## **Comparison Between the Mass Spectrometric Behaviour and Condensed-phase Reactivity of Products of Addition of Phthalimidesulphenyl Chloride to Aryl Acetylenes**

#### G. Capozzi, S. Menichetti and C. Nativi

Centro CNR 'Chimica dei Composti Eterociclici,' Dipartimento di Chimica Organica, Università di Firenze, Via G. Capponi 9, I-50121 Firenze, Italy

**R. Seraglia and P. Traldi** CNR, Area della Ricerca, Corso Stati Uniti 4, I-35100 Padova, Italy

The electron impact-induced mass spectrometric behaviour of six products of the addition of phthalimidesulphenyl chloride to aryl acetylenes was studied with the aid of daughter ion spectroscopy. The electron impact-induced decomposition processes parallel those observed in the condensed phase. In particular for the diaryl adducts the formation of 3-chlorobenzothiophene derivatives results in a highly favoured process under the two sets of operating conditions.

## **INTRODUCTION**

Phthalimidesulphenyl chloride belongs to the class of functionalized sulphenyl halides, and it has a sulphurchlorine bond and a sulphur-nitrogen bond whose reactivity can be modulated by appropriate reactions.

The reaction between phthalimidesulphenyl chloride and alkynes has recently been studied.<sup>1</sup> The regioselectivity of the addition was found to be very similar to that shown by other simple alkanes or arensulphenyl chlorides.<sup>2–5</sup> The reaction of the adducts with nucleophiles



0030-493X/93/020101-06 \$08.00 © 1993 by John Wiley & Sons, Ltd.

of different types led to substitution of the phthalimide residue with the formation of new classes of vinyl sulphides and vinylsulphenamides.<sup>1,6</sup>

The mass spectrometric behaviour of some adducts of phthalimidesulphenyl chloride with some alkyl acetylenes has been the subject of a previous paper.<sup>7</sup> In that case the electron impact-induced decomposition patterns were strongly influenced by both the substituents and the phthalimide moiety. In particular we observed that the loss of Cl<sup>•</sup> was strongly dependent on the alkyl substituents and that the formation of protonated phthalimide was a favoured process in all cases.

It can be expected that the presence of an aryl group  $\alpha$  to the chlorine atom should strongly affect the decomposition routes, thus allowing the formation of new species.

Pursuing our interest in the study of adducts between phthalimidesulphenyl chloride and alkynes, we report here the electron impact-induced decomposition pattern of compounds 1-6.

## **EXPERIMENTAL**

#### Synthesis of vinylsulphenamides 1-6

The synthesis of sulphenamides  $1,^6 2^{1b}$  and  $3^{1b}$  has been described. Compounds 4-6 were similarly prepared by addition of phthalimidesulphenyl chloride to the appropriate alkyne in dry dichloromethane. Purification was achieved by column chromatography and recrystallization. Pure sulphenamides 4-6 showed the correct elemental analysis and consistent spectroscopic data. Yields and melting points were as follows: 4, 75%, 152 °C; 5, 87%, 132–133 °C; 6, 65%, 142–145 °C.

Received 27 May 1992 Revised manuscript received 16 October 1992 Accepted 17 October 1992

	1		2		3		4		5		6	
	EI	MIKE	El	MIKE	El	MIKE	El	MIKE	Ei	MIKE	El	MIKE
lonic	m/z	m/z	m/z	m/z	m/z	m/z	m/z	m/z	m/z	m/z	m/z	m/z
species	(R.A.)*	(A.A.) <sup>b</sup>	(R.A.)	(A.A.)	(R.A.)	(A.A.)	(R.A.)	(A.A.)	(R.A.)	(A.A.)	(R.A.)	(A.A)
M+.	329	-	391	-	419	-	451	-	379	-	379	-
	(7)		(5)		(15)		(45)		(18)		(68)	
[M – H]+	_	-	-	390			-	-	-	-	-	-
				(8)								
$[M - H_2O]^+$	-	311	-	-	-	-	-	-	-	-	-	-
		(13)										
[M – Cl] +	-	294	-	356	-	384	-	416	-	344	-	344
		(30)		(30)		(12)		(4)		(9)		(4)
[M - PhthH]+*	182	182	244	244	272	272	304	304	232	232	232	232
	(23)	(42)	(32)	(46)	(86)	(32)	(12)	(7)	(100)	(83)	(40)	(22)
[M - PhthS]+	-	-	213		241	241	273	273	201	-	201	
			(3)		(10)	(42)	(18)	(72)	(7)		(25)	
[M – PhthSH]+*	-	-	-	-	-	-	-	-	200	200	200	200
									(15)	(8)	(45)	(74)
[R <sup>1</sup> R <sup>2</sup> C <sub>2</sub> S] <sup>+</sup>	148	-	210	210	238	238	270	270	198	-	198	-
	(18)		(9)	(14)	(23)	(7)	(20)	(4)	(41)		(60)	
$[R^1R^2C_2]^+$	116	-	178	178	206	206	238	238	166	-	166	-
	(52)		(73)	(2)	(100)	(7)	(100)	(7)	(33)		(100)	
[PhthH]+•	147	147	147	-	147	_	147	_	147	-	147	
	(100)	(15)	(100)		(68)		(39)		(30)		(18)	
[C <sub>7</sub> H <sub>4</sub> O] <sup>+</sup>	104	-	104	_	104	-	104	-	104	-	104	-
	(50)		(65)		(33)		(25)		(25)		(17)	
$[R^1R^2C_2S - CH_3]^+$	_	-	-	-	-	-	255	-	-	-	-	
							(12)					
$[R^{1}R^{2}C_{2} - CH_{3}]^{+}$		-	-	-	-	-	223	223		_	-	-
							(54)	(6)				
<sup>a</sup> Relative abundance (	(%).											
<sup>®</sup> Absolute abundance	(%).											

