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MASS SPECTRA OF SULFINAMIDE DERIVATIVES AND IDENTIFICATION OF THEIR THERMAL DECOMPOSITION PRODUCTS†

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Abstract—The mass spectra of 30 sulfinamide derivatives (RSONHR′, R′ = alkyl or p-XC_6H_4) are reported. Most of the spectra had peaks attributable to thermal decomposition products. For some compounds these were identified by pyrolysis under similar conditions to be: RSO_2NHR', RSO_2SR, RSSR and NH_2R' (in all kinds of sulfinyl amides); RSNHR′ (in the case of arylsulfinyl arylamides); $RSO_2C_6H_4NH_2$, $RSOC_6H_4NH_2$ and $RSC_6H_4NH_2$ (in the case of arylsulfinyl arylamides of the type of X = H).

The mass spectra of the three thermally stable compounds showed that there are several kinds of common fragment ions. The mass spectra of the thermally labile compounds had two groups of ions; (i) characteristic fragment ions of the intact molecules and (ii) the molecular ions of the thermal decomposition products. It was concluded that the sulfinamides give the following ions after electron impact: $[M]^{+\cdot}$, $[M - R]^+$, $[M - R + H]^{+\cdot}$, $[M - SO]^{+\cdot}$, $[RS]^+$, $[NHR']^+$, $[NHR' + H]^{+\cdot}$, $[RSO]^+$, $[RSO + H]^{+\cdot}$, $[R]^+$, $[R + H]^{+\cdot}$, $[R']^+$ and $[M - OH]^+$, and that the thermal decomposition products give the following ions: $[RSO_2SR]^{+\cdot}$, $[RSSR]^{+\cdot}$, $[M - O]^{+\cdot}$, $[M + O]^{+\cdot}$ and $[RSOC_6H_4NH_2]^{+\cdot}$.

ALTHOUGH the mass spectra of a variety of organic compounds having a S—O linkage have been reported, no report on the mass spectra of sulfinamide derivatives is available. We have prepared 30 sulfinamides to investigate their physicochemical properties, and this paper reports and discusses their electron impact mass spectra. Because thermal decomposition of the sulfinamide derivatives in the mass spectrometer was found to be unavoidable, care was taken to distinguish between the ions due to the sulfinamide and those from their pyrolysis products.

RESULTS AND DISCUSSION

The compounds studied in this work are as follows.

Ethanesulfinyl amides (C_2H_5SONHR')

1 $R' = n\text{-}C_4H_9$
2 $R' = C_6H_{11}$(cyclohexyl)
3 $R' = C_6H_5$

Benzenesulfinyl amides (C_6H_5SONHR')

4 $R' = H$
5 $R' = n\text{-}C_3H_7$
6 $R' = C_6H_5$
7 $R' = p\text{-}CH_3C_6H_4$
8 $R' = p\text{-}CH_3OC_6H_4$
9 $R' = p\text{-}ClC_6H_4$
10 $R' = p\text{-}C_2H_5CO_2C_6H_4$
11 $R' = p\text{-}CH_3COC_6H_4$

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p-*Toluenesulfinyl amides* (p-$CH_3C_6H_4SONHR'$)

12	$R' = H$	**13**	$R' = n$-C_3H_7
14	$R' = n$-C_4H_9	**15**	$R' = C_6H_{11}$(cyclohexyl)
16	$R' = C_6H_5$	**17**	$R' = p$-$CH_3C_6H_4$
18	$R' = p$-$CH_3OC_6H_4$	**19**	$R' = p$-ClC_6H_4
20	$R' = p$-$C_2H_5CO_2C_6H_4$	**21**	$R' = p$-$CH_3COC_6H_4$

p-*Methoxyberzenesulfinyl amides* (p-$CH_3OC_6H_4SONHR'$)

22	$R' = p$-$CH_3C_6H_4$	**23**	$R' = p$-$CH_3OC_6H_4$
24	$R' = p$-ClC_6H_4		

p-*Chlorobenzenesulfinyl amides* (p-ClC_6H_4SONHR')

25	$R' = C_6H_5$	**26**	$R' = p$-$CH_3C_6H_4$
27	$R' = p$-$CH_3OC_6H_4$	**28**	$R' = p$-ClC_6H_4
29	$R' = p$-$C_2H_5CO_2C_6H_4$	**30**	$R' = p$-$CH_3COC_6H_4$

Thermal decomposition products of sulfinamides

All the sulfinamides were introduced into the mass spectrometer through the all-glass direct inlet system without direct heating. However, a large number of compounds gave mass spectra having a few peaks at too high m/e values. The results of the high resolution mass measurements of four compounds (**4**, **6**, **11** and **19**) (Table 1) indicated that these unusual peaks correspond to the molecular ions of thiolsulfonates (RSO_2SR) and disulfides (RSSR). Therefore, it was suspected that the compounds decomposed thermally even if the indicated temperature range 50–90 °C of the sample chamber was much lower than the decomposition temperatures (110–135 °C) of most of the sulfinamides.

