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The fragmentation mechanism under electron impact of *N*-trifluoromethylsulfonyl derivatives of arenesulfonyl, imidoyl and di-imidoyl halides and amides

I.G. Krajnikova*, L.M. Yagupolskii, R. Yu. Garlyauskaite

Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str. 5, Kiev 252094, Ukraine

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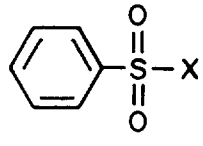
Abstract

The fragmentation mechanism of *N*-trifluoromethyl sulfonyl derivatives of arenesulfonyl, imidoyl, and di-imidoyl halides and amides by electron impact (70 eV) has been investigated in a mass-spectrometric study. The existence of molecular ion (MI) peaks in the mass spectra enables confirmation of their expected structures. An inverse dependence is observed between the MI stability and the electron-withdrawing power of a substituent. The fragmentation processes usually proceed along common pathways, and depend on the quantity of substituted oxygen atoms as well as the nature of the X substituent. The fragmentation of the sulfonyl chlorides, fluorides, amides and methyl sulfones and mono-*N*-(trifluoromethylsulfonyl)arenesulfonimidoyl derivatives proceeds via the formation of rearranged cations. Complex branched fragmentation connected with the elimination of both CF_3 and X groups is characteristic for the *N,N'*-bis(trifluoromethylsulfonyl)arenesulfonodi-imidoyl chlorides which contain more strongly electron-withdrawing substituents and exhibit the highest molecular polarization. The results observed allow fragmentation mechanisms to be suggested for one- or two-substituted derivatives of sulfones and sulfonic acids.

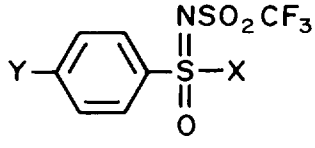
Keywords: Fragmentation mechanism; Arenesulfonyl halide derivatives; Arenesulfonyl amide derivatives; Imidoyl halide derivatives; Imidoyl amide derivatives; Di-imidoyl halide derivatives; Di-imidoyl amide derivatives

1. Introduction

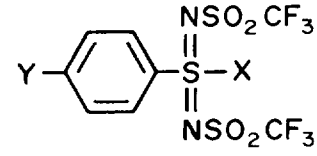
The principle of superstrong electron-withdrawing substituents with σ_n constants in the range 1.1–1.7 has recently been developed [1,2]. These compounds contain one or two NSO_2CF_3 groups in place of the corresponding oxygen atoms in sulfones, sulfonyl chlorides and fluorides. They may be classified into three groups:



1st group ($\sigma_n < 1.1$)



2nd group ($\sigma_n \simeq 1.4$)



3rd group ($\sigma_n \simeq 1.7$)

where X = NH_2, CH_3, H, F, Cl, CF_3; Y = H, F, Cl.

The sulfonyl halides differ principally from one another in their reactivity. In sulfonyl chlorides, the chlorine atoms are so positive that the compounds $ArS(=NSO_2CF_3)_2Cl$ chlorinate benzene and are also reduced by ammonia, forming ammonium salts with quadrivalent sulfur $[ArS(=NSO_2CF_3)-N^-SO_2CF_3]$-$NH_4^+$ [3]. The sulfonyl fluorides react in a standard manner with substitution of fluorine atoms by amino groups. This difference in reactivity should be reflected in the corresponding mass spectra, since fragmentation pathways as well as peculiarities of the rearrangement process are connected with the reactivity of the title compounds. Since mass-spectrometric data are not available in the literature, a detailed investigation of the fragmentation pathways was undertaken.

*Corresponding author.

