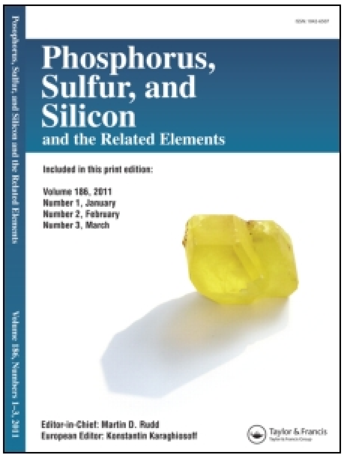

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THE MASS SPECTRA OF SOME SUBSTITUTED THIOPHENE-2-CARBOXYLIC ACIDS

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THE MASS SPECTRA OF SOME SUBSTITUTED THIOPHENE-2-CARBOXYLIC ACIDS

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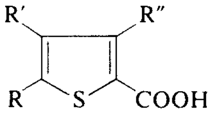
The mass spectra of some 3-, 4-, and 5-substituted thiophene-2-carboxylic acids at 70 eV are reported. The majority of isomeric 5- and 3-substituted compounds can be differentiated by mass spectrometry. In 3-methyl-, 3-methoxy, 3-thiomethyl-, 3-methylsulphinyl-, 3-formyl-thiophene-2-carboxylic acids the fragmentation is influenced by an "ortho-effect" which activates the H_2O elimination.

We recently studied the electron impact mass spectra of some 5- and 3-substituted thiophene-2-carboxamides[1] and some substituted thiophene-2-[2] and 3-carboxanilides.[3] The mass spectra of aromatic carboxylic acids have been widely discussed[4–15] but few investigations on thiophene carboxylic acids have been reported.[16] Here we report the electron impact mass spectra at 70 eV of some 3-, 4- and 5-substituted thiophene-2-carboxylic acids I



I

	R	R′	R″
1	H	H	H
2	H	H	CH_3
3	H	CH_3	H
4	CH_3	H	H
5	H	H	CH_3O
6	CH_3O	H	H
7	H	H	CH_3S
8	CH_3S	H	H
9	H	H	CH_3SO_2
10	CH_3SO_2	H	H
11	H	H	CH_3SO
12	H	H	CHO
13	C_2H_5	H	H
14	NO_2	H	H
15	H	H	F
16	H	H	Br
17	H	Br	H
18	Br	H	H
19	H	H	I

in order to study the effect of the substituent in 3-, 4- and 5-positions in the thiophene ring on the fragmentation.

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TABLE I

Mass spectra at 70 eV of substituted thiophene-2-carboxylic acids (% Relative intensity).