This was confirmed as follows. Insertion of compound **28**, which crystallizes as colourless needles with a decomposition temperature of 136 °C, into the mass spectrometer with the temperature of the sample chamber at 85 °C gave, on recovery, a purple solid. The latter substance had a different i.r. spectrum from **28**. Further, the i.r. spectrum of **28** after heating in a glass tube at 90 °C for 10 min was unchanged,

TABLE 1. RESULTS OF THE HIGH RESOLUTION MASS MEASUREMENTS OF **4**, **6**, **11** AND **19**

Compound	m/e	Ion	Compound	m/e	Ion
4	141	$[M]^{\dagger}$	**11**	125	$[C_6H_5SO]^{+}$
4	125	$[C_6H_5SO]^{+}$	**11**	126	$[C_6H_5SO + H]^{\dagger}$
4	126	$[C_6H_5SO + H]^{\dagger}$	**11**	109	$[C_6H_5S]^{+}$
4	109	$[C_6H_5S]^{+}$	**11**	110	$[C_6H_5S + H]^{\dagger}$
4	116	$[C_6H_5S + H]^{\dagger}$	**11**	250	$[C_6H_5SO_2SC_6H_5]^{\dagger}$
4	256	$[C_6H_5SO_2SC_6H_5]^{\dagger}$	**11**	218	$[C_6H_5SSC_6H_5]^{\dagger}$
6	217	$[M]^{\dagger}$ or $[C_6H_5SOC_6H_4NH_2]^{\dagger}$	**19**	139	$[CH_3C_6H_4SO]^{+}$
6	125	$[C_6H_5SO]^{+}$	**19**	140	$[CH_3C_6H_4SO + H]^{\dagger}$
6	109	$[C_6H_5S]^{+}$	**19**	123	$[CH_3C_6H_4S]^{+}$
6	92	$[NHC_6H_5]^{+}$	**19**	124	$[CH_3C_6H_4S + H]^{\dagger}$
6	201	$[C_6H_5SNHC_6H_5]^{\dagger}$ or $[C_6H_5SC_6H_4NH_2]^{\dagger}$	**19**	249	$[CH_3C_6H_4SNHC_6H_4Cl]^{\dagger}$
			19	278	$[CH_3C_6H_4SO_2SC_6H_4CH_3]^{\dagger}$
			19	246	$[CH_3C_6H_4SSC_6H_4CH_3]^{\dagger}$

which indicates clearly that in the mass spectrometer the compound must have been heated to a temperature higher than 85 °C. The comparatively hot ionization chamber temperature *c.* 130 °C located very close to the sample chamber is a possible cause of the thermal decomposition. The temperature of the ionization chamber for all other determinations was between 110–175 °C.

Thus, thermal decomposition was considered to be unavoidable for most sulfinamides, because the temperature of the ionization chamber was higher than that of the decomposition temperatures of the sulfinamides. Therefore, it became necessary to determine the thermal decomposition products prior to interpretation of the mass spectra.

In order to identify the thermal decomposition products seen in the mass spectrometer, **4** and **16**, representing the arylsulfinyl alkylamides and arylsulfinyl arylamides, were heated *in vacuo* at 150 °C for 5 min, which simulated the conditions employed in the determination of the mass spectra. The decomposition products were separated by high-speed liquid chromatography (h.l.c.) and/or by column chromatography (l.c.), and are listed in Table 2. The methods of identification are given in the Experimental section.

Although the decomposition products were not determined quantitatively, h.l.c. of the decomposition products of **4** and **16** heated at 150 °C for 30 min indicated that longer heating does not affect the composition of the decomposition products.

Compounds **6**, **14** and **19** were also thermolysed under the same conditions. Their major decomposition products (Table 2) were similarly separated and identified (see Experimental).

The results (Table 2) indicate that the following compounds, p,p'-$RC_6H_4SO_2$-$C_6H_4NH_2$, p,p'-$RC_6H_4SOC_6H_4NH_2$ and p,p'-$RC_6H_4SC_6H_4NH_2$, are formed only from arylsulfinyl arylamides which have no substituent at the *para* position of the benzene rings of the arylamide moieties of their molecules.

From the results mentioned so far it was concluded that almost all of the sulfinamides decompose by heating at 150 °C to give the following decomposition products.

Alkylamides (RSONHR′)

NH_2R', RSO_2NHR', RSO_2SR and RSSR.

