MASS SPECTROMETRY OF NEGATIVE IONS OF PYRIDINE N-OXIDES

V. S. Fal'ko, U. M. Dzhemilev,
V. I. Khvostenko, and G. A. Tolstikov

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The dissociative capture of electrons by N-oxides of pyridine and α-, β-, and γ-picolines was investigated by mass spectrometry [1]. The mass spectra of the negative ions were studied. The curves of the effective yields of the negative ions as a function of the energies of the electrons were obtained.

The interaction of electrons with pyridine and its alkylated derivatives [2] leads to the formation of two excited states of negative molecular ions, which then disintegrate via the energetically possible disintegration channels to form stable negative ions. Alkyl substituents in the pyridine molecule do not cause the appearance of new states of the molecular ions.

The experimental data on the dissociative capture of electrons by N-oxides of methylpyridines are presented in Table 1. The mass spectrum of the negative ions is a set of relative intensities of peaks of ions at the maxima of their effective yields, so that several peaks with respect to the number of resonance processes involving the formation of the given ions may correspond to one mass number. The relative intensities of peaks for two poorly resolved (from one another) resonance peaks are presented for the peak of maximum intensity.

The oxygen atom in pyridine N-oxides has a substantial effect on the processes of dissociative capture of electrons, causing both the appearance of new excited states of the negative molecular ions and a change in the number of possible channels of disintegration of the molecular ions. Five ground states of the excited molecular ions, which are designated by the letters a-e, can be distinguished from the position of the maxima of the effective yield of ions on the scale of the energy of the electrons and from the paths of disintegration. We will examine the indicated states for the pyridine N-oxide molecule.

Low-energy state a of the negative molecular ions is represented in the mass spectrum of pyridine N-oxide by the lines of the $(M-H)^-$, $NC_3H_3^-$, $NC_3H_2^-$, and NC_3^- fragment ions. The relative intensities of the peaks of the indicated ions are relatively low, and the maximum effectiveness of the formation of ions during the disintegration of the negative molecular ions of state a is observed at electron energies of 0.2-0.5 eV.

The disintegration of molecular ions of the b state is accompanied by ejection of a C_2H_3 group (ions with m/e 68). The maximum of the resonance peak on the curve of the effective yield of $(M-C_2H_3)^-$ ions is found at an electron energy of 0.8 eV.

The most intense peaks in the mass spectrum of pyridine N-oxide are affiliated with the ions formed during the dissociation of the negative molecular ions of the c state, and the maximum effective yield of ions is observed at electron energies of 3-3.2 eV. The disintegration of the molecular ions of this state is represented in the mass spectrum by peaks of the $(M-H)^-$, $(M-OH)^-$, $(M-OCH)^-$, O^-, and OH^- ions and of ions with m/e 64.

The states of the molecular ions enumerated above are observed only during the interaction of electrons with the pyridine N-oxide molecules, and the oxygen atom linked by a semipolar bond to the pyridine nitrogen atom affects their formation. The higher-energy states of the negative molecular ions have

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Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 661-665, May, 1974. Original article submitted April 2, 1973.

TABLE 1. Mass Spectra of the Negative Ions of N-Oxides of Pyridine and Its Methyl Derivatives

