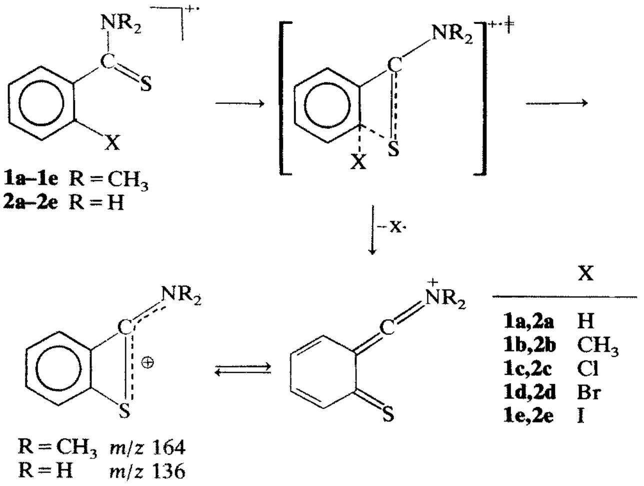
The Loss of *ortho* Halogeno Substituents From Substituted Thiobenzamide Ions†

Hans-Fr. Grützmacher
Fakultät für Chemie, Universität Bielefeld, Universitätsstraße, D-4800 Bielefeld 1, Germany

The loss of *ortho* substituents (CH_3, Cl, Br, I) from molecular ions of substituted thiobenzamides has been investigated by determination of the critical energy and kinetic energy released during this process to obtain some further insight into the corresponding reaction of *N,N*-dimethylthiobenzamide ions. In contrast to the latter compounds the *ortho* methyl substituent is not eliminated from the molecular ions of *o*-methylthiobenzamide, but the loss of *ortho* halogeno substituents occurs with identical reaction characteristics in both series of compounds. It is concluded that the loss of halogeno substituents from molecular ions in both series corresponds to a direct substitution reaction via a 4-membered transition state.

Recently it has been shown that the loss of *ortho* substituents from the molecular ions of *N,N*-dimethylthiobenzamides **1a–1e** by intramolecular, aromatic substitution occurs via two mechanisms, depending on the substituent.[2] In analogy to the corresponding *N,N*-dimethylbenzamides[3] a H-atom and a methyl group, respectively, are lost from the *ortho* position of **1a** and **1b** in a multistep reaction initiated by a H-migration from the *N*-methyl group to the S-atom. The second mechanism, which produces an isomeric $[M-X]^+$ ion, is observed for the loss of Cl, Br and I from **1c**, **1d** and **1e**, respectively. Although the structure of this second type of $[M-X]^+$ ions has not been established directly by comparison with reference ions of known structure, the data for the activation energy $\varepsilon_f^{\neq}$ and the kinetic energy release T for this process[2] are in accord with a direct displacement of these halogeno substituents via a 4-membered transition state, and it has been suggested that the substitution occurs by the sulfur atom of the thioamide group (Scheme 1, R = CH_3). In this case a similar loss of *ortho* halogeno substituents is also expected for the thiobenzamides **2c–2e** (Scheme 1, R = H).



Scheme 1

Table 1. Partial mass spectra[a] of substituted thiobenzamides 2a–2e

m/z	**2a**	**2b**	**2c**	**2d**	**2e**
$[M]^{+\cdot}$	100	64	119[b]	48[b]	31
$[M-H]^+$	(M−X)	100	6	1	1
$[M-X]^+$	13	<1	100	100	100
$[M-NH_2]^+$	33	6[c]	24	4	1
$[M-SH]^+$	60	45	30	5	1
120	1	—	3	5	4
119	—	7	1	—	—
118	—	(M−SH)	—	—	—
117	—	80	—	—	—
116	—	34	—	—	—
111	1	—	4	1	2
110	3	—	1	1	3
109	7	—	11	17	33
108	1	1	4	3	4
104	(M−SH)	3	1	3	4
103	9	—	5	10	19
102	2	1	24	17	17
93	3	1	2	1	3
92	1	5	—	—	1
91	—	30	1	1	2
90	—	28	1	—	1
89	—	21	—	—	—

[a] % base peak; only peaks >1% are given. With the exception of *m/z* 60 ($^{\oplus}CSNH_2$) and *m/z* 45 ($^{\oplus}CHS$) only fragments of the phenyl group are seen in the lower mass range.
[b] Sum of isotope peaks ($^{35}Cl + ^{37}Cl$) and ($^{79}Br + ^{81}Br$), respectively.
[c] $[M-NH_3] = 14\%$.

