Curie-point Pyrolysis of Saturated and Unsaturated Dicarboxylic Acids studied by Tandem Mass Spectrometry

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It is shown by tandem mass spectrometry that Curie-point pyrolysis of saturated α,ω-dicarboxylic acids $HOOC(CH_2)_nCOOH$ (n = 1—6) leads mainly to the formation of intramolecular anhydrides and cyclic ketones. In some cases products are formed which must be due to intermolecular interactions such as acetone formation for n = 1 and hydroxybenzoic acid formation for n = 3. Mechanisms for the formation of these products are presented where 1,5-hydrogen shifts from activated positions to a carbonyl group play a crucial role. The unsaturated dicarboxylic acids $HOOC(C_2H_2)COOH$ and $HOOC(C_3H_4)COOH$ show, in addition to structure dependent dehydration reactions, elimination of carbon dioxide. The latter reaction proceeds in some cases *via* a 1,5-hydrogen shift from the carbonyl group to the double bond, but also by a 1,4-hydrogen shift from the carboxy-group to the double bond followed by a 1,2-hydrogen shift prior to or during decarboxylation seems to occur as suggested by the products generated.

α,ω-Dicarboxylic acids and their derivatives are an important class of compounds. Well known are the malonic ester synthesis and the Dieckmann condensation reaction, but pyrolysis of the acids in the presence of a suitable base, such as $Ba(OH)_2$, leading to cyclic ketones is of particular interest.[1] Although many papers concerning the mechanisms of product formation upon pyrolysis of (un)saturated carboxylic acids have appeared,[2] no extensive gas-phase pyrolysis studies of dicarboxylic acids have been reported so far. The availability of a tandem mass spectrometer equipped with a simultaneous ion detection system[3] and a Curie-point pyrolysis inlet system has enabled us to study the low-pressure gas-phase pyrolysis of some saturated α,ω-dicarboxylic acids and unsaturated dicarboxylic acids. Not only the structures of their pyrolysis products, but also the mechanisms of pyrolysis have been elucidated by use of the collisonal activation (c.a.) method in combination with reference compounds. The combination of fast pyrolysis and on-line product determination has been shown to be especially advantageous for the study of the decarboxylation of the unsaturated dicarboxylic acids.

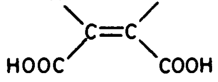
The results obtained are presented and discussed below.

$HOOC(CH_2)_nCOOH$

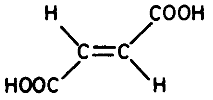
(I) $n = 1$
(II) $n = 2$
(III) $n = 3$
(IV) $n = 4$
(V) $n = 5$
(VI) $n = 6$

$HOOC-CH_2-C(O)-CH_2-COOH$

(VII)



(VIII)



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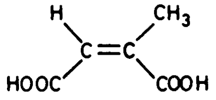

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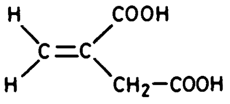

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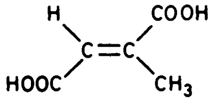
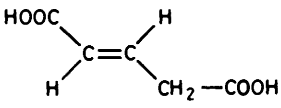


(XI)



(XIII)

Results

Compounds (I)—(XIII) have been pyrolysed. The completeness of the pyrolysis of the acids has been checked by comparing their Curie-point pyrolysis mass spectra with their standard mass spectra.[4]

Malonic Acid (I).—The Curie-point pyrolysis mass spectrum of this acid is presented in Table 1. Interesting pyrolysis fragments are found at *m/z* 42, 58, and 60 and their structures have been determined by tandem mass spectrometry (m.s./m.s.).

m/z 42. The c.a. spectrum of the ions with *m/z* 42 formed upon pyrolysis mass spectrometry (p.m.s.) of acid (I) is presented in Table 2 together with the c.a. spectra of the *m/z* 42 ions, generated from ionized cyclobutanone and ethoxyacetylene. From Table 2 it can be seen that the spectra are identical, thus indicating that all three ions have the same structure. This is ionized ketene as this is easily formed by a cycloreversion process from the molecular ion of cyclobutanone with expulsion of ethene. Note that the elimination of ethene from ionized ethoxyacetylene must proceed *via* a 1,5-H shift rather than a 1,3-H shift to give ionized ketene and not hydroxyacetylene.

m/z 58. The c.a. spectrum of this ionized pyrolysis product of acid (I) is presented in Table 3 together with the c.a. spectra of reference ions (**2a**—**f**) and of the ionized pyrolysis products of *m/z* 58 of acids (III), (VII), and (XIII) and the electron impact (e.i.) induced fragment at *m/z* 58 of but-3-enoic acid (**2g**). From Table 3 it can be seen that acetone is the pyrolysis product of acid (I). Another conclusion that can be drawn from Table 3 is

Table 1. Curie-point pyrolysis mass spectra of acids (I) and (II)[a]

Acid (I)		Acid (II)	
m/z	Rel. int.	*m/z*	Rel. int.
41	5.1	42	10.4
42	85.4	44	23.4
43	91.8	55	5.1
44	40.9	56	100
45	12.4	72	13.7
58	75.9	74	5.1
59	6.9		
60	100		

[a] Peaks with a relative intensity <5% have been omitted.

Table 2. C.a. spectra of *m/z* 42 ions[a,b]

m/z	(**1a**)	(**1b**)	(**1c**)[c]	(**1d**)[c]
12	8.8	7.1	7.6	7.2
13	26.2	26.5	23.9	22.0
14	47.6	48.4	54.0	55.4
16	0.8	0.9	0.6	1.1
21[d]	0.2	0.2	0.2	0.2
24	2.1	2.1	1.7	1.7
25	2.9	2.8	2.8	3.3
26	1.7	1.8	1.3	1.3
28	4.3	4.5	3.6	3.2
29	2.5	2.6	1.7	2.3
40	0.7	0.6	0.6	0.6
41	2.1	2.1	2.0	1.7

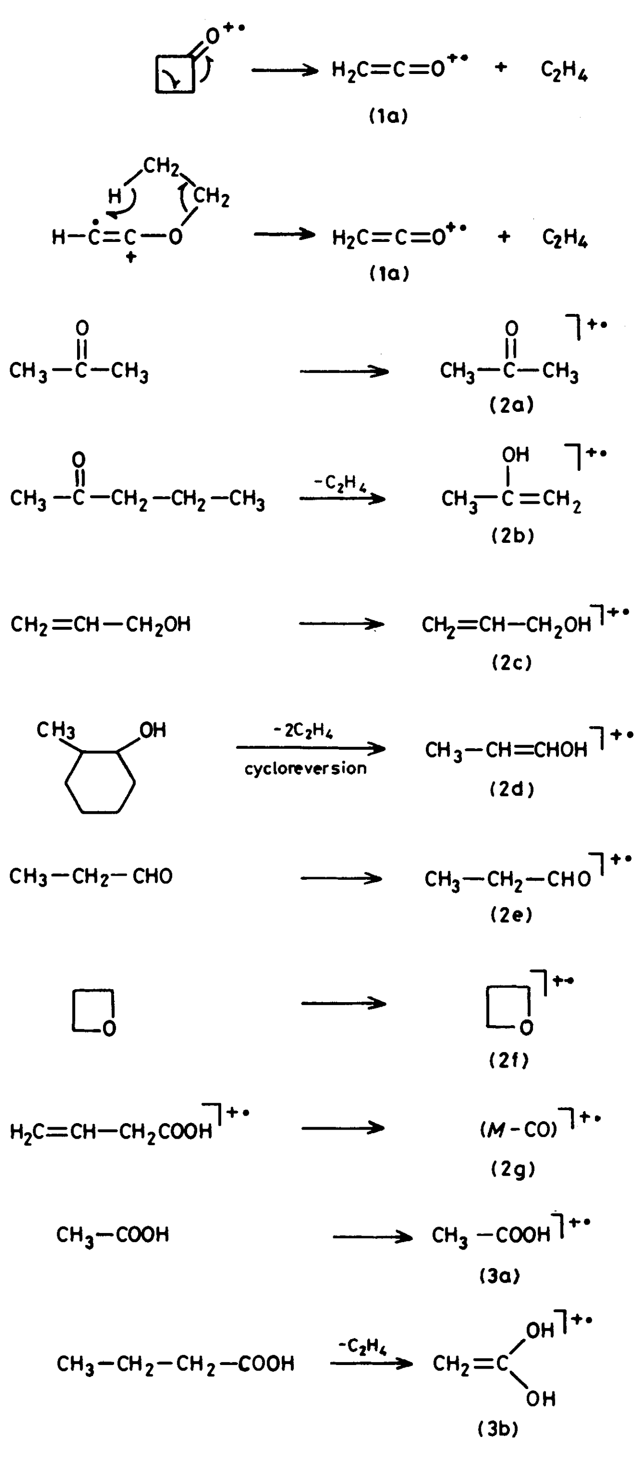
[a] See text for structures. [b] Σ_{12} = 100%. [c] (**1c**): fragment of acid (I); (**1d**): fragment of acid (III). [d] M^{2+} ion.

that pyrolysis of acid (**VII**) also leads to acetone as the product. This will be discussed in the mechanistic section of the paper.

m/z 60. Malonic acid is known[5] to decarboxylate upon heating in the liquid phase to yield acetic acid. This has been proposed[5] to proceed *via* a six-membered transition state, but the initially generated enolic form of acetic acid has not been observed so far. The low-pressure Curie-point pyrolysis m.s./m.s. system reduces the possibility of tautomerization of initially formed pyrolysis products and thus enhances the chance of observing the least stable tautomer if it is formed at all.