m/e	Pyridine N-oxide	α-Picoline N-oxide	β-Picoline N-oxide	γ-Picoline N-oxide
1	2	3	4	5
		16,8 (8,8)	17,8 (8,55)	37,6 (8,95)
108		100 (3,26)	100 (3,12)	67,5 (4,25)
		62 (0,2)	19,2 (0,4)	53 (0,2)
		5,2 (8,8)	0,98 (8,5)	27,3 (8,56)
107		1,0 (3,6)	2,2 (3,2)	2,6 (4,8)
			0,89 (0,3)	3,6 (0,2)
		0,67 (8,8)		1,43 (8,6)
106		0,6 (3,6)	0,79 (3,2)	1,04 (4,8)
			0,29 (0,3)	
	6,61 (8,8)*	3,78 (8,5)	0,5 (8,6)	2,6 (8,23)
94	100 (3,1)	65,3 (3,24)	15,7 (3,14)	16,1 (3,4)
	5,7 (0,3)	10 (0,36)	3,0 (0,3)	10,4 (0,34)
		0,4 (8,5)	0,29 (8,6)	5,71 (8,6)
93	4 (4,2)	1,86 (4)	0,74 (3,2)	1,95 (4,35)
			0,24 (0,3)	3,9 (0,3)
	0,25 (8,5)	5,05 (8,7)	2,32 (8,55)	67,5 (9,2)
92		9,3 (3,3)	3,94 (3,2)	9,1 (4,35)
		0,67 (0,34)	0,07 (0,3)	13 (0,32)
		1,46 (8,64)	0,39 (8,9)	8,3 (9,1)
91		5 (3,3)	1,38 (3)	3,9 (3,2)
		1,3 (0,24)	0,07 (0,3)	
		3,84 (8,25)	0,88 (8,56)	29,9 (9,12)
90		4,27 (3,2)	0,99 (3,32)	8,85 (4,64)
		1,27 (0,2)	0,14 (0.48)	23,4 (0,2)
		0,8 (8,5)	0,08 (8.48)	1,55 (9)
82		0,16 (4,2)	8,4 (1,1)	
		2,33 (1,2)		1,3 (1,1)
		0,67 (8,6)		2,08 (9)
81		0,47 (3,3)	1,57 (4,1)	6,35 (4,5)
		1,13 (8,8)	0,15 (8.4)	13 (9,2)
80		2,67	7,9 (3,2)	83 (4,28)
		0,2 (0,28)		1,3 (0,2)
	0,29 (8,8)	0,27 (9)	0,29 (8,2)	2,08 (9.2)
79		2 (4,7)	6,4 (4,25)	14,5 (4,56)
	1.0 (8,45)	2,06 (8,7)	0,49 (8,8)	5,7 (9,1)
78	3.14 (3,16)	2,33 (6,8)	0,69 (4,4)	8,85 (3,28)
		0,23 (4,8)		3,6 (0,24)
	1.07 (8,55)	0,23 (8,7)		0,78 (9.1)
76	1,15 (4,08)	0,53 (3,7)	0,1 (4)	1,04 (4,5)
	2,06 (8,1)	0,67 (8,8)	1,32 (8,45)	3,38 (8,8)
68	1,24 (3,8)			10 (4,28)
	1,87 (0.8)	26,7 (1.24)	18,5 (1,10)	1,04 (1,1)
	1.24 (8.1)	0,6 (8,6)	0,6 (8,56)	10,4 (9,28)
67				15 (5,84)
	6.2 (3,8)	14 (3,6)	0,74 (3,6)	100 (4.28)
		1,1 (9)	0,6 (8,6)	5,2 (9,2)
66	51.5 (3.2)	47,5 (3,7)	4,33 (3,52)	6 (4,32)
				1,65 (0,28)
	0,91 (8,3)	0,6 (8,65)	0,34 (8,6)	3.9 (9,1)
65	8,26 (4,2)	0,26 (4,25)	0,12 (3,6)	0,78 (4,2)
		0,36 (0,24)		
	3,47 (8,2)	1,6 (8,85)	0,94 (8,7)	46.7 (9,28)
64	0,57 (3,4)	0,26 (4,36)		10,9 (4,31)
				10,4 (0,2)
	0,58 (8,3)	0,8 (8,72)	0,69 (8.8)	1,82 (9,1)
63	0.16 (4,3)	0,13 (4)		
53	0,49 (8,2)	2,8 (8,96)	0,44 (8,7)	4,42 (9,2)
	0,44 (4,3)	0,13 (4,32)	0,49 (4,2)	0,78 (4,5)
	0,3 (0,2)			
	0,91 (8,1)	0,93 (9,16)	1,5 (8,32)	1,09 (9,2)
52	0,88 (4,0)	1,16 (3,64)	10,3 (4)	0,91 (4,2)
	0,22 (0,2)			
	1,65 (8,1)	1,93 (9)	0,49 (8,5)	2,47 (9,2)
51		0,13 (3,56)		
	6,83 (8,2)	4,0 (8,96)	1,72 (9)	1,95 (9,2)
50	1,93 (3,92)	1,0 (4,4)	0,29 (4,5)	1,18 (4,5)
	2,24 (0,2)	1,3 (0,2)	4,92 (0,2)	19,5 (0,3)
	3,72 (8,3)	0,87 (9)	0,24 (9)	1,3 (9)
49				
	0,62 (8)	0,4 (8,5)	0,49 (8,8)	2,86 (9)
43		0,33 (4,6)	0,49 (4,2)	2,6 (4,2)
	6,83 (8,28)	4,66 (8,6)	1,97 (8,48)	3,12 (8,9)
42	1,46 (3,28)	2,0 (4,3)	0,5 (3,9)	
	3,3 (0,12)	8,68 (0,2)	12 (0,12)	23 (0,2)
	6,72 (8,1)	7,34 (8,92)	11,3 (8,6)	10,4 (8,9)
41	3,06 (3,72)	5,33 (4,4)	1,48 (4,26)	5,7 (4,2)
	4,55 (8,3)	7,0 (8,95)	23 (8,4)	22,4 (8,95)
40	14 (3,94)	16,6 (3,88)	2,46 (3,8)	28,6 (5,8)
				57 (4,32)