TABLE 2. THERMOLYSIS PRODUCTS IDENTIFIED FROM COMPOUNDS **4**, **6**, **14**, **16** AND **19**

Compound	Products	Compound	Products
4	$C_6H_5SO_2NH_2$	**6**	$C_6H_5NH_2$
	$C_6H_5SONH_2$(**4**)		p-$C_6H_5SOC_6H_4NH_2$
	$C_6H_5SO_2SC_6H_5$		$C_6H_5SONHC_6H_5$(**6**)
	$C_6H_5SSC_6H_5$		$C_6H_5SO_2SC_6H_5$
16	$C_6H_5NH_2$		p-$C_6H_5SC_6H_4NH_2$
	p,p'-$CH_3C_6H_4SOC_6H_4NH_2$		$C_6H_5SSC_6H_5$
	p,p-$CH_3C_6H_4SO_2C_6H_4NH_2$	**14**	p-$CH_3C_6H_4SONHC_4H_9$(**14**)
	p-$CH_3C_6H_4SONHC_6H_5$(**16**)		p,p'-$CH_3C_6H_4SO_2SC_6H_4CH_3$
	p,p'-$CH_3C_6H_4SC_6H_4NH_2$		p,p'-$CH_3C_6H_4SSC_6H_4CH_3$
	p,p'-$CH_3C_6H_4SO_2SC_6H_4CH_3$	**19**	p-$ClC_6H_4NH_2$
	p,p'-$CH_3C_6H_4SSC_6H_4CH_3$		p,p'-$CH_3C_6H_4SO_2NHC_6H_4Cl$
			p,p'-$CH_3C_6H_4SO_2SC_6H_4CH_3$
			p,p'-$CH_3C_6H_4SSC_6H_4CH_3$

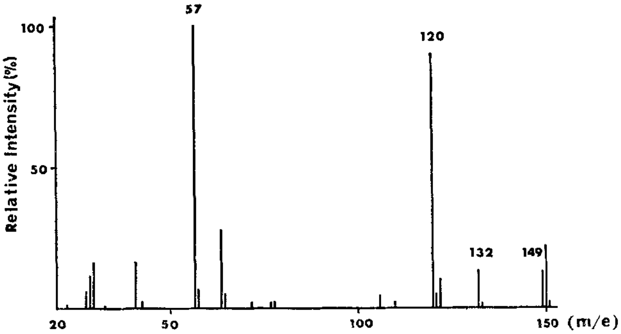


FIG. 1. Mass spectrum of **1**.

Arylamides ($RSONHC_6H_4X$)

$NH_2C_6H_4X$, $RSO_2NHC_6H_4X$, $RSNHC_6H_4X$, RSO_2SR and RSSR; when X = H three extra products are found, $RSO_2C_6H_4NH_2$, $RSOC_6H_4NH_2$ and $RSC_6H_4NH_2$.

Fragmentation pathways of sulfinamides

Although the thermal stability was not investigated for all the compounds, three sulfinamides (**1**, **2** and **15**) were shown to be stable on heating at 150 °C for 5 min. Thus, the h.l.c. of the heated compound had only one peak corresponding to the original molecule (**15**), or the i.r. spectra determined before and after the heating (**1** and **2**) were identical. The thermal stability of these compounds was also shown by the fact that the i.r. mass spectra determined after about 10 min in the vicinity of the hot ionization chamber did not show any peak attributable to pyrolysis products. Therefore, the mass spectra obtained could be considered to be those derived only from the original molecules (**1**, **2**, **15**).

The mass spectrum of **1** is shown in Fig. 1. The characteristic fragment peaks listed in Table 3 indicate that three compounds decompose in a similar fashion after electron impact (20 eV) to afford $[M - OH]^+$, $[M - R]^+$, $[M - R + H]^+$, $[RSO]^+$, $[RSO + H]^+$, $[NHR']^+$, $[R]^+$, $[R + H]^+$ and $[R']^+$ ions. Compound **15** showed three additional ions, $[M - SO]^+$, $[RS]^+$ and $[NHR' + H]^+$.

TABLE 3. CHARACTERISTIC FRAGMENT PEAKS OF INTACT MOLECULES (*m*/*e* AND RELATIVE INTENSITY)

Ion	**1**	**2**	**15**
$[M]^+$	149(15)	175(92)	237(25)
$[M - OH]^+$	132(13)	158(2)	220(11)
$[M - R]^+$	120(91)	146(97)	146(18)
$[M - R + H]^+$	121(8)	147(10)	147(3)
$[RSO]^+$	77(3)	77(2)	139(100)
$[RSO + H]^+$	78(3)	78(2)	140(50)
$[NHR']^+$	72(3)	98(11)	98(51)
$[NHR' + H]^+$		99(2)	99(5)
$[R]^+$	29(12)	29(4)	91(7)
$[R + H]^+$	30(16)	30(2)	92(22)
$[R']^+$	57(100)	83(100)	83(9)
$[M - SO]^+$			189(93)
$[RS]^+$			123(4)

