

Collisional Activation Spectra of Quaternary Phosphonium and Tertiary Sulfonium Cations Produced by Field Desorption

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The collisional activation spectra of a variety of tetraalkyl phosphonium and trialkyl sulfonium ions generated by field desorption are reported. The fragmentation behaviour of the onium ions is compared with that of ammonium ions, reported earlier [4] and the corresponding open shell amine, phosphine and sulfide molecular ions. Cleavage of the heteroatom-carbon bond, with or without hydrogen rearrangement (i.e. alkyl and alkane loss) leads to prominent fragment ions in all onium ions. Pronounced heterolytic cleavage of this bond was only observed in sulfonium ions. No direct α -cleavage of the cation is observed, however, α -cleavage can occur in a second step after elimination of a substituent. This process leads to the base peak with ammonium ions, occurs less frequently in sulfonium ions and cannot be observed unequivocally in phosphonium ions. In addition, the collisional activation spectra of phenylalkyl phosphonium ions and chlorine containing quaternary phosphonium ions are discussed. It is demonstrated that collisional activation in conjunction with field desorption is a useful technique for the structure elucidation of onium cations.

It has been shown in the past that organic mass spectrometry is not only an important method for structure elucidation of organic compounds, but yields rich information on the chemistry and thermochemistry of organic ions in the gas phase as well. Using conventional ionization techniques such investigations are usually confined to those compounds which can be vaporized without thermal decomposition, which makes it impossible to study strongly polar compounds, in particular, organic salts [1]. For such organic salts the field desorption (f.d.) technique [2] has proved to be the ionization method of choice [3]. With this technique, very simple mass spectra are observed which are dominated by the cation signal. In addition cluster ions of the type $[\text{Cat}_{n+1}\text{A}_n]^+$ (Cat = cation, A = anion) are detected. However, especially in the case of onium ions, structure specific fragments are often of low abundance or completely missing, which renders the structure elucidation of the organic cation difficult or impossible.

A combination of field desorption and collisional activation (c.a.) has therefore been proposed [4, 5] to overcome this difficulty. If after acceleration, the mass analyzed cation collides with a neutral target atom a large variety of collision induced fragments are formed. For the structure elucidation of unknown compounds it is especially important that

the electron impact and collision induced fragmentation behaviour of a given ion resemble each other closely [4].

In a first communication [5], c.a. spectra of quaternary ammonium cations were reported. In the present study, this investigation has been extended to phosphonium and sulfonium salts in order to test whether the c.a. spectra allow a structure elucidation of the cations also in these instances. Even more important is the fact that the c.a. spectra give information on the chemistry of such even electron phosphonium and sulfonium cations which is not available by any other method. Thus, special emphasis has been laid on a comparison of the fragmentation behaviour of ammonium, phosphonium, and sulfonium ions. Moreover the closed shell onium ions are compared with their open shell analogues (i.e. amine, phosphine, and sulfide ions).

Results

Phosphonium Ions

Tetraalkyl phosphonium ions. The c.a. spectra of four tetraalkyl phosphonium ions have been recorded (see Table 1). The c.a. spectrum of $[(i\text{-C}_3\text{H}_7)_3\text{CH}_3\text{P}]^+$ as a representative of these ions is shown in Figure 1.

The most abundant fragment in the c.a. spectra of all tetraalkyl phosphonium ions is due to loss of a hydrogen atom. The intensity of this fragment is