No	$[M]^{+\cdot}$	$[M-OH]^{+a}$	$[a\text{-}CO]^{+}$	$[M-H_2O]^{+\cdot}$	Other peaks													
1	128 (58)	111 (100)	83 (50)	—	100 (7)	82 (11)	81 (12)	71 (4)	69 (4)	58 (7)	57 (15)	56 (3)	49 (5)	45 (34)	39 (45)	38 (15)	37 (12)	36 (4)
2	142 (100)	125 (51)	97 (76)	124 (37)	141 (11)	99 (3)	98 (6)	96 (27)	85 (4)	71 (4)	70 (8)	69 (13)	62 (6)	58 (3)	57 (3)	53 (21)	51 (6)	50 (4)
					45 (28)	39 (8)	38 (3)	37 (3)										
3	142 (100)	125 (70)	97 (80)	—	141 (35)	113 (3)	96 (6)	95 (3)	82 (3)	71 (5)	70 (40)	69 (11)	63 (3)	58 (3)	57 (6)	53 (23)	51 (6)	50 (5)
					45 (18)	40 (4)	39 (9)	38 (4)										
4	142 (74)	125 (70)	97 (100)	—	*141* (22)	*115* (3)	*113* (7)	96 (7)	95 (6)	93 (4)	82 (3)	71 (7)	70 (7)	69 (16)	63 (3)	62 (4)	61 (3)	59 (8)
					58 (6)	57 (8)	53 (38)	51 (8)	50 (6)	45 (33)								
5	158 (100)	141 (26)	113 (9)	140 (4)	143 (5)	139 (13)	129 (30)	127 (4)	126 (15)	112 (11)	111 (50)	99 (3)	98 (3)	89 (3)	87 (9)	85 (19)	84 (4)	83 (3)
					81 (3)	72 (5)	71 (3)	70 (8)	69 (9)	59 (8)	58 (5)	57 (3)	55 (3)	53 (5)	45 (35)	39 (6)	38 (4)	37 (3)
6	158 (75)	141 (9)	—	—	143 (13)	126 (3)	115 (100)	114 (18)	99 (35)	98 (20)	89 (3)	87 (38)	82 (4)	81 (4)	71 (24)	70 (26)	69 (33)	68 (4)
					59 (9)	58 (3)	57 (8)	55 (19)	53 (7)	45 (41)	44 (26)	39 (11)	38 (10)	37 (7)				
7	174 (100)	157 (8)	129 (4)	156 (9)	159 (9)	141 (72)	128 (10)	127 (15)	111 (10)	88 (5)	85 (8)	84 (5)	71 (10)	70 (4)	69 (11)	45 (22)	39 (4)	38 (3)
8	174 (100)	157 (16)	129 (3)	—	159 (34)	131 (39)	130 (7)	115 (16)	114 (25)	103 (20)	97 (3)	88 (4)	85 (11)	82 (7)	81 (6)	71 (23)	70 (14)	69 (27)
					59 (3)	58 (4)	57 (9)	53 (3)	45 (27)	39 (8)	38 (7)	37 (4)						
9	206 (100)	189 (5)	—	—	175 (6)	174 (4)	143 (46)	141 (3)	127 (38)	115 (6)	110 (3)	99 (8)	85 (3)	83 (9)	82 (20)	81 (12)	77 (6)	71 (4)
					70 (3)	69 (9)	64 (4)	63 (3)	57 (3)	53 (3)	50 (3)	45 (21)	39 (32)	38 (7)	37 (3)			
10	206 (60)	189 (3)	—	—	191 (53)	175 (4)	162 (8)	147 (9)	143 (17)	127 (8)	*115* (100)	*111* (4)	110 (3)	99 (14)	98 (7)	87 (24)	85 (10)	84 (5)

					83 (9) 82 (26) 81 (19) 79 (3) 71 (17) 70 (11) 69 (26) 65 (3) 64 (4) 63 (10) 59 (6) 58 (4) 57 (18) 55 (8) 53 (9) 50 (4) 45 (41) 39 (21) 38 (6)
11	190 (86)	173 (3)	145 (3)	172 (4)	189 (3) 175 (100) 174 (12) 159 (3) 158 (6) 147 (4) 144 (25) 143 (8) 142 (4) 141 (10) 131 (26) 129 (5) 128 (7) 127 (17) 126 (20) 124 (5) 111 (7) 110 (9) 104 (5) 99 (5) 97 (4) 87 (20) 85 (6) 84 (5) 83 (4) 82 (12) 81 (10) 77 (4) 76 (4) 71 (5) 70 (4) 69 (10) 64 (5) 63 (3) 59 (6) 58 (5) 57 (4) 45 (47) 39 (14) 38 (7) 36 (5)
12	156 (62)	139 (6)	111 (100)	138 (3)	155 (7) 128 (72) 110 (11) 84 (8) 83 (12) 82 (9) 81 (7) 77 (3) 69 (8) 58 (5) 57 (6) 55 (4) 53 (3) 50 (3) 45 (22) 39 (30) 38 (6) 37 (5) 29 (4)
13	156 (50)	139 (5)	111 (15)	—	155 (4) 141 (100) 113 (11) 97 (6) 96 (3) 95 (3) 85 (3) 77 (4) 69 (3) 67 (3) 65 (3) 53 (3) 45 (7) 39 (4)
14	173 (100)	156 (4)	—	—	143 (4) 115 (33) 112 (3) 110 (6) 99 (5) 98 (4) 97 (3) 96 (3) 87 (19) 85 (4) 84 (3) 83 (4) 82 (15) 81 (13) 71 (9) 70 (6) 69 (14) 59 (3) 57 (11) 55 (5) 53 (6) 45 (21) 39 (34) 38 (11) 37 (6) 30 (10)
15	146 (90)	129 (100)	101 (11)	—	102 (6) 82 (3) 81 (3) 75 (5) 69 (7) 57 (28) 45 (8)
16	208 (100) 206 (97)	191 (75) 189 (71)	163 (4) 161 (4)	—	137 (3) 135 (3) 119 (5) 117 (5) 83 (5) 82 (21) 81 (9) 50 (3) 45 (25) 39 (9) 38 (7) 37 (6)
17	208 (100) 206 (97)	191 (73) 189 (69)	163 (3) 161 (3)	—	137 (4) 135 (4) 119 (3) 117 (3) 83 (6) 82 (15) 81 (6) 50 (4) 45 (18) 39 (10) 38 (8) 37 (5)
18	208 (100) 206 (97)	191 (87) 189 (85)	163 (7) 161 (7)	—	193 (3) 119 (8) 117 (8) 83 (15) 82 (70) 81 (40) 80 (3) 69 (12) 58 (7) 57 (35) 53 (9) 50 (5) 45 (40) 44 (15) 39 (55) 38 (46) 37 (38)
19	254 (100)	237 (63)	209 (6)	—	183 (3) 165 (6) 164 (11) 128 (3) 110 (7) 84 (4) 83 (6) 82 (20) 81 (12) 71 (3) 69 (3) 57 (4) 55 (6) 45 (22) 39 (18) 38 (10) 37 (8)