The c.a. spectra of the ionized pyrolysis product *m/z* 60 of acids (I) and (III) and the c.a. spectra of the ions (**3a** and **b**) are presented in Table 4. The latter two spectra are similar to those reported by Levsen *et al.*[6] It can be seen from the spectra that the pyrolysis product of acid (I) is acetic acid.

Succinic Acid (**II**).—The Curie-point pyrolysis mass spectrum of this acid is presented in Table 1 and shows only one large peak at *m/z* 56. The e.i. mass spectrum of succinic acid anhydride, however, does not show a molecular ion peak, but a very large peak at *m/z* 56 corresponding to $[M - CO_2]^{+\cdot}$. It is not therefore clear from the pyrolysis mass spectrum whether the anhydride is formed pyrolytically and detected as its $[M - CO_2]^{+\cdot}$ ion or that the peak at *m/z* 56 is due to the molecular ion of a pyrolysis product, such as cyclopropanone. The c.a. spectra of the *m/z* 56 ions generated by e.i. from succinic acid anhydride and by p.m.s. of acid (**II**) are presented in Table 5. Their similarity indicates that the pyrolysis product is the anhydride, which appears in the pyrolysis mass spectrum as the $[M - CO_2]^{+\cdot}$ ion.



Glutaric Acid (**III**).—The Curie-point pyrolysis mass spectrum of this acid is presented in Figure 1a. The fragments of interest which have been examined with m.s./m.s. are found at *m/z* 42, 58, 60, 70, and 86. Figure 1b shows the corresponding pyrolysis mass spectrum for a Curie-point temperature of 510 °C instead of the standard Curie-point temperature of 610 °C. Note the increase of intensity of the peaks at *m/z* 84, 112, and 138 at this particular T_{Curie}, a phenomenon which has only been observed for acid (**III**), but not for the other acids investigated. The origin of this phenomenon will be discussed in the mechanistic section.

m/z 42. The c.a. spectrum of the *m/z* 42 ions, generated upon p.m.s. of acid (**III**) and having the elemental composition

Table 3. C.a. spectra of *m/z* 58 ions[a,b]

m/z	(2a)	(2b)	(2c)	(2d)	(2e)	(2f)	(2g)[c]	(2h)[d]	(2i)[d]	(2j)[d]	(2k)[d]
24	0.6	0.6	0.7	0.4	0.4	0.2	0.5	0.4	0.6	0.6	0.5
25	2.0	2.3	2.3	2.4	1.8	1.5	2.2	2.2	2.4	2.3	2.5
26	9.0	8.1	7.4	9.8	11.6	8.3	11.5	7.0	7.2	8.3	9.0
27	16.2	14.9	12.2	18.1	23.4	13.0	20.2	9.7	15.5	16.3	17.9
28	3.6	3.6	6.5	9.2	20.6	46.0	9.6	3.6	3.7	6.9	9.0
29	8.9	17.0	20.3	24.9	28.9	16.6	24.9	12.0	13.9	22.9	29.5
30	0.3	1.6	7.5	8.9	4.8	11.4	7.1	0.4	0.4	4.7	7.6
31	0.5	12.9	9.9	12.3	3.3	2.8	12.8	0.4	1.2	6.7	11.5
32			0.5	0.6			0.3				
36	0.4	0.9	1.8	0.4	0.2		0.4	0.3	0.4	0.3	0.3
37	1.3	2.9	4.5	1.6	0.7		1.7	1.1	1.2	1.3	1.3
38	1.5	3.7	6.2	2.2	0.8		1.9	1.4	1.6	1.7	1.8
39	3.0	8.7	12.6	4.6	1.5		4.2	2.5	2.7	3.2	3.7
40	1.3	1.9	3.9	1.5	0.4		0.9	1.0	1.0	0.9	0.8
41	3.3	3.3	2.1	0.7	0.5		0.5	3.1	3.0	1.6	0.6
42	9.9	6.2	4.7	1.1	0.7		0.7	8.9	8.4	4.2	1.1
43	38.3	11.5	3.0	1.2	0.2		0.6	46.0	36.9	18.2	2.7

[a] See text for structures. [b] Σ_{24} = 100%. [c] Ion formed upon e.i.-induced decarbonylation of but-3-enoic acid. [d] Pyrolysis fragments of (**2h**): acid (I); (**2i**): acid (VII); (**2j**): acid (III); (**2k**): acid (XIII).

Table 4. C.a. spectra of *m/z* 60 ions[a,b]

m/z	(3a)	(3b)	(3c)[c]	(3d)[c]
12	0.7	1.1	0.6	0.8
13	1.6	2.8	1.6	2.1
14	3.1	7.7	3.8	4.6
15	7.9	5.7	7.4	8.2
16	1.7	0.4	1.3	1.6
17	0.4	0.6	0.7	1.1
18	0.1	0.6	0.1	0.2
19		0.2		0.1
24	0.6	0.9	0.4	0.9
25	1.2	2.1	1.4	1.6
26	1.4	1.6	1.6	1.7
27	0.3	0.2	0.4	0.3
28	5.1	5.2	5.4	6.7
29	11.6	22.0	14.0	15.4
30	0.4	1.6	0.4	0.6
31	3.6	10.7	3.6	4.6
40	0.8	1.1	0.7	0.8
41	1.8	3.3	2.1	2.0
42	5.3	16.8	6.0	6.7
43	34.8	6.6	33.2	26.2
44	1.9	0.6	2.2	1.8
45	15.9	7.2	13.2	11.6
46		1.0		0.6

[a] See text for structures. [b] Σ_{12} = 100%. [c] Pyrolysis fragments of (**3c**): acid (I); (**3d**): acid (III).

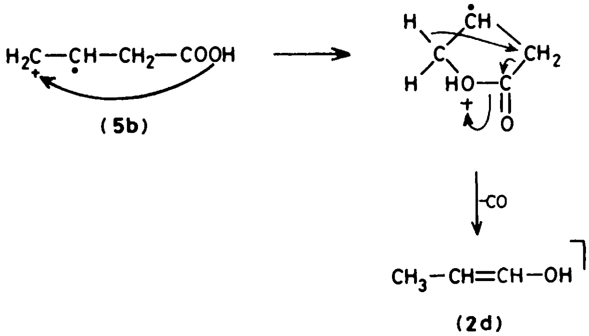
Table 5. C.a. spectra of *m/z* 56 fragments: a, generated upon pyrolysis of acid (II), b, generated upon e.i. from succinic acid anhydride

	Rel. int.[a]	
m/z	a	b
24	1.9	2.1
25	7.1	7.9
26	32.0	30.8
27	20.7	20.7
28	36.3	36.1
29	2.0	2.4

[a] Σ_{24} = 100%.

C_2H_2O, is presented in Table 2. It can be seen that in this case again the ketene structure is present.

m/z 58. The c.a. spectrum of the ions *m/z* 58, generated upon p.m.s. of acid (**III**), is presented in Table 3. This spectrum points to a mixture of ion structures, *i.e.* (**2d** and **a**) (*ca.* 1:1). However, the formation of but-3-enoic acid upon pyrolysis of acid (**III**) (see below under *m/z* 86) and the similarity of the c.a. spectra of ions (**2d** and **g**), derived from but-3-enoic acid, show that a substantial part of the *m/z* 58 fragments is generated by e.i. rather than by pyrolysis. The formation of (**2d**) from but-3-enoic acid can be rationalized as follows:



m/z 60. Like acid (I) glutaric acid yields acetic acid upon pyrolysis, as established by m.s./m.s. (Table 4).

m/z 70. As noted for the formation of *m/z* 56 upon p.m.s. of acid (II), the peak at *m/z* 70 in the pyrolysis mass spectrum of acid (III) might be due to either the e.i.-induced loss of CO_2 from the pyrolytically formed anhydride or to the pyrolytically formed cyclobutanone or to both. The relevant c.a. spectra are presented in Table 6. From the data in Table 6 it can be calculated that *ca.* 75% of the intensity of the peak at *m/z* 70 in the pyrolysis mass spectrum of acid (III) is due to cyclobutanone and the remaining 25% to the $[M - CO_2]^{+\bullet}$ ion of glutaric acid anhydride.

m/z 86. The formation of pyrolysis product(s) with this molecular weight is of particular interest as this formal loss of $[H_2CO_2]$ from acid (III) is not observed for any of the higher acid homologues. The c.a. spectra of the *m/z* 86 species and of reference ions (**5a**—**d**) are presented in Table 7. From the data in Table 7 it can be calculated that the pyrolysis fragments of *m/z* 86 consist of a mixture of crotonic acid (**5a**) and but-3-enoic acid (**5b**) in a ratio of *ca.* 70:30.