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2. Results and discussion

The primary purpose of the mass-spectrometric study was the determination of the composition and the confirmation of the structure of the compounds synthesized. An analysis of the mass spectra, and in particular the existence of the molecular ion (MI) and characteristic cation peaks in the mass spectra of these compounds, has allowed confirmation of the expected structural formulae. Molecular ions were always present in the mass spectra under observation. The intensity of the mass-spectral cations depended mainly on several external factors (temperature, environment, etc.) and the number of cations formed. The number of cations of each kind depends both on their stability and their subsequent rate of fragmentation. The more stable the cation the lower the probability of its subsequent fragmentation. An estimate of the stability of the cations from their relative intensities in the mass spectrum seems to be feasible since such spectra were recorded under identical experimental conditions and, in our opinion, did not exhibit any cations which could be ascribed to secondary reaction products.

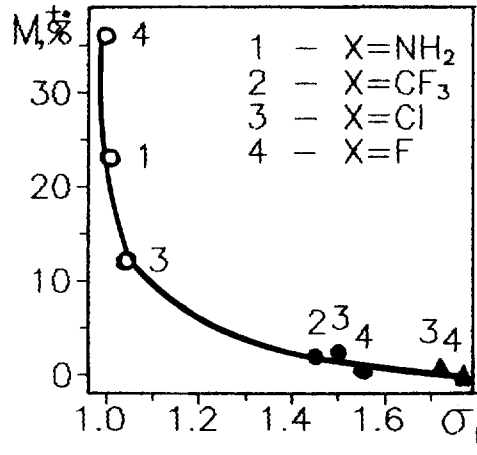
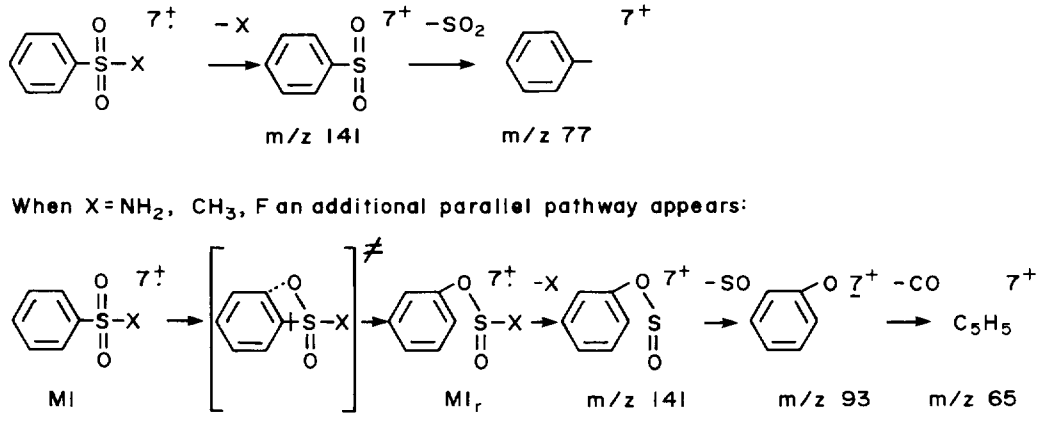


Fig. 1. A plot of the MI stability ($M^{+\cdot}$, %) versus the electron-withdrawing function (σ_n) for compounds of the first (○), second (●) and third (▲) groups.

A mutually inverse dependence has been observed between the MI stability and the electron-withdrawing power of a given substituent (Fig. 1). The electron-withdrawing function increased and the MI stability fell in going from the first to the third group of compounds listed above. The relative intensity of MI varied from 12% to 35% for first group compounds and decreased to 0.5%–2.5% and 0.1%–1.0% for compounds of the second and third groups. Thus, the third group of compounds with the strongest electron-withdrawing substituents seems to include the most unstable substances with respect to electron impact with their MI peaks having a low intensity in their mass spectra. This feature corresponds with the high reactivity of third group compounds.