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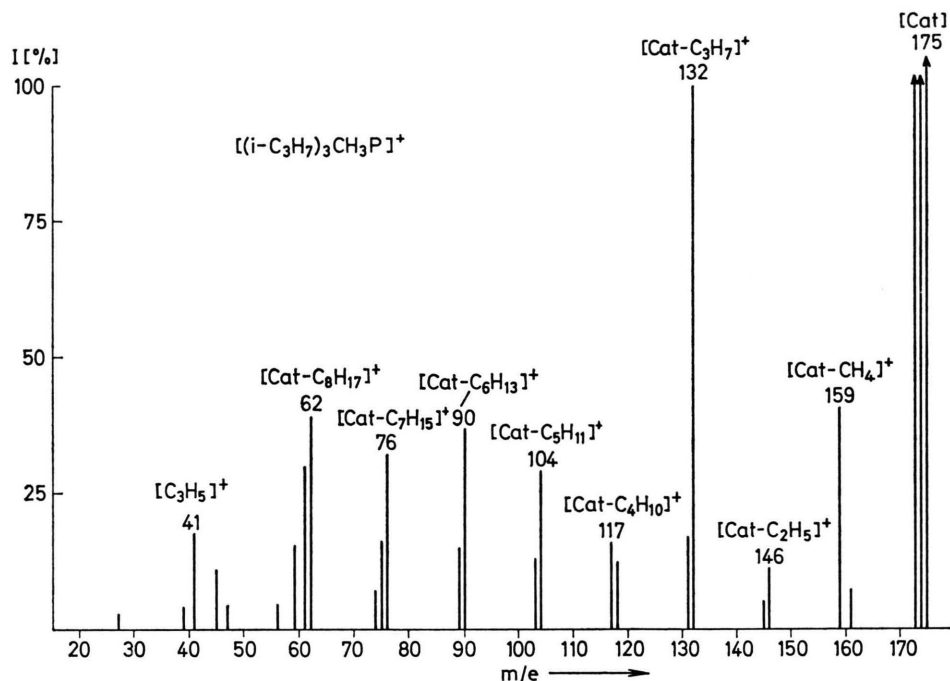


Fig. 1. Collisional activation mass spectrum of $(i\text{-C}_3\text{H}_7)_3\text{CH}_3\text{P}^+$.

2 ÷ 20 times that of the most abundant fragment not formed by hydrogen abstraction. In addition, loss of additional hydrogen atoms from the cation is observed with significant abundance. The corresponding fragment is of much lower intensity in the ammonium* and sulfonium ions (10 ÷ 70% of the base peak). The high stability of the [Cat-H]⁺ ion obviously results from a participation of d-orbitals in the bond formation leading to ylene type ions, e.g. [R₃P=CH₂]⁺. Such d-orbital participation is more pronounced with phosphorous than with sulfur [6]. Thus it is known from solution chemistry that phosphorous ylens are much more stable than sulfur ylens.

Excluding the hydrogen abstraction processes all spectra are dominated by loss of an alkyl group from the quaternary phosphonium ion leading to trialkyl phosphine molecular ions



In the case of an asymmetrical substituted cation the largest substituent is lost preferentially. On the other hand, heterolytic cleavage with charge migration to the alkyl group is not a significant process.

* This process has not been reported in [5].

All other abundant fragments in the upper mass range ($> m/e$ 61) arise from loss of either $\text{C}_n\text{H}_{2n+1}$ or $\text{C}_n\text{H}_{2n+2}$ from the cation, i.e. the heteroatom is retained in the ionic fragment. The relative abundances of these processes are listed in Table 1. It is obvious that the formation of most of these ions involves carbon-carbon cleavage with successive skeletal rearrangement (e.g. loss of C_5H_{11} from $[(i\text{-C}_3\text{H}_7)_3\text{CH}_3\text{P}]^+$), and thus is rather uncharacteristic with respect to the original structure of the cation. For instance, methyl substituents give rise to [Cat-CH₃]⁺ ions of low or medium intensity. As this ion is part of the fragment series



the c.a. spectra do not allow an unequivocal confirmation of the presence of a methyl substituent.

Loss of alkene molecules, which is an important process with sulfonium ions (vide infra), is only observed with low abundance, if at all. In contrast, the e.i. spectrum of $(\text{C}_2\text{H}_5)_3\text{P}$ (one of the few phosphine spectra published so far) is dominated by successive loss of three ethylene molecules [7].

Secondary decomposition leads to uncharacteristic hydrocarbon fragments in the lower mass range among which the [C₃H₅]⁺ ion is always observed (even with sulfonium ions).

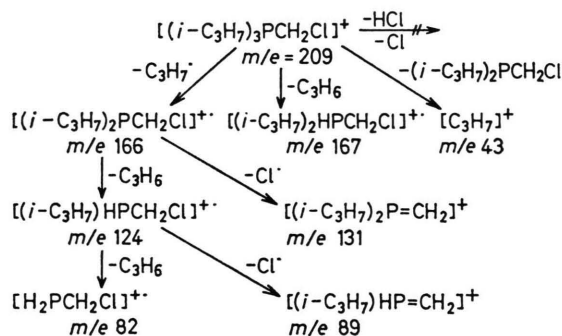
Table 1. The c.a. spectra of tetraalkyl phosphonium ions^a.

