DISSOCIATION OF 2-METHYL-2-OXAZOLINE AND 2-ETHYL-2-OXAZOLINE MOLECULES INDUCED BY LOW-ENERGY ELECTRON IMPACT

Ján Blaško, Peter Papp, Štefan Matejčík

Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovakia
E-mail: jan.blasko@fmph.uniba.sk

Experimental investigation of electron ionization of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline was carried out using crossed electron beam and molecular beam method. We have recorded the mass spectra of positive ions at ~ 70 eV and assigned detected masses to possible fragments. The ionization energies of the 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline were determined to be 9.5 eV and 9.13 eV respectively. Appearance energies for the main fragments were for the first time estimated, too.

1. Introduction

Polyoxazolines are a significant group of polymers with a large scale of possible applications for example in materials as thermal sensors. Another application is a carrier system for active substances in drug delivery [1]. Due to their well-known biocompatibility, polyoxazolines have the potential to find a diversity of applications in biological systems. The cationic ring opening polymerization of 2-oxazolines was first publicated in the 1960s, which was later modified with microwave-assisted processes. This technique was used to achieve higher yields [2]. Microwave radiation shortens the polymerization time up to 400 times compared to hot heating [1]. During research in the 1960s, polymerization was investigated through NMR spectroscopy, chromatography, kinetic studies and MALDI-TOF MS [1].

The present work is focused to molecular properties of 2-methyl-2-oxazoline (2M2O) and 2-ethyl-2-oxazoline (2E2O) under electron impact. Using the mass spectrometry technique, the mass spectra of positive ions at ~ 70 eV and cross sections for both molecules was obtained. Threshold energies were determined from cross sections with a suggestion of possible chemical formulas of products.

2. Experimental setup

For investigation of electron induced processes of molecules an experiment with crossed electron and molecular beam was used (see scheme in Fig.1). The molecular beam source (MBS) was filled with the measured sample (2M2O, CAS: 1120-64-5, purity: 98%, Sigma Aldrich and 2E2O, CAS: 10431-98-8, purity > 99%, Sigma Aldrich) and generated the effusive beam passing into the vacuum through capillary. The electrons were produced by trochoidal electron monochromator (TEM) generating an electron beam with a well specified energy and colliding with the molecular beam from MBS. The positive ions were extracted by a weak electric field from the collisional region into the quadrupole mass spectrometer (QMS), where ions with selected *m/z* passed through QMS into the channeltron electron multiplier (CEM) detector.

The pressure in the vacuum chamber during the measurements was in the range of 1×10^{-7} mbar to 5×10^{-7} mbar. The apparatus was operated in two different modes. In the first one the mass spectrum was collected at a constant electron energy of ~70 eV in range from m/z 10 amu to 105 amu for 2E2O and from m/z 10 amu to 90 amu for 2M2O. In the second mode, the ion efficiency curves for particular ions with given *m/z* were measured as a function of incident electron energy (with a step of ~0.025 eV) around the threshold energy of selected ion fragment. The appearance energy (AE) of the selected process after electron ionization was estimated based on the Wannier law [3]. For calibration of the kinetic energy of the electrons we used Ar as well-established calibration gas with threshold energy of first ionization energy of 15.76 eV.
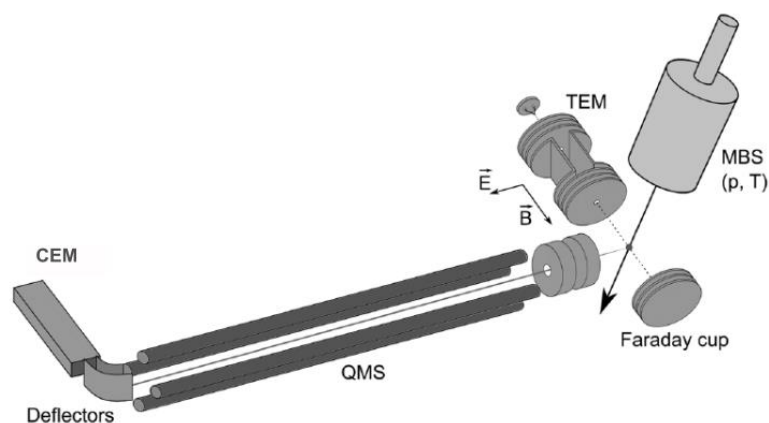
Fig.1. The schema of the electron and molecular crossed beams experiment CEMBIA based on [4].