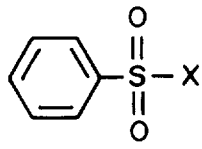
The fragmentation mechanism for the first group compounds seems to be the simplest. All species recorded are listed in Table 1. Possible fragmentation pathways deduced from these data are shown in Scheme 1. It will be noted that the first pathway at Scheme 1 is most probable when X=Cl (because only the corresponding cations are observed), but an additional parallel possibility appears with $X=NH_2$, CF_3 or F, where the four-centre cyclic rearrangement involving Ph–O bond formation and Ph–S bond cleavage occurs (Scheme 1). The relative intensity of the MI for the latter group of compounds increases abruptly; this is a characteristic of rearranged ions (MI_r) (Table 1). Mass spectra at lowered ionization energy were recorded in order to provide proof of the rearranged cation formation for $X=NH_2$, CF_3 or F. The observed increase in the relative intensities of MI_r may also be considered as support for the assumption mentioned above.

Peaks at $m/z=141$ and $m/z=93$ have been observed previously [4]. Since only benzenesulfonamides were studied in that work, the m/z 93 peak was identified with $[PhNH_2]^+$ and on that basis the existence of NH_2



Scheme 1. Schematic illustration of the fragmentation mechanism for first group compounds. The symbol ≠ in Schemes 1 and 2 designates a transition state in which the C–O bond has already formed while the C–S bond has not yet ruptured.

Table 1
Relative intensities (I_i (%)) of characteristic cations formed in the fragmentation of compounds of the first group

Characteristic cations[a]								
	X=CH_3		X=NH_2		X=F		X=Cl	
	m/z	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)
$M^{\cdot+}$	156	21.0	157	23.5	160	35.3	176	12.9
$[Ph-SO_2]^+$	141	14.0	141	9.9	141	5.6	141	31.4
$[Ph-O]^+$	93	4.2	93	17.4	93	11.8	–	–
$[Ph-OH]^{\cdot+}$	94	19.6	94	7.5	–	–	–	–
$[Ph]^+$	77	34.3	77	31.5	77	25.2	77	50.4
$[PhH]^{\cdot+}$	78	3.5	78	3.8	78	2.2	78	5.0
$[C_5H_5]^+$	65	3.2	65	0.5	65	17.4	–	–

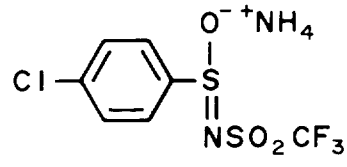
[a]The sequence of characteristic cations listed in Tables 1–3 is in accordance with their formation during fragmentation.

group migration was assumed [4]. In contrast, we have investigated a number of compounds with X=NH_2, CH_3, F, and *m/z* 93 peaks have always been observed in their mass spectra (Table 1). Thus this peak must correspond to a $[PhO]^+$ cation and its identification in Ref. [4] is apparently incorrect. Fragmentation occurs by stepwise elimination of X, SO and CO groups, a process which is only initiated after rearrangement from MI to MI_r (Scheme 1).

The fragmentation process is mainly determined by the number of substituted oxygen atoms as well as by the nature of the X substituent bound to the sulfur atom. The fragmentation pathway for compounds of the second and third group apparently consists of a number of competitive paths, but one is usually dominant. We believe that the NSO_2-CF_3 and S–X bonds are the weakest in compounds of these groups (Schemes 2 and 3), although the necessary subdivision of thermodynamic and kinetic factors is somewhat troublesome in these cases.

The fragmentation pathway involving CF_3 elimination dominates in compounds of the second group (Table 2). This trend may be explained reasonably by assuming the existence of a six-centre excited species giving rise to subsequent Ph–O bond formation and Ph–S bond cleavage (Scheme 2). An indication of the possibility of a rearrangement of this type is the increase in the relative intensities of the relevant ion peaks (see Table 2, ions with *m/z* 222 for X=F) which is common for the rearranged ions. It is probable that Ph–O (1) and O–S (2) bond rupture leads to the formation of *m/z* 77 or *m/z* 93 cations, respectively (refer to Table 2 for magnitudes of *m/z* 77 and 93 peaks). This path seems to predominate for compounds of the second group, although in the case of X=Cl or NH_2 an additional route involving elimination of the X group from the MI is evident. In this case, CF_3 and then SO_2 groups are also eliminated from MI. Cations formed with *m/z* 176 (for the second group at X=Cl) or with *m/z* 157 (X=NH_2) are protonated and their further fragmentation may be related both to X group elimination and X group migration to the benzene ring (see Scheme 2). The presence of *m/z* 272 cations (X=Cl, NH_2) in the mass spectra seems to prove the existence of a third fragmentation pathway connected with X elimination from MI. Cations formed via this path exhibit low intensities in the mass spectra, but their presence necessitates consideration of such a pathway. The insertion of a chlorine atom in the *para* position of a benzene ring does not involve any changes in fragmentation but confirms the proposed fragmentation path. All characteristic peaks of *p*-chlorine-substituted compounds are present in the mass spectra (Table 2).