Table 1. EI mass spectra and MIKE spectra of M<sup>++</sup> of compounds 1-6

# Cyclization of vinylsulphenamides 1–6 to the corresponding 2-substituted-3-chlorobenzothiophenes

To a solution of sulphenamides 1-6 (1 equiv.) in dry dichloromethane (5 equiv.) kept at room temperature under a nitrogen atmosphere, aluminium trichloride (2 equiv.) was added and the mixture was maintained at room temperature for an additional 15 min. Aqueous quenching and column chromatographic purification gave the pure cyclized products.<sup>8</sup> Correct microanalyses and consistent spectroscopic data were obtained for all the benzothiophenes synthesized. Cyclized products derived from sulphenamides 1 and 2 were also identified by comparison with authentic samples.<sup>9,10</sup>

#### Mass spectrometry

All mass spectrometric measurements were performed on a VG ZAB2F instrument,<sup>11</sup> operating under electron impact (EI) conditions (70 eV, 200  $\mu$ A, ion-source temperature 200 °C). Samples were introduced via a direct inlet system.

Metastable transitions were detected by massanalysed ion kinetic energy (MIKE) spectroscopy.<sup>12</sup> Collisional-activated decompositions (CAD) were obtained by 8 keV ions colliding with air in the second field-free region. In the collision cell the pressure was maintained such as to reduce the main beam intensity to 60% of its normal value.

### **RESULTS AND DISCUSSION**

The 70 eV EI mass spectra together with the MIKE spectra of  $M^+$  ions of 1–6 are reported in Table 1.

The relative abundances of the  $M^{+}$  ions of 1-6 increase in accordance with the electron donor properties of the substituents.

Even though the structures of 1-6 resemble those of the previously studied alkyl derivatives,<sup>7</sup> their mass spectrometric behaviour is significantly different. In fact, whereas with the alkyl derivatives most of the total ion current was due to phthalimide-containing moieties, in the present case the EI-induced decomposition is strongly dependent on the aryl substituents. The formation of protonated phthalimide [PhthH + H]<sup>+</sup> at m/z148, always detected in the MIKE spectra of M<sup>++</sup> ions of alkyl derivatives, was never observed for 1-6. Hence the presence of an alkyl group  $\alpha$  to the chlorine atom seems to be a necessary condition for the occurrence of such a process.

Moreover, the loss of Cl<sup> $\cdot$ </sup>, which readily occurred with the alkyl derivatives, was never detected in the EI mass spectra of 1–6 and MIKE spectra showed that it is not a kinetically favoured process.

The cleavage of the N—S bond with H rearrangement (Cleavage 1 in Scheme 1) leads to the molecular ion of phthalimide, [PhthH]<sup>+</sup>, at m/z 147 and to [M — PhthH]<sup>+</sup> ions. The former leads to the base peak in the EI mass spectra of 1 and 2; for 3, 4, 5 and 6 its



relative abundance decreases, while the abundances of the complementary fragments show a significative increase, reasonably owing to their lower ionization energies.