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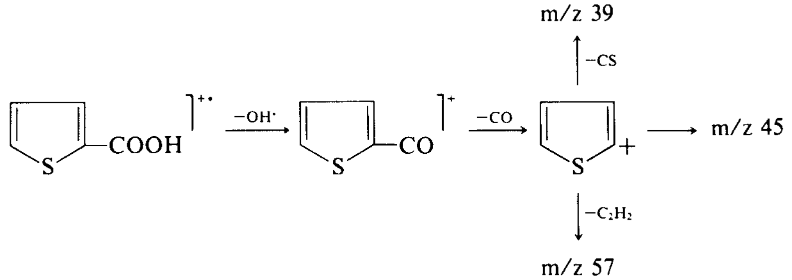
[a] $[M-OH]^+ = a$

RESULTS AND DISCUSSION

The mass spectra of the compounds I at 70 eV are listed in the table. The fragmentation processes discussed are supported by labelling experiments; transitions substantiated by an appropriate metastable peak (directly observed in the 70 eV mass spectrum) are indicated by an asterisk. The molecular ions are very intense, always greater than 50%, forming the base peak in many cases.

Thiophene-2-carboxylic acid[16] (compound no. 1) shows as primary main degradation reaction the loss of OH, confirmed by labelling experiments, followed by CO elimination (Scheme 1).



SCHEME 1

The fragmentation of 3-, 4- and 5-methyl-thiophene-2-carboxylic acids (compounds no. 2, 3 and 4) starts with the loss of the OH$^\bullet$ radical, followed by CO elimination to give an intense ion at m/z 97 characteristic for alkylthiophenes.[16–21] These compounds give intense $[M—H]^+$ peaks and the $[M—CH_3]^+$ peaks are absent, whereas the corresponding benzene derivatives do not show significant $[M—H]^+$ peaks and show relatively unimportant $[M—CH_3]^+$ peaks.[7] 3-Methyl-thiophene-2-carboxylic acid gives an intense $[M—H_2O]^{+\bullet}$ peak (rel. int. 37%) which is also observed at 15 eV; this transition is supported by the corresponding metastable peak. The expulsion of H_2O from the molecular ion is attributed to the *ortho*-interaction of the methyl group with the carboxylic function, this occurring between the OH of the carboxylic group and the H atom from the nearby methyl group. This transition involves a six-membered state and has been used to explain the formation of $[M—H_2O]^{+\bullet}$ peaks in the mass spectra of o-hydroxybenzylalcohol,[22] o-hydroxybenzoic acid,[12] anthranilic acid[23] and o-mercaptobenzoic acid.[14] The $[M—H_2O]^{+\bullet}$ peak is absent in 4- and 5-methyl derivatives and thus 3-methyl-thiophene-2-carboxylic acid can be distinguished from 4- and 5-isomers by mass spectrometry. 4- and 5-Methyl-thiophene-2-carboxylic acids also show loss of the carboxylic group in one step, this elimination being supported by the corresponding metastable peak.

The plots of relative intensity against nominal ionization energy of the more important primary fragmentation processes indicate that the loss of OH is the more energetically favorable decomposition process in 3-, 4- and 5-methyl-thiophene-2-carboxylic acids (Figure 1).