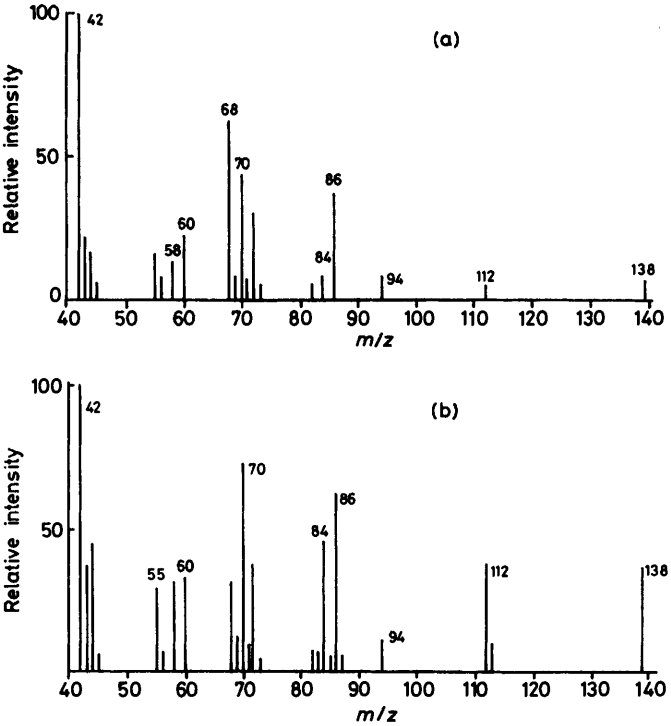


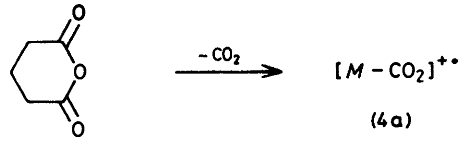
Figure 1. Curie-point pyrolysis mass spectra of glutaric acid (**III**) at 610 °C (a) and 510 °C (b)

Table 6. C.a. spectra of m/z 70 ions[a,b]

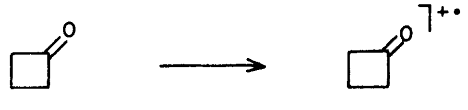
m/z	Ion (**4a**)	 (**4b**)	 (**4c**)*
24	0.4	0.4	0.4
25	2.2	2.2	2.2
26	10.5	11.1	11.6
27	23.0	17.4	19.5
28	7.9	12.9	10.0
29	5.9	2.0	3.2
36	0.9	0.7	0.7
37	3.5	2.9	3.0
38	5.7	5.3	5.3
39	14.9	15.5	13.8
40	3.6	3.1	3.2
41	6.2	4.7	4.9
42	12.2	21.3	20.1
43	0.5	0.5	1.0
55	2.5	0.1	1.1

[a] See text for structures. [b] Σ_{24} = 100%.

* Pyrolysis fragment of acid (**III**).



(4a)



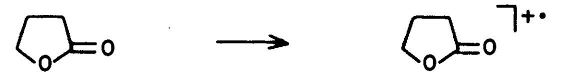
(4b)

$$CH_3{-}CH{=}CH{-}COOH \longrightarrow CH_3{-}CH{=}CH{-}COOH]^{+\bullet}$$

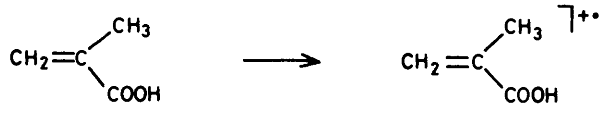
(5a)

$$CH_2{=}CH{-}CH_2{-}COOH \longrightarrow CH_2{=}CH{-}CH_2{-}COOH]^{+\bullet}$$

(5b)



(5c)



$$CH_2{=}C(CH_3)COOH \longrightarrow CH_2{=}C(CH_3)COOH]^{+\bullet}$$

(5d)

The occurrence of the exceptional peaks at m/z 84, 112, and 138 in the pyrolysis mass spectrum of acid (**III**), especially at a T_{Curie} of 510 °C (Figure 1), seems difficult to explain. At least the species corresponding to m/z 138 must be due to a bimolecular reaction. The c.a. spectra of the m/z 84 and 112 ions are presented in Tables 9 and 11, respectively. The large peak at m/z 84 in the c.a. spectrum of the m/z 112 pyrolysis fragment points strongly to a relationship between these two fragments. In fact, the m/z 84 fragment might be due to an e.i.-induced fragmentation of the pyrolysis product with M 112, as discussed in the mechanistic section. The c.a. spectrum of the m/z 138 ions formed upon p.m.s. of acid (**III**) and the c.a. spectra of reference ions (**6a**—**c**) are presented in Figure 2. From Figure 2 it will be clear that the pyrolysis products corresponding to the peak at m/z 138 in the pyrolysis mass spectrum of acid (**III**) consist of a mixture of (**6a**) and either (**6b** or **c**) or both.

Adipic Acid (**IV**).—The Curie-point pyrolysis mass spectrum of this acid is presented in Table 8. It shows that pyrolysis leads to the formation of fragments at m/z 82 and 84. The c.a. spectrum of the m/z 84 fragment is presented in Table 9 together with that of ion (**7a**). It can be seen from Table 9 that cyclopentanone is the main product found upon Curie-point p.m.s. of acid (**IV**). The fragment at m/z 82 will probably be due to a dehydrogenation reaction of the cyclic ketone formed; this reaction is also observed for the higher molecular weight homologues.

Pimelic Acid (**V**).—The Curie-point pyrolysis mass spectrum of this acid is presented in Table 8. The major pyrolysis product is found at m/z 98. Its c.a. spectrum is presented in Table 10 together with those of the reference ions (**8a** and **b**). From the data in Table 10 it can be seen that cyclohexanone is the pyrolysis product of acid (**V**). Table 8 also shows that its dehydrogenated products are formed as observed for acid (**IV**). The relatively large intensity of the peak at m/z 94 strongly indicates that the product of the two-fold dehydrogenation reaction might be phenol.

Suberic Acid (**VI**).—The Curie-point pyrolysis mass spectrum of this acid is presented in Table 8. The c.a. spectrum of the product at m/z 112 corresponding to $[M - H_2O - CO_2]$ is presented in Table 11 together with the c.a. spectrum of the reference ion (**9a**). Table 11 also gives the c.a. spectra of the

Table 7. C.a. spectra of m/z 86 ions[a,b]

m/z	(**5a**)	(**5b**)	(**5c**)	(**5d**)	(**5e**)[c]	(**5f**)[c]	(**5g**)[c]	(**5h**)[c]	(**5i**)[c]
26	2.1	2.3	1.6	2.2	2.0	1.8	1.8	1.7	2.0
27	2.6	4.7	1.9	6.2	3.3	2.2	2.2	2.2	3.2
28	1.1	1.6	0.8	8.2	1.4	0.9	0.9	0.9	1.2
29	5.7	8.8	4.7	7.7	7.4	5.5	5.6	5.4	6.8
30	0.3	0.7	0.3	0.7	0.6	0.3	0.3	0.3	0.5
31	1.0	1.5	0.8	0.3	1.7	1.0	1.0	1.0	1.5
36	1.1	0.5	1.1	0.3	1.1	0.9	1.1	1.0	1.0
37	5.5	3.3	6.4	1.3	6.0	4.7	4.9	4.7	6.2
38	10.5	6.0	8.9	1.9	7.7	9.6	9.9	9.7	8.0
39	29.3	21.0	30.7	7.4	26.1	29.3	29.6	30.4	27.0
40	8.3	5.4	10.0	2.9	6.5	9.5	9.2	9.6	6.7
41	11.4	9.1	11.9	7.4	9.3	11.6	11.3	11.5	9.7
42	5.3	17.4	4.7	51.1	8.6	5.8	5.7	6.1	7.7
43	1.2	2.8	1.3	0.8	2.4	2.3	2.1	1.9	2.3
44	1.0	2.0	0.9	0.7	1.2	1.0	1.0	1.1	1.2
45	8.2	5.9	7.3	0.3	6.7	7.2	7.2	6.8	7.3
46	0.8	0.3	1.4		0.7	1.1	1.1	1.1	0.7
53	0.3	0.2	0.8		0.4	0.5	0.5	0.5	0.4
54	0.04	0.2	0.2		0.1	0.1	0.1	0.1	0.1
55	0.2	0.9	0.3	0.4	0.5	0.3	0.2	0.3	0.4
57	0.5	0.5	0.7		0.9	0.7	0.6	0.6	0.9
58	0.6	3.8	1.2		1.7	0.9	0.9	1.1	1.4
68	2.7	0.9	1.7		3.1	2.3	2.1	1.8	3.1
71	0.5	0.2	0.3		0.5	0.5	0.5	0.4	0.6

[a] See text for structures. [b] Σ_{26} = 100%. [c] Pyrolysis fragments of (**5e**): acid (**III**); (**5f**): acid (**X**); (**5g**): acid (**XI**); (**5h**): acid (**XII**); (**5i**): acid (**XIII**).