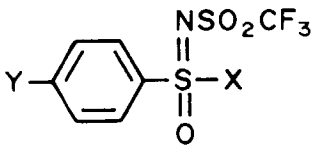
In an attempt to suppress the main fragmentation pathway for the second group compounds, we tried to stop the cation rearrangement and oxygen bridge formation. A mass-spectrometric study of the salt



was performed for this purpose. A peak with *m/z* 324 corresponding to the molecular mass of the salt (0.5%) was observed in the mass spectrum. The next peak occurred at *m/z* 322, i.e. elimination of two hydrogen atoms from the MI of the salt. This cation was detected in the mass spectrum as a quasi-molecular species. Hence, it may be assumed that some decrease in the

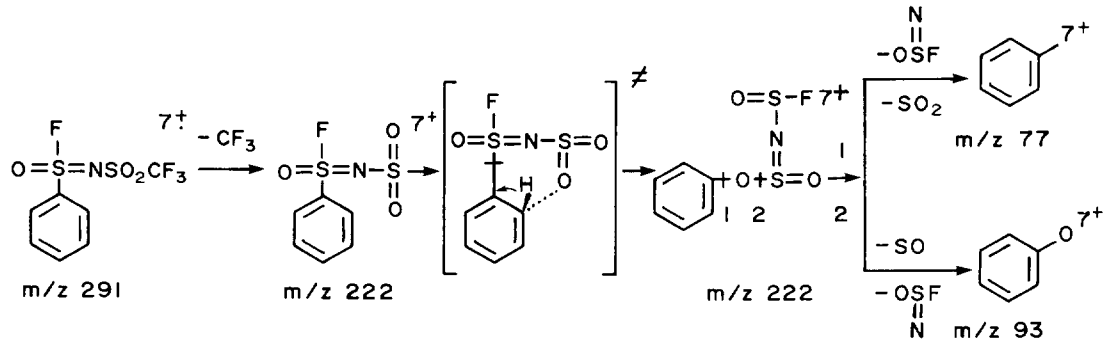
Table 2
Relative intensities (I_i (%)) of characteristic cations formed in consequence of the fragmentation of compounds of the second group