		Characteristic fragment ion series											Additional fragment ions
		<i>n</i>											Rel. Int. $\geq 10\%$
cation		1	2	3	4	5	6	7	8	9	10	11	<i>m/e</i> (rel. int.)
		rel. intensities											
$[(\text{CH}_3)_4\text{P}]^+$ <i>m/e</i> 91	$[\text{Cat-C}_n\text{H}_{2n+1}]^+$ $[\text{Cat-C}_n\text{H}_{2n+2}]^+$	100 66											41 (15), 45 (73) 46 (29), 57 (64), 58 (38), 59 (70), 73 (12), 90 (230)
$[(\text{C}_2\text{H}_5)_3\text{CH}_3\text{P}]^+$ <i>m/e</i> 133	$[\text{Cat-C}_n\text{H}_{2n+1}]^+$ $[\text{Cat-C}_n\text{H}_{2n+2}]^+$		8 100	18 10	29 15	6 24	8 10						45 (11), 57 (13) 59 (17) 131 (47), 132 (150)
$[(i\text{-C}_3\text{H}_7)_3\text{CH}_3\text{P}]^+$ <i>m/e</i> 175	$[\text{Cat-C}_n\text{H}_{2n+1}]^+$ $[\text{Cat-C}_n\text{H}_{2n+2}]^+$	20 40	11 5	100 17	12 15	29 13	36 15	32 16	39 30		5		41 (17), 45 (11) 59 (15) 173 (109) 174 (1000)
$[(n\text{-C}_4\text{H}_9)_3\text{CH}_3\text{P}]^+$ <i>m/e</i> 217	$[\text{Cat-C}_n\text{H}_{2n+1}]^+$ $[\text{Cat-C}_n\text{H}_{2n+2}]^+$	50 45	45 85	41 15	100 82	17 15	16 19	22 15	12 11	12 13	32 31	22 20	102 (13) 172 (10) 186 (25) 212 (15), 213 (35) 214 (200), 215 (600) 216 (1800)

^a Abundances relative to the base peak (excluding hydrogen abstraction reactions from the cation).

Mono- and Dichloromethyl Triisopropyl phosphonium ions

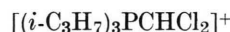
The c.a. spectrum of $(i\text{-C}_3\text{H}_7)_3\text{PCH}_2\text{Cl}^+$ (Fig. 2) demonstrates that the chlorine atom directs the fragmentation behaviour of this phosphonium ion (Scheme 1). Loss of the largest substituent ($\text{R} = \text{C}_3\text{H}_7$) still leads to an abundant fragment (m/e 166), but is no longer the base peak. This fragment



Scheme 1

decomposes by successive loss of two propene molecules (m/e 124 and m/e 82). In contrast to the tetraalkyl phosphonium ions, heterolytic cleavage of the phosphorous-carbon bond (m/e 43) is an important process and is obviously induced by the