Table 8. Curie-point pyrolysis mass spectra of acids (**IV**)—(**VI**)[a]

Acid (IV)		Acid (V)		Acid (VI)	
m/z	Rel. int.	m/z	Rel. Int.	m/z	Rel int.
55	43.3	42	10.4	42	44.0
56	19.1	43	7.4	43	28.6
82	22.7	55	26.1	44	22.2
84	100	56	9.6	55	37.3
85	5.5	68	13.0	56	50.8
		69	31.7	68	100
		70	26.1	69	41.3
		80	11.3	82	31.7
		83	12.2	84	36.5
		94	30.0	108	19.0
		96	15.2	110	31.0
		98	100	112	55.6
		99	8.3		

[a] Peaks with a relative intensity <5% have been omitted.

p.m.s. species at m/z 112 of acids (**III**) and (**XI**), the e.i.-induced fragment m/z 112 from acid (**XI**) and the reference ions (**9b** and **c**) which will be discussed in the following section. It is clear from Table 11 that cycloheptanone (**9a**) is formed upon pyrolysis of acid (**VI**), which by a one- or two-fold dehydrogenation can lead to the products at m/z 110 and 108 (Table 8).

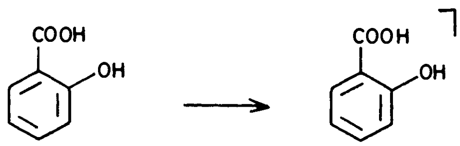
The Unsaturated Dicarboxylic Acids (**VIII**)—(**XIII**).—The unsaturated dicarboxylic acids (**VIII**)—(**XIII**) have been examined extensively with various mass spectrometric methods,[4a,7] most recently with field ionization, field desorption, and fast atom bombardment mass spectrometry.[8] In general they can be recognized easily from their spectra.

Curie-point p.m.s. of maleic acid (**VIII**) and fumaric acid (**IX**) gives rise to spectra which are rather different as shown in Figure 3. The main pyrolysis product of (**VIII**) is the anhydride (m/z 98), which upon e.i. decarboxylates to a great extent to give the ion with m/z 54 [compare this with the formation of

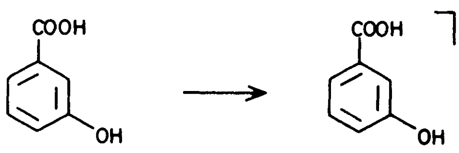
Table 9. C.a. spectra of m/z 84 ions[a]

	Ion			
m/z	(**7a**)[b]	(**7b**)[c]	(**7c**)[d]	(**7d**)[e]
24	0.3	0.3	0.4	0.4
25	1.9	1.8	0.5	0.7
26	5.6	5.5	2.2	1.6
27	6.9	6.6	5.1	3.2
28	3.0	2.6	2.1	2.1
29			4.2	3.6
30			0.3	0.5
31			0.5	0.3
36	0.1	0.1	0.6	1.0
37	0.6	0.5	2.5	4.2
38	1.1	0.9	3.3	5.8
39	5.5	5.6	8.2	9.7
40	1.3	1.1	1.9	3.5
41	6.3	7.1	4.1	3.3
42	5.1	4.5	4.9	3.8
43	0.9	0.8	7.4	5.9
44			0.7	0.6
45			0.5	3.2
46				0.2
48	0.1	0.2	0.1	0.2
49	0.3	0.3	0.5	0.3
50	0.7	0.7	1.6	0.7
51	0.9	0.9	1.4	0.7
52	0.9	0.9	1.1	1.0
53	3.0	3.0	4.0	3.3
54	2.8	2.4	2.6	2.3
55	39.2	37.7	13.5	9.1
56	11.3	14.6	6.0	4.7
57			0.9	1.4
58			0.4	0.5
65	0.3	0.3	1.6	1.2
66	0.4	0.3	1.8	3.0
67	0.7	0.5	1.2	2.2
68	0.4	0.3	2.1	2.9
69	0.5	0.6	11.7	13.1

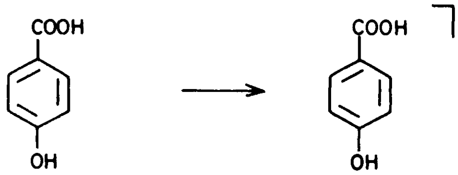
[a] Σ_{24} = 100%. [b] See text for structure. [c] Pyrolysis fragment of acid (**IV**). [d] Fragment of acid (**III**) (see text). [e] Fragment of acid (**XI**) (see text).



(6a)



(6b)



(6c)

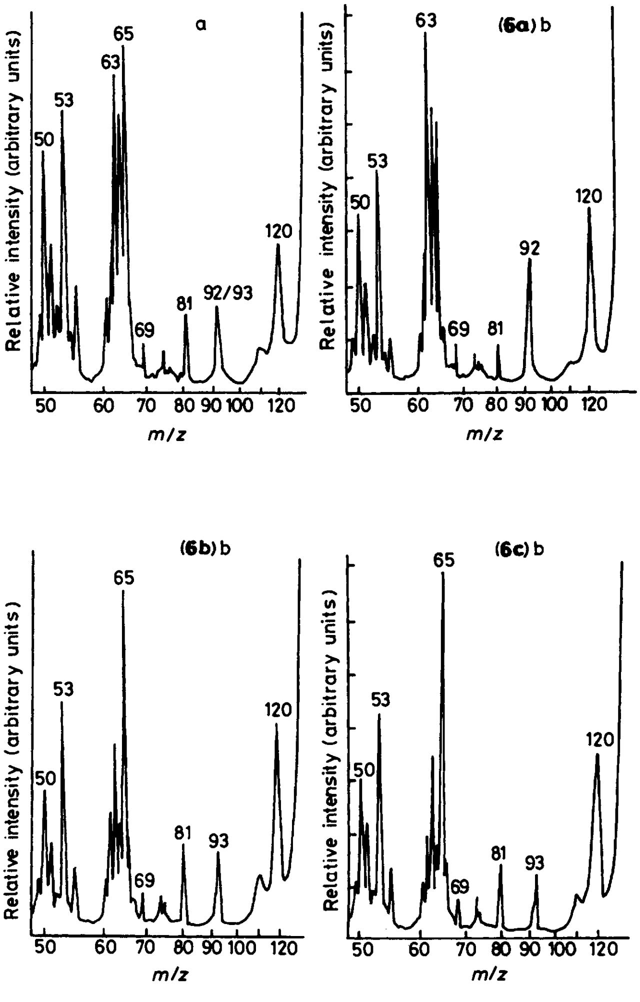
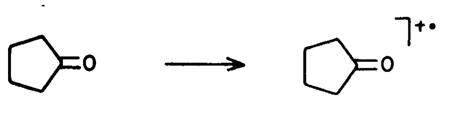
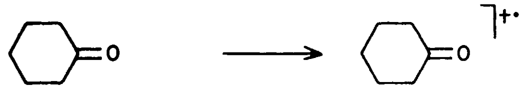


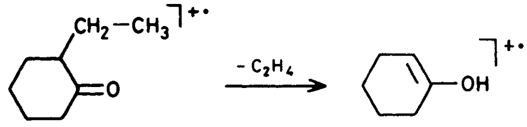
Figure 2. C.a. spectra of m/z 138 ions: a, ionized pyrolysis fragment m/z 138 of acid (III) at T_{Curie} 510 °C; b, see text for structures



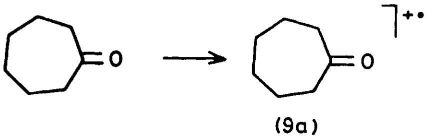
(7a)



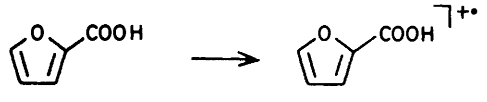
(8a)



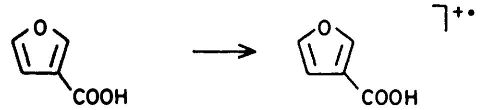
(8b)



(9a)



(9b)



(9c)

fragment of m/z 56 upon pyrolysis of acid (II)]. Acid (IX), however, suffers significantly decarboxylation upon pyrolysis to give the m/z 72 product, although it also appears to isomerize to some extent to acid (VIII) which then yields the products at m/z 98 and 54. The Curie-point pyrolysis mass spectra of the isomeric acids (X)—(XIII) are presented in Figure 4.