The mass spectrum of 3-methoxy-thiophene-2-carboxylic acid (compound no. 5) shows intense $[M—OH]^+$, $[M—CHO]^+$ and $[M—CHO—H_2O]^+$ peaks. The $[M—CHO]^+$ peak is due to the migration of an hydrogen atom from the methoxy group to the

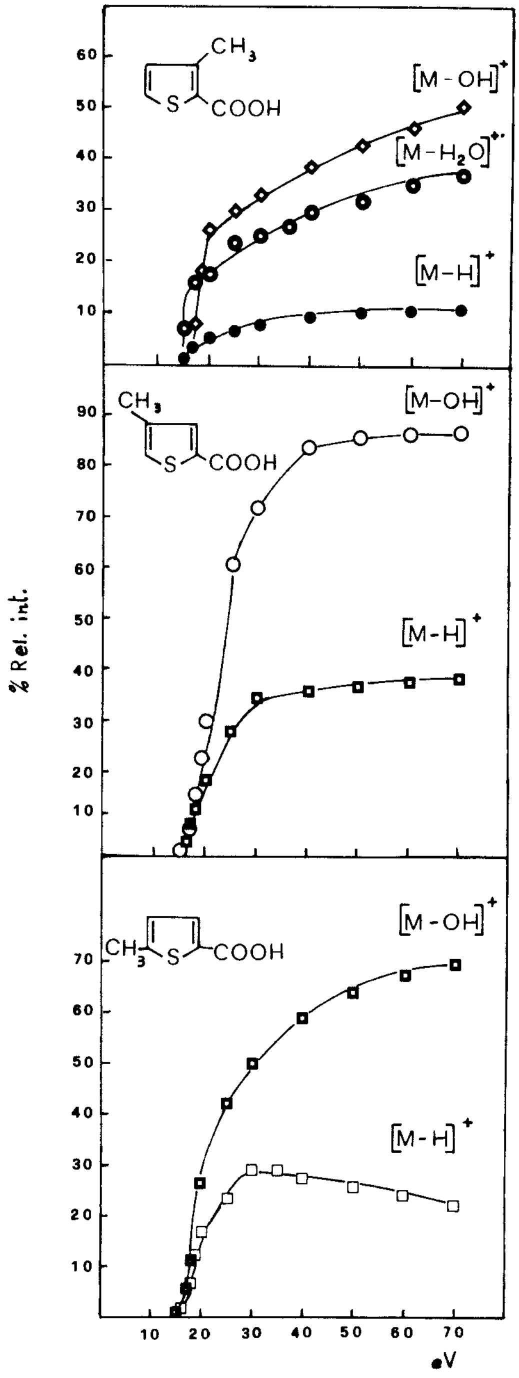
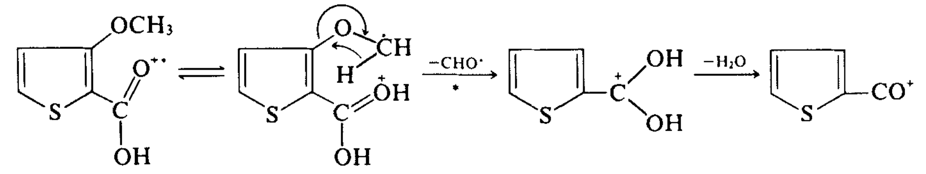


FIGURE 1 Plots of relative intensity against ionization nominal energy of the more important primary fragmentation processes of 3-, 4- and 5-methyl-thiophene-2-carboxylic acids.

carbonyl oxygen, leading to the rearranged molecular ion **b** which then expels a formyl radical[8] to give the ion **c** (Scheme 2).

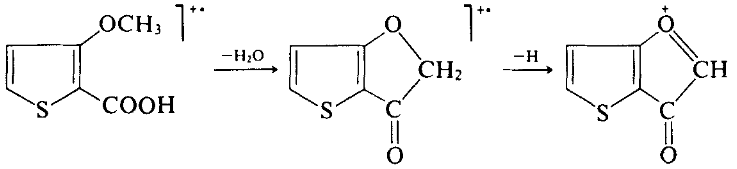


m/z 158 (100%) m/z 129 (30%) m/z 111 (50%)

a **b** **c**

SCHEME 2

In the spectrum of the corresponding labelled derivative (corrected for d_0 contributions) the expected total shift of the ion **c** at m/z 130 is not observed but the m/z 129 peak is also present, indicating the existence of an equilibrium between **a** and **b** before the occurrence of fragmentation. The 3-Methoxy derivative also shows a weakly $[M—H_2O]^{+\cdot}$ peak. The $[M—H_2O]^{+\cdot}$ peak found for 3-methoxy-thiophene-2-carboxylic acid is produced by a specific "ortho-effect"[11,24] similar to 3-methyl-thiophene-2-carboxylic acid. The $[M—H_2O]^{+\cdot}$ radical ion undergo H loss; the relative intensity of the $[M—H_3O]^+$ ion is 13% in the 3-methoxy derivative, while it is negligible in 3-methyl- and 3-thiomethyl-thiophene-2-carboxylic acids (Scheme 3)