The partial 70 eV mass spectra of thiobenzamide **2a** and the *ortho* substituted derivatives **2b–2e** are given in Table 1. These spectra show clearly the expected tendency for the formation of $[M-X]^+$ ions *m/z* 136 in the case of the halogeno derivatives. The mass spectrum of thiobenzamide **2a** has been published previously,[4] and it is known from labelling experiments that most of the H-atoms eliminated during the formation of *m/z* 136 ions originate from the amino group and only some of them are lost from the phenyl group. The main fragmentation pathways of **2a** in the

---

† See Ref. 1.

CCC-0030-493X/81/0016-0448$01.50

70 eV mass spectrum correspond to the elimination of a SH and a NH_2 radical, respectively. Metastable **2a** ions decompose mainly by loss of H and ˙SH, besides elimination of $NH_2^{\cdot}$, HCN and H_2CN, the two former processes giving rise to rather broad and flat-topped signals.

The increase in the intensity of the $[M-X]^+$ ions m/z 136, and the corresponding decrease in the intensities of the molecular ions, $[M-NH_2]^+$ ions and $[M-SH]^+$ ions in the series of the *ortho* halogeno substituted derivatives **2c–2e** clearly reflect the ease of substituent loss from these compounds. This is also seen from the metastable ion (MI) spectra of the corresponding molecular ions, which contain only one signal for loss of the halogen atom. This parallels the mass spectrometric behaviour of the *N,N*-dimethyl derivatives **1c–1e**[2] and shows that the *N*-methyl groups are not essential for this substitution reaction. As expected and in contrast to the fragmentation of **1b**, an abundant elimination of the *ortho* methyl substituent from **2b** is neither observed in the 70 eV mass spectrum, nor does it occur with metastable **2b** ions. Hence, compound **2b** has been omitted from further investigations.

Table 2. MI spectra and CA spectra of *m/z* 136 ions (M−X) from 2a, 2c–2e

	m/z	2a	2c	2d	2e
MI	109	100	100	100	100
	92	5	(+)	—	—
	77	2	2	3	3
CA	135	(285)	91	100	121
	134	78	39	39	42
	120	—	3	3	4
	119	8	2	2	2
	117	—	1	1	1
	109	(564)	(325)	(351)	(313)
	108	99	40	42	42
	103	71	59	60	58
	102	100	100	100	100
	92	(23)	(7)	+	+
	91	33	23	22	22
	84	+	5	5	5
	82	21	9	10	10
	77	(36)	(34)	(35)	(35)
	76	21	23	24	23
	75	20	21	22	21
	69	39	25	27	25
	65	31	23	25	23
	63	14	10	11	10
	60	—	9	9	8
	58	7	4	4	4
	57	4	2	3	2
	51	12	11	11	11
	50	10	9	10	8
	45	9	4	4	5
	39	10	4	4	4
	28	4	1	1	1

Table 3. Ionization energies (*I*(M)) and appearance energies (*A*(ion)) for thiobenzamides 2a, 2c–2e in eV

	2a	2c	2d	2e
I(M)	8.8	8.8	8.5	8.5
$A(M-NH_2)$	12.2	12.1	12.2	—
$A(M-X)$	11.8	10.4	9.6	9.3
$\varepsilon_f^{\neq}(M-X)$	3.0	1.6	1.1	0.8