All spectra show a peak at m/z 86 due to a one-fold decarboxylation of the molecules. The c.a. spectra of these m/z 86 pyrolysis fragments are presented in Table 7. From the data in this Table it can be calculated that pyrolysis of (XIII) leads to a mixture of crotonic acid (column 5a in Table 7) and but-3-enoic acid (column 5b in Table 7) in a 70:30 ratio. Note that the same mixture is formed upon pyrolysis of acid (III). Pyrolysis of the acids (X)—(XII) gives rise to mixtures of crotonic acid (column 5a in Table 7) and methacrylic acid (column 5d in Table 7) in the ratios of 54:46 (X), 51:49 (XI), and 43:57 (XII). Acid (X) shows in addition to decarboxylation a dehydration reaction (m/z 112) followed by an e.i.-induced decarboxylation, which leads to m/z 68 as the base peak in the pyrolysis mass spectrum [compare with the pyrolytic behaviour of acid (VIII)]. The fumaric acid homologue (XI) also appears to dehydrate upon pyrolysis leading to a peak at m/z 112 in the spectrum (Figure 4); note also the peak at m/z 84, which may be an e.i.-induced fragment of the dehydrated product. This view is supported by the c.a. spectrum of the m/z 112 ions (Table 11), which shows an intense peak at m/z 84.

Mechanisms.—A. *Combined* H_2O *and* CO_2 *loss from the saturated dicarboxylic acids* (I)—(VI). All the acids (I)—(VI)

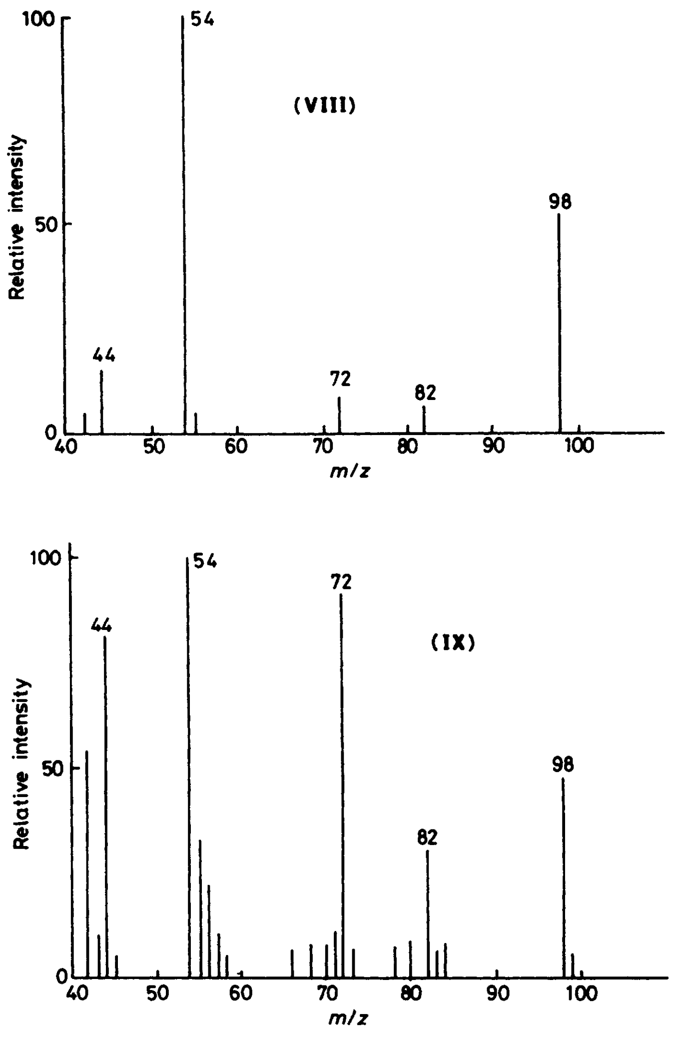


Figure 3. Curie-point pyrolysis mass spectra of acids (VIII) and (IX)

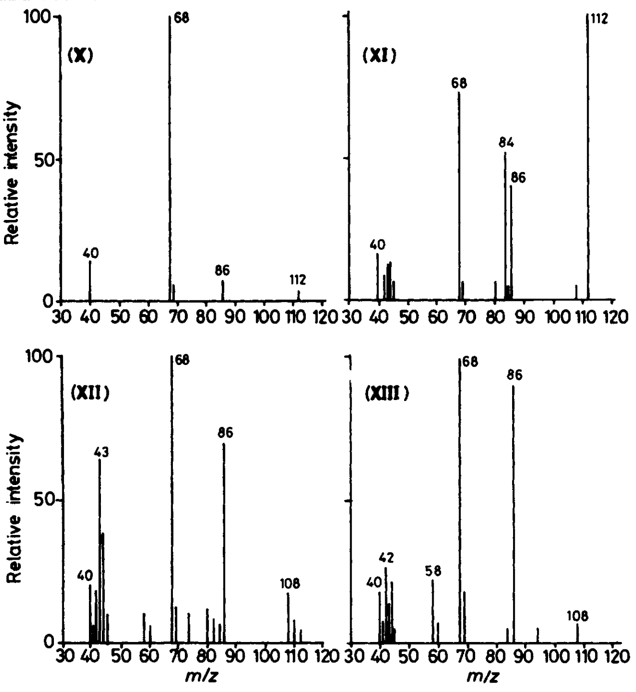


Figure 4. Curie-point pyrolysis mass spectra of acids (X)—(XIII)

Table 10. C.a. spectra of m/z 98 ions[a,b]

	Ion		
m/z	(8a)	(8b)	(8c)[c]
24	0.1	0.1	0.1
25	0.4	0.4	0.3
26	1.2	1.3	1.5
27	2.9	3.7	3.5
28	1.3	1.0	1.5
29	0.9	1.6	1.0
30		0.2	
31	0.1	0.5	0.1
36	0.3	0.3	0.3
37	1.4	1.1	1.4
38	2.4	1.8	2.4
39	9.1	5.8	8.5
40	2.1	1.2	2.0
41	8.1	4.1	7.3
42	8.2	1.9	7.9
43	1.9	2.5	1.9
44	0.3	0.3	0.3
45		0.2	
48	0.2	0.2	0.2
49	0.4	0.5	0.3
50	1.2	1.2	0.9
51	1.2	1.3	0.9
52	0.8	0.7	0.7
53	1.8	1.6	1.5
54	2.2	0.7	1.9
55	12.4	4.3	11.4
56	1.7	0.7	1.7
57	0.6	0.6	0.5
61	0.3	0.3	0.2
62	0.3	0.4	0.3
63	0.4	0.6	0.4
65	0.6	1.0	0.7
66	0.6	1.1	0.8
67	1.3	2.3	1.6
68	1.9	1.7	3.1
69	9.2	3.5	9.4
70	6.8	11.7	6.9
77	1.3	5.6	1.2
78	1.4	3.4	1.3
79	1.8	4.6	1.9
80	6.5	2.5	7.1
81		3.8	
83	4.4	17.9	5.2

[a] $\Sigma_{24} = 100\%$. [b] See text for structures. [c] Pyrolysis fragment of acid (V).

exhibit in their Curie-point pyrolysis mass spectra a large peak formally corresponding to $[M - H_2CO_3]$. The first step in the formation of this product will be the pyrolytic loss of water to give the cyclic anhydride, which may then eliminate carbon dioxide either pyrolytically or upon e.i. These are not easy to distinguish from each other: the absence of a peak corresponding to $[M - H_2O]$ in the pyrolysis mass spectra is not indicative of a pyrolytic loss of carbon dioxide, because the e.i. mass spectra of the anhydrides do not exhibit $M^{+\bullet}$ peaks, but strong $[M - CO_2]^{+\bullet}$ peaks instead. The c.a. spectrum of the ionized $[M - H_2CO_3]$ species from acid (III), however, suggests strongly that decarboxylation of the corresponding anhydride occurs both pyrolytically and upon e.i. (Table 6). The same may be true for the anhydrides from acids (IV)—(VI), especially because of the extensive dehydrogenation observed for their $[M - H_2CO_3]$ species (see Table 8). Such extensive dehydrogenation reactions are not seen to occur upon e.i. of the corresponding anhydrides or ketones themselves. Note also the preference for two-fold dehydrogenation in the case of acid (V) (Table 8), possibly the formation of phenol being the driving force.

