SECONDARY ION MASS SPECTRA OF ORGANIC CATIONIC DYESTUFFS

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Rules for the behavior under fast atom bombardment (FAB) have been established for 15 cationic dyes — quaternary ammonium salts of heterocyclic amines and heterocycles containing quaternary nitrogen atoms with aliphatic substituents. Intense peaks corresponding to the molecular mass of the cationic part of the dyes $[M-Hal]^+$ *are observed in the spectra of all the derivatives. Fragmentation of the azodyes is determined by the azo group and the heterocycle. The base peaks in the case of compounds containing a quaternary nitrogen atom with aliphatic substituents correspond to the ammonium ion and a fragment of amine type. The results obtained can be used to identify dyes of unknown structure from their secondary ion mass spectra (SIMS).*

Quaternary ammonium salts have low volatility and undergo thermal decomposition on heating [1]. Consequently the traditional methods of mass spectrometry (electron impact, chemical ionization, field ionization), which require preliminary heating and evaporation of the sample, are unsuitable for the analysis of compounds of this type.

Recently developed desorption methods are able to generate ions of thermally labile compounds in the gas phase without the heating and evaporation steps [2, 3]. Secondary ion mass spectrometry (SIMS) is one of these methods which is based on secondary ion emission by bombardment of a substance with fast atoms or ions [4].

The potential of SIMS in structural analytical determination of quaternary ammonium salts has been demonstrated with derivatives of simple aliphatic amines [5-9].

The object of the present work was to obtain and study secondary ion mass spectra of a series of quaternary ammonium salts of heterocyclic amines with mono- or polyheterocycles, and also heterocycles containing quaternary nitrogen atoms with aliphatic substituents, to study the rules of their behavior under fast ion bombardment (FAB) conditions, and to examine the analytical possibilities of SIMS for their identification. Fifteen water-soluble cationic dyes were studied. Some organic cationic dyes have been previously studied by SIMS [10-13].

The dyes studied may be divided into four groups of structurally similar compounds:

1) dyes containing polyheteroatom rings: imidazole (I), pyrazole (II), 1,2,4-triazole (III, IV), 1,3,4-thiadiazole (V), and benzimidazole (VI);

2) derivatives of indolenine (VII-IX) and benzo[1,2,3-*c,d*]indolenine (X);

3) optical bleaches, derivatives of coumarin with heterocyclic substituents in positions 3 and 7 (XI), (XII);

4) Compounds containing quaternary nitrogen atoms with aliphatic substituents (XIII-XV). A quaternary ammonium salt of similar structure with long chain aliphatic substituents (XVI), but which is not a dye, was also studied.

In contrast to the electron impact (EI) spectra, the SIMS of compounds (I-XVI) (Table 1) are characterized by a small number of lines and are readily interpreted. The spectra of the compounds studied contain both odd and even electron ions. In distinction from xanthane dyes [11], for example, the FAB spectra of the compounds we have studied do not contain peaks of clusters made up of molecules of the dye and glycerol. Peaks corresponding to products of thermolysis, which make the interpretation of EI spectra difficult, are also absent.

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*Deceased.

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TABLE 1. Partial Secondary Ion Mass Spectra of Dyes I–XVI*