The MI and collisional activation (CA) spectra of the $[M-X]^+$ ions, m/z 136, are shown in Table 2. The m/z 136 ions from **2c–2e** are certainly identical in structure, while m/z 136 ions from **2a** give somewhat different spectra. The MI spectrum of these latter ions contains a distinct peak for product ions m/z 92 (m/z 136 − CS), which is hardly visible in the MI spectrum of m/z 136 ions from **2c** and absent in those of **2d** and **2e**. The CA spectrum of m/z 136 ions from **2a** is distinguished from the other spectra mainly by intensity differences of the product ions. Considering also the labelling experiments[4] it is difficult to decide whether the m/z 136 ions from **2a** represent a single structure or a mixture of structures. In the latter case some of them may be of the same structure as the m/z 136 ions from **2c–2e**. Table 3 gives the ionization energies I(M) and the appearance energies $A(M-NH_2)$ and $A(M-X)$ of the $[M-NH_2]^+$ and $[M-X]^+$ ions, respectively, together with other thermochemical data. $A(M-X)$ clearly depends on the dissociation energy of the C−X bond, as observed for the corresponding fragment ions of **1c–1e**.[2] Moreover, the critical energy $\varepsilon_f^{\neq}$ for the loss of *ortho* halogeno substituents from **2c–2e**, evaluated from $A(M-X)-I(M)$, is in all cases 0.1–0.2 eV smaller than $\varepsilon_f^{\neq}$ for the same process of **1c–1e**. Therefore, the loss of halogeno substituents from the molecular ions of both series of compounds very probably occurs by the same mechanism. This is further corroborated by an analysis of the kinetic energy T released during these reactions (Table 4) and of the corresponding peak shapes. Only in the case of **2a** ions, which lose a H-atom in a different reaction,[4] is a flat-topped signal observed. The loss of Cl and Br from **2c** and **2d**, respectively, gives rise to Gaussian shaped peaks in the mass analysed ion kinetic energy (MIKE) spectra according to the test suggested by Holmes and Terlouw.[5] This has also been observed for the loss of Cl and Br from **1c** and **1d** ions.[2] The MIKE spectrum of **2e** ions contains a broad triangular peak for the loss of I, indicating a rather large amount of kinetic energy released during this reaction (Table 4). The peak shows a small inflection at its sides and the peak shape test clearly reveals its composite nature. Again this is in perfect agreement with the loss of I from **1e** ions.[2] However, it is not quite clear why a composite peak is observed for the loss of I from metastable **2e** ions (and **1e** ions). Since the CA spectra show that the same product ion m/z 136 is formed as in the case of the chloro and

Table 4. Kinetic energy released (*T*, meV) and metastable peak shapes[a] for loss of *ortho* substituents from 2a, 2c–2e

	2a	2c	2d	2e
$T_{0.8}$	85 (0.62)	9 (0.53)	11 (0.49)	42 (0.52)
$T_{0.5}$	230 (1.00)	31 (1.00)	46 (1.00)	158 (1.00)
$T_{0.2}$	372 (1.32)	83 (1.64)	130 (1.69)	297 (1.34)
$T_{0.1}$	484 (1.49)	128 (2.03)	186 (2.01)	364 (1.52)
T_B	495 —	97 —	157 —	400 —

[a] Relative peak width given in parentheses.

bromo derivatives, there are either two reacting configurations (different excited states?) of the molecular ions of the iodo compounds for this reaction or the neutral reaction product I is formed in two different electronic states.[11] The following conclusions can be drawn from a comparison of the mass spectrometric reactions of the *N*,*N*-dimethylthiobenzamides **1a**–**1e** and thiobenzamides **2a**–**2e**: (i) abundant loss of a H-atom and a methyl group from the *ortho* position of the phenyl group is observed only in the mass spectra of the *N*,*N*-dimethyl derivatives **1a** and **1b**, respectively, as expected from the mechanism of this reaction.[2] The loss of H from **2a** involves mainly the hydrogen atoms of the NH_2 group and is probably due to another type of reaction.[4] The *ortho* CH_3 group of **2b** is eliminated only to a very small extent, if at all. (*ii*) With respect to the loss of Cl, Br and I substituents from molecular ions, both series of compounds exhibit the same dependence on bond dissociation energies for $[M-X]^+$ ion intensities, critical energies $\varepsilon_f^{\neq}$ and kinetic energy T released with identical peak shapes. Furthermore, the magnitudes of $\varepsilon_f^{\neq}$ and T are very similar in both series. This strongly indicates the same mechanism for these reactions without much influence of the *N*-methyl groups present in **1c**–**1e**. (iii) In both series of compounds the loss of *ortho* halogeno substituents and the characteristics of this reaction are most easily explained by a direct substitution reaction via a 4-membered transition state as depicted in Scheme 1. However, there are only *indirect* arguments available for a displacement of the halogeno substituents by the S-atom of the thioamide group. The MI spectra of m/z 136 ions from **2c**–**2e** show that HCN is easily eliminated while sulfur-containing fragments are lost only by high energy processes in the CA spectra. This is in accord with the proposed transfer of the sulfur atom to the *ortho* position. The molecular ions of thioformanilide, which is isomeric to **2a** and some of its *ortho* substituted derivatives, but not of formanilide, fragment abundantly by attack of the S-atom of their thioamide group on the *ortho* position of the phenyl group.[6] This shows clearly that an intramolecular aromatic substitution in molecular ions by a S-atom occurs quite easily and is favoured compared with a substitution by N- or O-atoms. Therefore the mass spectra of the *ortho* halogeno benzamides contain only comparatively small peaks due to the loss of the substituents.