B. *Acetic acid formation upon pyrolysis of acids* (I) *and* (III). The formation of acetic acid upon pyrolysis of acids (I) and (III) can be described as the result of either a 1,2-elimination reaction leading directly to acetic acid or a 1,5-hydrogen shift *via* a six-membered cyclic transition state leading to the enol form of acetic acid. The latter would then ketonize by collisions to the walls or other gaseous species in the expansion tube prior to ionization.

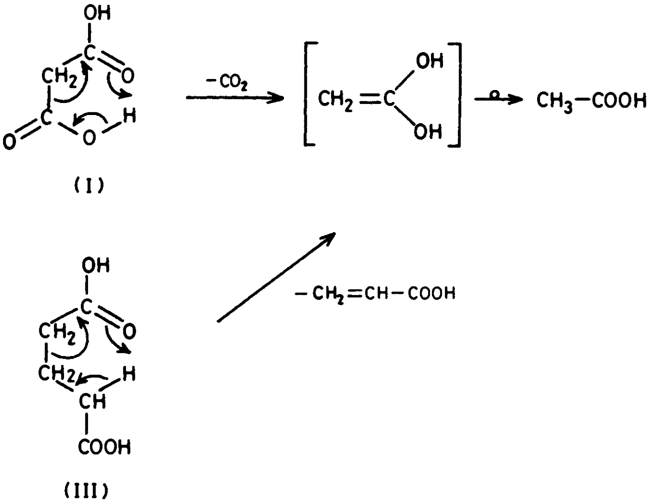
The fact that acetic acid is only formed from acids (I) and (III), in which a 1,5-shift of a mobile or *activated* hydrogen atom to a carbonyl group is possible, suggests strongly the 1,5-

Table 11. C.a. spectra of m/z 112 ions [a,b]

	Ion						
m/z	(9a)	(9b)	(9c)	(9d)[c]	(9e)[c]	(9f)[c]	(9g)[d]
36	0.2	1.5	1.5	0.2	0.1	0.5	1.1
37	1.0	7.0	7.7	0.9	0.8	2.4	5.9
38	1.5	12.5	12.8	1.8	1.3	4.5	10.3
39	7.5	14.1	13.3	7.0	4.0	9.5	17.5
40	1.8	1.9	1.0	1.8	1.3	3.7	2.9
41	7.4	2.1	1.2	8.0	3.9	3.6	1.4
42	5.2	1.3	0.8	5.2	9.8	1.6	1.3
43	2.7	0.2	0.2	2.5	4.7	3.4	1.1
44	0.2	0.8	0.5	0.2	0.3	0.5	0.5
45		7.4	6.1		0.2	1.5	6.7
49	0.2	0.7	0.8	0.2	0.2	0.4	0.6
50	1.0	0.8	0.9	0.8	0.5	0.8	1.0
51	1.3	0.4	0.3	1.3	0.6	0.8	0.3
52	0.8	0.3	0.3	0.7	0.3	0.5	0.4
53	2.4	2.0	2.7	1.9	0.9	2.1	2.6
54	1.9	0.6	0.4	2.1	0.5	0.8	0.5
55	9.7	3.6	3.4	9.9	4.9	2.8	2.7
56	3.2	1.1	0.9	4.3	1.0	1.4	0.5
57	0.7			0.7	0.4	0.6	0.1
58	0.4			0.5	0.2	0.1	
61	0.1			0.2			
62	0.1			0.2	0.2	0.2	
63	0.3			0.3	0.2	0.4	
65	0.5	0.9	1.2	0.7	0.5	0.8	0.5
66	0.7	3.0	3.2	0.7	0.5	1.4	2.7
67	2.1	2.8	4.4	3.0	1.1	3.8	4.0
68	12.4	1.1	0.7	12.4	1.6	24.0	0.8
69	8.7	0.5	0.4	6.2	3.0	7.4	1.5
70	2.0	0.3	0.2	2.2	3.0	3.7	0.8
84	13.1	7.1	2.7	13.3	52.7	13.5	28.2
94	7.4			7.3			
95		26.1	32.6				4.1
97	3.3			3.5	1.1	3.1	

[a] See text for structures. [b] $\Sigma_{36} = 100\%$. [c] Pyrolysis fragments of (9d): acid (VI); (9e): acid (III); (9f): acid (XI). [d] E.i. fragment of acid (XI).

hydrogen shift mechanism rather than the 1,2-elimination reaction to form eventually acetic acid as shown:

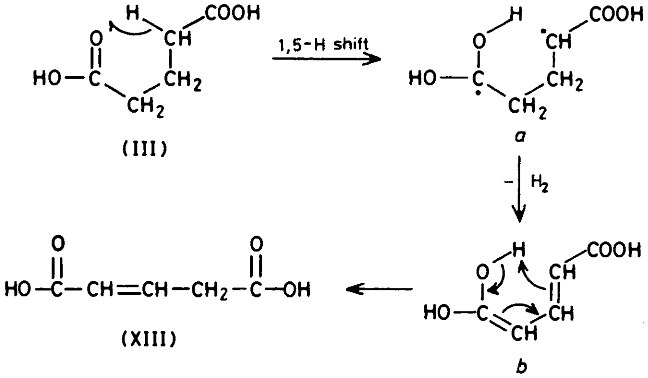


(I)

(III)

This mechanism is further supported by the occurrence of other specific pyrolysis reactions of acid (III) and by the formation of acetone upon pyrolysis of acids (I), (III), and (VII) as described in sections C and D.

C. *The importance of a* 1,5-H *shift as demonstrated by the deviating behaviour of acid* (III) *upon Curie-point pyrolysis.* Glutaric acid (III) is the only member of the saturated dicarboxylic acids investigated (I)—(VI) which shows an important peak in the pyrolysis mass spectrum due to formal loss of [H_2CO_2] at m/z 86 (see Figure 1). Direct 1,2-elimination of formic acid from (III) is very unlikely: there is no element in the structure of acid (III) that would favour such a reaction and no specialty in the molecule which could account for the specificity of the reaction. The possibility of water elimination prior to or following loss of carbon monoxide from acid (III) can be excluded as well: γ-butyrolactone would then be the product and this not found at all as shown by the c.a. results for m/z 86 (Table 7). A successive decarboxylation and dehydrogenation of acid (III) can also be excluded as the initially formed butyric acid, a rather volatile compound, would at least reach the ion source of the mass spectrometer partly undecomposed.



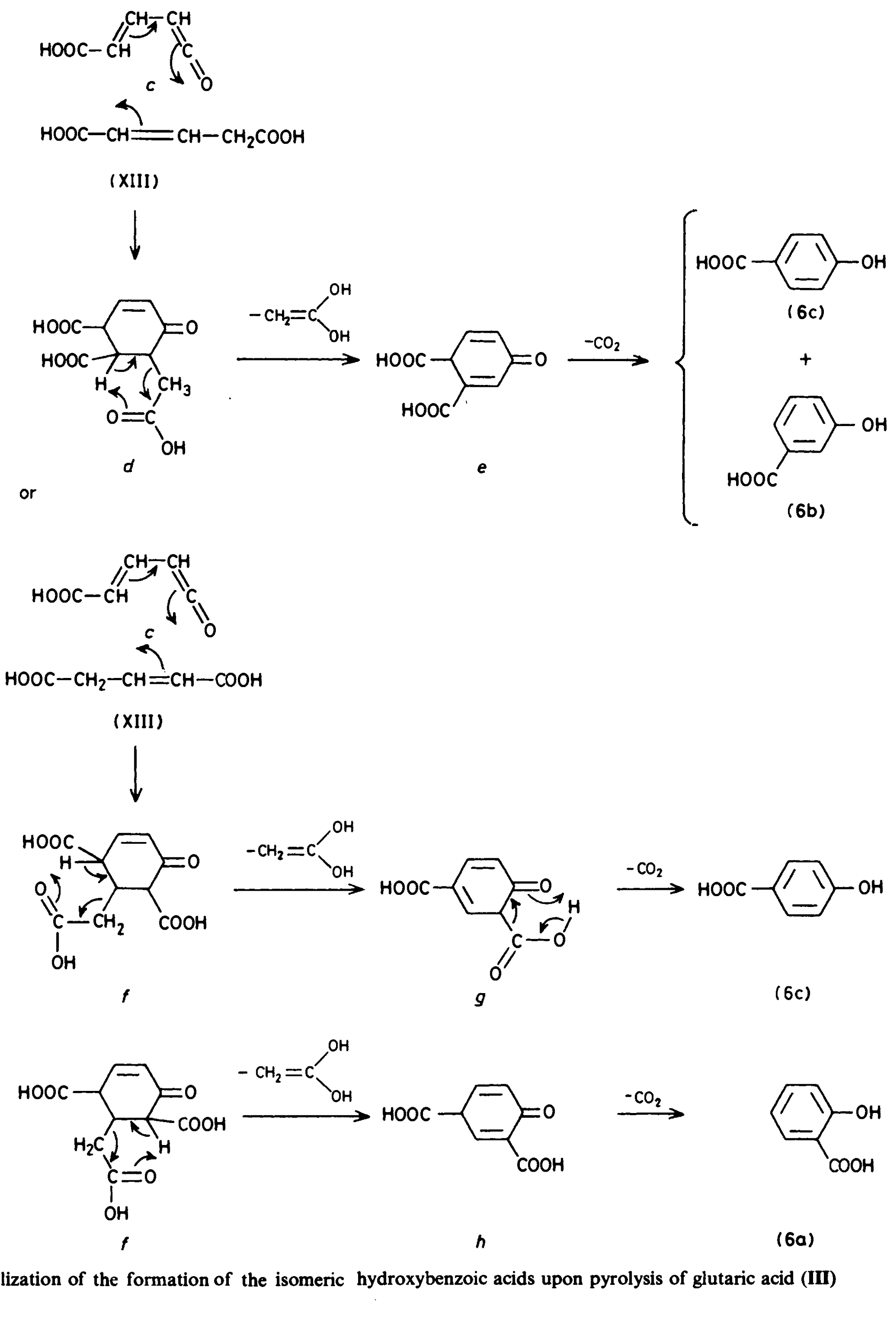
Scheme 1. Rationalization of the dehydrogenation of glutaric acid (III) upon Curie-point pyrolysis