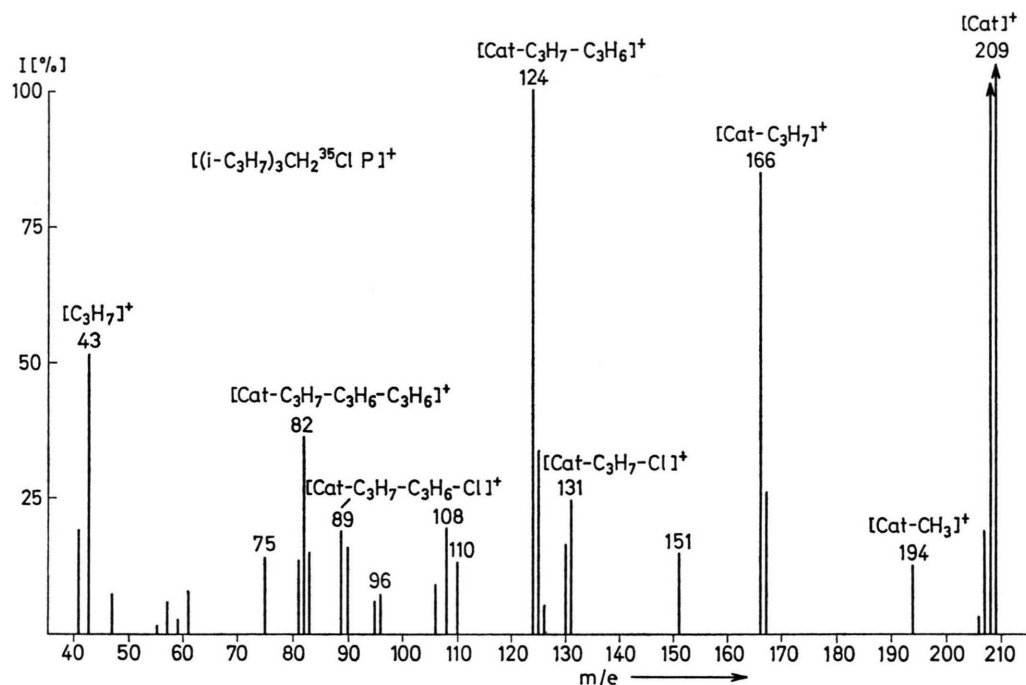
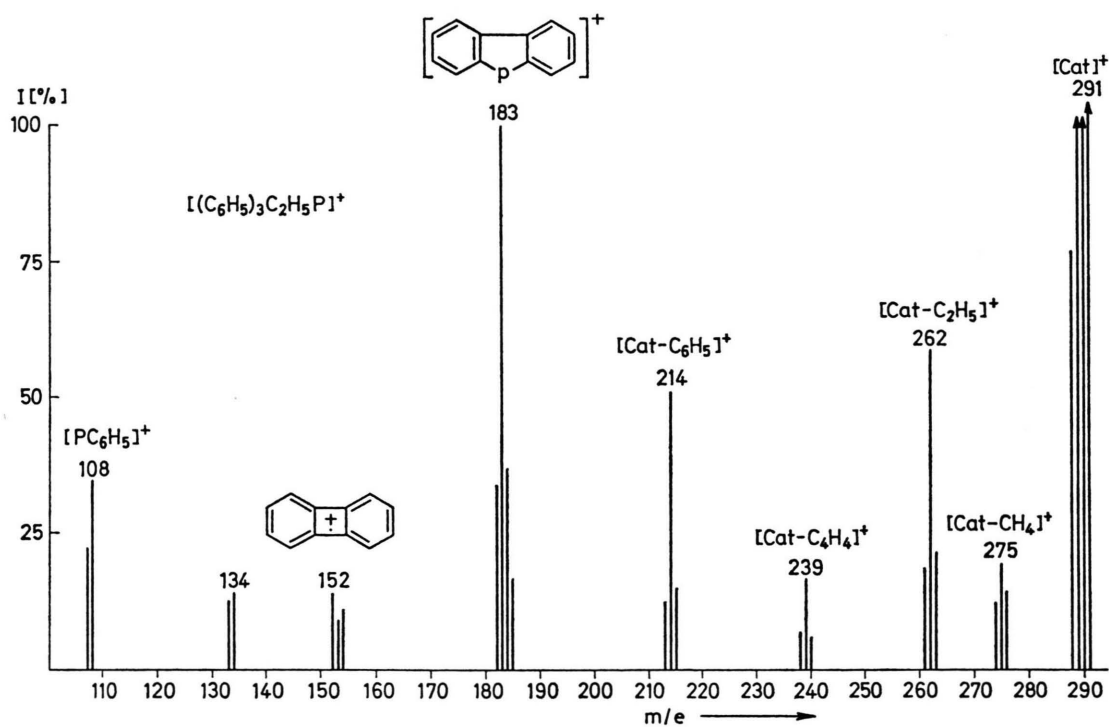
strong electronegativity of the chlorine atom. Comparison with the c.a. spectrum of



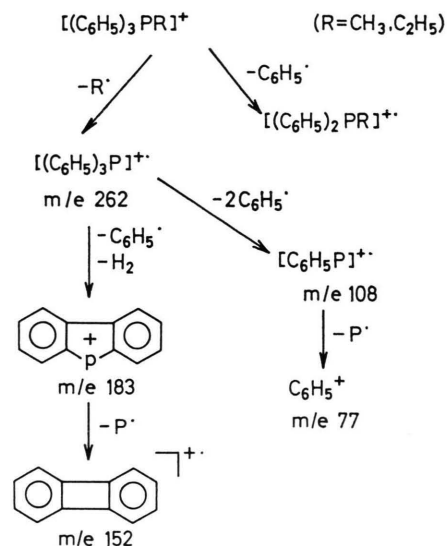
supports this view. The $[\text{C}_3\text{H}_7]^+$ fragment is the most abundant peak in this spectrum.*