The characteristic fragment peaks of **3**, **4**, **16** and **19**, which all undergo the thermal decomposition in the mass spectrometer, are listed in Table 4. In the Table, the $[M + O]^{\dagger}$ ion means the ion(s) $[RSO_2NHC_6H_5]^{\dagger}$ and/or $[RSO_2C_6H_4NH_2]^{\dagger}$ in the case of $X = H$ for the sulfinyl arylamide ($RSONHC_6H_4X$), and the ion $[RSO_2NHC_6H_4X]^{\dagger}$ in the case of $X \neq H$. The $[\text{'M'}]^{\dagger}$ ion means the ion(s) $[RSONHC_6H_5]^{\dagger}$ (the molecular ion) and/or $[RSOC_6H_4NH_2]^{\dagger}$ in the case of $X = H$, and the molecular ion in the case of $X \neq H$. The $[M - O]^{\dagger}$ ion means the ion(s) $[RSNHC_6H_5]^{\dagger}$ and/or $[RSC_6H_4NH_2]^{\dagger}$ in the case of $X = H$, and the ion $[RSNHC_6H_4X]^{\dagger}$ in the case of $X \neq H$. The mass spectrum of **16** is shown in Fig. 2. The elemental compositions of several ions in Table 4 marked (*) were ascertained by high resolution mass measurements. Table 4 shows that these compounds afforded two groups (A and B) of common fragment ions. The ions of the A group are the same as the characteristic ions of the intact molecules mentioned before, but the $[M - R]^{+}$ and $[M - R + H]^{\dagger}$ ions are missing in the spectra of **4**, **16** and **19**. It is not possible to conclude that all of the ions of group A were produced only from the intact molecules, because these ions could also be partially produced from the thermal decomposition products. However, from the results of the thermal decomposition reaction (cf. Table 2), not all molecules introduced into the mass spectrometer undergo thermal decomposition during the determination of mass spectra. Therefore the ions of this group were produced, at least partly, from the unchanged molecules. The ions of group B, $[RSO_2SR]^{\dagger}$, $[RSSR]^{\dagger}$, $[M + O]^{\dagger}$, $[\text{'M'}]^{\dagger}$ (if this is not the molecular ion) and $[M - O]^{\dagger}$, can be considered to arise from the artifacts.

Metastable ions indicated the formation of the following ions from the original molecular ions. Compound **1**—*m/e* 120 $[M - R]^{+}$, *m/e* 72 $[NHR']^{+}$ and *m/e* 132 $[M - OH]^{+}$; compound **2**—*m/e* 146 $[M - R]^{+}$ and *m/e* 158 $[M - OH]^{+}$; and compound **15**—*m/e* 98 $[R'NH]^{+}$, *m/e* 220 $[M - OH]^{+}$ and *m/e* 189 $[M - SO]^{\dagger}$.

The characteristic fragment ions and a few of the types of ions produced from the pyrolysis products of all compounds, except the seven derivatives already cited, are compiled in Table 5.

TABLE 4. FRAGMENT PEAKS OF **3**, **4**, **16** AND **19** (*m/e* AND RELATIVE INTENSITY)

Group	Ion	**3**	**4**	**16**	**19**
A	$[M - OH]^{+}$	152(6)		214(4)	248(6)
A	$[M - R]^{+}$	140(25)			
A	$[M - R + H]^{\dagger}$	141(4)			
A	$[RSO]^{+}$	77(9)	125(100)*	139(81)	139(26)*
A	$[RSO + H]^{\dagger}$	78(5)	126(8)*	140(8)	140(3)*
A	$[NHR']^{+}$	92(14)		92(14)	126(3)
A	$[NHR' + H]^{\dagger}$	93(100)		93(100)	127(100)
A	$[R]^{+}$	29(45)	77(68)	91(13)	91(14)
A	$[R + H]^{\dagger}$	30(11)	78(17)	92(14)	92(14)
A	$[R']^{+}$	77(9)		77(3)	
A	$[M - SO]^{\dagger}$		93(59)	183(8)	
A	$[RS]^{+}$		109(26)*	123(48)	123(17)*
B	$[\text{'M'}]^{\dagger}$	169(4)	141(83)*	231(4)	
B	$[RSO_2SR]^{\dagger}$		250(27)*	278(19)	278(22)*
B	$[RSSR]^{\dagger}$	122(6)			246(20)*
B	$[M + O]^{\dagger}$			247(19)	281(1)
B	$[M - O]^{\dagger}$			215(39)	249(12)*

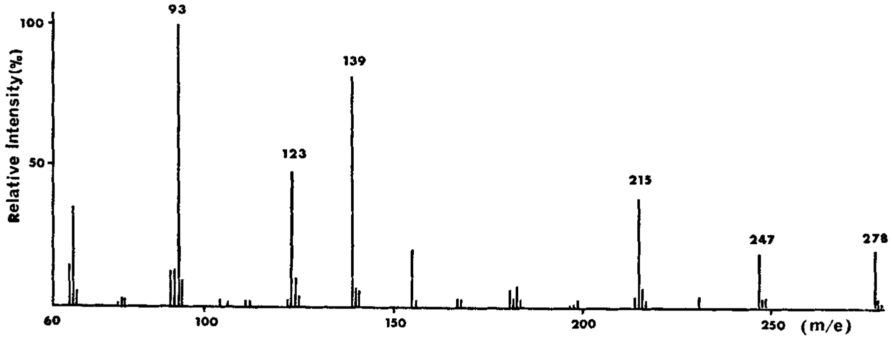


FIG. 2. Mass spectrum of **16**.

