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Thermal decomposition of 2-(4-aminophenyl)- and 2-(2,4-diaminophenyl)malonic acids and derivatives ☆

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Abstract

The thermal decomposition of the hydrochloride salts of 2-(4-aminophenyl)- and 2-(2,4-diaminophenyl)malonic acids, the corresponding diethyl esters, and the respective sodium carboxylates has been examined using thermogravimetry. Thermal decomposition of the hydrochlorides of the carboxylic acids occurs by sequential loss of two moles of carbon dioxide per mole of salt followed by loss of hydrogen chloride at approximately 400°C. The corresponding diethyl esters undergo initial degradation by loss of two moles of ethylene and a mole of carbon dioxide per mole of salt. This is followed, in sequence, by loss of a second mole of carbon dioxide and then one or two moles of hydrogen chloride depending on the identity of the amine salt undergoing decomposition. The sodium salts of the neutralized amino acids do not undergo significant decomposition below 800°C.

Keywords: Aminoaromatic acid; Decomposition; DTG; TGA

1. Introduction

The thermal decomposition of amine salts, principally quaternary ammonium hydroxides, has long been of interest as a means of preparing alkenes [1,2]. The thermal fragmentation of other amine salts has been much less well-documented [3–6].

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In addition to alkenes, products from the thermal decomposition of alkylammonium halides often include amine, alkyl halide and hydrogen halide [5,6]. The degradation of arylammonium salts has not been examined in any detail. In this work the thermal decomposition of the hydrochloride salts of 2-(4-aminophenyl)- and 2-(2,4-diaminophenyl)malonic acids, the corresponding diethyl esters and the respective sodium carboxylates, has been studied.

2. Experimental

2.1. Materials

Diethyl 2-(4-nitrophenyl)malonate and diethyl 2-(2,4-dinitrophenyl)malonate were obtained by synthesis as previously described [7]. Hydrogen chloride was commercial material from Matheson Gas Products (PA 18936-9969, USA). Palladium on charcoal (10% Pd/C) was obtained from Matheson, Coleman and Bell (OH 45212, USA). Hydrogen was high purity from Scott Specialty Gases, Inc. (PA 18949-9983, USA). Common solvents and mineral acids were supplied by the Fisher Scientific Company (IL 60143, USA).

2.2. Diethyl 2-(4-aminophenyl)malonate hydrochloride

A solution of 4.53 g (0.016 mol) of diethyl 2-(4-nitrophenyl)malonate in 80 ml of 95% aqueous ethanol and 0.50 g of 10% Pd/C was shaken at room temperature (Parr low-pressure hydrogenation apparatus) under 3 atm of hydrogen for 10 h. The mixture was filtered through Celite to remove the catalyst and the solvent was removed by rotary evaporation at reduced pressure. The residue was dissolved in 50 ml of ethyl acetate. Dry hydrogen chloride gas was bubbled through the solution until no more solid was being formed. The solid hydrochloride was collected by filtration at reduced pressure, washed with two 25 ml portions of ethyl acetate and three 25 ml portions of hexane, and allowed to dry to afford 4.63 g (90.5% yield) of 2-(4-aminophenyl)malonate hydrochloride, m.p. 192°C (DSC): IR (cm^{-1}, KBr) 2986 (m) (aromatic C–H), 2815 (s-broad) (amino group, N–H), 1730 (vs) (carbonyl), 1509 (m) (aromatic nucleus), 1217, 1147 (s) (ester C–O); proton NMR (δ, DMSO-d_6) 1.25 (t, 6 H, $J = 6.1$ Hz, methyl protons), 3.62 (broad s, 3 H, amino protons), 4.18 (q, 4 H, $J = 6.1$ Hz, methylene protons), 5.03 (s, 1 H benzylic proton), 7.40 (AB pattern, 4 H, $J_{AB} = 8.4$ Hz, $\Delta\nu_{AB} = 39.3$ Hz, aromatic protons); carbon-13 NMR (δ, DMSO-d_6) 14.0 (methyl carbon atoms), 56.2 (benzylic carbon atom), 61.6 (methylene carbon atoms), 122.8, 130.7, 132.2, 132.9 (aromatic carbon atoms), 167.9 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 178 (100%), 251 (29%), 106 (27%), 150 (15%), 103 (11%), 77 (9%), 36 (7%), 252 (4%).