Triphenylalkyl phosphonium ions. The phosphonium ions $[(\text{C}_6\text{H}_5)_3\text{RP}]^+$ ($\text{R} = \text{CH}_3$ and C_2H_5), have been studied. Figure 3 shows the c.a. spectrum of $[(\text{C}_6\text{H}_5)_3\text{C}_2\text{H}_5\text{P}]^+$. Again prominent fragments arise from loss of the substituents C_6H_5 and C_2H_5 , respectively. While in the case of the tetraalkyl phosphonium ions loss of the largest substituent gives rise to the most abundant fragment, in that of the triphenylalkyl phosphonium ions elimination of the alkyl substituent is clearly favoured. The comparison of the lower part of this spectrum ($m/e < 214$) with the e.i. spectrum of triphenyl phosphine [8] reveals a striking similarity. Thus the fragment at m/e 183 is observed as the base peak both in the e.i. spectrum of triphenyl phosphine and in the c.a. spectrum of triphenylalkyl phosphonium ions. This fragment has been formulated as 9-phosphafluorenyl ion [8],

* In discussing relative abundances, the mass discrimination which results from different multiplier response should be borne in mind (see Experimental).

Fig. 2. Collisional activation mass spectrum of $(i\text{-C}_3\text{H}_7)_3\text{CH}_2^{35}\text{ClP}^+$.Fig. 3. Collisional activation mass spectrum of $(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H}_5)\text{P}^+$.

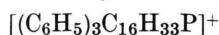
the ion at m/e 152 as o-biphenylene ion [8], while loss of ethyl and two phenyl substituents leads to the ion $[\text{C}_6\text{H}_5\text{P}]^+$ at m/e 108 (see Scheme 2). Finally the presence of a phenyl substituent is also indicated by the loss of C_4H_3^+ , C_4H_4 and C_4H_5^+ from the cation (m/e 238–240).



Scheme 2

The spectrum of $[(\text{C}_6\text{H}_5)_3\text{CH}_3\text{P}]^+$ resembles qualitatively that of the ethyl substituted ion except that loss of methyl (30%) is observed

instead of ethyl. The c.a. spectrum of



has recently been recorded by Veith [9] and corresponds qualitatively to the spectra reported here.

Sulfonium Ions

While only little is known about the e.i. induced dissociation of phosphines [7, 8, 10] the fragmentation behaviour of sulfides has been studied extensively [11]. The molecular ions of these compounds decompose mainly by α -cleavage, carbon-sulfur cleavage and alkene elimination forming mercaptane ions.

In the present study, eight trialkyl sulfonium ions were investigated under c.a. conditions (see Table 2). Typical examples are shown in Fig. 4 and Figure 5. In analogy to sulfides, carbon-sulfur cleavage and alkene elimination are the dominant fragmentation processes also of sulfonium ions, while the direct α -cleavage of the cation is not observed (vide infra)*. Alkyl and alkene eliminations are competing effectively with each other, but it is

* Some minor peaks such as loss of C_3H_7^+ from $[(n\text{-C}_4\text{H}_9)(\text{C}_2\text{H}_5)\text{CH}_3\text{S}]^+$

(4%) could in principle result from α -cleavage of the cation, but can also be rationalized otherwise.