It is also not clear why the reactions mentioned would only be valid for acid (III) and not for any of the other acids. An initial dehydrogenation of acid (III), however, can be understood very well on the basis of its structure as summarized in Scheme 1. Here a 1,5-shift of an activated hydrogen atom from one of the α-methylene groups to the carbonyl group at the other end of the molecule leads to the biradical species *a* which then can eliminate a hydrogen molecule to give the enolic species *b*. This on its turn may ketonize either intramolecularly by a 1,5-H shift or intermolecularly by collisions with other molecules or with the walls of the pyrolysis chamber and inlet lines to the mass spectrometer to yield acid (XIII).

The following observations further support this point of view. (1) The Curie-point pyrolysis mass spectrum of acid (III) contains peaks at m/z 72 and 60 due to products which can easily be formed by homolytic cleavage of the bond between the two methylene groups of the biradical species *a* (m/z 60 has been shown to be the ionized keto form of acetic acid and not the expected enol form; the neutral enolic form of acetic acid could ketonize rapidly by collisons with other molecules or with the walls of the pyrolysis chamber prior to ionization).

(2) The Curie-point pyrolysis mass spectrum of acid (III) contains rather intense peaks at m/z 112 and 84, especially at T_{Curie} 510 °C. Their formation can be explained readily from intermediate *b* (Scheme 1) by loss of water to give the ketene species *c*, $O=C=CH-CH=CH-COOH$ with M 112, which then can eliminate carbon monoxide by electron impact to give m/z 84.

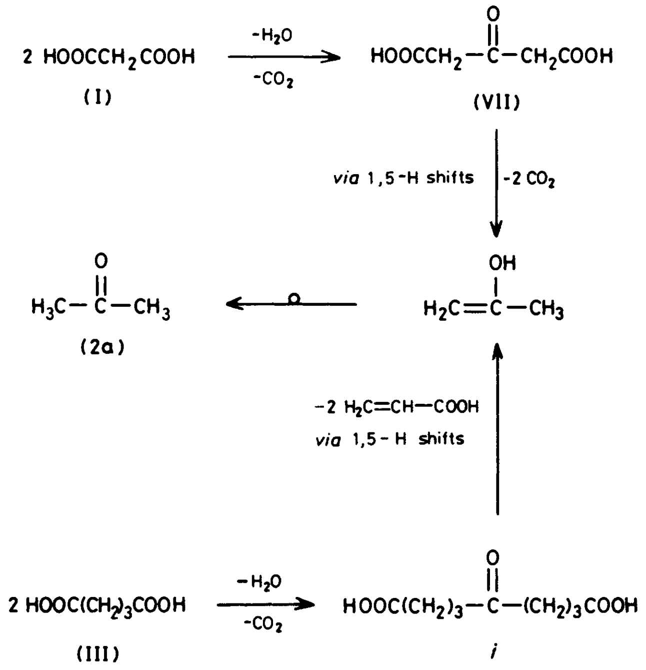
(3) The c.a. spectrum of products of m/z 86 generated upon p.m.s. of acid (III) is similar to that of products of m/z 86 generated upon p.m.s. of acid (XIII) (columns 5e and i of Table 7). This strongly supports the initial dehydrogenation of acid (III) as rationalized in Scheme 1 to give acid (XIII).



Scheme 2. Rationalization of the formation of the isomeric hydroxybenzoic acids upon pyrolysis of glutaric acid (III)

(4) The formation of the product *m*/*z* 138 from acid (**III**), especially at T_{Curie} 510 °C, can be understood and has even been predicted on the basis of a Diels–Alder reaction between the ketene species *c* (formed by dehydration of species *b* in Scheme 1) and the dehydrogenated glutaric acid, *i.e.* (**XIII**) (Scheme 1). Following the [2 + 4] cycloaddition reaction of these molecules elimination of enolic acetic acid and carbon dioxide in a series of steps results in the formation of hydroxybenzoic acids with *M* 138 as shown in Scheme 2 and proved to be the case by c.a. (Figure 2).

D. *Formation of acetone upon pyrolysis of acids* (**I**) *and* (**III**). The production of acetone upon Curie-point pyrolysis of acid (**I**) most probably proceeds *via* an initial intermolecular anhydride formation followed by decarboxylation of the anhydride function analogous to the intramolecular ketone formation from the higher acid homologues (**III**)—(**VI**). In this way acid (**VII**) will be the product formed. This view is supported by the results of Curie-point pyrolysis of (**VII**) itself, which show acetone to be the only detectable product. The latter demonstrates again the importance of the 1,5-shift of an activated hydrogen atom to a carbonyl group and the ketonization of an initially formed enolic species (Scheme 3). A similar intermolecular anhydride formation followed by decarboxylation of the anhydride in the case of acid (**III**) leads



Scheme 3. Rationalization of the formation of acetone upon Curie-point pyrolysis of malonic (I) and glutaric acid (III)

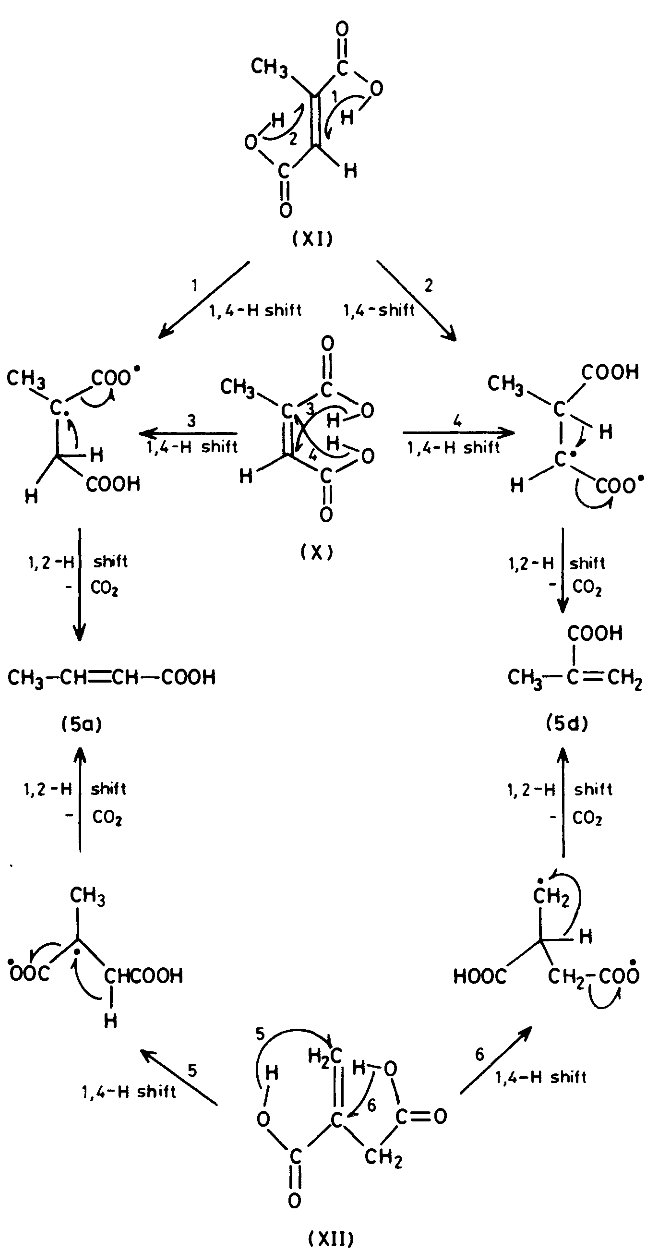
to product *i* which after a two-fold acrylic acid elimination *via* 1,5-H shifts also leads to acetone as the pyrolysis product (Scheme 3).

