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Thermal decomposition of 2-(4-nitrophenyl)- and 2-(2,4-dinitrophenyl)malonic acids and derivatives [☆]

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Abstract

The thermal decomposition of 2-(4-nitrophenyl)- and 2-(2,4-dinitrophenyl)malonic acids, the corresponding diethyl esters, and the respective sodium carboxylates has been examined using thermogravimetry. Thermal decomposition of the carboxylic acids occurs by sequential loss of two moles of carbon dioxide per mole of acid followed by volatilization of the nitroaromatic formed. The corresponding diethyl esters undergo rapid decomposition at temperatures approaching 200°C to afford in addition to volatile products (carbon dioxide) significant amounts of nonvolatile residue.

Keywords: Decomposition; DTG; Nitroaromatic acid; TGA

1. Introduction

The thermal decomposition of aryl carboxylic acids and derivatives has long been of interest [1–4]. Many of these materials find application in the manufacture of explosives and polymers. The behavior of malonic acid derivatives under thermal stress has also been explored [5]. The acids themselves generally undergo decarboxylation to afford the corresponding acetic acid as the initial thermally-stimulated event.

In this work the decomposition of 2-(4-nitrophenyl)- and 2-(2,4-dinitrophenyl)malonic acid, the corresponding diethyl esters, and the sodium carboxylates have been examined by thermogravimetry and/or mass spectrometry.

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2. Experimental

2.1. *Materials*

Diethyl malonate, 4-nitrochlorobenzene, 2,4-dinitrochlorobenzene, dimethyl sulfoxide (DMSO), and potassium *t*-butoxide were obtained from Aldrich Chemical Company, WI 53233, USA. Sodium hydride was obtained from Ventron/Alfa Inorganics, Inc., MA 01835-0147, USA. Hydrogen chloride was commercial material from Matheson Gas Products, PA 18936-9969, USA. Common solvents and mineral acids were supplied by the Fisher Scientific Company, IL 60143, USA.

2.2. *Diethyl 2-(4-nitrophenyl)malonate*

To a stirred solution of 14.01 g (0.125 mol) of potassium *t*-butoxide in 100 ml of freshly-distilled DMSO maintained in an atmosphere of dry nitrogen was added, dropwise over a period 0.35 h, 20.0 g (18.9 ml, 0.125 mol) of diethyl malonate. Heat was evolved and the solution acquired a light yellow color. Solid 4-nitrochlorobenzene (9.84 g, 0.065 mol) was added portionwise over 0.5 h. Heat was evolved (the temperature rose to 60°C) and the color of the solution darkened to a deep purple. After the addition was complete the mixture was stirred at 95–105°C for 3 h, allowed to cool to near room temperature, and poured with vigorous stirring into a slurry of 300 ml of ice and 10 ml of concentrated (37%) aqueous hydrochloric acid solution. The pale yellow precipitate which formed was collected by filtration at reduced pressure, washed with five 60 ml portions of water, allowed to dry, and crystallized from ethyl acetate/hexane (1 : 5) to afford 13.44 g (84.2% yield) of diethyl 2-(4-nitrophenyl)malonate as pale yellow needles: m.p. 61°C (by DSC); IR (cm^{-1}, KBr) 2989 (w), 2985 (m), 2975 (w) (aliphatic C–H), 1740 (vs), 1720 (s) (carbonyl group), 1604 (m) (aromatic nucleus), 1524 (s), 1348 (s) (aromatic nitro group, N–O), 1228 (s), 1142 (s) (ester C–O), 861 (s) (aromatic nitro group, C–N); proton NMR (δ, $CDCl_3$) 1.27 (t, 6 H, $J = 7.2$ Hz, methyl protons), 4.23 (q, 4 H, $J = 7.2$ Hz, 4 H, methylene protons), 4.72 (s, 1 H, benzylic proton), 7.92 (AB pattern, 4 H, $J_{AB} = 9.1$ Hz, $\Delta\nu_{AB} = 185.8$ Hz, aromatic protons); carbon-13 NMR (δ, $CDCl_3$) 14.0 (methyl carbon atoms), 57.6 (methylene carbon atoms), 62.4 (benzylic carbon atoms), 123.7, 130.5, 139.6, 147.8 (aromatic carbon atoms), 167.0 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 209 (100%), 181 (85%), 163 (42%), 137 (30%), 136 (22%), 89 (22%), 78 (17%), 63 (15%), 106 (14%), 237 (9%), 281 (9%).

