

# MASS SPECTRA OF NEGATIVE IONS FROM THIOPHANE AND ITS ALKYL DERIVATIVES

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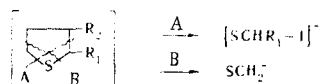
The mass spectra of the negative ions from the dissociative capture of electrons were obtained for thiophane and its alkyl derivatives. With a few exceptions, all of these negative ions of the spectrum contain sulfur atoms: electron capture is not observed in cyclic compounds — cyclopentane and methylcyclopentane. The principle routes of dissociation during electron capture were isolated for thiophane and alkylthiophanes and explain the greater portion of the observed lines.

The use of mass spectrometry of negative ions for the solution of structural and analytical problems of organic chemistry has deficiencies with respect to information relating to the fundamental principles of disintegration of molecules of organic compounds during the addition of a "superfluous" electron to the molecule.

The negative ions of aliphatic sulfides and disulfides have been studied in a number of papers [1-3]; in the present paper, we have for the first time studied the mass spectra of negative ions of alkylthiophanes. The relative intensities of the observed negative ions are presented in Table 1. (The intensity of the maximum yield ions was taken as 100%.)

In contrast to aliphatic sulfides, the mass spectra of the negative ions of alkylthiophanes contain intense  $M-1$  peaks, the relative amount of which is insignificant for thiophane itself and increases as the length of the alkyl chain increases. The  $S^-$  ions and rearranged  $SH^-$  ions characteristic for organosulfur compounds are observed in high relative yields. The mass spectra of thiophane and alkylthiophanes contain a line with a mass number of 47, to which the  $SCH_3^-$  ions, also formed by rearrangement of the bonds, correspond.

An examination of the mass spectra presented in Table 1 made it possible to establish that the larger group of spectral lines is explained by disintegration of the negative molecular ion via schemes A and B:



(In scheme A, the ring disintegrates with detachment of still another hydrogen atom.) According to this scheme,  $SCH_2^-$  ions are formed in all of the compounds except 2,5-dimethylthiophane (in which the intensity of the peak with  $m/e$  46 is insignificant, since only process A to form  $SC_2H_3^-$  is possible),  $SC_3H_3^-$  ions in 2,4-dimethylthiophane,  $SC_4H_7^-$  ions in 2-propylthiophane, etc. This scheme explains the higher intensity of the lines of  $SCH_2^-$  ions in  $\beta$ -substituted compounds as compared with  $\alpha$ -substituted compounds (amyl- and hexylthiophanes).

All of the mass-spectral ions except  $C_3H_5^-$ , which has a low relative yield, contain sulfur atoms. The center of capture of electrons is probably the sulfur atom, since electron capture does not occur in cyclopentane and methylcyclopentane molecules.

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TABLE 1. Mass Spectra of the Negative Ions of Thiophane and Its Alkyl Derivatives

Ion	m/e	T	2-Ethyl-thiophane	2,4-Di-methyl-thiophane	2,5-Di-methyl-thiophane	2-Propyl-thiophane	2-Butyl-thiophane	3-Amino-thiophane	2-(2,2-Di-methylpro-pylthio)-phane	2-Hexyl-thiophane	3-Hexyl-thiophane
SC <sub>10</sub> H <sub>19</sub> <sup>-</sup>	171									100	100
SC <sub>9</sub> H <sub>17</sub> <sup>-</sup>	157							100	100		
SC <sub>8</sub> H <sub>15</sub> <sup>-</sup>	143						100			2,4	—
SC <sub>7</sub> H <sub>13</sub> <sup>-</sup>	129					100		7,1	8,6	11,0	—
SC <sub>6</sub> H <sub>11</sub> <sup>-</sup>	115		26,3	22,5	16,4		2,8		17,2	0,1	—
SC <sub>5</sub> H <sub>9</sub> <sup>-</sup>	101		—	—	—	3,1	33,1	—	2,1	1,2	0,8
SC <sub>4</sub> H <sub>7</sub> <sup>-</sup>	87	0,6	1,2	—	—	53,3	0,3	2,2	0,7	—	3,0
SC <sub>4</sub> H <sub>5</sub> <sup>-</sup>	85	0,03	—	—	—	—	—	2,1	0,6	—	2,2
SC <sub>3</sub> H <sub>3</sub> <sup>-</sup>	73	—	33,4	3,0	2,1	0,4	1,5	—	—	—	—
SC <sub>2</sub> H <sub>3</sub> <sup>-</sup>	59	3,7	5,7	17,5	100	6,2	7,3	8,3	8,6	10,4	12,0
SCH <sub>3</sub> <sup>-</sup>	47	0,4	4,3	25,0	—	2,3	2,1	12,2	3,9	2,7	16,0
SCH <sub>2</sub> <sup>-</sup>	46	13,9	9,7	31,0	0,3	6,0	4,4	12,7	7,7	7,1	12,8
C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	41	1,5	3,8	—	—	1,9	1,1	1,0	3,6	2,4	—
SH <sup>-</sup>	33	100	100	100	68,4	53,3	50,5	85,8	96,2	96,0	96,4
S <sup>-</sup>	32	11,0	32,0	12,5	38,1	16,0	20,2	73,5	51,8	68,4	90,0
Relative sensitivity		6,4	2,6	2,7	3,6	2,1	1,5				1,2

It is apparent from Table 1 that the relative probability of disintegration of the ring during the addition of an electron is high for thiophane and 2,4- and 2,5-dimethylthiophane and decreases in molecules with longer alkyl substituents.

When a "superfluous" electron is added, a much smaller amount of charged fragments is formed as compared with fragmentation of molecules of alkylthiophanes during the formation of positive ions [4]. No correlation was observed between the disintegrations of the positive and negative molecular ions.

The last line of Table 1 contains the relative sensitivity, which is the ratio of the current of the ions of maximum intensity (100%) to the current of ions with m/e 77 in the spectrum of benzene [5] when identical volumes of the investigated substance and benzene are admitted into the device.

In addition to the ions of the mass spectrum described here, S<sup>-</sup> and SC<sub>2</sub>H<sub>3</sub><sup>-</sup> ions are observed when thiophane and alkylthiophanes are admitted into the device at electron energies of 5 ± 0.5 eV.

## EXPERIMENTAL

The experiments were carried out with an MKh-1303 mass spectrometer equipped for recording negative ions. The electron energies at which the maximum yields of ions of the mass spectrum presented are observed are grouped about 8 eV with a scatter of ±0.5 eV. The conditions for obtaining the mass spectra are as follows: the temperature of the ionization chamber was 150 ± 1°C, the ionizing electron current was 4.0 μA, and the half-width of the distribution of electrons with respect to energy was 0.5-0.6 eV.

In addition to thiophanes, cyclopentane and methylcyclopentane vapors were admitted into the ion source, but the formation of negative ions by these molecules was not detected in the range of electron energies from 0 to 50 eV.

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