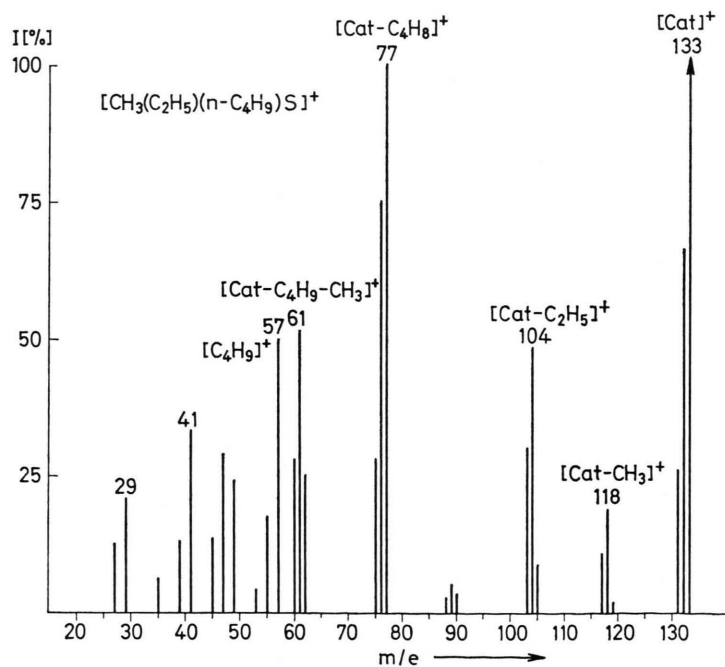


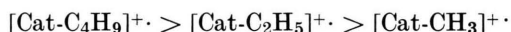
Fig. 4. Collisional activation mass spectrum of $\text{CH}_3(\text{C}_2\text{H}_5)(n\text{-C}_4\text{H}_9)\text{S}^+$.

Table 2. The c.a. spectra of tertiary sulfonium cations^a.

Cation		Characteristic fragment ion series ^b								Additional fragment ions Rel. int. $\geq 10\%$ <i>m/e</i> (rel. int.)
		<i>n</i>								
		1	2	3	4	5	6	7	8	
		Rel. intensities								
[(CH ₃) ₃ S] ⁺ <i>m/e</i> 77	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	100	22							27 (18), 35 (11), 45 (81) 46 (60)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺	75	60							
[(CH ₃) ₂ C ₂ H ₅ S] ⁺ <i>m/e</i> 91	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺		100							27 (26), 29 (21), 35 (14) 41 (12), 45 (49), 46 (40) 58 (18), 59 (32), 74 (12) 89 (14), 90 (79)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	42	88	30						
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺	40	78	5						
[(C ₂ H ₅) ₂ CH ₃ S] ⁺ <i>m/e</i> 105	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺		53		22					27 (23), 29 (19), 45 (43) 46 (24), 58 (18), 59 (25) 104 (50)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	8	100	6	20					
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺		61	39 ^c	38					
[(C ₂ H ₅) ₃ S] ⁺ <i>m/e</i> 119	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺		43		25					29 (13), 45 (13), 46 (14) 58 (15), 59 (36), 60 (33) 88 (18), 118 (32)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺		100		30	15				
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺		31	32 ^c	59	13				
[CH ₃ (C ₂ H ₅)(<i>n</i> -C ₄ H ₉)S] ⁺ <i>m/e</i> 133	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺		9		100		24			27 (12), 29 (21), 39 (13) 41 (33), 45 (14), 55 (17) 57 (50), 60 (28), 131 (26) 132 (66)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	19	49	4	75	25				
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺	11	30	5	28	52 ^c	29			
[(<i>i</i> -C ₃ H ₇) ₂ CH ₃ S] ⁺ <i>m/e</i> 133	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺			89			38			39 (17), 40 (10), 41 (26) 42 (12), 43 (37), 59 (10) 131 (14), 132 (49)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	10	4	100	5	6				
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺	4	6	32	28 ^c	7	12			
[(<i>i</i> -C ₃ H ₇) ₂ C ₂ H ₅ S] ⁺ <i>m/e</i> 147	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺			86		5	59			27 (20), 29 (17), 35 (15), 39 (29), 41 (38), 42 (30) 43 (75), 59 (23), 145 (15) 146 (90)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	11	34	100		5	15			
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺		3	36	30 ^c	13	50	32		
[(<i>n</i> -C ₄ H ₉) ₂ CH ₃ S] ⁺ <i>m/e</i> 161	[Cat-C _{<i>n</i>} H _{2<i>n</i>}] ⁺				100				39	41 (14), 45 (15), 57 (39) 160 (17)
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+1}] ⁺	19	19	5	75	6	18			
	[Cat-C _{<i>n</i>} H _{2<i>n</i>+2}] ⁺		10	16	60		26 ^c		31	

^a Abundances relative to the base peak.^b Values in italics characterize fragments formed by carbon-sulfur cleavage with or without hydrogen rearrangement.^c Ions formed most likely by loss of the largest substituent with successive α -cleavage.

not possible to predict a priori which process will dominate. It is noteworthy that alkene elimination is not observed with phosphonium ions (vide supra). The abundance of the fragments formed by loss of a substituent (either as alkyl radical or alkene molecule) reflects its size: The largest substituent is lost preferentially followed by the second and third largest one as illustrated for example in Fig. 4 for the [(*n*-C₄H₉)(C₂H₅)CH₃S]⁺ ion:



and



Alkyl loss which does not correspond to loss of one or two substituents (i.e. cleavage of a sulfur-carbon bond) is largely suppressed in sulfonium ions. Thus even the presence of a methyl substituent is in general detectable. The specificity of the fragmenta-

tion is even more pronounced for the alkene elimination. Only those alkene losses are observed which correspond to the elimination of one or two substituents of the cation. It is obvious that this simple fragmentation pattern allows an unambiguous structure elucidation of the cation. This is in contrast to the fragmentation behaviour of tetraalkyl phosphonium ions which is rather unspecific if one excludes the loss of the largest substituent (see Table 1).

