$	0.52	C_2H_2
57	$C_3H_5O^+$	9.81	C_2H_3
56	$C_3H_4O^+$	27.97	C_2H_4
55	$C_4H_7^+$	100.00	HCO
54	$C_4H_6^+$	26.07	H_2CO
53	$C_4H_5^+$	7.60	$H_2CO+ H$
52	$C_4H_4^+$	0.53	$H_2CO + H_2$
51	$C_4H_3^+$	0.56	$H_2CO + H_2 + H$
45	$C_2H_5O^+$	1.24	C_3H_3
44	$C_3H_8^+$	1.94	C_2O
43	$C_2H_3O^+$	6.10	C_3H_5
42	$C_3H_6^+$	4.50	C_2H_2O
41	$C_3H_5^+$	23.14	C_2H_3O
40	$C_3H_4^+$	3.60	C_2H_4O
39	$C_3H_3^+$	17.85	$C_2H_4O + H$
31	CH_3O^+	1.21	C_4H_5
30	CH_2O^+	1.15	C_4H_6
29	$C_2H_5^+$	35.07	C_3H_3O
28	$C_2H_4^+$	52.51	C_3H_4O
27	$C_2H_3^+$	20.42	$C_3H_4O + H$
26	$C_2H_2^+$	6.16	$C_3H_4O + H_2$
18	H_2O^+	10.00	C_5H_6
17	OH^+	0.73	C_5H_7
16	CH_4^+	0.29	C_4H_4O
15	CH_3^+	0.73	C_4H_5O

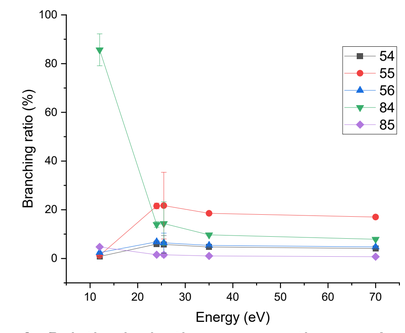


Figure 3. Relative ionization cross section as a function of electron-impact ionization.

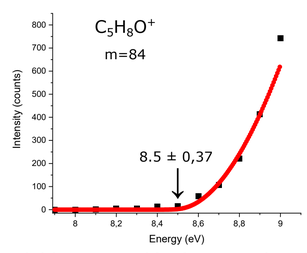


Figure 4. Ionic yield measured in the near-threshold region.

Table 3. Apperance energy of fragments: m = 54, 55, 56, 84, 85.

Mass	Apperance energy	Thresholds [4]
85	8.53 ± 0.35	———
84	8.50 ± 0.37	8.37 ± 0.02
56	11.60 ± 0.35	———
55	12.00 ± 0.36	———
54	11.63 ± 0.39	———

Photon-induced ionization

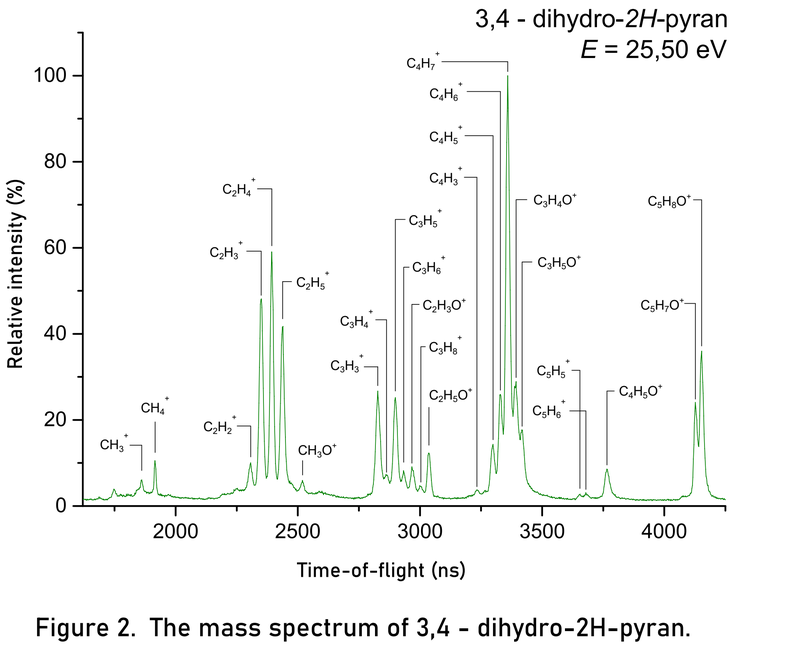


Figure 2. The mass spectrum of 3,4 - dihydro-2H-pyran.