3. Results

The positive ion mass spectrum of 2M2O recorded at ~70 eV is shown in Fig. 2. The parent molecular ion (P^+) with m/z 85 was detected, as well as other fragments already identified in NIST database [5]. The spectrum is in good agreement with the NIST spectrum regardless of intensity of some fragments. The peaks in the spectrum are labeled according to the possible products, more products for one peak are noted if there are more possibilities for one m/z. To reveal exact products quantum chemical calculations will be performed in the future. The second heaviest fragment is m/z 84 where the hydrogen is dissociated from the molecule. Without the support of theoretical calculations, it is not possible to determine the position from which the H atom dissociated. The highest peak is at mass m/z 55, there are three possibilities for this fragment C_2HNO^+, $C_3H_3O^+$, $C_3H_5N^+$. For 2M2O we did not detect formation of product via loss of the CH_3 side chain group. But in the spectrum at the mass m/z 15 the cation of methyl group is visible.
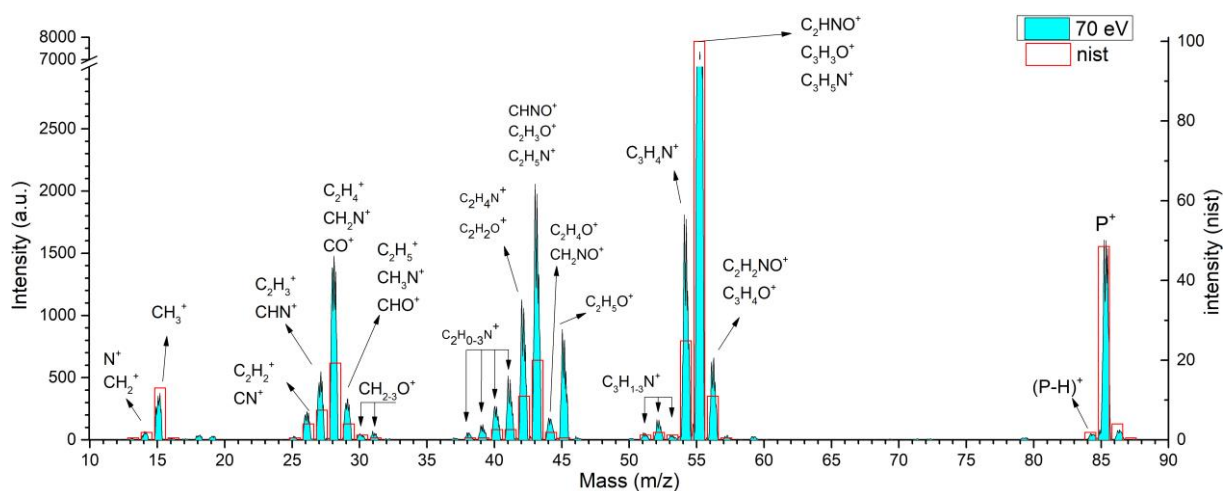

Fig. 2. Mass spectra of measured 2-methyl-2-oxazoline molecule at ~70 eV in comparison with mass spectra from NIST.

The positive ion mass spectrum of 2E2O recorded at ~70 eV is shown in Fig. 3. The parent molecular ion (P^+) has the mass m/z 99 which was identified as well as fragments m/z 98 where the hydrogen is dissociated from the molecule and m/z 69 $(P-CH_2-CH_3-H)^+$ or $(P-CH_2-O)^+$. The peak at mass m/z 100 is isotope of the parent. In the mass spectrum of 2E2O measured at ~70 eV we have again identified the supposed fragments in agreement with NIST database [6] regardless on intensity of some fragments. Only exclusion is that in the NIST spectrum there is a weak fragment at the mass m/z 97 which we did not identify in our spectrum. On the other hand, the fragment at mass m/z 49 and m/z 45 is seen in our spectrum, and the doubly charged parent ion at m/z 48.5. The first fragment is at mass m/z 15 which represents methyl group (not shown in the NIST spectrum starting at m/z 20). Also, the side chain cation is visible, the ethyl group $(CH_3-CH_2)^+$ at mass m/z 29, however there is the