E. *The unsaturated dicarboxylic acids* (VIII) *and* (IX). The pyrolytic anhydride formation and subsequent e.i.-induced decarboxylation of maleic acid (VIII) are similar to those of the saturated acid (II) and will not be further discussed here.

The decarboxylation of fumaric acid (IX) is also not discussed as it can be compared directly with the results obtained for acids (X)—(XIII) discussed in section F. The pyrolysis fragment at *m/z* 82 of acid (IX) is most probably due to a reaction similar to that presented in Scheme 3 for acids (I) and (III), *i.e.* initial intermolecular anhydride formation followed by successive decarboxylation of the anhydride and two-fold decarboxylation of the carboxy-groups.

F. *Decarboxylation of the unsaturated dicarboxylic acids* (X)—(XIII). The acids (X)—(XII) all decarboxylate upon pyrolysis to give a mixture of crotonic and methacrylic acid as established by c.a. experiments. Although an isomerization of acids (X) and (XI) to (XII) *via* a high-energy 1,3-H sigmatropic shift might explain the decarboxylation of all three acids *via* an eventual 1,5-H shift, this can account for the formation of methacrylic acid, but not of crotonic acid. Furthermore, a reversed 1,3-H shift in acid (XII) would lead to the formation of acid (XI) which hardly takes place, if it occurs at all, as can be concluded from the very low abundance of fragments with *m/z* 112 and 84 in the Curie-point pyrolysis mass spectrum of (XII), although this acid can be calculated[9] to be *ca.* 20 kJ mol^{-1} less stable than (XI) (see Figure 4).

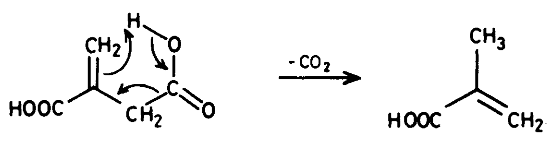
Two alternative mechanisms remain for the decarboxylation reactions. (i) A 1,2-elimination of CO_2 takes place at either end of the acid thus leading to a mixture of products. This mechanism can account for the formation of crotonic and methacrylic acid from acids (X) and (XI), but would predict a mixture of methacrylic acid and but-3-enoic acid as the pyrolysis products of acid (XII). But-3-enoic acid, however, is not found and a complete isomerization of this possibly formed acid to crotonic acid can be excluded, because of its abundant formation from acids (III) and (XIII) under the same pyrolytic conditions.



Scheme 4. Rationalization of the decarboxylation of acids (X)—(XII) upon Curie-point pyrolysis

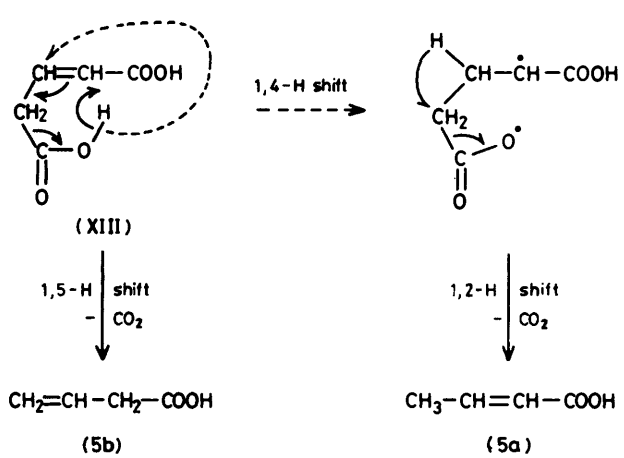
(ii) An initial 1,4-H transfer occurs from either of the carboxylic acid groups to the double bond. The decarboxylation reaction might then either occur simultaneously with or follow a thermodynamically controlled 1,2-H shift as reported in a recent Curie-point pyrolysis study of some unsaturated carboxylic acids.[2i] This mechanism can account for all products formed upon pyrolysis of the acids (X)—(XII) and is presented in Scheme 4.

The larger yield of methacrylic acid upon pyrolysis of acid (XII) than that upon pyrolysis of the acids (X) and (XI) can readily be explained as being due to a *ca.* 20% additional contribution of the 1,5-H shift-induced decarboxylation reaction, as described in the literature: [2a]



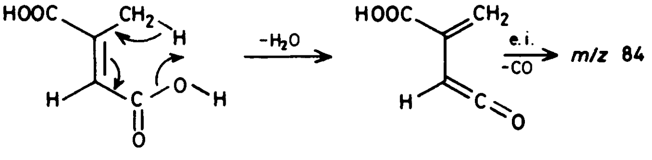
(XII)

The formation of crotonic acid upon pyrolysis of acid **(XIII)** can be explained by the same mechanism as involved in the decarboxylation of acids **(X)**—**(XII)** if CO_2 originates from the saturated end of the molecule, *i.e.* by successive 1,4- and 1,2-H shifts (Scheme 5). This CO_2 molecule can also be eliminated *via* a 1,5-H shift to give but-3-enoic acid, which accounts for 25% of the total decarboxylated products of acid **(XIII)** (Scheme 5).



Scheme 5. Rationalization of the decarboxylation of glutaconic acid **(XIII)** from the saturated end of the molecule, leading to crotonic and but-3-enoic acid

G. *Other pyrolytic reactions of the unsaturated dicarboxylic acids* **(X)** *and* **(XI)**. The main peak in the Curie-point pyrolysis mass spectrum of the maleic acid homologue **(X)** is found at *m/z* 68 (Figure 4). The origin of this peak can readily be explained by dehydration of the acid to form the anhydride followed by an e.i.-induced decarboxylation [compare with the behaviour of acid **(VIII)**]. The large peak at *m/z* 112 accompanied by the peak at *m/z* 84 in the Curie-point pyrolysis mass spectrum of acid **(XI)** can also be explained by an abundant dehydration of the molecule leading to a pyrolysis product with *M* 112, which then decarbonylates upon e.i. to produce the fragment ion of *m/z* 84. The pyrolytic dehydration may proceed *via* a mechanism similar to that of the e.i.-[4a] and f.i.-induced[8] dehydration of the molecular ion of acid **(XI)**:



(XI) *M* 112

Experimental

Instruments.—The complete pyrolysis mass spectra were recorded with a quadrupole mass spectrometer equipped with a Curie-point pyrolysis inlet system; details of this instrument and of the Curie-point pyrolysis method have been described elsewhere.[10] The c.a. spectra were obtained with a tandem mass spectrometer constructed at the FOM Institute in Amsterdam. A detailed description of this instrument has been given by Louter *et al.*[3]

The reference compounds were introduced into the ion source *via* a septum inlet system (100—150 °C) with the exception of the hydroxybenzoic acids which were introduced *via* a direct insertion probe at room temperature. Ions were generated by electron impact (70 and 14 eV) and accelerated to 6 keV kinetic energy.

The pyrolysis of the acids was performed on line in high vacuum by means of a Curie-point pyrolysis inlet system to a maximum temperature of 610 °C (standard conditions) and 510 °C [acid **(III)**], reached in 0.1 s[10] and using sample amounts of 2 μg. The gaseous pyrolysis products leaked during 4.5 s *via* an expansion chamber into the ion source. Molecular ions were generated by e.i. (13—14 eV) and accelerated to 6 keV kinetic energy.

In the c.a. experiments the first magnet of the tandem mass spectrometer was set to transmit the ions under investigation. Helium was used as the collision gas and its pressure in the collision cell was adjusted in such a manner that the total fragment ion current reached an optimum value for the reference ions investigated at a particular *m/z* value. This pressure was used and kept constant during all c.a. experiments of the p.m.s. products with the same *m/z* value. The adjustment of the collision cell gas pressure was repeated for every other *m/z* value studied.

The post-acceleration voltage was set on 15 kV during all experiments. Every c.a. spectrum reported in this work was recorded simultaneously and with unit mass resolution in the mass regions tabulated.

Materials.—The various dicarboxylic acids and reference compounds used were commercially available.

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