2.3. 2-(4-Aminophenyl)malonic acid hydrochloride

A solution of 5.01 g (0.017 mol) of diethyl 2-(4-aminophenyl)malonate and 4.88 g (0.087 mol) of potassium hydroxide in 60 ml of 50% aqueous ethanol was stirred

for 1 h at 60°C and most of the solvent was removed by rotary evaporation at reduced pressure. The residual syrup was dissolved in 100 ml of ethyl acetate. Dry hydrogen chloride was bubbled into the solution until no further solid was formed. The pale yellow precipitate was collected by filtration at reduced pressure, washed with four 25 ml portions of ethyl acetate, and dried at reduced pressure (2 Torr; over Dririte) to afford 3.72 g (93.3% yield) of 2-(4-aminophenyl)malonic acid hydrochloride: m.p. 201°C (DSC) IR (cm^{-1}, KBr) 3387, 3146, 2885 (s-broad) (N–H and O–H), 2604 (s-broad) (amine salt, N–H), 1639, 1609 (s) (carbonyl), 1509 (vs) (aromatic nucleus), proton NMR (δ, DMSO-d_6) 3.38 (broad s, 3 H, amino protons), 4.40 (s, 1 H, benzylic proton), 6.80 (AB pattern, 4 H, $J_{AB} = 8.4$ Hz, $\Delta\nu_{AB} = 138.1$ Hz, aromatic protons); carbon-13 NMR (δ, DMSO-d_6) 56.7 (benzylic carbon atom), 114.4, 114.5, 124.1, 129.7 (aromatic carbon atoms), 173.1 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 106 (100%), 144 (30%), 151 (27%).

2.4. *Sodium 2-(4-aminophenyl)malonate*

A suspension of 1.02 g (4.31 mmol) of 2-(4-aminophenyl)malonate hydrochloride and 0.69 g (6.51 mmol) of sodium carbonate in 150 ml of benzene was stirred at solvent reflux under a Dean-Stark trap (to collect water as it was formed) for 12 h. The solvent was removed by rotary evaporation at reduced pressure to afford sodium 2-(4-aminophenyl)malonate as a yellow solid: IR (cm^{-1}, KBr) 3390, 3331 (s-broad) (N–H), 1586 (s), 1441 (m) (carbonyl), 1357 (m) (aromatic nucleus); proton NMR (δ, D_2O) 4.34 (s, 1 H, benzylic proton), 6.93 (AB pattern, 4 H, $J_{AB} = 9.1$ Hz, $\Delta\nu_{AB} = 89.6$ Hz, aromatic protons); mass spectrum, m/z (% of base) 151 (31%), 107 (11%), 106 (100%), 77 (15%), 52 (10%), 44 (68%).

2.5. *Diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride*

Diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride was prepared in 91.4% yield by reduction of the corresponding dinitro compound as described above for diethyl 2-(4-aminophenyl)malonate: IR (cm^{-1}, KBr) 2925 (s-broad) (N–H), 1629 (s) (carbonyl), 1594 (m) (aromatic nucleus); proton NMR (δ, DMSO-d_6) 1.33 (t, 6 H, $J = 7.2$ Hz, methyl protons), 4.48 (broad s, 6 H, amino protons), 4.27 (q, 4 H, $J = 7.2$ Hz, methylene protons), 4.44 (s, 1 H, benzylic proton), 7.48 (AB portion of ABX pattern, 2 H, $J_{AB} = 8.3$ Hz, $\Delta\nu_{AB} = 194.9$ Hz, $J_{BX} = 1.5$ Hz, aromatic protons), 7.07 (X portion of ABX pattern, 1 H, aromatic proton); mass spectrum, m/z (% of base) 220 (22%), 174 (18%), 171 (13%), 148 (26%), 147 (100%), 119 (14%), 65 (10%), 57 (14%), 55 (12%), 46 (10%), 45 (25%), 43 (17%), 41 (14%), 38 (26%), 36 (75%), 35 (13%).

2.6. *2-(2,4-Diaminophenyl)malonic acid dihydrochloride*

A mixture of 0.51 g (1.47 mmol) of diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride, 4.02 g (17.3 mmol) of formic acid and three drops of concentrated

aqueous sulfuric acid solution was stirred at 50–60°C for 2.3 h. Formic acid/ethyl formate was removed by rotary evaporation at reduced pressure. The residue was collected and dried at reduced pressure (2 Torr) over Drierite to afford 2-(2,4-diaminophenyl)malonic acid dihydrochloride (86.7% yield) as a fine brown powder, m.p. 240°C (DSC): IR (cm^{-1}, KBr) 2925 (s, broad, N–H), 1629 (s, carbonyl), 1508 (m, aromatic nucleus); proton NMR (δ, DMSO-d_6) 3.50 (s, 1 H, benzylic proton), 3.84 (broad s, 6 H, amino protons) 7.06 (AB portion ABX pattern, 2 H, $J_{AB} = 7.8$ Hz, $\Delta\nu_{AB} = 126.4$ Hz, $J_{BX} = 1.3$ Hz, aromatic protons), 6.79 (X portion of ABX pattern, 1 H, aromatic proton); carbon-13 NMR (δ, DMSO-d_6) 35.3 (benzylic carbon atom), 103.8, 115.2, 125.1, 125.4, 131.1, 144.7 (aromatic carbon atoms), 176.3 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 171 (88%), 148 (100%), 120 (55%), 119 (71%), 71 (54%), 57 (91%), 55 (46%), 41 (73%).