TABLE 1 (Continued)

m/e	Pyridine N-oxide	α-Picoline N-oxide	β-Picoline N-oxide	γ-Picoline N-oxide
1	2	3	4	5
	6,61 (7,92)	8 (8,68)	3,45 (8,25)	2,86 (8,9)
39	1,23 (4,52)		0,34 (4,16)	
	24,8 (8,2)	18,6 (8,72)	8,13 (8,2)	12,5 (9)
25				
	24,8 (8,15)	21,8 (8,8)	8,2 (8,2)	6,23 (9,1)
17	14 (3,2)	48 (3,54)	18,5 (3,64)	3,9 (4,4)
	89,6 (8)	120 (8)	17,3 (8,92)	33,8 (8,25)
16	268 (3,12)	630 (3,48)	185 (3,16)	83 (4,36)
	0,49 (8,2)	2,8 (8,96)	0,44 (8,7)	4,42 (9,2)

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*The energy of the electrons of the maximum yield is given in parentheses in electron volts.

already been observed during a study of the dissociative capture of electrons by pyridine molecules.

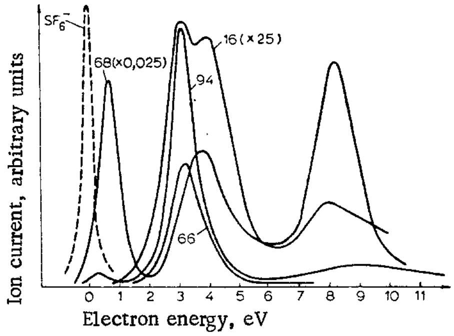

Fig. 1. Dependence of the effective yield of negative ions on the electron energy in pyridine N-oxide (the mass numbers are indicated by the numbers beside the curves).

The d state of the molecular ions is revealed distinctly from the curves of the effective yield of O^- ions, on which there are two poorly resolved peaks (see Fig. 1). The first peak has a maximum at an electron energy of 3.2 eV and corresponds to state c of the negative molecular ions. The second peak, with a maximum at an electron energy of 4 eV, shows the existence of yet another state of the negative molecular ions, which disintegrates with the formation of O^- ions. The dissociation of the negative molecular ions of the indicated state also leads to the formation of $(M-CH_3)^-$, $(M-OCH)^-$, $(M-NO)^-$, $NC_3H_3^-$, $NC_3H_2^-$, NC_3^-, and $(M-2H)^-$ ions and of ions with m/e 68, 41, 40, and 39. In contrast to processes of dissociative capture of electrons by pyridine molecules [only $(M-H)^-$, NC_3^-, C_2H^-, and C_2^- ions are formed in this range of electron energies], the disintegration of the molecular ions of pyridine N-oxide proceeds via a considerably larger number of channels. Moreover, a channel for the formation of C_2H^- and C_2 ions is opened. Ions with m/e 65 are formed by detachment of an NO group and apparently have the structure of the cyclopentadienyl anion. The inflection of the peak on the curve of the effective yield of ions with m/e 65 on the lower electron-energy side shows that the ions are also formed during the disintegration of the molecular ions of the c state, but with a lower probability. Similar processes are also noted on the curves of the effective yield of ions with m/e 53, 52, and 50.