possibility of creation of another product CHO$^+$ at this mass. The hydrogen loss is now more efficient than for 2M2O, the P-H$^+$ ion is more intensive than the parent ion. The most intensive product is at mass m/z 54.
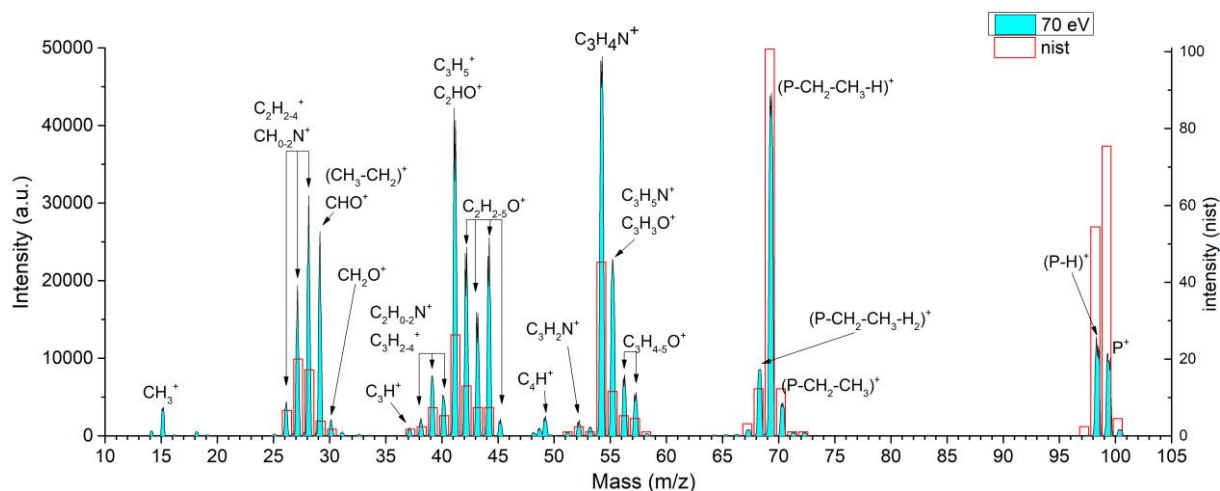

