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ELECTRON-IMPACT FRAGMENTATION OF MONO- AND DIACYLHYDRAZINES OF FLUOROCARBOXYLIC ACIDS

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The mechanism of electron-impact dissociative ionization of mono- (I) and diacylhydrazines (II) of fluorocarboxylic acids RC(O)NHNHR$_1$ (I) and RC(O)NHNR$_1$C(O)R (II) with R = CH_3, CH_2F, CHF_2, CF_3, C_2F_5, C_3F_7, C_4F_9, C_6F_{13}; R$_1$= H, CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_9H_{19}, C_6H_5 has been studied. The fragmentation of (I) with R$_1$= H involves direct cleavage of C(O)-C and C(O)-N bonds. The accumulation of fluorines in the molecule increases the portion of dissociates at the C(O)-C bond and, starting from R$_1$= C_2F_5, no fragmentation at the C(O)-N bond occurs. When an alkyl group is introduced into the hydrozine fragment some arrangements involving N-N bond cleavage become prevailing processes. Elongation of perfluoroalkyl groups does not affect much the molecular ion fragmentation, the mass spectra pattern being dependent on only the size and character of the substituent R$_1$ attached to the nitrogen atom.

The fragmentation of fluorine-containing diacylhydrazines (II) proceeds analogously to that of (I) with R$_1$= H, independently of substituent R$_1$. The major contribution to the total ion current is from ions generated by dissociation of the perfluoroacyl fragment.

The main trends in dissociation of parent ions and fragments have been considered and compared with fragmentation of some non-fluorinated analogs. Some mechanisms for the rearrangement processes have been suggested.