Compound	m/z, (relative intensity of ion peaks, % of maximal peak)
I	245 (26), 244 (M^+, 67), 148 (A, 6), 135 (, 69), 120 (B, 25), 112 (C, 100)
II	335 (27), 334 (M^+, 100), 211 (E, 25), 196 (B,E, 31), 126 (C, 18), 124 (10), 111 (D, 22), 109 (7), 91 (82)
III	322 (27), 321 M^+, 100), 231 (11), 224 (A, 14), 211 (E, 18), 196 (B,F, 93), 180 (9), 113 (C, 35), 98 D, 23), 91 (92)
IV	394 (22), 393 (M^+, 62), 296 (A, 3), 284 (24), 283 (E, 100), 268 (B, 4), 224 (18), 149 (98), 133 (62), 113 (C, 48), 105 (98), 98 (D, 17)
V	348 (27), 347 (M^+, 57), 215 (C, 37), 200 (D, 10), 148 (A, 42), 136 (23), 135 (E, 100), 134 (30), 120 (B, 85), 43 (53)
VI	370 (37), 369 (M_+, 100), 278 (23), 263 (11), 91 (93),
VII	318 (26), 317 (M^+, 100), 302 (7)*, 184 (6), 158 (5)
VIII	323 (24), 322 (M^+, 100), 171 (11), 170 (5), 161 (13), 160 (D, 41), 159 (7), 158 (18), 145 $[D-CH_3]^+$, (7), 144 (9), 137 (8), 136 (, 46)
IX	333 (30), 322 (M^+, 100), 317 (13), 160 (D, 21), 159 (10), 158 (18), 145 $[D-CH_3]^+$, (8), 144 (10), 134 (22), 132 (12), 131 (10)
X	367 (30), 365 (M^+, 100), 307 (12), 305 (34)
XI	309 (20), 308 (M^+, 100), 212 (7), 84 (D, 5)
XII	338 (10), 337 (M^+, 100), 84 (D, 97)
XIII	422 (36), 420 (M^+, 100), 361 (19), 271 (30), 257 (30), 255 (78), 167 (30), 152 (70), 132 (81), 131 (70), 129 (81)
XIV	326 (55), 325 (90), 324 (M^+, 100), 297 (30), 280 (12), 253 (14)
XV	436 (10), 434 (M^+, 26), 333 (20), 331 (60), 161 (14), 160 (21), 147 (62), 146 (8), 145 (15), 132 (D, 60), 119 (10), 118 (12), 102 (14), 72 (21), 58 (100), 44 (24)
XVI	550 (M^+, 10), 548 (40, 552 (12), 520 (8), 494 (6), 492 (2), 466 (2), 464 (2), 296 (7), 268 (5), 201 (10), 199 (14), 84 (23), 58 (100), 55 (67)

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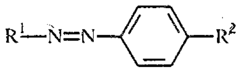
*The intensities of the ions are known to >1% of the maximal ion: the M^+ ion has the composition $[M-Hal]^+$

TABLE 2. ^1H NMR Spectra of the Dyes Studied

Compound	Chemical shifts, δ, ppm
II	2,32 (3H, s, $C—C\underline{H}_3$), 3,05 (3H, s, $N—C\underline{H}_3$); 4,20 (3H, s, $N—C\underline{H}_3$); 4,38 (3H, s, $N—C\underline{H}_3$), 4,66 (2H, s, $C\underline{H}_2Ph$), 6,51 (1H, s, $=C\underline{H}$), 6,87 (2H, d, arom.), 7,0...7,3 (5H, br.m, Ph), 7,92 (2H, d, 1—H)
IV	1,36 (3H, t, $CH_2—C\underline{H}_3$), 3,76 (2H, q, $C\underline{H}_2—CH_3$), 4,02 (2H, t, $NC\underline{H}_2CH_2—$), 4,18 (3H, s, $NC\underline{H}_3$), 4,24 (3H, s, $NC\underline{H}_3$), 4,62 (2H, t, $CH_2C\underline{H}_2O—$), 7,01 (2H, d, arom), 7,43 (2H, t, $H_{(4)}$), 7,58 (1H, t, 5—H), 7,97 (4H, d, 1—H and 3—H), 9,18 (1H, s, =CH)
VII	1,51 (3H, d, $=CH—C\underline{H}_3$, J = 6,4Hz), 1,72, 1,78 (3H, 3H, s, $=C—(C\underline{H}_3)_2$), 2,86 d, 3,64 dd (1H, 1H, $=C\underline{H}_2$, J = 16,5 Hz, J = 8,5 Hz), 4,02 (3H, s, $=N^+—C\underline{H}_3$), 5,74 (1H, q, $=C\underline{H}—CH_3$, J = 7,0Hz), 6,40 (1H, d $—C\underline{H}=CH—$, J = 13,1Hz), 7,2...7,5 br.m (8H, arom.), 8,41 (1H, d, $—CH=C\underline{H}—N=$, J = 13,1Hz)
IX	1,58 (3H, d, $=CH—C\underline{H}_3$), 1,79 s 1,83 s (3H, 3H, $=C(C\underline{H}_3)_2$), 2,38 (3H, s, $=C—C\underline{H}_3$), 3,82, 4,36 (1H, 1H, dd, $=C\underline{H}_2$), 4,27 (3H, s, $=N^+—C\underline{H}_3$), 5,26 (1H, m, $=C\underline{H}—CH_3$), 7,2...7,5 (8H, m, arom.)
X	1,22 (3H, t, $CH_2—C\underline{H}_3$), 3,68 (6H, br.m., $—N(C\underline{H}_2—CH_3)(C\underline{H}_2C\underline{H}_2OH)$, 4,20 (3H, s $=N^+—C\underline{H}_3$), 7,16 d 8,0...8,3 , 8,58 d, 8,74 (2H, 6H, 1H, 1H, arom)
XIII	1,80 (3H, d, $=CH—C\underline{H}_3$), 3,07 (2H, t, $=C—C\underline{H}_2—CH_2$), 3,52 (9H, s, $NC\underline{H}_3$), 3,68 (2H, t, $CH_2C\underline{H}_2—N=$), 4,10 (1H, m $C\underline{H}—CH_3$), 7,3...7,9 (8H, q arom.)
XV	1,14 (3H, t, $—CH_2C\underline{H}_3$), 1,37 (3H, d, $=CH—C\underline{H}_3$), 3,63 (2H, q, $—C\underline{H}_2CH_3$), 3,77 s 3,85 s (6H, $N—C\underline{H}_3$), 4,0...4,3 (6H, br.m., $N(CH_3)_2$, 7,06 (2H, d, arom), 7,71 (1H, d, 3—H), 8,03 (2H, d 4—H), 8,10 (1H, dd, 2—H), 8,35 (1H, d, 1—H)