In addition to the alkyl and alkene elimination discussed above abundant fragments due to a formal loss of alkane molecules, which again correspond to the elimination of one or two substituents, are also observed in the c.a. spectra of sulfonium ions (see Table 2). Moreover, additional prominent peaks due to formal alkane elimination are observed which can be rationalized by the loss of the largest substituent with subsequent α -

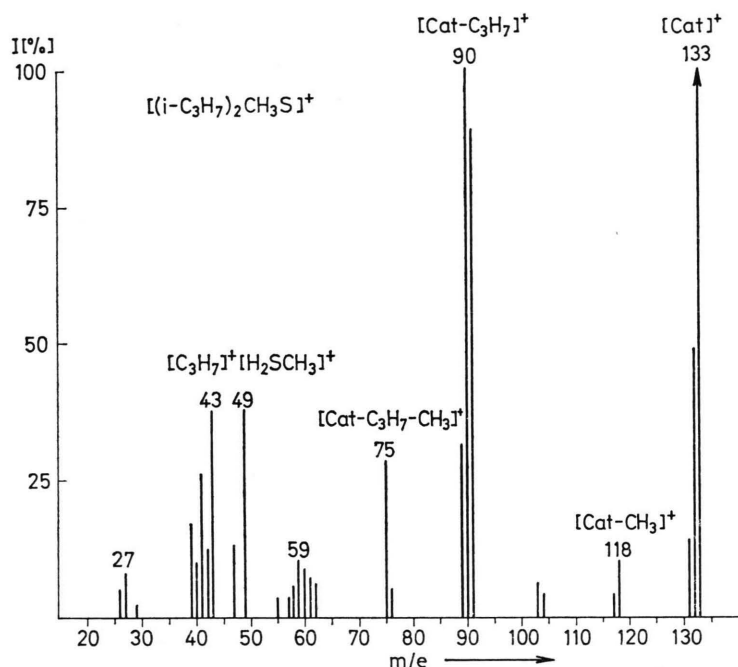
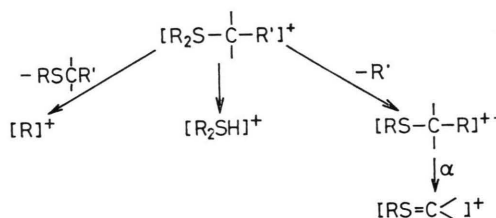


Fig. 5. Collisional activation mass spectrum of $(i\text{-C}_3\text{H}_7)_2\text{CH}_3\text{S}^+$.

cleavage (Scheme 3) as also indicated in Table 2. Thus in $[(n\text{-C}_4\text{H}_9)(\text{C}_2\text{H}_5)\text{CH}_3\text{S}]^+$, loss of the *n*-butyl substituent with subsequent α -cleavage leads to a dominant peak at m/e 61 (Fig. 4), while in $[(i\text{-C}_3\text{H}_7)_2\text{CH}_3\text{S}]^+$ loss of the isopropyl substituent



Scheme 3

with subsequent α -cleavage gives rise to m/e 75 (Figure 5).

Finally, heterolytic cleavage of the sulfur-carbon bond leads to abundant alkyl ions ($[\text{C}_4\text{H}_9]^+$ in Fig. 4 and $[\text{C}_3\text{H}_7]^+$ in Figure 5). The corresponding heterolytic cleavage is not observed with tetraalkyl phosphonium ions.