In order to investigate the structure of  $[M - PhthH]^+$  ions and the feasibility of cyclization reactions, MIKE experiments were performed on them (see Figs 1 and 2). The MIKE spectra of  $[M - PhthH]^+$  ions originating from 1, 3, 4, 5 and 6 did not give clear information about the structures of these ionic species. The detected fragment ions were due to losses of H<sup>\*</sup> and Cl<sup>\*</sup> for 1, 3, 5 and 6 and to the loss of CH<sub>3</sub><sup>\*</sup> for 4. The MIKE spectrum of  $[M - PhthH]^+$  ions originating from 2 shows several fragment ions. The ions at m/z 212 and 200 can be attributed to the losses of S and CS<sup>\*</sup>, respectively, typical of benzothiophene derivatives.



Figure 1. MIKE spectra of  $[M - PhthH]^{++}$  ions originating from (a) compound 1, (b) compound 2 and (c) compound 3.

The comparison of the CAD-MIKE spectrum of  $M^{+}$  of 3-chloro-2-phenylbenzothiophene with that of  $[M - PhthH]^{+}$  ions originating from 2 proves the identity of the two structures (see Fig. 3). Similarly, the benzo-thiophene structure of the other  $[M - PhthH]^{+}$  ions was proved.

This particular reactivity has been also found in the condensed phase.<sup>8</sup> In fact, when 1-6 were dissolved in dichloromethane and aluminium trichloride was added, high yields of 3-chlorobenzothiophene derivatives were obtained. Under these conditions Lewis acid catalysis is needed to activate the intramolecular cyclization which, in turn, is a spontaneous process for radical cations of 1-6.

The formation of  $[M - PhthS]^+$  ionic species (arising from cleavage 2 in Scheme 1), not observed for 1 and detected only in the EI mass spectra of 5 and 6, can be explained by the resonance stability of the product ions, owing to the presence of the aryl moieties. In fact, in both the EI and MIKE spectra the abundance of  $[M - PhthS]^+$  ions increases according to the electron donor properties of the aryl substituents, which stabilize the cation produced (for 4  $[M - PthS]^+$  leads to the base peak of the MIKE spectrum of  $M^+$ ).

Cleavage 2 with H rearrangement (see Scheme 1) leads to  $[M - PhthSH]^{+}$  ions, detected only for 5 and 6, and highly favoured for the latter. It can be rationalized by invoking the formation of acenaphthylene derivatives (see Scheme 2).

The formation of  $[R^1R^2C_2]^+$  ions is also worth noting. These ionic species were detected in high yield in the EI mass spectra of all the compounds. Possibly  $[R^1R^2C_2]^+$  ions could arise from thermal decomposition. Measurements in the probe temperature range 80-280 °C do not show any variation of their relative



Scheme 2



Figure 2. MIKE spectra of [M - PhthH]<sup>++</sup> ions originating from (a) compound 4, (b) compound 5 and (c) compound 6.

abundances; further, the presence of the peaks corresponding to  $[R^1R^2C_2]^{+\cdot}$  ions in the MIKE spectra of  $M^{+\cdot}$  of 2-4 seems to suggest that  $[R^1R^2C_2]^{+\cdot}$  formation must be considered to be an EI-induced and not a thermal process. However, a clear variation of the  $M^{+\cdot}/[R^1R^2C_2]^{+\cdot}$  abundance ratio is observed on varying the ion source temperature (see Table 2): such a dependence is fairly high for 1, whereas it becomes smaller or negligible for the other compounds. Such

results can be explained by considering that with typical ion source temperature of 200 °C the  $[R^1R^2C_2]^{++}$  ions are formed by two different decomposition processes, viz. EI and thermally induced, the latter being more significant for 1. The electron donor properties of the aryl substituents seem to assist the process leading to these ionic species. The m/z values of these ionic species correspond to the relative molecular mass of the arylalkynes used in the synthesis of 1–6. It should be noted that in



Figure 3. CAD-MIKE spectra of (a) [M - PhthH]<sup>++</sup> ions originating from compound 2 and (b) M<sup>++</sup> ions of 3-chloro-2-phenylbenzothio-phene.



Scheme 3

the case of 1,2-diphenyl-2-chlorovinyl methyl sulphide<sup>13</sup> this retrosynthetic process is not operative under EI conditions and, consequently, it can be ascribed to the presence of the phthalimido residue.