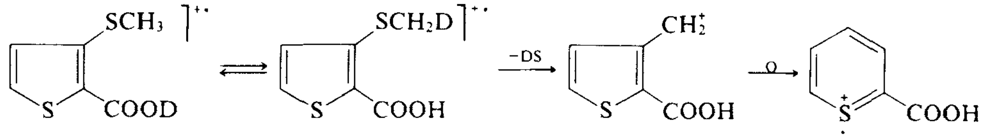
d

SCHEME 3

as is also found for corresponding 3-substituted thiophene-2-carboxamides.

5-Methoxy-thiophene-2-carboxylic acid (compound no. 6) has a different mass spectrum than that of the 3-analogue. In fact in this compound $[M—H_2O]^{+\cdot}$, $[M—CHO]^+$ and $[M—CHO—H_2O]^+$ peaks are absent and the base peak is the $[M—CH_3—CO]^+$ ion (m/z 115). The $[M—CH_3—CO]^+$ peak for 3-methoxy derivative is only 2%. Only in the 5-methoxy-thiophene-2-carboxylic acid is the $[M—CO_2]^{+\cdot}$ peak present, as is also found in some methyl-substituted benzoic acids.[7]

3-Methylthio-thiophene-2-carboxylic acid (compound no. 7) gives $[M—OH]^+$, $[M—H_2O]^+$, $[M—CH_3]^+$ and $[M—SH]^+$ peaks. The $[M—SH]^+$ peak is the most intense; SH loss is a feature of SCH_3 group fragmentation.[1,15] In the spectra of the deuterated acid (corrected for d_0 contributions), there appears a $[M—DS]^+$ peak, indicating that the deuterium of the acid is not retained solely in the carboxyl group after ionization; it appears to be partially scattered in the S-methyl group[15] (Scheme 4).



SCHEME 4

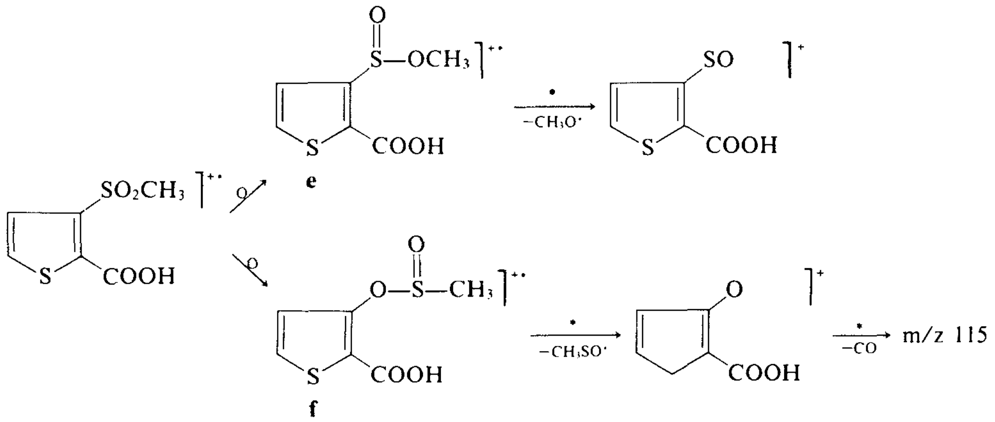
This skeletal rearrangement, which affords the $[M-SH]^+$ ion, becomes more prominent when the formation of $[M-CH_3]^+$ ion is not especially favorable.