Fig. 3. Mass spectra of 2-ethyl-2-oxazoline molecule at ~70 eV in comparison with mass spectra from NIST.
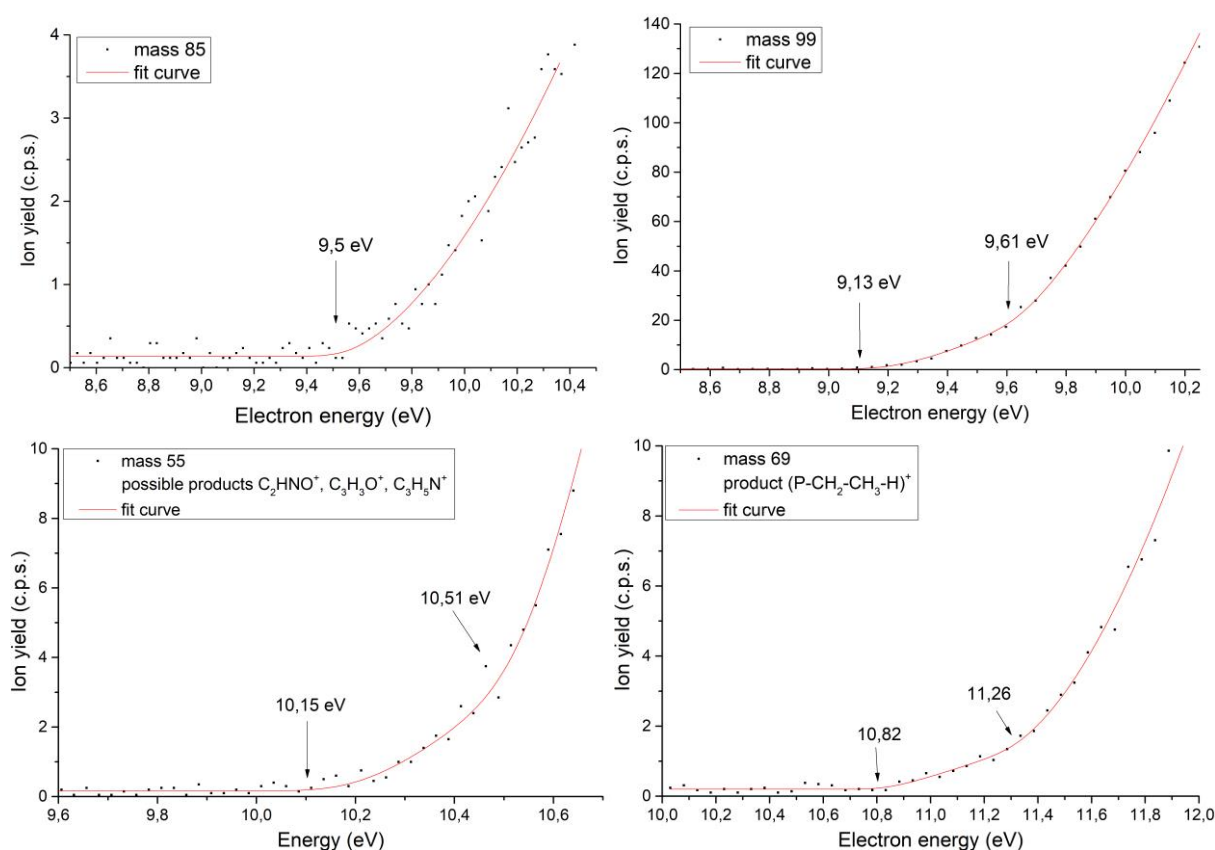

Fig. 4. Region of threshold of cross section of molecule ionization 2-methyl-2-oxazoline (left) and 2-ethyl-2-oxazoline (right)

The ionization energy (IE) for 2M2O is showed at Fig. 4. (top left) and is estimated on 9.5 eV. The IE for 2E2O is 9.1 eV with a second threshold at 9.6 eV, what we can see at Fig. 4 (top right). Subsequently we determine appearance energies for most of the fragments showed in the Tab. 1. From the differences of IE and AE it is possible to determine the dissociative energies (DE) of the products. In the mass spectra and in Tab. 1, we observe some sequences. There are several peaks originating

from hydrogen losses for example for 2M2O at masses m/z 51 – 55 representing $C_3H_{1-5}N$. Very similar dissociation is at masses m/z 39 – 43 $C_2H_{1-5}N^+$, where H is sequentially dissociated. Carbon was most likely dissociated from the product at m/z 55 C_2HNO^+, $C_3H_3O^+$, $C_3H_5N^+$ to give fragment at mass m/z 43 $CHNO^+$, $C_2H_3O^+$, $C_2H_5N^+$, and subsequently fragment at mass m/z 31 CH_3O^+, CH_5N^+.

In the case of 2E2O, there are also visible sequences for example at masses m/z 41 – 45 representing $C_2H_{1-5}O^+$. Carbon with hydrogen was most likely sequentially dissociated from product at the mass m/z 57 $C_3H_5O^+$ to give product at mass m/z 44 $C_2H_4O^+$. This fragment was dissociated to product at mass m/z 31 CH_3O^+. Another type of sequential dissociation is the CH_2 dissociation from product m/z 57 $C_3H_5O^+$ to the products m/z 43 $C_2H_3O^+$ and m/z 29 CHO^+. At the mass m/z 98 H is dissociated from the parent and fragment $(P-H)^+$ is created. Next fragment is $(P-CH_2-CH_3)^+$, where the side chain – ethyl group CH_2-CH_3 is dissociated. The dissociation energy for the side chain is 2.4 eV, what is about 1,19 eV less than in literature for dissociation C-C bond [7]. We did not observe this kind of dissociation in 2M2O, what is according to the NIST. The next 2 peaks are m/z 69 $(P-CH_2-CH_3-H)^+$ or $(P-CH_2-O)^+$ and m/z 68 $(P-CH_2-CH_3-H_2)^+$, where, in addition to the ethyl group, the carbon – bond hydrogens from the ring are also dissociated.

