MASS SPECTRA AND STRUCTURES OF SUBSTITUTED CARBAZoles

R. A. Khmel'nikskii, P. B. Terent'ev, and O. A. Solovev

The anomalous character of the dependence of the stability with respect to electron impact on the size of the alkyl group in alkylacetylcarbazoles leads to the conclusion that the molecular ion undergoes profound rearrangement prior to detachment of the first neutral particle, during which the effect of the functional group on this process is manifested weakly. The functional group is not always the determining factor in the formation of the primary fragment ions, particularly if the processes involving the participation of the alkyl group lead to more stable ions than the processes involving the participation of a labile functional group.

Research on carbazoles by a number of investigators [1-3] has led to the conclusion that polycyclic condensed systems containing a carbazole fragment and alkylcarbazoles have anomalously high stabilities with respect to electron impact (W_M). The assumption of profound rearrangement of the molecular ion leading to specific fragmentation of these systems was advanced in a study of 9-alkylcarbazoles [3].

It seemed of interest to examine the effect of electron-donor groups on the W_M values and pathways of fragmentation of substituted carbazoles.

In the present research we studied the mass spectra of the following substituted carbazoles:

The mass spectra of the investigated compounds were obtained with a modified MKh-1303 mass spectrometer with direct introduction of the substances into the ion source at various ionizing-electron ener-
As expected, the introduction of a nitro group in the carbazole molecule lowers the \( W_M \) value, but, as before, this value remains very high.

The mass spectra obtained at an ionizing-electron energy of 50 eV (>3% of the maximum peak), the \( W_M \) values, and the fragmentation selectivities \( (S_{1/2}) \) are presented in Table 1. The intensities of the peaks in the mass spectra are expressed in percent of the total ion current; the fragmentation pathways in the schemes are confirmed by the corresponding metastable peaks.

As expected, the introduction of a nitro group in the carbazole molecule lowers the \( W_M \) value, but, as before, this value remains very high.

The fragmentation of I proceeds via the pathways characteristic for nitro-substituted heterocyclic compounds. The fragmentation selectivity is quite high \( (S_{1/2} = 6) \), and the fraction of ions depicted in the scheme