For 5-methylthio-thiophene-2-carboxylic acid (compound no. 8) the most intense peaks are $[M-CH_3]^+$ and $[M-CH_3-CO]^+$. The intensity of the $[M-SH]^+$ ion in the 5-methylthio derivative is drastically suppressed in comparison with that of the 3-analogue, as is found in the corresponding benzene derivatives.[15] For the 5-methylthio derivatives the routes of fragmentation are:

1) $[M]^{+\cdot} \longrightarrow [M-OH]^+ \longrightarrow [M-OH-CO]^+ \longrightarrow [M-OH-CO-CH_3]^{+\cdot}$

2) $$\begin{tikzcd} & & {[M-CH_3-CO]^+} \\ {[M]^{+\cdot}} \arrow[r, "\cdot"] & {[M-CH_3]^+} \arrow[ur, "\cdot"] \arrow[dr] & \\ & & {[M-CH_3-CS]^+} \end{tikzcd}$$

3-Methylsulphonyl-thiophene-2-carboxylic acid (compound no. 9) shows a weak peak at m/z 175 due to $CH_3O^\cdot$ loss from the rearranged molecular ion **e**, similar to phenylalkylsulphones[25] and diarylsulphones.[26] This loss is confirmed by the mass spectra of the labelled derivatives. The 3-methylsulphonyl derivative gives also an intense m/z 143 peak due to $CH_3SO^\cdot$ loss from the rearranged molecular ion **f** (Scheme 5).



SCHEME 5

Another route of fragmentation is:

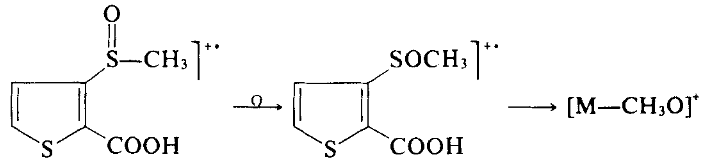
$$[M]^{+\cdot} \xrightarrow{\cdot} [M-CH_3]^+ \xrightarrow{\cdot} [M-CH_3-SO_2]^+ \longrightarrow$$
$$\longrightarrow [M-CH_3-SO_2-OH]^{+\cdot} \longrightarrow [M-CH_3-SO_2-OH-CO]^{+\cdot}$$

The fragmentation of the 5-methylsulphonyl-thiophene-2-carboxylic acid (compound no. 10) is the same than that of 3-derivative. However in the 3-derivative the base peak is the molecular ion, in the 5-derivative the base peak is the ion corresponding to m/z 115.

For 3-methylsulphinyl-thiophene-2-carboxylic acid (compound no. 11) the base peak is the $[M—CH_3]^+$ ion. The main route of fragmentation is:

$$[M]^{+\cdot} \longrightarrow [M—CH_3]^+ \longrightarrow [M—CH_3—SO]^+ \longrightarrow [M—CH_3—SO—OH]^{+\cdot} \longrightarrow$$
$$\longrightarrow [M—CH_3—SO—OH—CO]^{+\cdot}$$

similar to that found for the 3-methylsulphonyl derivative. The 3-Methylsulphinyl derivative also shows H_2O and HCOOH eliminations from the molecular ion, indicated by metastables. The 3-methylsulphinyl compound shows a m/z 159 weak peak due to $CH_3O^\cdot$ loss from the rearranged molecular ion **g** as found for 3-methylsulphonyl derivative (Scheme 6).



SCHEME 6

3-Formyl-thiophene-2-carboxylic acid (compound no. 12) has a $[M—OH—CO]^+$ base peak and gives also $[M—H_2O]^{+\cdot}$ (supported by the corresponding metastable peak), $[M—H]^+$ and $[M—CO]^+$ peaks. The $[M—H]^+$ peak is also given by phthalaldehydic acid[5] and has almost the same intensity. The molecular ion and $[M—CO]^{+\cdot}$ radical ion are the only peaks present in the mass spectrum at 12 eV.

3-Methyl-, 3-methoxy-, 3-thiomethyl-, 3-methylsulphinyl-, 3-formyl-thiophene-2-carboxylic acids give the $[M—H_2O]^{+\cdot}$ peak which is due to an "ortho-effect", the plots of relative intensity of this fragmentation process against nominal ionization energy for these compounds are shown in Figure 2. It is evident that 3-methyl-thiophene-2-carboxylic acid shows the more energetically favorable decomposition. Steric factors probably inhibit the occurrence of the $[M—H_2O]^{+\cdot}$ peak in 3-methylsulphonyl-thiophene-2-carboxylic acid, as is found for corresponding 3-substituted thiophene-2-carboxamide.[1]

For 5-ethyl-thiophene-2-carboxylic acid (compound no. 13) the base peak is the $[M—CH_3]^+$ ion and shows the metastable supported COOH loss from the molecular ion to give the ion at m/z 111. Another feature observed is the following degradation:

$$[M]^{+\cdot} \longrightarrow [M—OH]^+ \xrightarrow{\bullet} [M—OH—C_2H_2]^+$$

which gives a m/z 113 ion.