From the results shown in Tables 3–5 it can be concluded that the characteristic fragment ions of the intact sulfinamides are correlated with the chemical structure as follows. (1) The $[M - R]^+$ and $[M - R + H]^{\dagger}$ ions are observed, particularly in the spectra of alkylsulfinyl amides. (2) The $[M - SO]^{\dagger}$ and $[RS]^+$ ions are observed only in the spectra of arylsulfinyl amides. (3) The $[NHR']^+$ and $[NHR' + H]^{\dagger}$ ions are generally observed in all kinds of sulfinamides, but either one (or both) is (are) characteristically very abundant in the spectra of sulfinyl arylamides. (4) The $[RSO]^+$ and $[RSO + H]^{\dagger}$ ions are generally observed in all kinds of sulfinamides, but the $[RSO]^+$ ion is characteristically abundant in the spectra of arylsulfinyl amides. (5) The $[R]^+$ and $[R + H]^{\dagger}$ ions are always observed in all kinds of sulfinamides. (6) The $[R']^+$ and $[M - OH]^+$ ions are sometimes missing.

With regard to the ions from the pyrolysis products it can be concluded as follows. (1) The $[RSO_2SR]^{\dagger}$ and $[M - O]^{\dagger}$ ions are observed in almost all spectra of the thermally unstable sulfinamides. (2) The $[M + O]^{\dagger}$ ion is frequently missing. (3) The $[\text{'M'}]^{\dagger}$ and $[RSSR]^{\dagger}$ ions are sometimes missing.

The mass spectra of a number of compounds were also determined at 75 eV, but no significant differences could be observed.

TABLE 5. FRAGMENT PEAKS (*m/e* AND RELATIVE INTENSITY)

Ion	**5**	**6**	**7**	**8**	**9**	**10**[a]	**11**[a]	**12**
$[M - OH]^+$	166(10)	200(4)	214(2)		234(3)		242(1)	138(1)
$[M - R]^+$	106(27)		154(3)					
$[M - R + H]^{\dagger}$	107(2)							
$[RSO]^+$	125(100)	125(33)	125(30)	125(16)	125(41)	125(48)	125(47)	139(100)
$[RSO + H]^{\dagger}$	126(16)	126(3)	126(3)	126(2)	126(37)		126(4)	140(11)
$[NHR']^+$	58(4)	92(52)	106(78)	122(100)	126(37)	164(2)	134(3)	
$[NHR' + H]^{\dagger}$		93(100)	107(100)	123(43)	127(100)	165(55)	135(38)	
$[R]^+$	77(6)	77(18)	77(34)	77(18)	77(14)	77(35)	77(49)	91(31)
$[R + H]^{\dagger}$	78(23)	78(4)	78(7)	78(6)	78(6)	78(4)	78(9)	92(6)
$[R']^+$	43(22)	77(18)	91(3)	107(3)			119(6)	
$[M - SO]^{\dagger}$	135(49)	169(5)	183(1)					107(48)
$[RS]^+$	109(2)	109(11)	109(21)	109(5)	109(9)	109(20)	109(43)	123(4)
$[\text{'M'}]^{\dagger}$	183(23)	217(18)	231(4)	247(12)	251(20)		259(3)	155(65)
$[RSO_2SR]^{\dagger}$		250(13)	250(12)	250(3)	250(41)	250(30)	250(18)	278(2)
$[RSSR]^{\dagger}$		218(5)	218(7)		218(16)		218(15)	
$[M + O]^{\dagger}$								
$[M - O]^{\dagger}$	167(4)	201(18)	215(13)		235(14)		243(9)	139(100)

TABLE 5 (*continued*)

Ion	**13**	**14**	**17**	**18**	**20**[a]	**21**[a]	**22**	**23**
$[M - OH]^+$	180(4)	194(26)			286(1)	256(4)		
$[M - R]^+$	106(3)	120(30)				182(2)		
$[M - R + H]^{\dagger}$	107(2)	121(4)						
$[RSO]^+$	139(100)	139(100)	139(100)	139(26)	139(23)	139(69)	155(17)	155(12)
$[RSO + H]^{\dagger}$	140(6)	140(17)	140(10)	140(3)	140(3)	140(8)	156(2)	156(1)
$[NHR']^+$	58(2)	72(6)	106(96)	122(100)	164(2)		106(100)	122(3)
$[NHR' + H]^{\dagger}$	59(1)		107(25)	123(57)	165(77)	135(57)	107(98)	123(100)
$[R]^+$	91(11)	91(6)	91(87)	91(16)	91(12)	91(51)	107(98)	107(1)
$[R + H]^{\dagger}$	92(13)	92(9)	92(10)	92(3)	92(15)	92(45)	108(9)	108(82)
$[R']^+$	43(8)	57(5)	91(87)	107(2)		119(3)	91(4)	107(1)
$[M - SO]^{\dagger}$		163(30)					213(15)	
$[RS]^+$	123(4)	123(20)	123(45)	123(56)	123(24)	123(55)	139(6)	139(20)
$['M']^{\dagger}$	197(15)	211(9)	245(2)	261(6)		273(6)	261(1)	
$[RSO_2SR]^{\dagger}$	278(1)		278(25)	278(9)	278(17)	278(24)		310(8)
$[RSSR]^{\dagger}$	246(2)	246(19)	246(10)	246(3)	246(35)	246(27)		278(11)
$[M + O]^{\dagger}$					319(1)	289(5)		
$[M - O]^{\dagger}$	181(4)	195(7)	229(7)			257(15)		261(1)