Characteristic cations

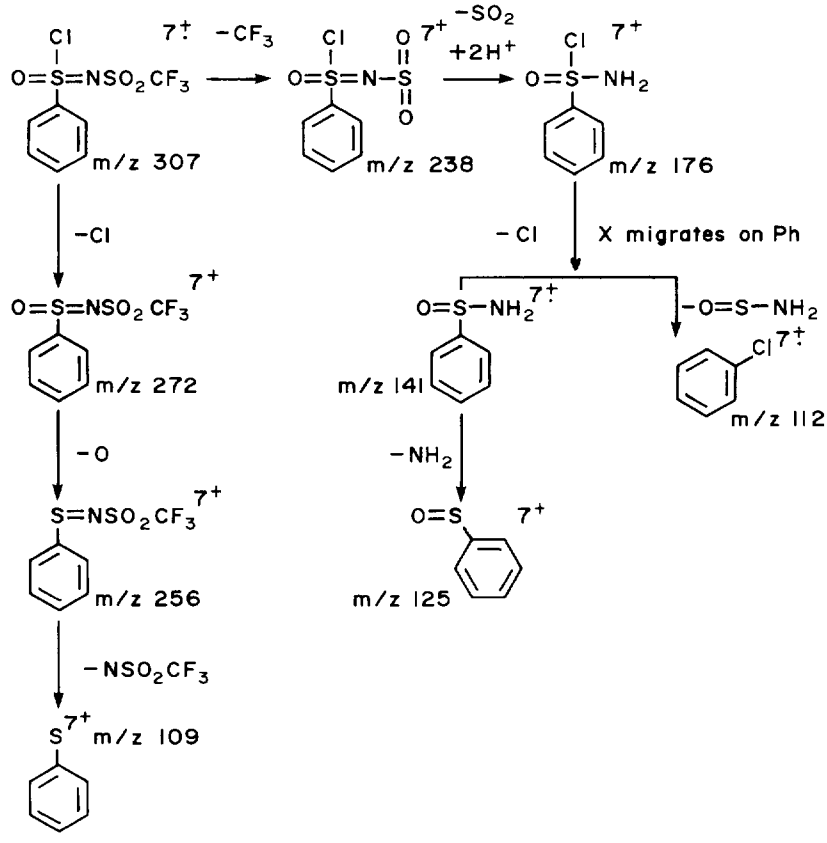


	X=NH$_2$ Y=H		X=F Y=H		X=Cl Y=H		X=NH$_2$ Y=Cl		X=Cl Y=Cl		X=CF$_3$ Y=Cl		X=NH$_4^+$ Y=Cl	
	m/z	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)
$M^{\cdot+}$	288	1.5	291	2.5	307	0.5	322	0.9	341	0.5	375	1.8	324	0.5
$[M-X]^+$	272	1.7	–	–	272	7.3	306	4.6	306	6.5	306	68.1	306	1.8
$[M-CF_3]^+$	219	21.6	222	54.0	238	12.5	253	19.5	272	9.0	306	68.1	253	0.5
$[Y-Ar-O]^+$	94[a]	6.6	93	7.2	93	9.3	128[a]	21.4	127	6.6	127	12.9	$[MI-2H]^+$	0.5
$[Y-Ar]^+$	77	11.6	77	30.6	77	24.0	111	6.5	111	16.0	111	17.5	111	2.5
$[Y-Ar-OS(X)NH_2]^+$	157	7.5	–	–	176	2.5	191	6.8	210	5.1	–	–	–	–
$[Y-Ar-OS-NH_2]^{\cdot+}$	140[a]	15.8	–	–	141	9.0	174[a]	15.5	175	13.3	–	–	175	1.3
$[Y-Ar-OS]^+$	–	–	–	–	125	9.8	–	–	159	8.0	–	–	159	20.5
$[Y-Ar-X]^{\cdot+}$	93	3.3	–	–	112	2.7	127	4.3	146	3.1	–	–	–	–
$[SO_2-NH_2]^+$	80	3.3	–	–	80	2.7	80	11.8	80	2.3	–	–	80	24.0
$[SO_2]^{\cdot+}$	–	–	–	–	64	4.8	64	4.6	64	2.9	–	–	64	4.8
$[CF_3]^+$	–	–	–	–	69	7.5	–	–	69	3.3	–	–	69	4.8

[a]These cations can add (or eliminate) a proton.



When $X=NH_2$ or Cl groups are added two additional ways appear:

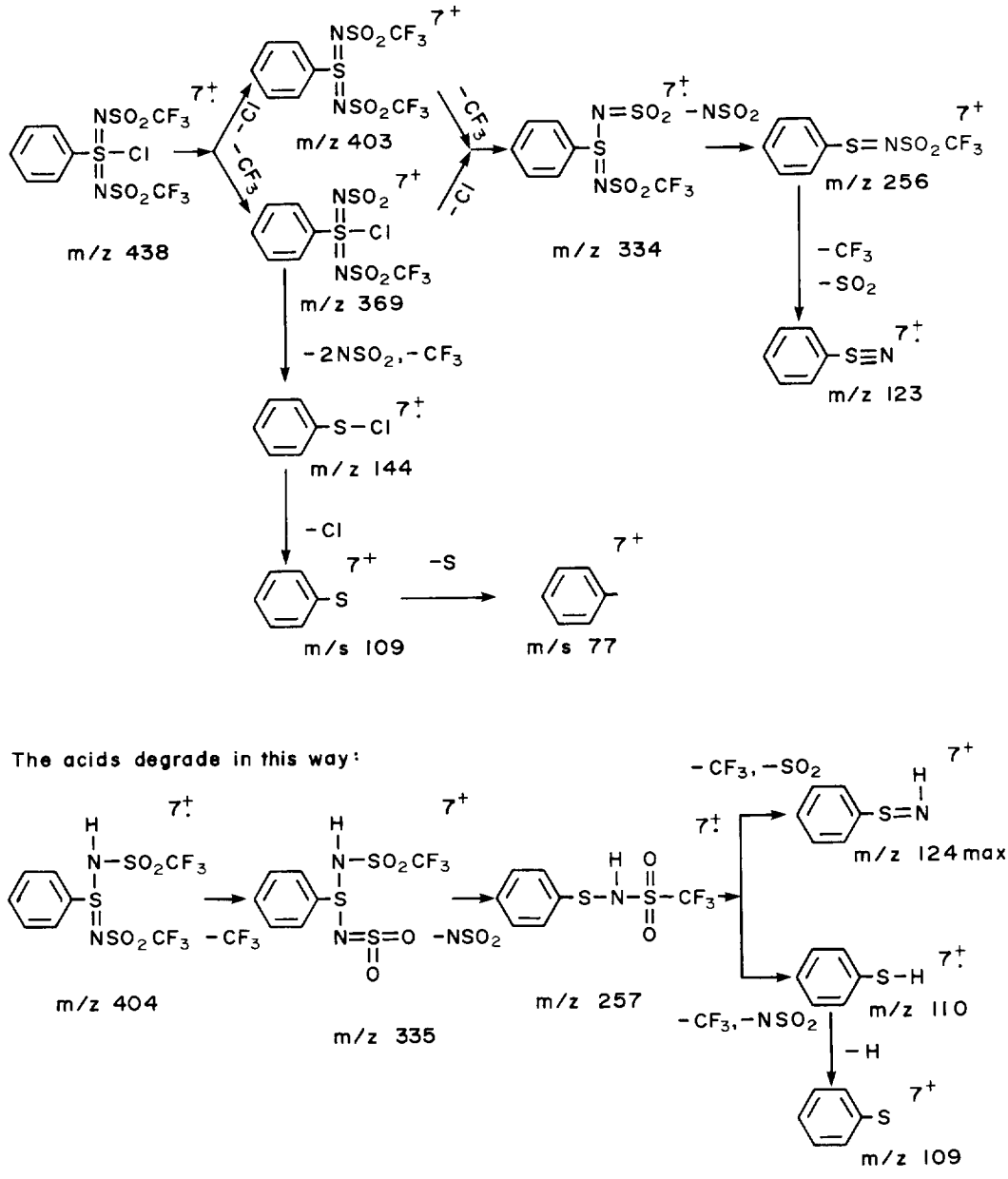


Scheme 2. Schematic illustration of the fragmentation mechanism for second group compounds.

ionic component and an increase in the covalent component of the O–N bond is inherent to the cation with *m/z* 322 although its exact structure is not known for certain. Consequently, two bonds (S–O and $O-NH_2$) appear to be the weakest and determine the next stage of fragmentation. The basic fragmentation pathway for second group compounds which starts with $S-CF_3$ bond degradation and involves cation rearrangement has not been observed.