2.3. *2-(4-Nitrophenyl)malonic acid*

A mixture of 6.00 g (0.02 mol) of diethyl 2-(4-nitrophenyl)malonate and 7.02 g (0.125 mol) of potassium hydroxide in 60 ml of 50% aqueous ethanol was stirred for 1 h at 60°C. The mixture was allowed to cool to room temperature and extracted with four 30 ml portions of diethyl ether to remove most of the ethanol present. The aqueous solution was acidified by the careful addition of 10 ml of concentrated aqueous (37%) hydrochloric acid solution. The white precipitate which formed was collected by filtration at reduced pressure, washed with four 30 ml portions of water, allowed to dry, and recrystallized from methanol/water (5 : 2) to afford 4.42 g (92.1% yield) of 2-(4-nitrophenyl)malonic acid as white plates, m.p. 153–154°C: IR (cm^{-1}, KBr) 3116 (m), 3086 (m), (aromatic C–H), 3016 (m), 2956 (m), (broad, O–H), 1689 (vs), (carbonyl), 1609 (s), (aromatic nucleus), 1539 (vs), 1348 (s), (aromatic nitro group), 1217 (s), 1197 (s) (ester C–O), 851 (m) (aromatic nitro group, C–N); proton NMR (δ, DMSO-d_6) 3.97 (s, 1 H, benzylic proton), 7.89 (AB pattern, 4 H, $J_{AB} = 8.6$ Hz, $\Delta\nu_{AB} = 188.8$ Hz, aromatic protons); carbon-13 NMR (δ, DMSO-d_6) 38.7 (benzylic carbon atom), 121.8, 129.5, 141.7, 144.9 (aromatic carbon atoms), 170.3 (carbonyl carbon atoms); mass spectrum, *m/z* (% of base) 181 (100%), 91 (79%), 89 (53%), 77 (48%), 63 (43%), 78 (42%), 29 (41%), 79 (39%), 136 (36%), 45 (27%), 51 (27%), 90 (25%), 107 (25%), 106 (22%), 44 (19%), 43 (15%), 62 (15%), 65 (15%), 171 (13%), 50 (12%), 57 (12%), 41 (11%), 55 (11%), 182 (11%).

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

A suspension of 0.76 g (3.41 mmol) of 2-(4-nitrophenyl)malonic acid and 0.36 g (3.41 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 10 h. The solvent was removed by rotary evaporation at reduced pressure to afford sodium 2-(4-nitrophenyl)malonate as white powder (0.814 g, 89.9% yield): IR (cm^{-1}, KBr) 3080 (w) (aromatic C–H), 2954 (w), 2846 (w) (aliphatic C–H), 1606 (vs) 1394 (s) (carbonyl) 1517 (vs), 1358 (s) (aromatic nitro group), 853 (m) (aromatic nitro group C–N stretch); proton NMR (δ, D_2O) 3.64 (s, 1 H, benzylic proton), 7.80 (AB pattern, 4 H, $J_{AB} = 8.9$ Hz, $\Delta\nu_{AB} = 212.8$ Hz, aromatic protons); mass spectrum, *m/z* (% of base) 254 (25%), 240 (100%), 194 (28%), 193 (29%), 178 (51%), 177 (41%), 176 (51%), 164 (42%), 165 (91%), 152 (32%), 136 (51%), 106 (24%), 90 (18%), 89 (28%), 78 (23%), 76 (27%), 63 (33%), 51 (27%).