Ion	**24**	**25**	**26**	**27**	**28**	**29**[a]	**30**[a]
$[M - OH]^+$							
$[M - R]^+$							
$[M - R + H]^{\dagger}$							
$[RSO]^+$	155(39)	159(39)	159(11)	159(11)	159(38)	159(4)	159(76)
$[RSO + H]^{\dagger}$	156(4)	160(5)	160(2)	160(1)	160(4)		160(7)
$[NHR']^+$	126(2)	92(100)	106(100)	122(100)	126(26)	164(18)	134(2)
$[NHR' + H]^{\dagger}$	127(100)	93(52)	107(51)	123(16)	127(100)	165(44)	135(51)
$[R]^+$	107(9)	111(12)	111(7)	111(9)	111(22)	111(19)	111(63)
$[R + H]^{\dagger}$		112(4)	112(2)	112(1)	112(5)	112(2)	112(14)
$[R']^+$		77(4)	91(2)	107(1)	111(22)		
$[M - SO]^{\dagger}$		203(3)					
$[RS]^+$	139(87)	143(7)	143(11)	143(5)	143(31)	143(8)	143(64)
$['M']^{\dagger}$		251(11)	265(6)				
$[RSO_2SR]^{\dagger}$	310(35)		318(6)		318(15)		318(28)
$[RSSR]^{\dagger}$	278(41)		286(4)		286(12)	286(3)	286(8)
$[M + O]^{\dagger}$	297(11)	267(1)			301(4)	339(5)	
$[M - O]^{\dagger}$	265(2)	235(6)	249(4)		269(7)	307(10)	277(2)

[a] $[NH_2C_6H_4CO]^{\dagger}$ was the most abundant ion.

EXPERIMENTAL

Preparation of materials

All sulfinamides were synthesized and purified according to the method reported previously.[1] Compounds **1**, **2**, **14** and **15** have not been reported previously.

N-*Butylethanesulfinamide* (**1**). Yellow oil, b.p. 80–85 °C (bath temperature)(0·005–0·01 mmHg). (Found: C, 47·86; H, 10·34; N, 9·26. $C_6H_{15}ONS$ requires C, 48·28; H, 10·13; N, 9·39).

N-*Cyclohexylethanesulfinamide* (**2**). Yellow oil, b.p. 60–70 °C (bath temperature) (0·005–0·01 mmHg). (Found: C, 54·38; H, 9·44; N, 7·93. $C_8H_{17}ONS$ requires C, 54·81; H, 9·78; N, 7·99).

N-*Butyl*-p-*toluenesulfinamide* (**14**). Yellow oil, b.p. 125–127 °C (bath temperature) (0·005–0·01 mmHg). (Found: C, 62·33; H, 8·13; N, 6.17. $C_{11}H_{17}ONS$ requires C, 62·52; H, 8·11; N, 6·63).

N-*Cyclohexyl*-p-*toluenesulfinamide* (**15**). Colourless plates, m.p. 70·5 °C (ex petroleum ether). (Found: C, 65·28; H, 7·96; N, 5·87. $C_{13}H_{19}ONS$ requires C, 65·79; H, 8·08; N, 5·91).

Mass spectral determination

The spectra were recorded with a JEOL JMS-01SG mass spectrometer at 20 and 75 eV, an acceleration voltage of 62 kV and a 100 μa emission current. Samples were introduced into the ionization chamber through an all-glass direct inlet system. The high resolution mass measurements were carried out using perfluorokerosene as the standard.

Identification of the thermal decomposition products

General. Unless otherwise specified in all cases the products were identified by comparison of their retention times (figures in parentheses in minutes) and their u.v. spectra. All melting points are uncorrected.