2.7. (4-Aminophenyl)acetic acid hydrochloride

Reduction of 5.00 g (0.028 mol) of (4-nitrophenyl)acetic acid using the method described above afforded 4.21 g (87.9% yield) of (4-aminophenyl)acetic acid hydrochloride as a white crystalline solid, m.p. 247°C (DSC): IR (cm^{-1}, KBr) 3026 (s-broad, O–H and N–H), 1695 (vs, carbonyl), 1505 (s, aromatic nucleus); proton NMR (δ, DMSO-d_6) 3.61 (s, 2 H, methylene protons), 7.34 (AB pattern, 4 H, $J_{AB} = 8.6$ Hz, $\Delta\nu_{AB} = 12.5$ Hz, aromatic protons), 10.35 (broad s, 4 H, N–H and O–H protons); carbon-13 NMR (δ, DMSO-d_6) 38.4 (methylene carbon atom), 121.4, 129.2, 129.3, 133.3 (aromatic carbon atoms), 170.9 (carbonyl carbon atom); mass spectrum, m/z (% of base) 106 (100%), 151 (23%), 36 (15%), 77 (10%).

2.8. 4-Aminotoluene hydrochloride

Reduction of 2.04 g (0.015 mol) of 4-nitrotoluene using the method described above afforded 1.87 g (89.3% yield) of 4-aminotoluene hydrochloride as a white crystalline solid: IR (cm^{-1}, KBr) 2845 (s-broad, N–H), 1504 (m, aromatic nucleus); proton NMR (δ, DMSO-d_6) 2.25 (s, 3 H, methyl protons), 7.33 (AB pattern, 4 H, $J_{AB} = 8.3$ Hz, $\Delta\nu_{AB} = 35.3$ Hz, aromatic protons), 7.59 (broad s, 3 H, amino protons); carbon-13 NMR (δ, DMSO-d_6) 20.4 (methyl carbon atom), 122.9, 129.2, 129.9, 137.3 (aromatic carbon atoms); mass spectrum, m/z (% of base) 106 (100%), 107 (59%), 36 (31%), 77 (17%).

2.9. Structural characterization

All new compounds were fully characterized spectroscopically. Infrared (IR) spectra were recorded using dilute (1%) solid solutions in anhydrous potassium bromide (as pressed discs) and a Perkin-Elmer model 1600 FTIR spectrometer (Perkin-Elmer, CT 06859, USA). Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded using dilute (5–20%) solutions in perdeuterodimethyl sulfoxide (DMSO-d_6) or deuterium oxide (D_2O) and a General Electric QE-300 NMR spectrometer (General Electric NMR Instruments, CA 94539-7482, USA).

Melting points were determined by differential scanning calorimetry (DSC) using a TA Instruments model 2910 DSC unit (Hewlett-Packard, CA 94304, USA). Mass spectra were obtained using a Hewlett-Packard 5995 A GC–MS instrument with inlet via a direct insertion probe (TA Instruments, Inc., DE 19720, USA).

2.10. Thermogravimetry

The thermal degradation characteristics of 2-(aminoaryl)malonic acid derivatives were examined by thermogravimetry using a TA Instruments 2100 thermal analyzer coupled with a 2910 TGA unit. In a typical run the temperature was ramped at a rate of 10°C min^{-1} from 50°C to 1000°C (or beyond the temperature of maximum decomposition). The TGA cell was swept with nitrogen at 50 ml min^{-1} during degradation runs and the sample (approximately 20 mg) was contained in a platinum sample pan. Decay plots (mass loss versus temperature) were generated by feeding the analyzer output (TA Instruments software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter supplied by TA Instruments. Extrapolated onset temperature for degradation and the temperature of maximum degradation were obtained from the derivative plot of mass loss versus temperature.