The formation of  $[\mathbb{R}^1\mathbb{R}^2\mathbb{C}_2]^{+}$  ions can be explained by an E-Z isomerization process followed by syn elimination of phthalimidesulphenyl chloride from molecular ions (see Scheme 3). In solution, sulphenyl chloride elimination from alkyne-sulphenyl chloride adducts has only once been observed under solvolytic conditions and occurred with a different mechanism.<sup>2</sup> In contrast acid-catalysed E-Z isomerization of compounds similar to 1-6 has often been observed<sup>14</sup> in the condensed phase. In particular we found<sup>8</sup> that for 4 this process occurs even in the presence of a trace amount of acid. Indeed, in solution, reversible protonation of a double bond may be regarded as a process which reduces the

Table 2. M<sup>+</sup>·/[R<sup>1</sup>R<sup>2</sup>C<sub>2</sub>]<sup>+</sup> abundance ratios obtained at different ion source temperatures

lon source temperature (°C)	1	2	3	4	5	6
200	0.13	0.34	0.15	0.45	0.54	0.68
150	0.18	0.25	0.25	0.40	0.58	0.67
100	1.17	0.15	0.40	0.32	0.50	0.60
50	1.70	0.10	0.45	0.25	0.40	0.58

energy barrier for rotation around this bond. A similar effect may be envisaged for extraction of one electron from the neutral molecule, which reduces the  $\pi$ -bond order, to give a delocalized radical cation.

Finally, the formation of  $[R^1R^2C_2S]^{+}$  ions can also be explained by assuming that the same isomerization process is operative (see Scheme 3). These ions, which are present in the EI mass spectra of all the compounds, are detected in the MIKE spectra of of M<sup>+•</sup> of 2-4. Several structures can be drawn for  $[R^1R^2C_2S]^+$  ionic species. In our opinion a thiirene derivative is a good candidate. Thiirenes are antiaromatic species which have been synthesized and characterized at 8 K in a matrix;<sup>15</sup> on the other hand, thiirenium ions are relatively stable species both in solution and in the solid state.<sup>2</sup> In our system, the presence of the two aryl groups conjugated with the three-membered ring might delocalize electron density stabilizing the cyclic structure. Indeed, charge delocalization is an important factor for the formation of  $[R^1R^2C_2S]^{+}$  ions and other ionic species such as  $[R^1R^2C_2]^{+}$ . In fact, these ions are absent in the MIKE spectra of 1, 5 and 6, which are monoaryl-substituted derivatives.

In conclusion, compounds 1-6 show similar reactivity in EI mass spectrometry and in the condensed phase. This behaviour might be useful since analysis of the ions detected in the mass spectra can assist in the design of suitable reaction conditions in order to generate the same species in the condensed phase.

#### REFERENCES

- (a) G. Capozzi, L. Gori and S. Menichetti, *Tetrahedron Lett.* 31, 6213 (1990); (b) G. Capozzi, L. Gori, S. Menichetti and C. Nativi, *J. Chem. Soc.*, *Perkin Trans.* 1 1923 (1992).
- G. Capozzi, V. Lucchini and G. Modena, *Rev. Chem. Intermed.* 2, 347 (1979).
- 3. G. Capozzi, G. Modena and L. Pasquato, in The Chemistry of

Sulphenic Acids and Their Derivatives, ed. by S. Patai, p. 403. Wiley, Chichester (1990).

- G. H. Schmid, in *The Chemistry of the Carbon–Carbon Triple* Bond, ed. by S. Patai, p. 275. Wiley, Chichester (1975).
- G. Capozzi, G. Romeo, V. Lucchini and G. Modena, J. Chem. Soc., Perkin Trans. 2 831 (1983).

- 6. E. Busi, G. Capozzi, S. Menichetti and C. Nativi, Synthesis 643 (1992).
- 7. R. Seraglia, P. Traldi, G. Capozzi and S. Menichetti, *Org. Mass Spectrom.* **27**, 529 (1992).
- 8. G. Capozzi, F. De Sio, S. Menichetti, C. Nativi and P. L. Pacini, in Proceedings of 15th International Symposium on the Organic Chemistry of Sulfur, ISOCS 15, Caen, France, June 28–July 3, 1992, p. 119.
- P. Geneste, J. Grimaud, J. L. Olivè and S. N. Ung, *Bull. Soc. Chim. Fr.* 271 (1977).
- 10. T. J. Barton and Z. Zika, J. Org. Chem. 35, 1729 (1970).
- R. P. Morgan, J. H. Beynon, R. H. Bateman and B. N. Green, Int. J. Mass Spectrom. Ion Phys. 28, 171 (1978).
  R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester,
- Metastable lons. Elsevier, Amsterdam (1973).
- 13. C. Paradisi, G. Scorrano, A. Visentini and P. Traldi, Org. Mass Spectrom. 21, 171 (1986).
- 14. V. Caló, G. Modena and G. Scorrano, J. Chem. Soc. C 1344 (1968).
- 15. A. Krantz and J. Laurene, J. Am. Chem. Soc. 99, 4842 (1977).