m/z	Supposed products	Energy (eV)
85	P^+	9.5 (IE)
84	$(P-H)^+$	9.89
56	$C_2H_2NO^+$, $C_3H_4O^+$	10.42
55	C_2HNO^+, $C_3H_3O^+$ $C_3H_5N^+$	10.15 & 10.51
54	$C_3H_4N^+$	13.39
53	$C_3H_3N^+$	14.62
52	$C_3H_2N^+$	13.1
51	C_3HN^+	15.72 & 16.71
45	$C_2H_5O^+$	15.37
44	$C_2H_4O^+$, CH_2NO^+	10.52
43	$CHNO^+$, $C_2H_3O^+$ $C_2H_5N^+$	10.37
42	$C_2H_4N^+$, $C_2H_2O^+$	11.37 & 12.11
41	$C_2H_3N^+$	12.56
40	$C_2H_2N^+$	14.15
39	C_2HN^+	14.63
31	CH_3O^+	12.5 & 13.51
30	CH_2O^+	11.27
29	$C_2H_5^+$, CH_3N^+, CHO^+	13.03 & 13.97
28	$C_2H_4^+$, CH_2N^+, CO^+	13.39
27	$C_2H_3^+$, CHN^+	13.93 & 14.53
26	$C_2H_2^+$, CN^+	11.77 & 14.78
15	CH_3^+	15.46
14	N^+, CH_2^+	16.33

m/z	Supposed products	Energy (eV)
99	P^+	9.13 & 9.61 (IE)
98	$(P-H)^+$	10.39 & 11.02
70	$(P-CH_2-CH_3)^+$	11.53 & 12.41
69	$(P-CH_2-CH_3-H)^+$ $(P-CH_2-O)^+$	10.82 & 11.26
68	$(P-CH_2-CH_3-H_2)^+$	12.29 & 12.66
57	$C_3H_5O^+$	11.56 & 12.17
56	$C_3H_4O^+$	10.65 & 11.22
55	$C_3H_5N^+$, $C_3H_3O^+$	12.25 & 13.13
54	$C_3H_4N^+$	12.19 & 12.67
49	C_4H^+	16.5
45	$C_2H_5O^+$	10.61
44	$C_2H_4O^+$	10.53
43	$C_2H_3O^+$	10.26 & 10.8
42	$C_2H_2O^+$	10.96 & 12.02
41	$C_3H_5^+$, C_2HO^+	11.99 & 12.49
40	$C_2H_2N^+$, $C_3H_4^+$	12.29
39	C_2HN^+, $C_3H_3^+$	14.68
38	C_2N^+, $C_3H_2^+$	20.37 & 24.85
32	NH_2O^+, CH_4O^+	12.16
31	HNO^+, CH_3O^+	11.79 & 12.81
30	CH_2O^+	11.13 & 12.17
29	$(CH_3-CH_2)^+$, CHO^+	12.1 & 12.65
28	$C_2H_4^+$, CH_2N^+	10.87 & 12.26
27	$C_2H_3^+$, CHN^+	13.98
26	$C_2H_2^+$, CN^+	11.5
17	OH^+	10.63
15	CH_3^+	15.37 & 16.65

Tab. 1.: Main products of 2-ethyl-2-oxazoline (right) and 2-methyl-2-oxazoline (left) fragmentation and appearance energies of ions as determined in the present work.