3. Results and discussion

The thermal decomposition of 2-(4-aminophenyl)malonic acid hydrochloride and 2-(2,4-diaminophenyl)malonic acid dihydrochloride and derivatives has been exam-

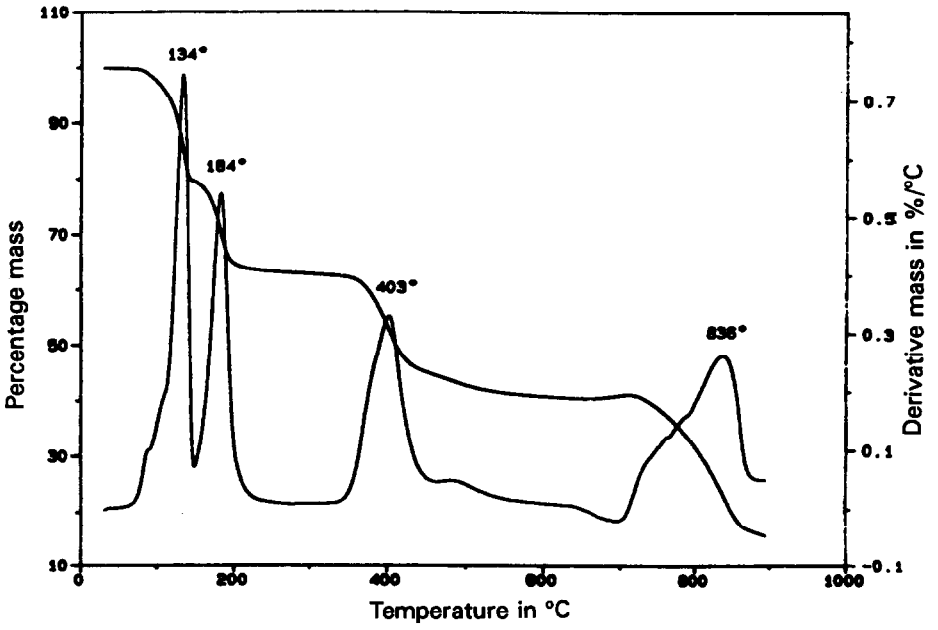
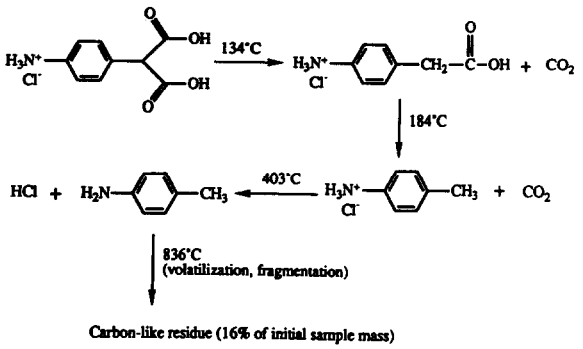


Fig. 1. Thermogram for the thermal degradation of 2-(4-aminophenyl)malonic acid hydrochloride.



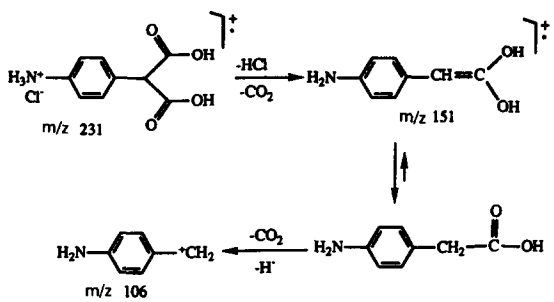
Scheme 1. Mode of thermal decomposition of 2-(4-aminophenyl)malonic acid hydrochloride.

ined using thermogravimetry. The decomposition of 2-(4-aminophenyl)malonic acid hydrochloride is depicted in Fig. 1 and occurs in four distinct major phases. The first major mass loss occurs at 134°C and corresponds to the loss of a first mole of carbon dioxide (19.4% of the initial sample mass lost). The second probably reflects the loss of a second mole of carbon dioxide (12.1% of the initial sample mass lost). The third occurs at 403°C and corresponds to the loss of hydrogen chloride (19.4% of the initial sample mass lost). The final mass loss occurs at 836°C and probably reflects volatilization of small products of the decomposition as well as some fragmentation (see peak shape). The proposed mode of decomposition is shown in Scheme 1. Support for the proposed mode of decomposition is available from several sources. First, the observed mass losses are in reasonably good agreement with those calculated (19.1%, 19.1%, 15.6%) for the sequential loss of two moles of carbon dioxide followed by a mole of hydrogen chloride. Second, malonic acids are known to undergo sequential loss of carbon dioxide when subjected to electron bombardment [8]. Third, the loss of hydrogen chloride at about 400°C occurs for a variety of other amine hydrochlorides. Fourth, phenylmalonic acid itself undergoes sequential loss of two moles of carbon dioxide at 136°C and 150°C, respectively. The scheme for decomposition of this salt is also supported by the decomposition of (4-aminophenyl)acetic acid hydrochloride prepared independently. The acetic acid salt loses carbon dioxide at 206°C and hydrogen chloride at 387°C. 4-Aminotoluene hydrochloride, in the absence of any residue matrix, undergoes complete volatilization at 188°C.

