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Mass-Spectrometric Fragmentation of *N,N*-Dimethyl-4-methoxy-6-polynitromethyl-1,3,5-triazin-2-amines

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Abstract — Mass-spectrometric fragmentation of *N,N*-dimethyl-4-methoxy-6-X-1,3,5-triazin-2-amine (X = fluorodinitromethyl, chlorodinitromethyl, bromodinitromethyl, trinitromethyl, 1,1-dinitroethyl, 2-hydroxy-1,1-dinitroethyl) under electron impact was studied. The stability of the molecular ion and the main fragmentation pathways are discussed.

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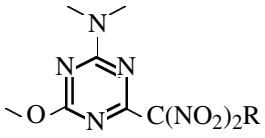
We found no mass-spectrometric data for polynitromethyl derivatives of 1,3,5-triazine. The mass-spectrometric fragmentation of some amino, arylamino, alkoxy, aryloxy, and alkyl derivatives of 1,3,5-triazine was studied in [1–5]. To reveal the effect of the polynitromethyl substituent on the stability of the molecular ion, fragmentation pattern, and structure of fragment ions, we examined the fragmentation of *N,N*-dimethyl-4-methoxy-6-polynitromethyl-1,3,5-triazin-2-amines **I**–**VI**.



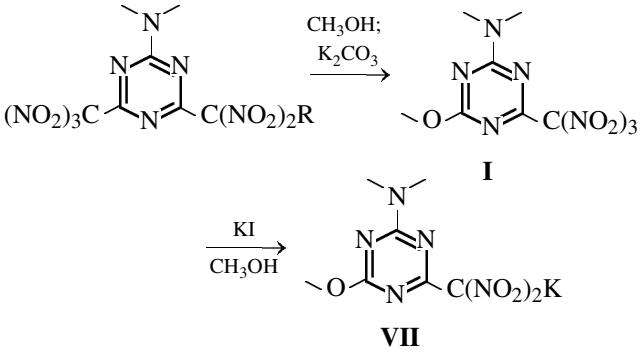
I–**VI**

R = NO_2 (**I**), F (**II**), Cl (**III**), Br (**IV**), CH_3 (**V**), CH_2OH (**VI**).

Compound **I** was prepared by the reaction of *N,N*-dimethyl-4,6-bis(trinitromethyl)-1,3,5-triazin-2-amine with methanol in the presence of potassium carbonate [6]. By denitration with KI in methanol, we prepared potassium salt of *aci*-nitro(4-dimethylamino-6-methoxy-1,3,5-triazin-2-yl)nitromethane **VII** [6].

Compounds **II**–**VI** were prepared from **VII**: compound **II**, by fluorination with XeF_2 [6]; **III**, by chlorination with Cl_2 [7]; **IV**, by bromination with Br_2 [7]; **V**, by reaction with CH_3I [8]; and **VI**, by reaction with formaldehyde [8].

The mass spectra of **I**–**VI** are given in the table.