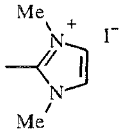
No peaks were observed in the FAB spectra corresponding to molecular ions. As in the case of aliphatic derivatives [5-9] and the cationic dyes studied previously [10-13], peaks with the cationic composition $[M - Hal]^+$ (M^+) were present in the FAB spectra of the quaternary salts (I-XVI). With the exception of a few cases (compounds I, IV, V, XV, and XVI) the cation peak is maximal in the spectra of the compounds studied (see M^+, Table 1).

In the case of compounds I, IV, V and XIV, the actual values of the relative intensities of the peaks $[M+H]^+$ and $[M+2H]^+$ are considerably larger than calculated from the molecular formula [3]: (actual/calculated in % relative to the M^+ peak for $[M+H]^+$ and $[M+2H]^+$ respectively) : (I) 42/16, (IV) 50/25, (V) 46/20, (XIV) 97/23; (I) 13/1, (IV) 14/3, (V) 17/6, (XIV) 61/2. From previous results [12], it may be assumed that reduction of these dyes occurs under FAB conditions

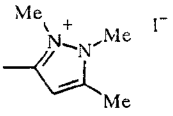


I-V

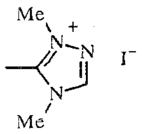
$R^1 =$



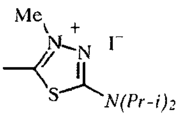
I



II

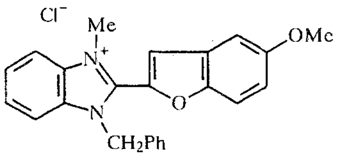


III. IV

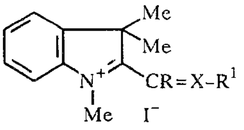


V

I,V R^2= NMe_2; II,III R^2= $NMeCH_2Ph$; IV R^2= $NEtCH_2CH_2OCOPh$



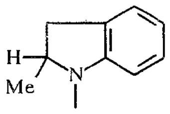
VI



VII, VIII R = H; IX R = Me

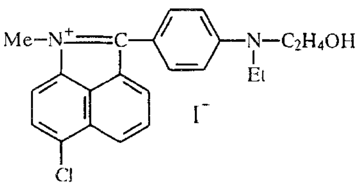
VII X = CH; VIII, IX R = N

$R^1 =$

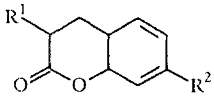


VII, IX

VIII

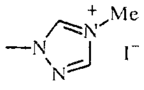


X



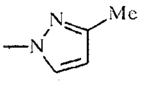
XI, XII

$R^1 =$

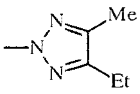


XI, XII

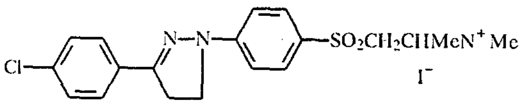
$R^2 =$



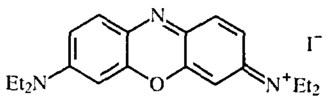
XI



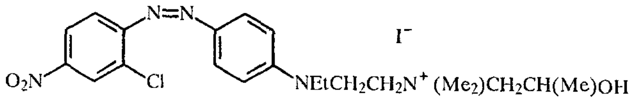
XII



XIII



XIV

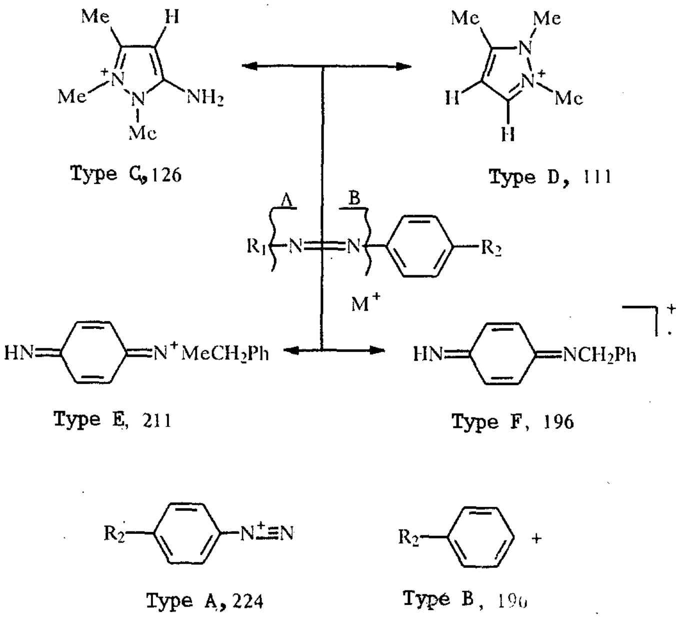


XV

$Me_2N^+(C_{18}H_{37})_2 \cdot Cl^-$

XVI

Characteristic fragmentation patterns for the azo compounds I-V under FBA conditions are shown below for compound II*:



Comparison with previous results [10], in which the dyes were bombarded with 4.5 keV argon atoms and the primary ion current was 10^{-9} A/mm^2, shows that the spectra consist of ions of a single type. The fragmentation process typical for the azodyes studied previously [10] is retained to some extent for compounds I-V: rupture of the exocyclic C—N bond (Table 1, ions