By h.l.c. A few mg of sample **4** or **16** were taken in a glass tube (diameter 0·4 cm, length about 10 cm) and the tube was evacuated to a pressure of a few mmHg. The sealed tube was heated in an oil bath at 150 °C for 5 min. The reaction products of **4** were dissolved in methanol and the solution was subjected to the separation by h.l.c. The reaction products of **16** had an intense bluish violet colour, and were dissolved in ethanol and decolourized with activated charcoal. The decolourized solution was evaporated *in vacuo* at room temperature and the residue was dissolved in methanol. The activated charcoal used was dried at room temperature and was extracted with diethyl ether. The solvent was removed *in vacuo* and the residue was dissolved in methanol. Both solutions were separated by h.l.c.

The thermal decomposition reactions and the separations by h.l.c. of the decomposition products of **6**, **14** and **19** were performed by the same procedure as used for **4** and **16**.

The h.l.c. was recorded by an Hitachi Liquid Chromatograph 635 equipped with both a u.v. monitor and a single beam spectrophotometer, Union 303 Spectrophotometer. The operating conditions were as follows. Column: Hitachi gel #3011, 0·21 × 100 cm; Solvent: methanol; Flow rate: 0·9 ml min^{-1}; Temperature: room temperature; Detector: u.v. monitor; Chart speed: 5 mm min^{-1}. The u.v. spectra of all fractions were recorded by repeated scanning every 5 s over the wavelength range of 210–310 nm.

The h.l.c. of the decomposition products of **4** showed six major peaks. The following compounds were identified: $C_6H_5SO_2NH_2$ (4·1); **4** (4·5); $C_6H_5SO_2SC_6H_5$ (10·7) and $C_6H_5SSC_6H_5$ (31·0), respectively. The other two compounds (3·7 and 6·4) and a few minor products could not be identified.

The h.l.c. of the decolourized solution of the decomposition products of **16** consisted of six major peaks. The h.l.c. of the activated charcoal extract showed one more peak (54·0). The products were identified as aniline (4·4), **16** (6·4); *p,p′*-$CH_3C_6H_4SC_6H_4NH_2$ (13·0), *p,p′*-$CH_3C_6H_4SO_2SC_6H_4CH_3$ (15·0) and *p,p′*-$CH_3C_6H_4SSC_6H_4CH_3$ (54·0). The u.v. spectra of the first and the last eluent fractions for the peak having a retention time of 5·4 min were quite different. The corresponding two compounds were shown to be *p,p′*-$CH_3C_6H_4SOC_6H_4NH_2$ and *p,p′*-$CH_3C_6H_4SO_2C_6H_4NH_2$, respectively. The other major product (7·4) and a few minor products could not be identified.

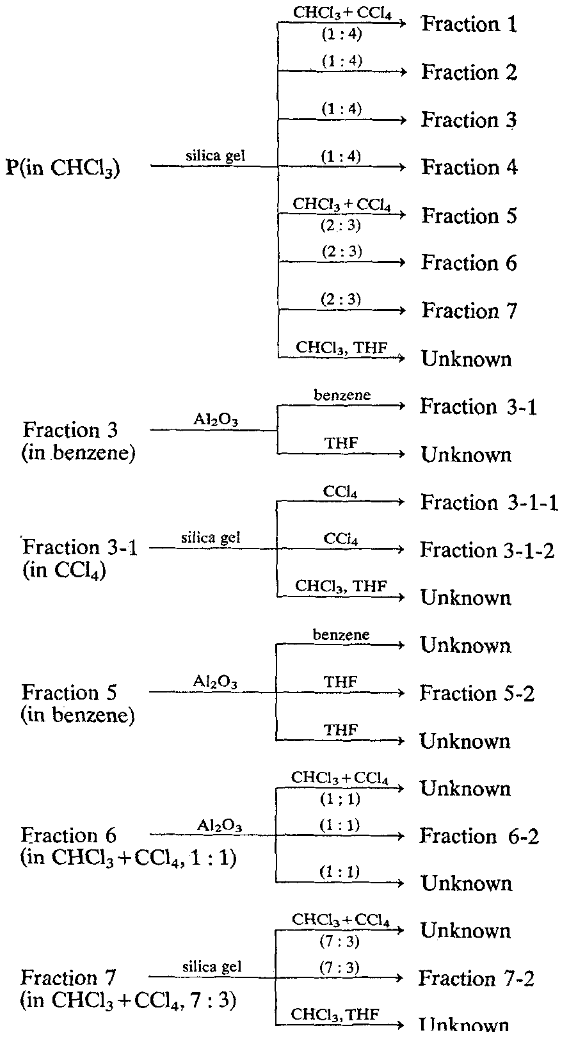
The h.l.c. of the decolourized solution of the decomposition products of **6** consisted of four major peaks. The h.l.c. of the activated charcoal extract had one more peak (31·0). The following compounds were identified: aniline (4·7); **6** (6·3) and $C_6H_5SO_2SC_6H_5$ (31·0). *p*-$C_6H_5SOC_6H_4NH_2$ (5·0) was identified by the coincidence of the wavelength of its u.v. absorption maximum with that of the known value.[2] The u.v. spectra of the initial fraction and the last fraction of the elution of the peak having the retention time of 10·5 min were quite different. The first fraction contained $C_6H_5SO_2SC_6H_5$ and the last fraction contained *p*-$C_6H_5SC_6H_4NH_2$, this being identified by the coincidence of the wavelength of the u.v. absorption maximum with that of the known value.[2] The few minor peaks could not be identified.

