

DIFFERENTIAL THERMAL GRAVIMETRIC ANALYSIS OF UNSATURATED SULTAM DERIVATIVES

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ABSTRACT

The thermal decompositions in a nitrogen atmosphere of different unsaturated sultam derivatives is reported: they are in accordance with our data for electron-impact mass spectrometry fragmentation pathways. For comparison the unsaturated sultone and the saturated sultam derivatives are included together with the DTG profiles for all the studied compounds.

INTRODUCTION

It has been reported that pyrolysis of 2,4-dimethyl-1,3-butadiene sultam derivatives releases SO_2 giving rise to the pyrrol ring [1]. Trials to prepare pyrrol derivatives from different unsaturated sultams gave poor yields [2].

Thermogravimetry (TG) continuously measures the loss of weight of a material as a function of temperature, so the application of this technique to different sultam derivatives may help to explain the reason for the low yield of the pyrolysis product, i.e. pyrrol. In addition, in DTG the derivative of the mass change with respect to time is recorded as a function of temperature which is an additional advantage.

In this study, we report the DTG curves of different unsaturated sultam rings as an adjunct to our mass spectrometric studies [3,4]. Thermal decomposition in an atmosphere of flowing dry nitrogen gives further information, as does the consideration of the description of the sultone ring [5] and its saturated sultam ring [6] systems under TG conditions.

EXPERIMENTAL

A known amount of each compound was weighed into pans (alumina crucibles) and sealed; the pan lid was pricked with a pin before being tared.

Thermal analysis was carried out in a nitrogen atmosphere, at a flow rate of 200 cc min⁻¹, using a Mettler TA 3000 [7]. The starting temperature ranged between 40 and 50 °C and the finishing temperature was 400 °C. The compounds studied are shown in Table 1.

TABLE 1
Compounds studied and TG details

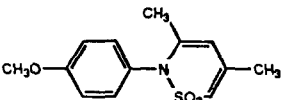
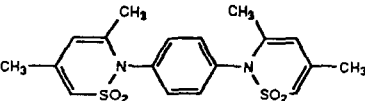
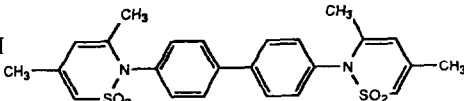
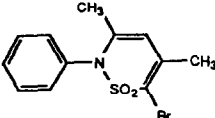
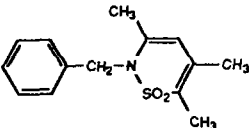
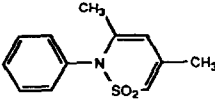
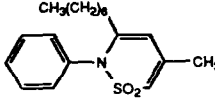
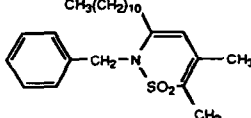
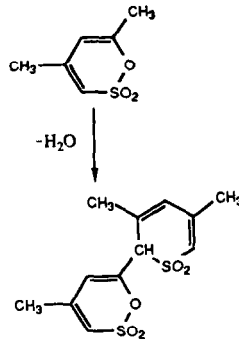
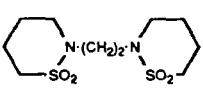
Compound	Weight (mg)	Calc.	Found	Start temp./end temp. (°C)	Peak temperature (°C)
I 	8.487	59.62	59.22	50/300	288.3
II 	9.350	80.61	82.33	50/400	284.2
III 	10.762	32.47	32.522	50/300	278.2
IV 	5.197	29.93	29.96	40/180	142.2
V 	10.140	34.60	36.105	50/400	276.7
VI 	10.649	93.6	94.99	50/280	261.7
VII 	9.724	all evap.	100	50/400	277.5
VIII 	7.567	all evap.	100	50/400	265

TABLE 1 (continued)

Compound	Weight (mg)	Calc.	Found	Start temp./end temp. (°C)	Peak temperature (°C)		
IX		10.127	11.25	13.18	50/250	151.7	
			26.15	25.81		181.7	
				0.044	40/180	40	
				0.123		45	
				0.88		65	
X		11.340	stable	0.035		110	
					0.052		127
					0.044		135
					0.070		156

Compounds I–X were prepared by previously published procedures [1,2,5,6,8,9]. Each substance was crystallised from the appropriate solvent until further crystallisation caused no change in melting points.

RESULTS AND DISCUSSION

The general pattern shown from the TG curves for compounds I, II and III indicated loss of a moiety, or moieties, from the molecule without the elimination of SO₂ to give rise to the pyrrol rings. The peak temperature was nearly the same in all cases, i.e. 288, 284 and 278°C respectively.