Complex branched fragmentation connected with the elimination of both CF_3 and X groups is characteristic for third group compounds which contain stronger electron-withdrawing substituents and exhibit higher molecular polarization (Table 3). After sequential fragmentation of X and then CF_3 or of CF_3 and then X groups, the two competitive pathways merge into one and the *m/z* 334 cation appears irrespective of the previous fragmentation direction (Scheme 3). Degradation of the *m/z* 334 cation leads to an *m/z* 123 cation. The *m/z* 369 (X = Cl) cation which appears after initial CF_3 elimination can exhibit a parallel fragmentation pattern resulting in an *m/z* 77 cation.

It was important to prove the correctness of the structural formula for compounds of the third group with X = H. In particular, it was interesting to ascertain if the hydrogen atom was connected to the sulfur atom



Scheme 3. Schematic illustration of the fragmentation mechanism for third group compounds involving acids.

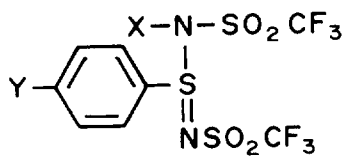
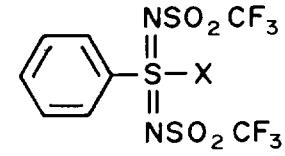
bound to the aryl group or to nitrogen in the N–SO_2CF_3 group. An analysis of characteristic peaks shown in Table 3 leads to the conclusion that these compounds have acidic structures and that the hydrogen atom is placed near the nitrogen atom in the NSO_2CF_3 group. We have recently demonstrated this kind of H atom localization (Table 3, compound with X = H and Y = H) by X-ray structural analysis [3]. Sulfur is tetravalent in such compounds. The fragmentation mechanism of acids (see the (A) and (B) columns in Table 3) is similar to that of third group compounds and proceeds with the formation of analogous cations. The CF_3 group in the MI is eliminated from the NSO_2CF_3 group but not from $NHSO_2CF_3$ for acids, since the majority of cations formed during fragmentation contain hydrogen atoms (see cations with *m/z* 335, 257, 124 and 110).

For all third group compounds, the main fragmentation direction leading to the formation of $[Ph-S=N]^+$ (*m/z* 123) cations for the acids: $[Ph-S=NH]^+$ (*m/z* 124) and $[F-Ar-S=NH]^+$ (*m/z* 142) is important.

3. Experimental details

Mass spectra of all compounds were recorded on an MS 1302 mass spectrometer. The sample was introduced into the ion source via the direct inlet and was ionized

Table 3
Relative intensities [I_i (%)] of characteristic cations formed in the fragmentation of compounds of the third group

Characteristic cations						
	X=H Y=H (A)		X=H Y=F (B)		X=Cl Y=H	
	m/z	I_i (%)	*m/z*	I_i (%)	*m/z*	I_i (%)
$M^{+\cdot}$	404	1.0	422	trace	438	trace
$[M-X]^+$	–	–	–	–	403	0.9
$[M-CF_3]^+$	335	1.6	353	1.6	369	1.0
$[M-CF_3,-X]^{+\cdot}$	–	–	–	–	334	0.9
$[Y-Ar-S=NSO_2CF_3]^+$	257[a]	11.8	275[a]	10.8	256	4.75
$[Y-Ar-S-N]^+$	124[a]	34.8	142[a]	37.2	123	15.0
$[Y-Ar-S-NH]^+$	125	3.0	143	5.6	124[a]	8.8
$[Y-Ar-S-X]^{+\cdot}$	110	3.0	128	5.6	144	7.8
$[Y-Ar-S]^+$	109	3.7	127	9.0	109	9.5
$[Y-Ar]^+$	–	–	95	3.2	77	5.8
$[SO_2-NH_2]^+$	80	19.2	80	12.4	80	8.5
$[CF_3]^+$	69	8.1	69	5.2	69	11.0
$[SO_2]^+$	64	6.7	64	5.2	64	12.0

[a]Hydrogen atom is placed at the nitrogen atom in these cations.

by electron impact (70 and 20 eV). The evaporation temperature was chosen individually for each sample within the range 25–80 °C. The peak intensity of each cation was normalized to total ion current. The compounds investigated were prepared according to the procedures described elsewhere [1,2].

Acknowledgement

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