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Article

Electron impact fragmentation of some mixed cyclotetraphosphazenes

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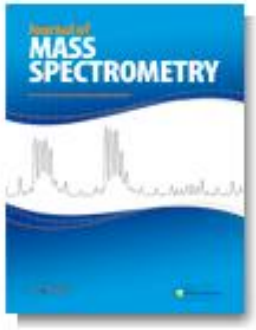

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Abstract

The electron impact fragmentations of some cyclotetraphosphazenes are reported and discussed. The major fragmentation path involves loss of two amine radicals and one chlorine radical in the series $P_4N_4Cl_{8-n}(NMe_2)_n$ when n=2, and subsequent stages involve a ring contraction process with elimination of a P = N fragment, when n = 5 loss of amine radicals predominates on statistical grounds with little evidence of ring contraction. In the series $P_4N_4F_{8-n}(NMe_2)_n$ fragmentation is dominated by loss of amino radicals when n = 4 and loss of fluorine radicals predominates on statistical grounds when n = 2. In the series $P_4N_4F_{8-n}X_n$ (n = 2 or 4, X = Cl or Br), when n = 2 and X = Br the major fragmentation path is the loss of two bromine radicals, whereas when X = Cl the more favoured path is the loss of two chlorine radicals. In both, subsequent stages involve ring contraction reactions with elimination of a PN fragment. When n = 4 and X = Br or Cl on bond energy grounds the more favoured fragmentation pattern is the loss of bromine or chlorine radicals, respectively.