The mass spectra of 2-(4-aminophenyl)malonic acid hydrochloride, (4-aminophenyl)acetic acid hydrochloride, and 4-aminotoluene hydrochloride are illustrated in Table 1. These spectra contain several similarities, including a base peak at m/z 106, and suggests that fragmentation of 2-(4-aminophenyl)malonic acid hydrochloride occurs as depicted in Scheme 2. The mass spectral fragmentation of 2-(4-aminophenyl)malonic acid hydrochloride is thus reminiscent of the thermal degradation of this salt in that loss of carbon dioxide and hydrogen chloride are the major events which characterize the fragmentation.

Table 1
Mass spectral framentation of 2-(4-aminophenyl)malonic acid hydrochloride, (4-aminophenyl)acetic acid hydrochloride, and 4-aminotoluene hydrochloride

2-(4-Aminophenyl)malonic acid hydrochloride		(4-Aminophenyl)acetic acid hydrochloride		4-Aminotoluene hydrochloride	
Fragment (m/z)	Intensity (% of base)	Fragment (m/z)	Intensity (% of base)	Fragment (m/z)	Intensity (% of base)
171	3	151	23	107	59
152	3	107	6	106	100
151	27	106	100	79	10
107	7	77	10	77	17
106	100	36	15		
77	11				
44	30				
43	4				



Scheme 2. Mass spectral fragmentation of 2-(4-aminophenyl)malonic acid hydrochloride.

The thermal decomposition of the hydrochloride salt of the corresponding ester, diethyl 2-(4-aminophenyl)malonate hydrochloride, is more complex and is depicted in Fig. 2. Three thermal events can be detected and a substantial residue (37% of the initial sample mass) remains at 900°C. The major event occurs at 174°C and corresponds to a loss of 36% of the initial sample mass. This is probably reflective of the loss of two moles of ethylene and a mole of carbon dioxide per mole of salt. Subsequent losses occur with maxima at 287°C (13% of the initial sample mass) and 465°C (15% of the initial sample mass). These might be attributed to the loss of a second mole of carbon dioxide and a mole of hydrogen chloride, respectively. However, the shape of the derivative plot (see Fig. 2) for these events suggest that neither may represent a well-defined transformation.

Mass spectral data for the diethyl ester hydrochloride are contained in Table 2 and the fragmentation pattern for this salt is shown in Scheme 3.

As observed for the corresponding acid, the initial loss is a molecule of hydrogen chloride. This is followed by the concerted loss of carbon dioxide and ethylene to