The h.l.c. of the decomposition products of **14** showed three major peaks. The compounds were **14** (5·7), *p,p′*-$CH_3C_6H_4SO_2SC_6H_4CH_3$ (14·5) and *p,p′*-$CH_3C_6H_4SSC_6H_4CH_3$ (54·0). The few minor peaks could not be identified.

The h.l.c. of the decolourized solution of the decomposition products of **19** consisted of four major peaks. The h.l.c. of the activated charcoal extract had one more peak (54·0). The compounds were identified to be *p*-chloroaniline (5·0), *p,p′*-$CH_3C_6H_4SO_2SC_6H_4CH_3$ (15·0) and *p,p′*-$CH_3C_6H_4SSC_6H_4CH_3$ (54·0). *p,p′*-$CH_3C_6H_4SO_2NHC_6H_4Cl$ (6·5) was identified by the coincidence of the wavelength of the u.v. absorption maximum with that of the known value.[3] The major peak (9·0) and a few minor peaks could not be identified.

By l.c. Decomposition of **4**. 300 mg of **4** were taken in a glass tube (diameter 0·4 cm, length about 10 cm) and the tube was evacuated to be the pressure of a few mmHg. The sealed tube was then heated in an oil bath at 150 °C for 3 min. Ammonia was identified by inserting a piece of filter paper impregnated with the Nessler reagent immediately after the opening of the tube.

CCl_4 was added to the decomposition products. The filtrate precipitated fairly quickly a small amount of colourless material. This substance was identified by h.l.c. to be a mixture of **4** and $C_6H_5SO_2NH_2$. In another experiment benzene was added to the decomposition products. The benzene insoluble part afforded colourless leaflets m.p. 160 °C after recrystallization from water. The melting points, the i.r. and u.v. spectra of this substance coincided with those of $C_6H_5SO_2NH_2$. The CCl_4 soluble part was separated by the column chromatography using silica gel as the adsorbent. The residue left by the evaporation of the first CCl_4 eluate was recrystallized from ethanol to afford colourless needles m.p. 60·5–62 °C. The recrystallization of the residue left by the evaporation of the second eluate from petroleum ether afforded colourless prisms m.p. 45 °C. These two substances were identified to be $C_6H_5SSC_6H_5$ and $C_6H_5SO_2SC_6H_5$ by the same method. The CCl_4 insoluble part was a solid substance at first, but changed into a mixture of a solid and an oily substance by treatment with organic solvents. It was not possible to isolate any pure compound which must be



present in this fraction at first, but instead $C_6H_5SO_3^-NH_4^+$ was isolated. Because this compound did not exist in the thermal decomposition products of **4**, it must be produced from an unknown decomposition product by the chemical treatment.

Decomposition of **16**. 700 mg of **16** were taken in a sealed evacuated glass tube of a similar size to that used for the decomposition of **4**. The tube was then heated in an oil bath at 150 °C for 30 min. After the reaction the i.r. spectrum of the yellowish oil on the inside wall of the upper part of the tube was identical with that of aniline. The dark blue viscous reaction products (P) were subjected to the separation by the repeated column chromatography as shown in the scheme on page 1035.

After recrystallization the crystals obtained were identified by the comparison of their melting points, the i.r. and the u.v. spectra with those of the authentic samples. The solvent used for the recrystallization, the appearance, the melting point and the chemical structure of each decomposition product are given in Table 6, the compounds being listed in order of their elution.

TABLE 6. DECOMPOSITION PRODUCTS OF **16** ($RSONHC_6H_5$, $R = p\text{-}CH_3C_6H_4$)

Fraction number	Appearance	m.p.(°C)	Solvent	Chemical structure
1	Colourless prisms	46–7	Ethanol	RSSR
2	Colourless prisms	78	Petroleum ether	RSO_2SR
3–1–1	Colourless prisms	86–7	Petroleum ether+ ether	$RSNHC_6H_5$
3–1–2	Colourless prisms	74–5	Ligroin	$RSC_6H_4NH_2$
4	Yellowish oil			$C_6H_5NH_2$
5–2	Colourless prisms	104–6	Ethanol	$RSO_2NHC_6H_5$
6–2	Colourless needles	189–193	Ethanol	$RSO_2C_6H_4NH_2$
7–2	Colourless prisms	170–2·5	Benzene	$RSOC_6H_4NH_2$

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REFERENCES

1. K. Mori and Y. Ueda, *Yakugaku Zasshi* **91**, 940 (1971).
2. H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.
3. A. E. Lutskii, Z. A. Tret'yak and S. I. Burmistrov, *Zh. Obshch. Khim.* **35**, 2090 (1965).