5-Nitro-thiophene-2-carboxylic acid (compound no. 14) shows as base peak the molecular ion. For this compound the main routes of fragmentation are:

1) $[M]^{+\cdot} \longrightarrow [M—OH]^+ \longrightarrow [M—OH—NO_2]^+ \longrightarrow [M—OH—NO_2—CO]^+$

2) $[M]^{+\cdot} \longrightarrow [M—NO]^+ \longrightarrow [M—NO—CO]^+ \longrightarrow [M—NO—CO—CO]^+$

The halogenoderivatives (compounds no. 15–19) show the following fragmentation route:

$$[M]^{+\cdot} \xrightarrow{\bullet} [M—OH]^+ \xrightarrow{\bullet} [M—OH—CO]^+ \longrightarrow [M—OH—CO—CS]^+$$

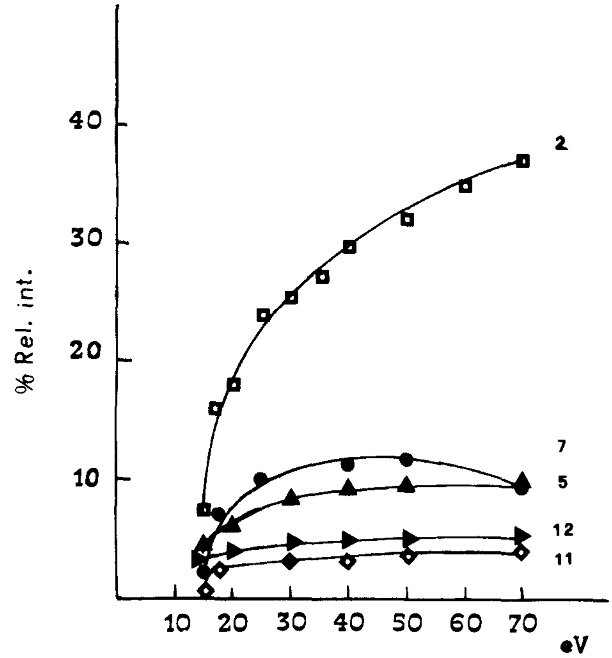


FIGURE 2 Plots of relative intensity of the $[M—H_2O]^{+\cdot}$ peak against ionization nominal energy of 3-methyl-(2), 3-methoxy-(5), 3-thiomethyl-(7), 3-methylsulphinyl-(11), 3-formyl-(12)-thiophene-2-carboxylic acids.

3-, 4- and 5-Bromo-thiophene-2-carboxylic acids (compounds no. 16–18) give a similar fragmentation route and thus it is not possible to distinguish between the isomeric bromo derivatives by mass spectrometry.

EXPERIMENTAL

3-Methyl-,[27] 4-methyl-,[28] 5-methyl-,[29] 3-methoxy-,[30] 5-methoxy-,[31] 3-methylthio-,[32] 5-methylthio-,[33] 3-methylsulphonyl-,[34] 5-methylsulphonyl-,[33] 3-methylsulphinyl-,[33] 3-formyl-,[35] 5-ethyl-,[36] 5-nitro-,[37] 3-fluoro-,[38] 3-bromo-,[39] 4-bromo-,[40] 5-bromo-,[41] 3-iodo-,[39] and thiophene-2-carboxylic acid[27] were prepared as reported.

The mass spectra were recorded on LKB 9000 S mass spectrometer with ion source temperature 250°C, using direct inlet probe technique at an ionizing voltage of 70 eV and at room temperature.

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REFERENCES

1. S. Occhipinti, G. Alberghina, S. Fisichella, O. Puglisi and L. Ceraulo, *Org. Mass Spectrom.*, **15**, 632 (1981).
2. S. Fisichella, S. Occhipinti, G. Alberghina and M. E. Amato, *J. Heter. Chem.*, **18**, 1011 (1981).
3. S. Fisichella, S. Occhipinti, G. Alberghina and M. E. Amato, *Phosphorus and Sulfur*, **10**, 317 (1981).