The disintegration of the molecular ions of high-energy state e forms a mass spectrum with many mass peaks, although their relative intensities are relatively low. In addition to the purely "pyridine" $NC_3H_2^-$, NC_3H^-, $NC_2H_2^-$, NC_2H^-, and C_2H^- ions, one also observes fragments, the formation of which is explained by participation of the oxygen atom in the dissociation processes: $(M-OH)^-$, $(M-H_3O)^-$, $(M-OC)^-$, $(M-OCH)^-$, O^-, and OH^-, and ions with m/e 68, 49, 43, 42, and 41. The maxima of the resonance peaks of the formation of the indicated ions are situated at 8-9 eV along the electron-energy scale.

Just as in the case of alkylpyridines, replacement of the hydrogen atom in the pyridine N-oxide molecule by a methyl group does not cause the formation of new states of the negative molecular ions. One observes only a certain redistribution of the probabilities of the various disintegrative channels.

Detachment of a methyl group from the molecular ions occurs during the dissociative capture of electrons by N-oxides of methylpyridines with a quite high probability, while for the methylpyridines themselves the indicated process is noted only during the capture of electrons by 2-methylpyridine molecules, and the probability of the process is very low. Depending on the electron energy, the curves of the effective yield of $(M-CH_3)^-$ ions contain three peaks of resonance processes. The first peak corresponds to disintegration of the molecular ions of the a state at an electron energy of 0.2 eV. The maximum of the second peak is situated at 3-3.2 eV on the electron-energy scale, and $(M-CH_3)^-$ ions are formed during the disintegration of the negative molecular ions of the c state. The third peak – a maximum at 8-8.6 eV – is caused by dissociation of the molecular ions of the e state.

Peaks of $(M-H_3O)^-$ ions are observed in the mass spectra of all of the investigated compounds. It should be noted that during the capture of electrons by N-oxides of pyridine and γ-picoline, $(M-H_3O)^-$ ions are formed during the disintegration of the molecular ions of the c state. Capture of electrons by N-oxides of α-picoline and β-picoline is accompanied by the formation of $(M-H_3O)^-$ ions, which are caused by disintegration of the molecular ions of both state c and state d with different degrees of effectiveness of formation; this is confirmed by the presence of inflections on the curves of the effective yield of ions.

The peaks of the resonance processes involved in the formation of $(M-H)^-$ ions during the disintegration of the negative molecular ions of the c state have a symmetrical form for the molecules of the first three compounds. The formation of $(M-H)^-$ ions during the interaction of electrons with γ-picoline N-oxide molecules occurs in a more complex manner. There are two breaks on the curve of the effective yield of ions at electron energies of 2.8 and 3.1 eV; in addition, $(M-H)^-$ ions are formed during the disintegration of the negative molecular ions of γ-picoline N-oxide of the d state with a high effective yield. The relative intensity of the lines of the fragment ions formed by disintegration of the negative molecular ions of the d state increases in the mass spectrum of γ-picoline N-oxide.

EXPERIMENTAL

The mass spectra were recorded with an MKh-1303 spectrometer remodeled for the recording of negative ions. The conditions maintained during the recording of the mass spectra were as follows: the ionizing electron current was 1 μA, and the ionization chamber temperature was 150°. The electron-energy scale was monitored from the curve of the effective yield of SF_6^- ions. The curves of the effective yield of negative ions as a function of the electron energy were obtained by means of an automatic recording device with a PDS-021M two-coordinate potentiometer.

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