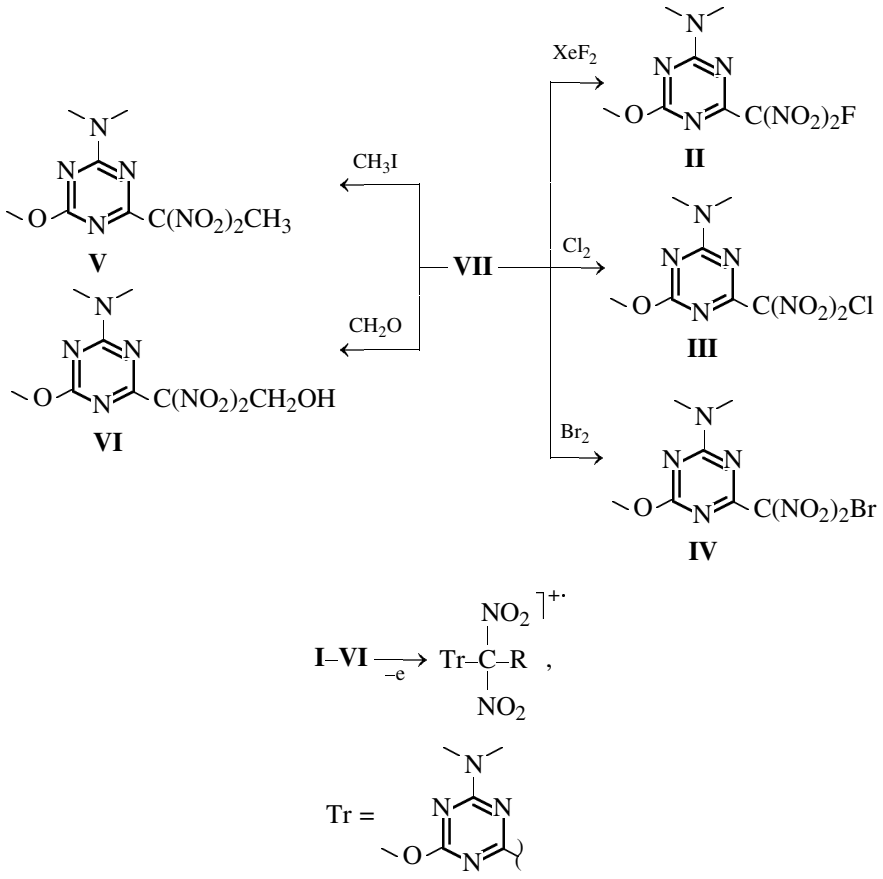
I

VII

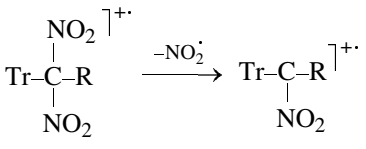
All these compounds exhibit a relatively strong (15–30%) peak of molecular ion, which distinguishes them from aliphatic nitro compounds which do not give a molecular peak [9, 10].

The most probable cause of the stabilization of the molecular ion is participation of the 1,3,5-triazine ring in the delocalization of the unpaired electron. With respect to the stability of the molecular ion, compounds **I**–**VII** can be ranked in the following order: $TrC(NO_2)_2CH_2OH > TrC(NO_2)_2CH_3 > TrC(NO_2)_2Cl > TrC(NO_2)_3 > TrC(NO_2)_2F \approx TrC(NO_2)_2Br$.

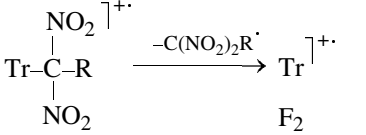
The molecular ion undergoes fragmentation along several pathways. Two fragmentation pathways are characteristic of all the compounds **I**–**VI**: (1) loss of NO_2 in the form of radical with the formation of even-electron ion F_1 and (2) loss of the whole polynitro-



methyl fragment in the form of radical with the formation of even-electron ion F_2.

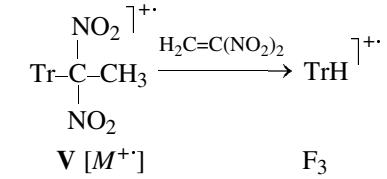


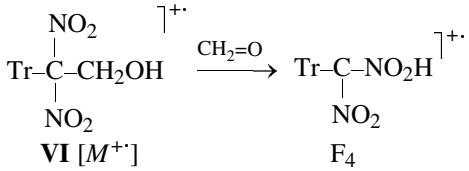
(1)



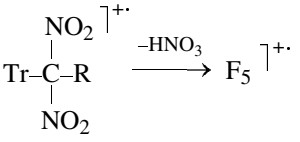
(2)

At the same time, other fragmentation pathways determined by the structure of substituent R bonded to the dinitromethyl group are also observed. The first of them is the loss of neutral molecules of dinitroethylene (from **V**) and formaldehyde (from **VI**) with the formation of odd-electron ions F_3 and F_4, respectively.

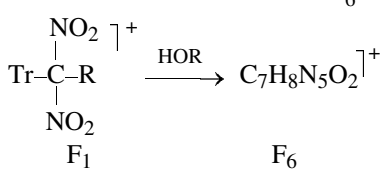




The second pathway is the loss of an HNO_3 molecule (from **II**–**V**), which can be considered as successive loss of two radical species ($M - NO_2 - OH$), with the formation of odd-electron ion F_5:



Similar elimination of the hydroxy group from the $[M - NO_2]^+$ ion was observed in the mass spectra of dinitromethylpyridines [11]. Further fragmentation of the resulting ions occurs along several pathways. In the fragmentation of **I**–**IV**, the F_1 cation eliminates a neutral molecule of HOR (R = NO_2, F, Cl, Br) with the formation of even-electron ion F_6:

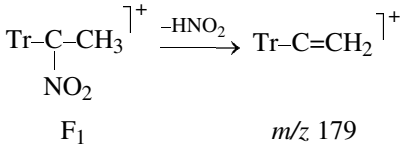


Mass spectra of **I**–**VI**[a]