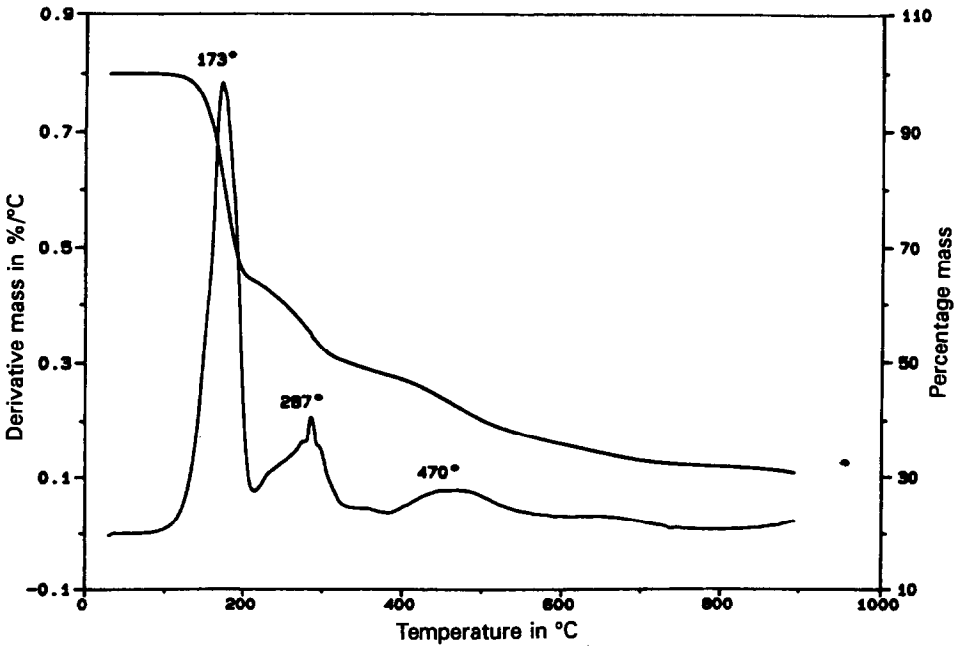


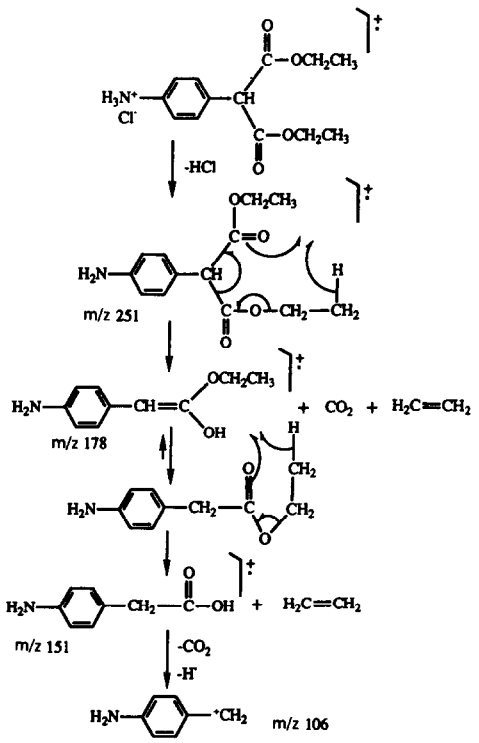
Fig. 2. Thermogram for the thermal degradation of diethyl 2-(4-aminophenyl)malonate hydrochloride.

Table 2
Mass spectral fragmentation of diethyl 2-(4-aminophenyl)malonate hydrochloride

Fragment (m/z)	Intensity (% of base)	Fragment (m/z)	Intensity (% of base)
251	27	104	11
178	100	94	10
150	16	77	9
122	14	51	4
106	35	37	5

generate ethyl (4-aminophenyl)acetate radical cation corresponding to the base peak in the spectrum. Further McLafferty-type loss of ethylene affords the radical cation of (4-aminophenyl)acetic acid (m/z 106) as noted before for the fragmentation of (4-aminophenyl)malonic acid hydrochloride. The mass spectral fragmentation involving an initial loss of hydrogen chloride, ethylene, and carbon dioxide does not directly parallel the thermal decomposition of the salt for which the loss of both ethylene and carbon dioxide apparently precedes the loss of hydrogen chloride.

In contrast to behavior of the hydrochlorides of either 2-(4-aminophenyl)malonic acid or the diethyl ester, the sodium salt of the neutralized acid does not undergo significant decomposition at temperatures below 800°C (see Fig. 3).



Scheme 3. Mass spectral fragmentation of diethyl 2-(4-aminophenyl)malonate hydrochloride.

The thermal decomposition of 2-(2,4-diaminophenyl)malonic acid dihydrochloride is, in the initial stages, reminiscent of that of the corresponding hydrochloride salt of the monoamino acid. As can be seen in Fig. 4 the initial thermal event corresponds to sequential loss of two moles of carbon dioxide at 202°C and 267°C, respectively. Additional loss occurs but much more gradually. A shoulder in the thermogram at about 400°C may be suggestive of the loss of hydrogen chloride. By 650°C, 57% of the initial sample mass, which would correspond to the loss of two moles of carbon dioxide and two moles of hydrogen chloride per mole of salt, has been lost. No other major fragmentation occurs below 800°C.

The thermal decomposition of diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride is depicted in Fig. 5. An initial mass loss corresponding to approximately 30% of the initial sample mass occurs at 186°C and reflects the loss of two moles of ethylene and a mole of carbon dioxide per mole of salt. This is followed by loss of a second mole of carbon dioxide (291°C; 13% of the initial sample mass) and slow loss of two moles of hydrogen chloride (centered at 464°C, complete by 600°C; 21% of the initial sample mass). The thermal fragmentation of this material is outlined in Scheme 4. It might be noted that this scheme parallels that observed for the decomposition of the monoamino compound (same heating rate) except that