4. R. S. Gohlke and F. W. McLafferty, 4th Annual Meeting A.S.T.M. Committee E-14, San Francisco p. 373, (1955).
5. J. L. Holmes and F. Benoit, *Org. Mass Spectrom.*, **4,** 97 (1970).
6. F. Benoit, *Org. Mass Spectrom.*, **7**(3), 295 (1973).
7. T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33,** 386 (1961).
8. D. V. Ramana and N. Sundaram, *Org. Mass Spectrom.*, **15,** 220 (1980).
9. S. Meyerson and J. L. Corbin, *J. Am. Chem. Soc.*, **87,** 3045 (1965).
10. M. J. Lacey, C. G. Macdonald and J. S. Shannon, *Org. Mass Spectrom.*, **5,** 1391 (1971).
11. F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31,** 3076 (1959).
12. E. M. Emery, *Anal. Chem.*, **32,** 1495 (1960).
13. K. Biemann, *Angew. Chem.*, **74,** 102 (1962).
14. S.-O. Lawesson, J. Ø. Madsen, G. Schroll, J. H. Bowie and D. H. Williams, *Acta Chem. Scand.*, **20,** 2325 (1966).
15. J. H. Bowie, S.-O. Lawesson, J. Ø. Madson, G. Schroll and D. H. Williams, *J. Chem. Soc.* (*B*), 951 (1966).
16. J. H. Bowie, R. G. Cooks, S.-O. Lawesson and C. Nolde, *J. Chem. Soc.* (*B*), 616 (1967).
17. I. W. Kinney, Jr. and G. L. Cook, *Anal. Chem.*, **24,** 1391 (1952); **25,** 1729 (1953).
18. V. Hanus and V. Cermàk, *Collect. Czech. Chem. Commun.*, **24,** 1602 (1959).
19. N. G. Foster and R. W. Higgins, *Org. Mass Spectrom.*, **1,** 191 (1968).
20. J. G. Pomonis, C. L. Fatland and R. G. Zaylskie, *J. Chem. Eng. Data*, **21,** 380 (1976).
21. J. Gimenez-Plata and J. M. Paraja Jmenez, *Afinidad*, **36,** 151 (1979).
22. J. S. Shannon, *Austral. J. Chem.*, **15,** 265 (1962).
23. K. Biemann, *Angew. Chem.*, **74,** 102 (1962).
24. J. H. Bowie and P. Y. White, *J. Chem. Soc.* (*B*), 89 (1969).
25. S. Meyerson and J. D. McCollenn, "Division of Physical Chemistry, 136th Meeting, ACS, Atlantic City, N. J., 1959."
26. S. Meyerson, H. Drews and E. K. Fields, *Anal. Chem.*, **36,** 1295 (1964).
27. H. D. Hartough and L. G. Conley, *J. Amer. Chem. Soc.*, **69,** 3096 (1947).
28. V. Ramanathan and R. Levine, *J. Org. Chem.*, **27,** 1667 (1962).
29. H. Behringer and K. Falkenberger, *Chem. Ber.*, **99,** 3309 (1966).
30. S. Gronowitz, *Arkiv. Kemi*, **12,** 239 (1958).
31. J. Sicé, *J. Amer. Chem. Soc.*, **75,** 3697 (1953).
32. S. Gronowitz, *Arkiv. Kemi*, **13,** 269 (1958).
33. Ya. L. Gol'dfarb, M. A. Kalik and M. L. Kirmalova, *Zhur. obshchei Khim.*, **29,** 3631 (1959).
34. F. Arndt, F. Kirsch and P. Nachtwey, *Ber. dtsch. Chem. Ges.*, **59,** 1079 (1926).
35. S. Gronowitz, Bo Gestblom and B. M. Maltesson, *Arkiv för Kemi*, **20,** 407 (1962).
36. E. Schleicher, *Ber. dtsch. Chem. Ges.*, **18,** 3015 (1885).
37. I. J. Rinkes, *Rec. Trav. Chim.*, **51,** 1134 (1932).
38. S. Gronowitz and U. Rosén, *Chemica Scripta*, **1,** 33 (1971).
39. W. Steinkopf, H. F. Schmitt and H. Fiedler, *Liebigs. Annalen Chem.*, **527,** 237 (1937).
40. S.-O. Lawesson, *Arkiv. Kemi*, **11,** 317 (1957).
41. S. Gronowitz, *Arkiv. Kemi*, **8,** 87 (1955).