2.5. *Diethyl 2-(2-4-dinitrophenyl)malonate*

To a stirred solution of 9.02 g (0.080 mol) of potassium *t*-butoxide in 100 ml of freshly distilled DMSO maintained in an atmosphere of dry nitrogen was added, dropwise over a period of 0.2 h, 13.01 g (0.081 mol) of diethyl malonate. To the stirred light yellow solution was added, portionwise over a period of 0.5 h, 9.03 g (0.044 mol) of 2,4-dinitrochlorobenzene. Heat was evolved and the reaction mixture acquired a dark-purple color. After the addition was complete, the mixture was stirred at 80–90°C for 3 h, allowed to cool to room temperature, and poured with vigorous stirring into a slurry of 200 ml of ice and 10 ml of concentrated (37%) aqueous hydrochloric acid solution. The yellow precipitate which formed was collected by filtration at reduced pressure, washed with four 40 ml portions of water, allowed to dry, and recrystallized from ethanol/water (5 : 1) to afford diethyl 2-(2,4-dintriophenyl)malonate (13.42 g, 93.5% yield) as brown needles, m.p. 47–48°C: IR (cm^{-1}, KBr) 3086 (w), 3081 (w) (aromatic C–H), 2986 (w), 2946 (vw), 2875 (vw) (aliphatic C–H), 1745 (vs), 1725 (vs) (carbonyl, 1604 (m) (aromatic nucleus), 1534 (vs), 1353 (vs) (nitro group), 1238 (m) (ester C–O); proton NMR (δ, $CDCl_3$) 1.30 (t, 6 H, $J = 7.2$ Hz, methyl protons), 4.29 (q, 4 H, $J = 7.2$ Hz, methylene protons), 5.36 (s, 1 H, benzylic proton), 8.15 (AB portion of ABX pattern, 2 H, $J_{AB} = 9.1$ Hz, $\Delta\nu_{AB} = 199.2$ Hz, $J_{BX} = 2.3$ Hz, aromatic protons), 8.91 (X portion of ABX pattern, 1 H, aromatic proton); carbon-13 NMR (δ, $CDCl_3$) 14.3 (methyl carbon atoms), 54.6 (methylene carbon atoms), 63.2 (benzylic carbon atom), 120.9, 127.6, 133.5, 134.7, 147.9, 149.3 (aromatic carbon atoms), 166.4 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 147 (100%), 36 (75%), 37 (26%), 148 (26%), 45 (25%), 20 (22%), 174 (18%).

2.6. 2-(2,4-Dinitrophenyl)malonic acid

A mixture of 40.1 g (0.17 mol) of formic acid, 0.52 g (0.015 mol) of diethyl 2-(2,4-dinitrophenyl)malonate, and ten drops of concentrated aqueous (98%) sulfuric acid solution was stirred at 50–60°C for 10 h. Formic acid/ethyl formate was removed by evaporation. The crystalline material that formed was collected, washed successively with two 30 ml portions of ethyl acetate and four 30 ml portions of water, and dried at reduced pressure (20 Torr over Dririte) to afford 2-(2,4-dinitrophenyl)malonic acid (3.79 g, 91.5% yield) as brown needles, m.p. 192°C (DSC): IR (cm^{-1}, KBr) 3056 (w), 3016 (w) (aromatic C–H), 2946 (w), 2875 (w), 2745 (vw) (aliphatic C–H), 3106–2875 (w, broad) (carboxyl), 1700 (vs) (carbonyl), 1604 (m) (aromatic nucleus), 1534 (vs), 1348 (vs) (aromatic nitro group); proton NMR (δ, DMSO-d_6) 4.16 (s, 1 H, benzylic proton), 8.20 (AB portion of ABX pattern, 2 H, $J_{AB} = 8.5$ Hz, $\Delta\nu_{AB} = 199.9$ Hz, $J_{BX} = 2.6$ Hz, aromatic protons), 8.90 (X portion of ABX pattern, 1 H, aromatic proton); carbon-13 NMR (δ, DMSO-d_6) 41.8 (benzylic carbon atom), 199.9, 127.6, 135.1, 137.2, 146.6, 148.4 (aromatic carbon atoms), 168.3 (carbonyl carbon atoms); mass spectrum, m/z (% of base) 180 (35%) 165 (100%), 119 (21%), 91 (10%), 90 (23%), 89 (52%), 78 (25%), 72 (28%), 63 (68%), 52 (23%), 51 (33%), 44 (74%), 39 (34%).