By comparison of the 2M2O and 2E2O table (Tab. 1.), it is possible to notice a supposed common product at m/z 55 for 2M2O and m/z 69 for 2E2O. However, looking at DE, it can be seen that DE for 2E2O is 1.69 and for 2M2O is 0.65, what makes difference of approximately 1.04 eV. Therefore, it can be concluded that this will not be a common product. For the supposed product CH_3^+, the DE for 2M2O is 5.96 and for 2E2O is 6.24. At the m/z 26 with the supposed products $C_2H_2^+$, CN^+ the DE for

2M2O is 2.27 and for 2E2O is 2.37. According to the DE, which is very similar for *m/z* 26, it is very likely that it will be the same product.

The potential fragmentation pathway for the 2E2O is shown in the Fig. 5. In the scheme there is assigned options for a given mass, thanks to that it is possible to assign dissociation energy to some specific bond. Subsequently, the results of bonds energies which represents DE are compared with the tabular values from the literature.
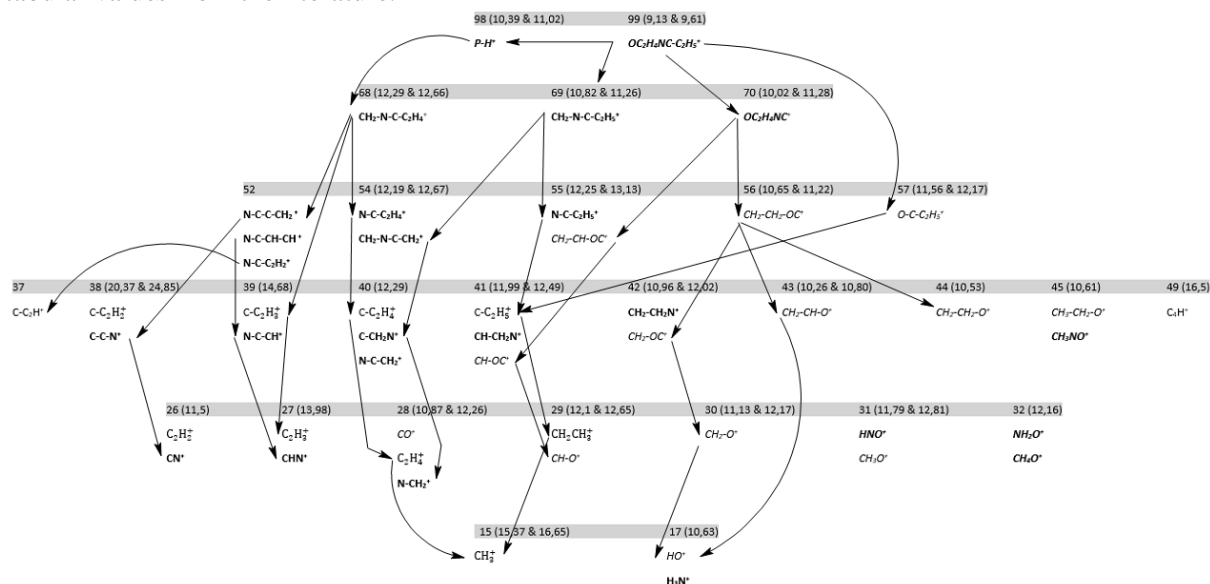

Fig. 5.: Possible fragmentation pathway of 2-ethyl-2-oxazoline.

4. Conclusion

We have studied formation of the positive ions formed by electron impact ionization of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline by means of crossed electron and molecular beam experiment. We have measured the mass spectra of the molecules at electron energy 70 eV. The measurements at 70 eV showed products of molecules fragmentation in accordance with NIST published data [5,6]. We recorded the ion efficiency curves in the threshold region of the most dominant fragments and estimated the appearance energies of the ions. The ionization energy of the 2-methyl-2-oxazoline´s parent ion was estimated to be 9,5 eV and the ionization energy of the 2-ethyl-2-oxazoline´s parent ion was estimated to be 9,13 eV. The formation of cationic methyl product *m/z* 15 CH_3^+ from 2M2O was observed, in contrast to 2E2O, where not only cationic ethyl product *m/z* 29 CH_2-CH_3 was observed bud also side chain – ethyl group CH_2-CH_3 is dissociated and the cationic fragment *m/z* 70 is formed. Although the appearance energies of ions were determined to reveal the accurate identifications quantum chemical calculations will be performed in the future to provide more insight.

5. References

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