EXPERIMENTAL

The *thiobenzamides* **2a**–**2e** were prepared from the corresponding benzonitriles by addition of H_2S in pyridine by standard procedures and crystallized from benzene/petroleum ether. The *mass spectra* of **2a**–**2e** were measured with a Varian MAT 311A mass spectrometer, electron energy 70 eV, emitted current 3 mA, accelerating voltage 3 kV, ion source temperature 150 °C, sample introduction via the direct inlet system, mass resolution *c.* 1000.

The *MI and CA spectra* were obtained with a VG ZAB-2F mass spectrometer (electron energy 70 eV, trap current 200 μA, acceleration voltage 6 kV, ion source temperature *c.* 180 °C, sample introduction via direct inlet system), from decomposition of the selected ions in the second field free region between the magnet and the electrostatic analyser. For collision induced decomposition He was introduced into the gas cell within the region at such a rate that the intensity of the main beam was reduced to *c.* 30% of its original intensity.

The *kinetic energy release* was measured with the same instrument under identical conditions and calculated from the width of the appropriate peaks in the MIKE spectra in the usual manner.[7] The values given in Table 4 are the mean values of at least three independent measurements.

The *ionization energies* and *appearance energies* of the relevant ions were obtained with a VG MM 12B-mass spectrometer modified as described previously,[8] using the semilog plot method[9] and $CH_3I(I(M) = 9.5\ eV^{10})$ as a reference introduced with the sample. Operation conditions: trap current 20 μA, acceleration voltage 4 kV, ion source temperature *c.* 200 °C, mass resolution *c.* 600. The mean values of two independent measurements are reported in Table 3. The reproducibility ±0.1 eV.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. Mechanisms of mass spectrometric fragmentation reactions—XXXII. For Part XXXI, see B. Schaldach, B. Grotemeyer, J. Grotemeyer and H. F. Grützmacher, *Org. Mass Spectrom.* submitted for publication.
2. D. V. Ramana and H. F. Grützmacher, *Org. Mass Spectrom.* **16**, 227 (1981).
3. C. W. Fong and C. R. Hameister, *Org. Mass Spectrom.* **13**, 711 (1978).
4. J. L. Holmes and F. Benoit, *Org. Mass Spectrom.* **5**, 525 (1971).
5. J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **15**, 383 (1980).
6. (a) W. Walter, R. F. Becker and H. F. Grützmacher, *Tetrahedron Lett.* 3515; (1968). (b) H. F. Grützmacher and H. Kuschel, *Org. Mass Spectrom.* **3**, 605 (1970).
7. M. A. Baldwin, P. J. Derrick and R. P. Morgan, *Org. Mass Spectrom.* **11**, 440 (1976).
8. B. Schaldach and H. F. Grützmacher, *Int. J. Mass Spectrom. Ion Phys.* **31**, 257 (1979).
9. F. P. Lossing, A. N. Tickner and W. A. Bryce, *J. Chem. Phys.* **19**, 1254 (1951).
10. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data* **6**, Suppl. No. 1 (1977).
11. The formation of excited I atoms from the dissociation of $[C_2H_5I]^+$ ions has also been suggested by T. Baer, U. Büchler and C. E. Klots, *J. Chim. Phys.* **77**, 739 (1980), from an analysis of the kinetic energy release distribution.

Received 24 April 1981; accepted 22 June 1981