2.7. Sodium 2-(2,4-dinitrophenyl)malonate

A suspension of 0.51 g (1.81 mmol) of 2-(2,4-dinitrophenyl)malonic acid and 0.195 g (1.81 mmol) of sodium carbonate in 150 ml of benzene was stirred at solvent reflux under a Dean-Stark trap for 12 h. The solvent was removed by rotary evaporation at reduced pressure to afford sodium 2-(2,4-dinitrophenyl)malonate as a pale yellow powder (0.47 g, 79.5% yield): IR (cm^{-1}, KBr) 3016 (m) (aromatic C–H), 2875 (w) (aliphatic C–H), 1584 (vs), 1382 (s) (carbonyl), 1538 (vs), 1349 (s) (aromatic nitro group), 835 (s) (aromatic nitro group, C–N); proton NMR (δ, D_2O) 4.00 (s, 1 H, benzylic proton), 8.08 (AB portion of ABX pattern, 2 H, $J_{AB} = 8.5$ Hz, $\Delta\nu_{AB} = 241.3$ Hz, aromatic protons), 8.95 (X portion of ABX pattern, $J_{BX} = 2.9$ Hz); mass spectrum, m/z (% of base) 181 (10%), 165 (100%), 119 (16%), 90 (16%), 89 (43%), 78 (10%), 63 (27%), 51 (12%), 44 (93%), 39 (20%).

2.8. 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 deuterochloroform ($CDCl_3$) or perdeuterodimethyl sulfoxide (DMSO-d_6) 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 (TA Instruments, Inc., DE 19720, USA). Mass spectra were obtained using a Hewlett-Packard 5995 A GC–MS instrument with inlet via a direct insertion probe (Hewlett-Packard Co., CA 94304, USA).

2.9. Thermogravimetry

The thermal degradation characteristics of 2-(nitroaryl)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 degradation characteristics of 2-(4-nitrophenyl)malonic acid and 2-(2,4-dinitrophenyl)malonic acid, the corresponding diethyl esters and the respective sodium salts have been examined using thermogravimetry and/or mass spectrometry. A plot of mass loss versus temperature with the temperature increasing at a rate of 10°C min^{-1} for 2-(4-nitrophenyl)malonic acid is shown in Fig. 1. By analogy with the decomposition of 2-phenylmalonic acid, depicted in Fig. 2, this probably reflects sequential loss of two moles of carbon dioxide per mole of acid followed by volatilization of the 4-nitrotoluene formed. A residue (approximately 20% of the initial sample mass) suggests that these processes are accompanied by some carbonization of the sample.

The mass spectral fragmentation of 2-(4-nitrophenyl)malonic acid follows a similar course (see Table 1). The base peak in the spectrum appears at m/z 181 and

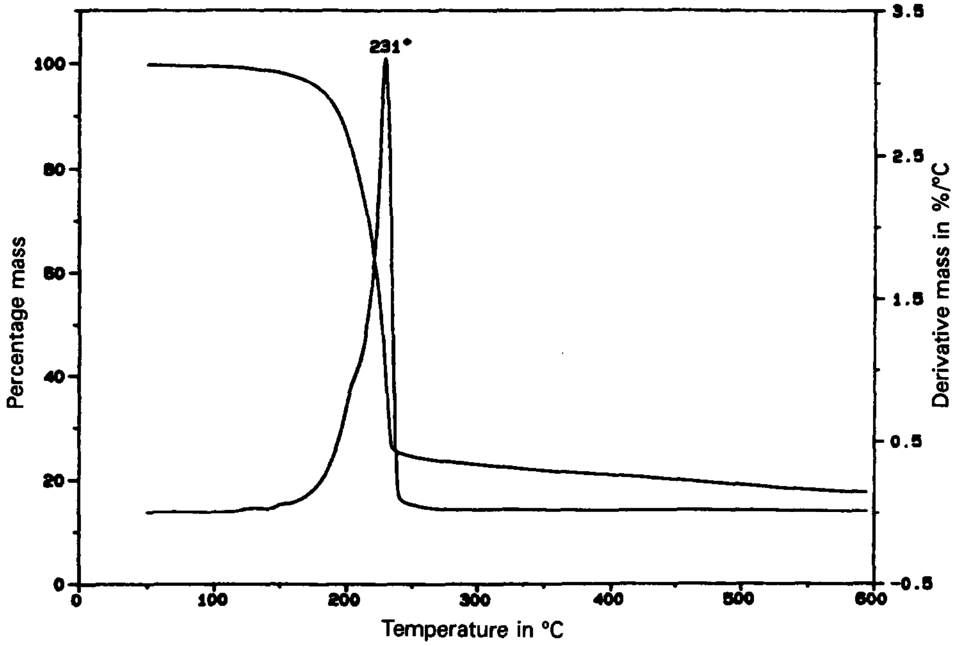


Fig. 1. Thermogram for the degradation/volatilization of 2-(4-nitrophenyl)malonic acid.