A and B) and of the N=N bond with hydrogen atom transfer to give ions E and F (Table 1). The presence of the heterocyclic substituent R_1 is characterized by peaks of the ions C and D (Table 1, scheme), formed by scission of the N=N bond and double migration of hydrogen. In the FAB spectra of compounds II-V there are also peaks which are characteristic of substituents capable of stabilizing a positive charge well. For example, the peak for the tropylium cation $C_7H_7^+$ (91) appears with high intensity in the spectra of compounds II and III which contain the benzyl group. The most intense peaks in the spectrum of dye IV correspond to the fragment ions from the substituent $C_6H_5C(O)OCH_2CH_2^+$ (149) and $C_6H_5C\equiv O^+$ (105). In the case of compound V the peak of the hydrocarbon ion $C_3H_7^+$ (43), corresponding to the substituent at nitrogen, also has high intensity.

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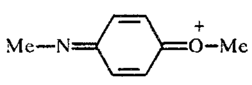
*In this scheme and later in the text the numbers which characterize the ion are the values of *m/z*.

In the FAB spectrum of the benzimidazole derivative (VI) the base peak is formed by loss of the benzyl group from nitrogen with localization of the charge either on the leaving group ($C_7H_7^+$, 91) or on the heterocyclic fragment with formation of the ion $[M - C_6H_5CH_2]^+$ (278) which then eliminates a methyl radical to form the ion 263 (Table 1).

A small number of fragmentation paths is observed in the FAB spectra of the indolenine (VII-IX, X) and coumarin (XI, XII) derivatives. Like the dyes with polyheteroatom rings I-V, the FAB spectra of the analogs VIII and IX and the substituted coumarins XI and XII contain ions of type D, characteristic of the heterocyclic part of the initial cation: 160 for compounds VIII and IX and 84 for compounds XI and XII (Table 1). There are additional peaks identifying the heterocycle in the spectra of compounds VIII and IX: $[D - 2H]^+$ (158), $[D - CH_3]^+$ (145). In the case of compound VIII the substituent R_1 is established by the ion peak 136

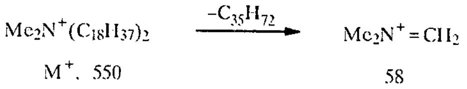


Demethylation of the initial cation is characteristic of dyes VII and IX: ions 302 and 317 respectively (Table 1). Dye X has a unique direction of decomposition: consecutive loss of the radicals CH_2OH and C_2H_5 from the initial cation to form the ion 305/307 (Table 1).

