LETTERS TO THE EDITOR

MASS SPECTRA OF THE NEGATIVE IONS OF 2- AND 4-THIOBARBITURIC ACIDS

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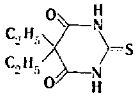
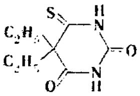
The difference in the behavior under electron impact of the structural isomers for 2- and 4-thiobarbituric acid derivatives have been previously discussed [1]. We have found that isomers I and II also differ substantially with respect to the spectra of dissociative capture of slow electrons (DCSE).



I



II

Mass spectra, m/e values (relative intensities in percent; energy of the electrons in the maximum of the peak in electron volts): I 200 (M^-) (0.7; 0), 199 (8; 1.2), 171 (100; 0.4), 171 (10; 3.3), 128 (0.3; 4.7), 58 (5; 5.4), 41 (1.8; 5.7), II 200 (M^-) (not observed), 199 (1.5; 1.2), 171 (100; 0.4), 171 (4.7; 3.3), 128 (0.3; 4.7), 58 (5; 5.4), 42 (1.6; 5.7).

The maximum-intensity peaks in the DCSE spectra of both isomers correspond to $[M - C_2H_5]^-$ ions with m/e 171; in both cases this may be explained by the effective stabilization of the resulting anions. The $[M - C_2H_5]^-$ ion peak has two maxima at 0.4 and 3.3 eV.

However, a long-lived negative molecular ion (M^-) with a lifetime relative to spontaneous splitting out of an electron of $\tau = 280 \cdot 10^{-6}$ sec is observed in the spectrum of I. A negative molecular ion is not observed for II. Its lifetime is probably shorter than the smallest measurable value of $5 \cdot 10^{-6}$ sec and cannot be recorded. Consequently, as in the case of electron impact [1], under the DCSE conditions the stability of the I molecule is considerably higher than that of isomer II. It follows from the IR and UV spectral data that isomer I, in contrast to isomer II, is characterized by strong intramolecular hydrogen bonds and the presence of several tautomeric forms. An increase in τ because of intramolecular hydrogen bonds and tautomeric transformations in a number of isomeric nitrophenols is indicated in [2]. This can apparently explain the high stability of M^- in the case of I and the observed differences in the intensities of the lines of $[M - H]^-$ (199) and SCN^- (58) ions in the mass spectra of isomers I and II.

Thus we have demonstrated the possibility of identification of the structural isomers of thiobarbituric acid derivatives by means of mass spectrometry of the negative ions. The DCSE mass spectra were measured with an MKh-1303 spectrometer remodeled for recording negative ions.

LITERATURE CITED

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