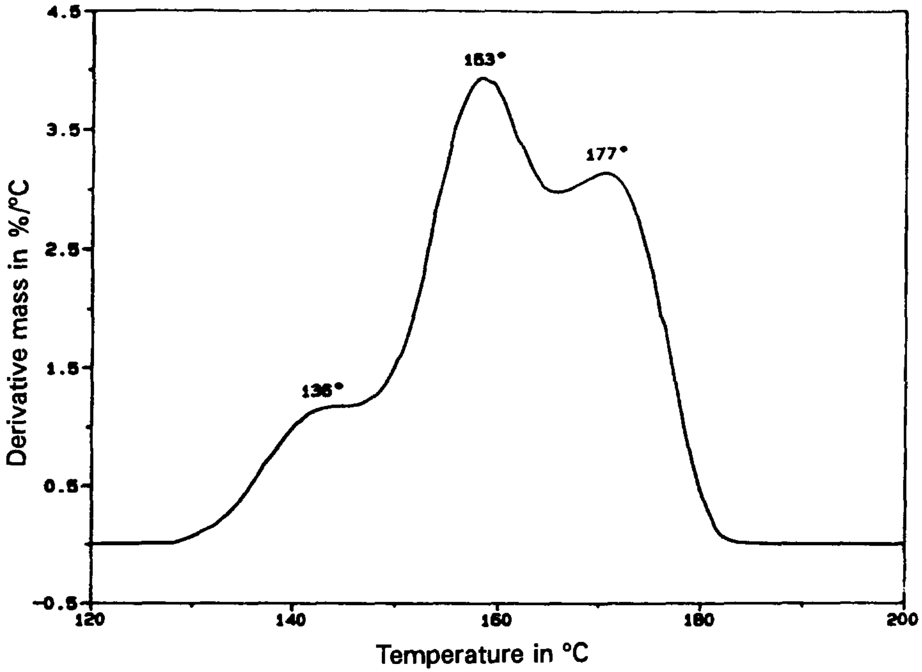


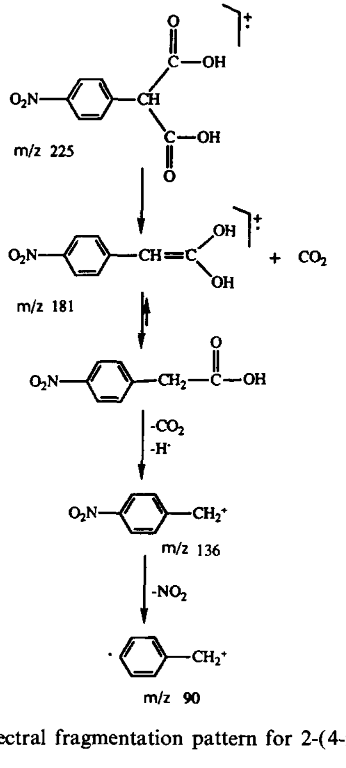
Fig. 2. Thermogram for the degradation/volatilization of 2-phenylmalonic acid.

Table 1
Mass spectral fragmentation of 2-(4-nitrophenyl)malonic acid

Fragment (*m*/*z*)	Intensity (% of base)	Fragment (*m*/*z*)	Intensity (% of base)
181	100	79	39
171	13	78	42
136	36	63	43
107	25	51	27
106	22	50	12
91	79	45	27
90	25	44	19
89	53	39	41

corresponds to the loss of carbon dioxide from the molecular ion. A prominent peak is also observed at *m*/*z* 136 corresponding to a second loss of carbon dioxide. The most probable fragmentation pattern for 2-(4-nitrophenyl)malonic acid is shown in Scheme 1.

The corresponding diethyl ester undergoes volatilization without fragmentation at 228°C while the corresponding sodium carboxylate undergoes catastrophic loss



Scheme 1. Partial mass spectral fragmentation pattern for 2-(4-nitrophenyl)malonic acid.

of carbon dioxide and perhaps nitrogen dioxide at about 200°C to yield a stable residue corresponding to approximately half of the initial sample mass (see Fig. 3).