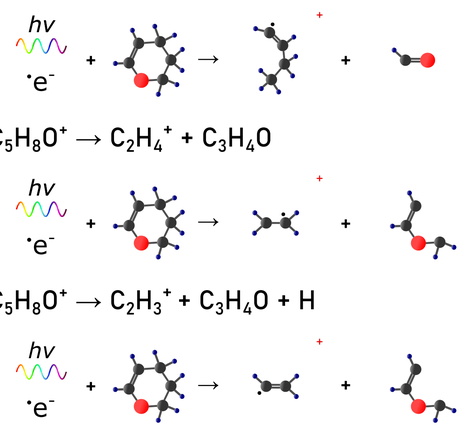
Table 2. Relative intensities of the cations, their assignments, and the most probable neutral fragments.

M (u)	Cation assignment	I_{Rel} at E = 25.50 eV	Possible neutral products
84	$C_5H_8O^+$	36.00	
83	$C_5H_7O^+$	24.08	H
69	$C_4H_5O^+$	8.62	$CH_2 + H$
66	$C_5H_6^+$	3.11	$O + H_2$
65	$C_5H_5^+$	2.77	$O + H_2 + H$
57	$C_3H_5O^+$	17.70	C_2H_3
56	$C_3H_4O^+$	28.93	C_2H_4
55	$C_4H_7^+$	100.00	HCO
54	$C_4H_6^+$	25.92	H_2CO
53	$C_4H_5^+$	14.34	$H_2CO+ H$
51	$C_4H_3^+$	3.81	$H_2CO + H_2 + H$
45	$C_2H_5O^+$	12.30	C_3H_3
44	$C_3H_8^+$	4.76	C_2O
43	$C_2H_3O^+$	9.11	C_3H_5
42	$C_3H_6^+$	8.24	C_2H_2O
41	$C_3H_5^+$	25.19	C_2H_3O
40	$C_3H_4^+$	7.32	C_2H_4O
39	$C_3H_3^+$	26.73	$C_2H_4O + H$
31	CH_3O^+	5.97	C_4H_5
29	$C_2H_5^+$	41.76	C_3H_3O
28	$C_2H_4^+$	59.08	C_3H_4O
27	$C_2H_3^+$	48.12	$C_3H_4O + H$
26	$C_2H_2^+$	10.06	$C_3H_4O + H_2$
16	CH_4^+	10.55	C_4H_4O
15	CH_3^+	6.09	C_4H_5O

Probable fragmentation reactions triggered by single ionization of DHP

$hv + C_5H_8O \rightarrow C_5H_8O^+ + e^-$ / $e^- + C_5H_8O \rightarrow C_5H_8O^+ + 2e^-$

$C_5H_8O^+ \rightarrow C_4H_7^+ + HCO$



$C_5H_8O^+ \rightarrow C_2H_4^+ + C_3H_4O$

$C_5H_8O^+ \rightarrow C_2H_3^+ + C_3H_4O + H$

References

[1] M. J. Han et al., *J Bioact. Compat. Polym.* **5**,80-88 (1990).
[2] J. Li et al., Bioorg. Med. Chem. Lett. 25, 5520-5523 (2015).
[3] M. Jurkowski, A. Kivimäki, R. Richter, T. J. Wasowicz, XLVI Extraordinary Congress of Polish Physicists the Polish Physical Society, 16-18.10.2020, Warsaw, Poland.
[4] P. J. Linstrom and W. G. Mallard, Eds., **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303, (retrieved June 6, 2021).

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