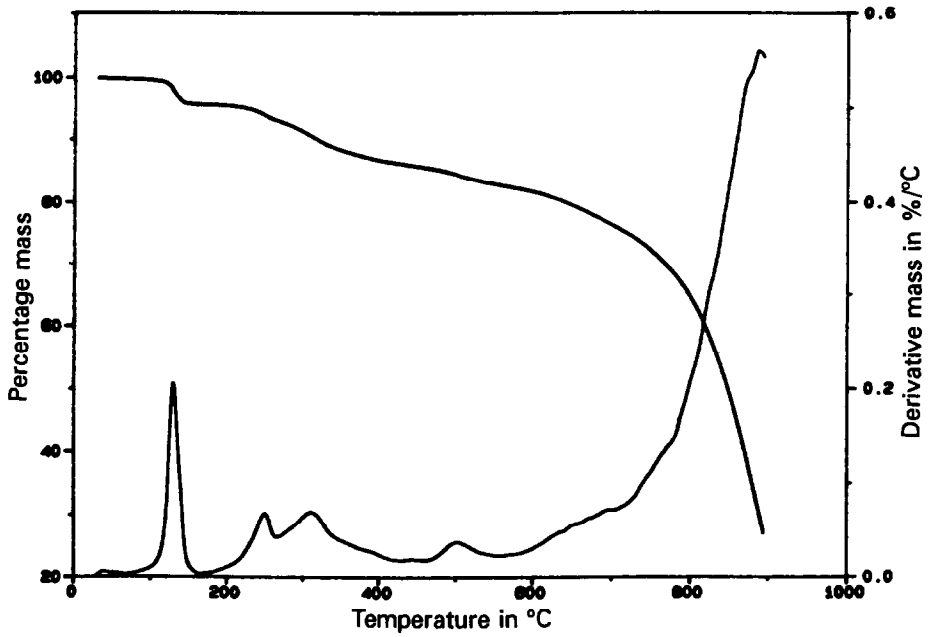


Fig. 3. Thermogram for the thermal decomposition of sodium 2-(4-aminophenyl)malonate.

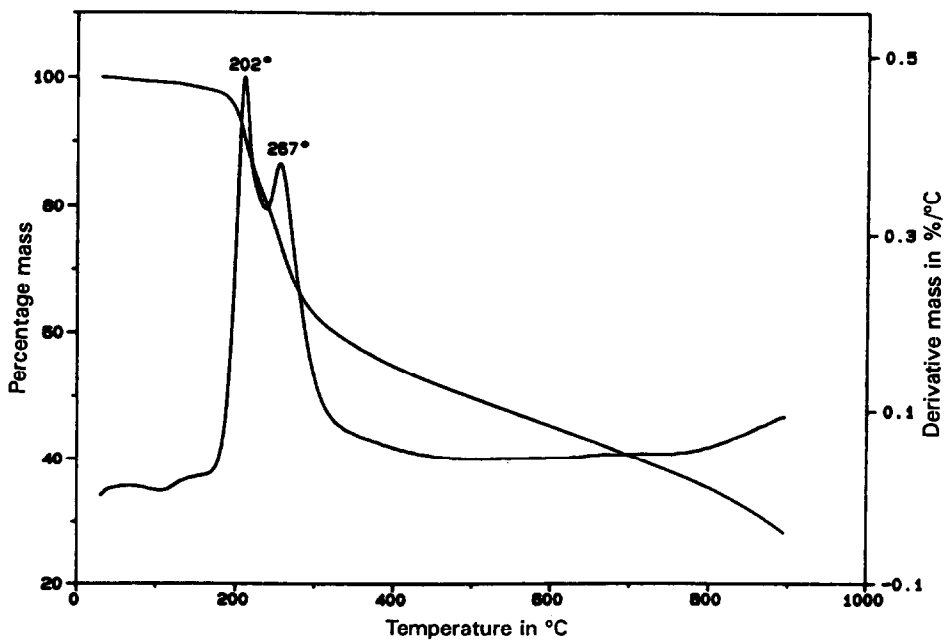


Fig. 4. Thermogram for the thermal degradation of 2-(2,4-diaminophenyl)malonic acid dihydrochloride