The mass spectral data for diethyl 2-(4-nitrophenyl)malonate are displayed in Table 2. The base peak in the spectrum appears at *m/z* 209 and corresponds to loss of ethylene from the molecular ion. This is followed by sequential loss of ethylene and carbon dioxide. The fragmentation pattern is displayed in Scheme 2.

Fragmentation/volatilization similar to that which occurs for the mononitro acid is also observed for 2-(2,4-dinitrophenyl)malonic acid at 218°C. The thermal fragmentation of the corresponding ester, diethyl 2-(2,4-dinitrophenyl)malonate, also occurs readily with sequential loss of ethylene and carbon dioxide. This decomposition is displayed in Fig. 4. Several stages of decomposition are apparent.

By analogy with the fragmentation observed for other malonate esters [6], the decomposition of this ester may be rationalized as shown in Scheme 3. The mass spectrum of the ester contains a base peak at *m/z* 181 (2,4-dinitrobenzyl cation) suggesting that the fragmentation occurring there is similar to that for thermal decomposition.

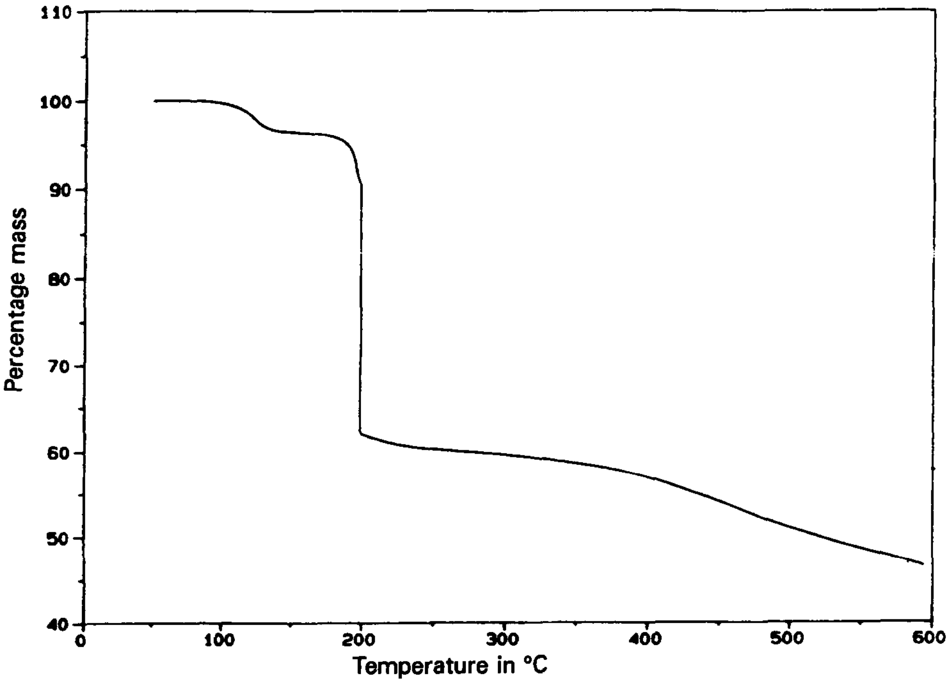
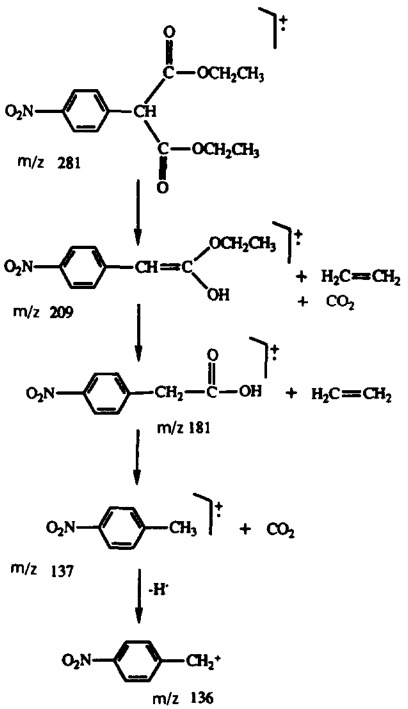


Fig. 3. Thermogram for the decomposition of sodium 2-(4-nitrophenyl)malonate.