The spectrum of compound XIII is also dominated by a single fragmentation pathway with removal of the aliphatic substituent containing the quaternary nitrogen atom. Charge is localized on the aromatic fragment $[M - CH_3SO_2CH_2CH(CH_3)N(CH_3)_2]^+$ (255/257).

Like its previously studied analog [10], processes of elimination of the hydrocarbon fragments and the nitrogen containing substituent from the initial cation to give the ions $[MH - C_2H_4]^+$ (297), $[M - C_2H_5-CH_3]^+$ (280), and $[MH - N(C_2H_5)_2]^+$ (253) are characteristic for dye XIV (Table 1).

Decompositions with participation of the quaternary nitrogen atom are characteristic and dominant for the other derivatives with aliphatic substituents XV and XVI. For XV removal elimination of $(CH_3)_2NCH_2CH(OH)CH_3$ from the initial cation occurs to give the ion with *m/z* 331/333 together with fragmentation of the substituent to give the stable ammonium ions $CH_3(OH)CHCH_2N^+(CH_3)_2R$, where R = $NHCH_3$ (161), NCH_3 (160), NH_2 (147), and H (132), and the amine fragments $CH_3(HO)CHCH_2N^+(CH_3){=}CH_2$ (102), $(CH_2)_2N^+(CH_3)_2$ (72), and $(CH_3)_2N^+{=}CH_2$ (58, Table 1). For compound XVI amine fragmentation occurs with elimination of an alkane from the initial cation:



$$\underset{M^{+},\ 550}{Me_2N^+(C_{18}H_{37})_2} \xrightarrow{-C_{35}H_{72}} \underset{58}{Me_2N^+{=}CH_2}$$

This type of fragmentation has been observed earlier [9] for low molecular analogs.

The results obtained indicate that SIMS is a potential structural analytical method for the identification of cationic dyes. The analytical possibilities of SIMS in this case are as follows. 1. The molecular mass of the cationic part of the dye is determined unambiguously from the M^+ peak. 2. The diagnostic ions A, B, E, and F can establish the presence of an azo group. 3. Heterocyclic substituents are established by peaks of ions with cyclic structures of types C, D, $[D - 2H]^+$, and $[D - CH_3]^+$. 4. Substituents which stabilize the positive charge well are identified by peaks corresponding to their masses. 5. Diagnostic signs which identify derivatives with aliphatic substituents are the presence of ammonium ions and amine fragments. The results obtained can be used to identify cationic dyes of unknown structure.

EXPERIMENTAL

The structures of the dyes studied were confirmed by ^1H NMR spectroscopy. The ^1H NMR spectra were obtained in $CDCl_3$ (compounds IV, VII, VIII, IX), DMSO-D_6 (compound X), and pyridine-D_5 solutions (compounds II, XIII, XV) with Bruker CXP-200 (200 MHz) and WH-90 (90 MHz) machines using HMDS as internal standard. The ^1H NMR spectra of compounds I, III, VIII, and XIV agreed with previously reported spectra [14].

Mass spectra were recorded on a Hitachi M80A double focusing mass spectrometer with an MOOZ data treatment system over the mass range 1-600 amu with a resolution of 1000. Ions of the compounds studied were formed by secondary emission resulting from bombardment of a solution of a dye in a glycerol matrix on a gold target by a primary beam of 8 keV Xe^+ ions with a current density of 10^{-7} A/cm^2. The ionization chamber pressure was $2.7 \cdot 10^{-4}$ Pa. The angle of incidence of the ions was 20°. Five μg dye was placed on the target and 1 μl analytically pure glycerol was added. This concentration was enough in most cases to give a FAB mass spectrum which lacked ion peaks from the matrix (glycerol). For dyes which dissolved well in glycerol a stable reproducible mass spectrum was observed for 5-8 min. For those compounds which were insoluble or poorly soluble in glycerol, the target with the suspension of dye in the glycerol matrix was heated to form a clear drop, was placed into the machine via the direct inlet, evacuated rapidly, and the mass spectrum recorded. In these cases the spectrum was stable for 30-60 s.

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