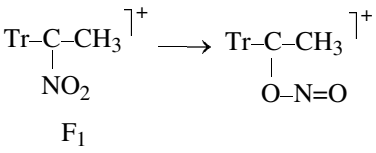
Comp. no.	*m/z* (I_{rel}, %)
I	303 (20, $M^{+\cdot}$), 257 (38, F_1), 194 (84, F_6), 182 (19), 165 (19), 153 (44, F_2), 96 (100, F_{10}), 83 (43, F_7), 69 (52, F_{11}), 58 (18, F_8), 46 (19), 44 (45), 43 (25), 42 (56)
II	276 (16, $M^{+\cdot}$), 230 (43, F_1), 213 (71, F_5), 194 (11, F_6), 183 (15), 153 (39, F_2), 137 (30), 112 (22), 99 (29), 96 (30, F_{10}), 83 (44, F_7), 69 (96, F_{11}), 67 (28), 58 (32, F_8), 46 (23), 44 (100), 43 (39), 42 (89)
III	292 (24, $M^{+\cdot}$), 246 (45, F_1), 229 (19, F_5), 216 (14), 194 (59, F_5), 182 (11), 153 (100, F_2), 137 (16), 115 (11), 96 (48, F_{10}), 83 (21, F_7), 69 (41, F_{11}), 58 (18, F_8), 44 (46), 43 (25), 42 (43)
IV	338 (15, $M^{+\cdot}$), 336 (15, $M^{+\cdot}$), 292 (29, F_1), 290 (30, F_1), 275 (10, F_5), 273 (10, F_5), 194 (30, F_6), 181 (23), 153 (100, F_2), 127 (10), 96 (87, F_{10}), 83 (12, F_7), 69 (27, F_{11}), 58 (13, F_8), 44 (18), 42 (23)
V	272 (27, $M^{+\cdot}$), 226 (100, F_1), 209 (68, F_5), 196 (44), 181 (73), 180 (26), 179 (83), 167 (14), 154 (16, F_3), 153 (11, F_2), 139 (65), 112 (14), 96 (40, F_{10}), 83 (25, F_7), 71 (26, F_9), 69 (54, F_{11}), 58 (17, F_8), 44 (36), 43 (29), 42 (33)
VI	288 (31, $M^{+\cdot}$), 258 (48, F_4), 242 (24, F_1), 224 (100), 212 (21), 208 (40), 196 (59), 195 (46), 182 (33), 180 (29), 178 (36), 168 (48), 153 (36, F_2), 139 (54), 125 (14), 96 (55, F_{10}), 83 (32, F_7), 71 (59, F_9), 69 (48, F_{11}), 58 (24, F_8), 44 (34), 43 (15), 42 (33)

[a] Peaks with the relative intensity exceeding 10% are given.

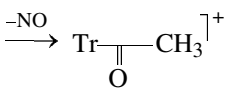
In the case of **V**, cation F_1 undergoes fragmentation along several pathways: loss of an HNO_2 molecule with the formation of an ion with *m/z* 179; loss of an NO molecule (apparently, after rearrangement of the nitro compound into the nitrite form, C–NO_2 → C–ONO) with the formation of an ion with *m/z* 196:



F_1 *m/z* 179

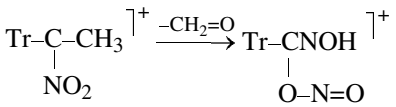


F_1



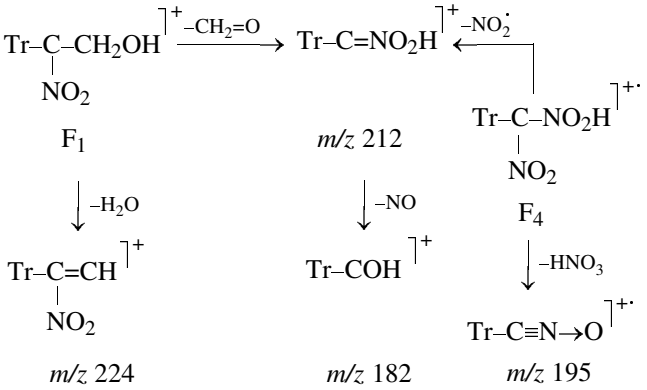
m/z 196

The other possible pathway of the fragmentation of F_1 with the formation of an ion with *m/z* 196 can be the loss of a formaldehyde molecule:



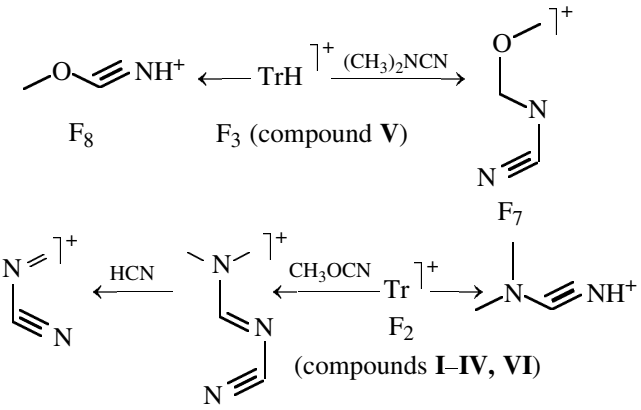
F_1 *m/z* 196

In the case of **VI**, ions F_1 and F_4 undergo fragmentation along several pathways: loss of NO_2, NO, CH_2=O, HNO_3, H_2O:



F_1 *m/z* 212 *m/z* 224 *m/z* 182 *m/z* 195

We also observed the fragmentation of the 1,3,5-triazine ring with the loss of neutral RCN molecules of $RCNH^+$ cations (R = OMe, NMe_2):



EXPERIMENTAL

The mass spectra of **I**–**VI** were recorded on a Finnigan Trace DSQ mass spectrometer in the electron impact mode (70 eV) with direct sample inlet.

Compounds **I**, **II**, **VII** [6]; **III**, **IV** [7]; and **V**, **VI** [8] were prepared by published procedures.

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