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

Fragment (*m*/*z*)	Intensity (% of base)	Fragment (*m*/*z*)	Intensity (% of base)
281	9	137	30
209	100	136	22
208	19	89	22
181	85	78	17
163	42	63	15
152	20	39	10



Scheme 2. Mass spectral fragmentation pattern for diethyl 2-(4-nitrophenyl)malonate.

Sodium 2-(2,4-dinitrophenyl)malonate undergoes decomposition at about 150°C to afford a residue corresponding to approximately 45% of the initial sample mass.

4. Conclusions

The thermal decomposition of 2-(4-nitrophenyl)malonic acid and 2-(2,4-dinitrophenyl)malonic acid occurs at moderate temperatures (less than 250°C) and in-

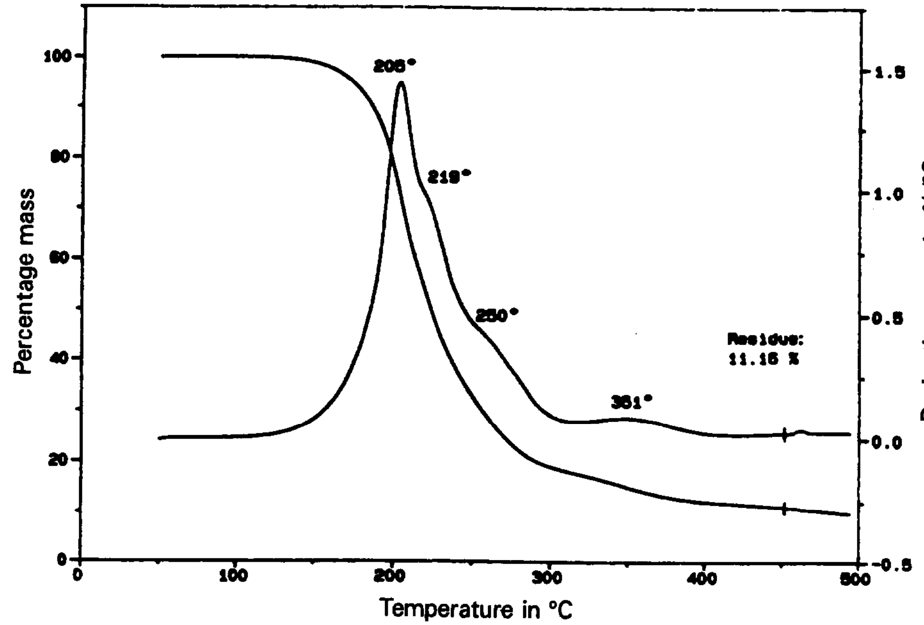
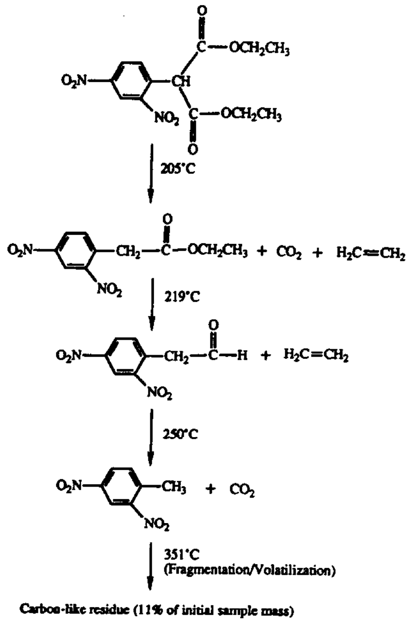


Fig. 4. Thermogram for the decomposition of diethyl 2-(2,4-dinitrophenyl)malonate.



Scheme 3. Mode of thermal degradation for diethyl 2-(2,4-dinitrophenyl)malonate.

volves sequential loss of carbon dioxide as initial steps. The decomposition of the corresponding ethyl esters involves an initial loss of ethylene and carbon dioxide followed by the sequential loss, firstly of a second mole of ethylene and then carbon dioxide. Decomposition of the sodium carboxylates occurs catastrophically at 150–200°C (loss of carbon dioxide and perhaps nitrogen dioxide) to yield a stable residue corresponding to approximately 45% of the initial sample mass.

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