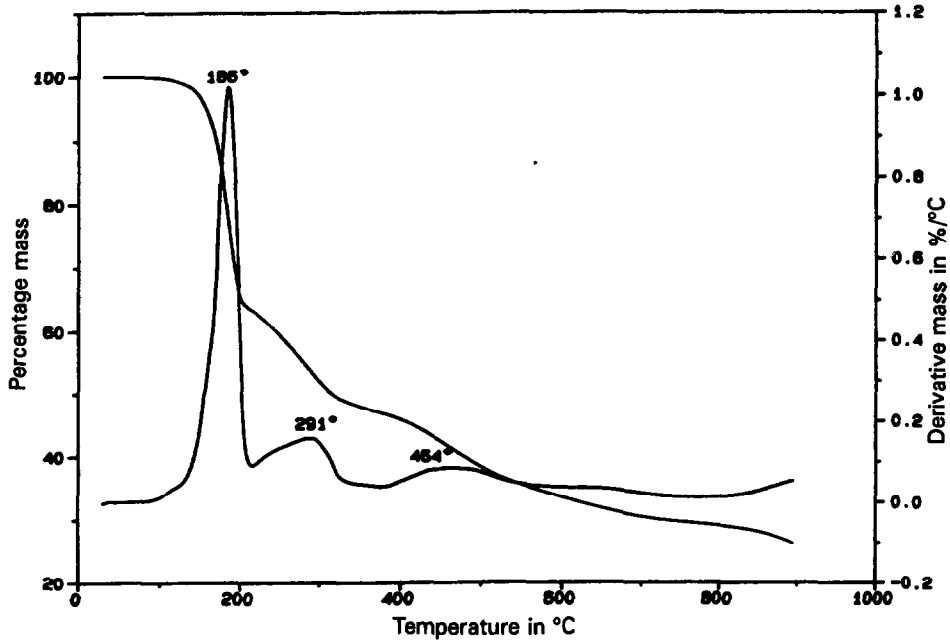
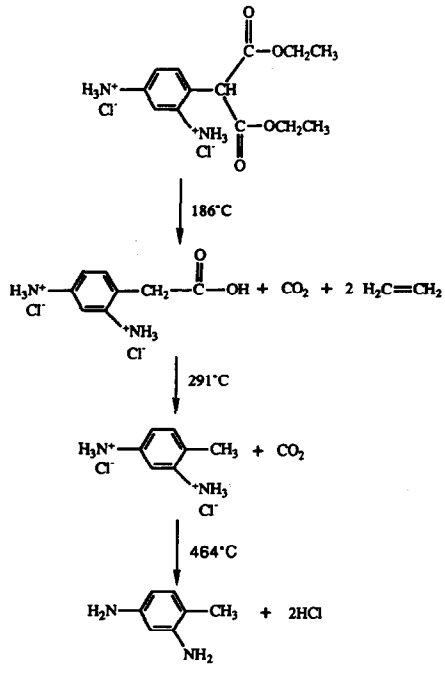


Fig. 5. Thermogram for the thermal degradation of diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride.



Scheme 4. Mode of thermal decomposition of diethyl 2-(2,4-diaminophenyl)malonate dihydrochloride

the temperatures for the various stages of decomposition are somewhat higher and less sharply delineated.

4. Conclusions

The thermal decomposition of 2-(4-aminophenyl)malonic acid hydrochloride occurs by sequential loss of carbon dioxide, at 134°C and 184°C, followed by loss of hydrogen chloride (403°C), and finally volatilization/fragmentation at 836°C. The hydrochloride of the corresponding diethyl ester also undergoes stepwise thermal fragmentation involving an initial loss (174°C) of two moles of ethylene and a mole of carbon dioxide per mole of salt. Subsequent losses may be attributed to carbon dioxide (287°C) and hydrogen chloride (465°C). Sodium 2-(4-aminophenyl)malonate does not undergo significant thermal decomposition at temperatures below 800°C. The thermal decomposition of the hydrochlorides of the corresponding 2,4-diamino acid and ester parallels that observed for the monoamino compounds.

Acknowledgments

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References

[1] S. Patai (Ed.), The Chemistry of the Amino Group, John Wiley, New York, NY, 1968, pp. 409–416.
[2] W.H. Saunders, Jr. and A.F. Cockerill, Mechanisms of Elimination Reactions, John Wiley, New York, NY, 1973, p. 405.
[3] C. Ainsworth and N.R. Easton, J. Org. Chem., 27 (1962) 4118.
[4] N.I. Singh and S. Mitra, Thermochim. Acta, 197 (1992) 341.
[5] E. Bourgeat-Lami, F. DiRenzo, F. Fajula, P.H. Mutin and T. Des Courineres, J. Phys. Chem., 96 (1992) 3807.
[6] P. Charlier, R. Jerome, P. Teyssie and R.E. Prud'homme, J. Polym. Sci., Polym. Chem. Ed., 31 (1993) 129.
[7] B.A. Howell and M. Liu, Thermochim. Acta, 243 (1994) 169.
[8] S.W. Tam, in S. Patai (Ed.), The Chemistry of Acid Derivatives, Pt. 1, John Wiley, New York, NY, 1979, Chapter 4.