Discussion

Amines, Phosphines and Sulfides

For a discussion of the fragmentation behaviour of the closed shell onium ions, a comparison of the decomposition of the corresponding open shell

amines, phosphines and sulfides is useful. α -cleavage leading to a stable, even electron fragment is by far the dominant fragmentation process in amines and still a significant process in sulfides leading to the base peak in the case of many compounds [12]. However, judging from available experimental data, this process is of lesser importance in the phosphine case. (α -cleavage gives rise to the base peak in diethyl sulfide [11], while the corresponding fragment in triethylphosphine [7] has a relative abundance of 24%.) While in molecular ions containing first row heteroatoms the tendency for α -cleavage decreases from nitrogen to halogen, this is not the case for the second row heteroatoms. The exceptional behaviour of the phosphorous compounds must result from a pronounced participation of d-orbitals in bond formation leading to a better stabilization of the electron deficiency in the molecular ion [12]. It is known that d-orbital participation is more pronounced in phosphorous than in sulfur compounds [6].

Onium Ions

In contrast to the open shell amine, phosphine, and sulfide ions, the corresponding closed shell onium ions do not show a direct α -cleavage of the cation as the radical site assumed to initiate this reaction [14] is lacking. Moreover, α -cleavage would

lead to rather instable odd electron fragments. α -cleavage is, however, possible as secondary decomposition: loss of a substituent leads to odd electron fragments which can undergo α -cleavage in a second step. As expected from the fragmentation behaviour of amine, phosphine and sulfide ions discussed above, loss of a substituent with subsequent α -cleavage leads to the base peak in the c.a. spectra of ammonium ions. This process is less abundant in sulfonium ions and not unequivocally detectable with phosphonium ions as a result of the stronger d-orbital participation in phosphorous containing ions. This d-orbital participation also explains the exceptional high proportion of hydrogen elimination from phosphonium ions.

Furthermore, ammonium and phosphonium ions differ in their fragmentation behaviour from sulfonium ions in so far as the alkene elimination from the cation is either missing or of low abundance. This result is surprising as in both cases the alkene elimination leads to energetically more favourable products (even electron ions + alkenes) than alkyl elimination (odd electron ions + alkyl radicals). Thus, steric factors possibly explain the observed differences. The alkene elimination proceeds via a hydrogen rearrangement with a cyclic transition state. Such a cyclic transition state can be sterically better accommodated in a tri-substituted than in a tetra-substituted ion. Thus alkene elimination is observed in trialkyl sulfonium ions and trialkyl phosphine ions, but not in tetraalkyl phosphonium ions.

Finally, it is noteworthy that heterolytic cleavage (with charge migration to the alkyl substituent) is dominant in trialkyl sulfonium ions, but not observed with tetraalkyl phosphonium ions. Heterolytic cleavage is obviously favoured by the higher electronegativity of sulfur as compared to phosphorous.

The present results demonstrate that structure elucidation of phosphonium and sulfonium ions using collisional activation can readily be made. Such structure elucidation is more straight forward in sulfonium ions where alkyl and alkene elimination as well as heterolytic cleavage give unambiguous information on the substituents.

Experimental

A self-constructed double focusing mass spectrometer with the magnetic sector arranged in front

of the electric sector was used to record collisional activation spectra. The collision cell was placed between the two sectors near the energy resolving slit. The ion source was a conventional field ionization/field desorption source which allowed a rapid replacement of the field ion emitter via a vacuum lock system.

For field desorption of the phosphonium and sulfonium iodides activated and also non activated $10\text{ }\mu\text{m}$ tungsten wire emitters were used. After dipping the wires into a saturated solution of the sample and applying an anode cathode potential difference of about 12 kV a high and almost smooth ion emission was obtained at emitter heating currents between 20 and 35 mA depending on the type of substance and loading of the emitter.

The translational energy of the cations before collision is determined by the anode potential which was set to 10 kV. The target gas helium was introduced into the collision cell up to a pressure at which the intensity of the precursor ion decreased to one third of the corresponding value without target gas due to scattering and decomposition processes. The c.a. spectrum of a mass selected cation was obtained by scanning the electric sector voltage. The mass spectra shown are the average of $3 \div 7$ measurements. Peaks were at least partially resolved up to a precursor mass of m/e 170. The reproducibility of the spectra differed considerably from compound to compound. The standard deviation was $\pm 15\%$ in favourable cases, but only $\pm 30\%$ in other instances.

It is important to note that in all spectra the fragment ion intensities are not corrected for a different multiplier response. This multiplier response is approximately proportional to the kinetic energy of the ions impinging on the first dynode (including the post acceleration of -2.5 kV between exit slit and multiplier). The onium iodides were prepared using standard procedures.

Acknowledgement

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