Such results were in accord with an earlier publication [3] in which the elimination of SO₂, studied by impact mass spectrometry, was shown to be governed by the relative strengths of the alkyl sulphur bond. The presence of an electron-attracting group, such as a chlorine atom, exerts a weakening influence on the alkyl sulphur bond, and hence tends to facilitate the loss of

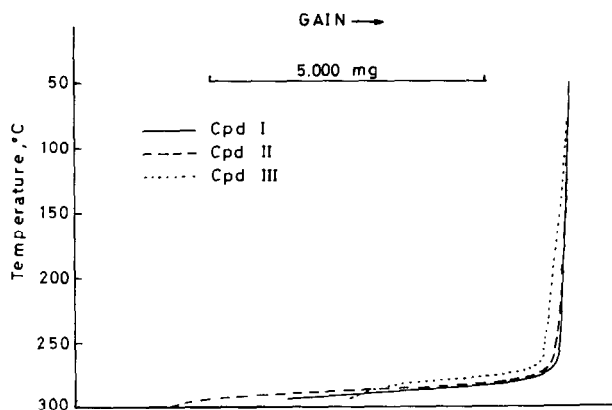


Fig. 1. TG profile for compounds **I**, **II** and **III**.

SO₂. On the other hand, the presence of electron-donating groups, such as the methyl group, will strengthen the bond and lowers the probability of the elimination of SO₂.

The thermal behaviour (TG) of compounds **I**, **II** and **III** is shown in Fig. 1. The DTG profile of these sultam derivatives has a single peak at 288, 284 or 278°C, as shown in Figs. 2–4 respectively.

It is clear that all C–C bonds have relatively high “s”-character since they are sp²–sp² bonds on sp³-hybridised carbon atoms. The weakest bonds are those between N, the phenyl moiety and that of the neighbouring SO₂, as the latter bond will be strengthened due to the presence of the methyl groups. This means that only the former bond is insignificant in thermal analysis. This method of fragmentation leads to splitting of whole moieties from the sultam derivatives.

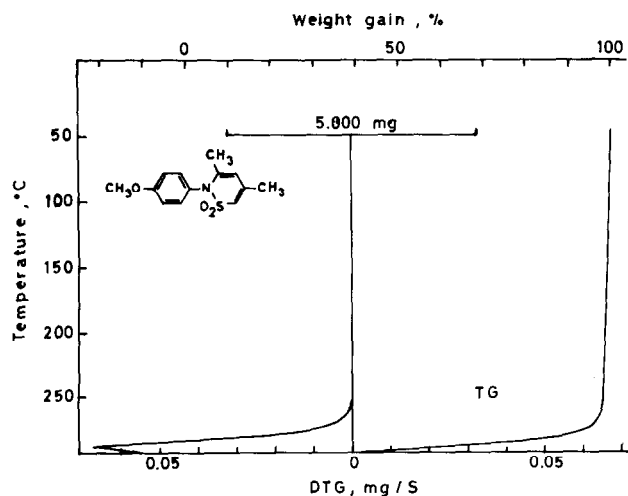


Fig. 2. DTG/TG of compound **I**.

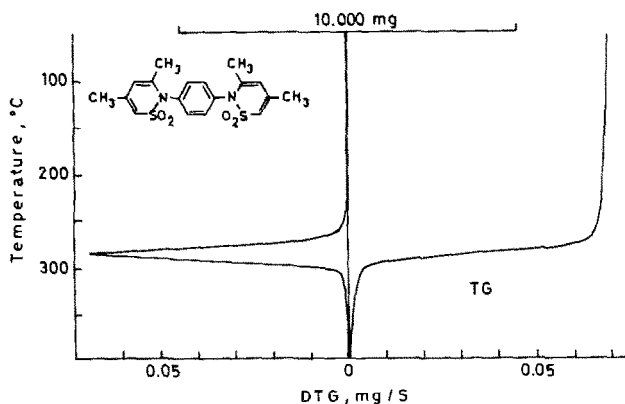


Fig. 3. DTG/TG of compound II.

In compound IV, the alkyl sulphur bond is weaker due to the presence of a bromine atom at C₁; hence, elimination of SO₂ occurred easily with the two methyl groups.

This is emphasised by the decrease in the peak temperature (DTG) to 152.5°C, compared with the other aforementioned compounds. Figure 5 shows the TG and DTG results for compound IV. It has been observed that leaving these bromo-compounds under ambient conditions in Egypt for about 2 years led to the complete decomposition of these derivatives.

In compound V, another methyl group is present on the sultam ring at C₁, instead of the bromine atom (as in compound IV); in addition the sultam ring is separated from the phenyl moiety by a methylene group. The DTG (Fig. 6) profile now has two peaks, one at 276.7 and the other at 343.3°C.

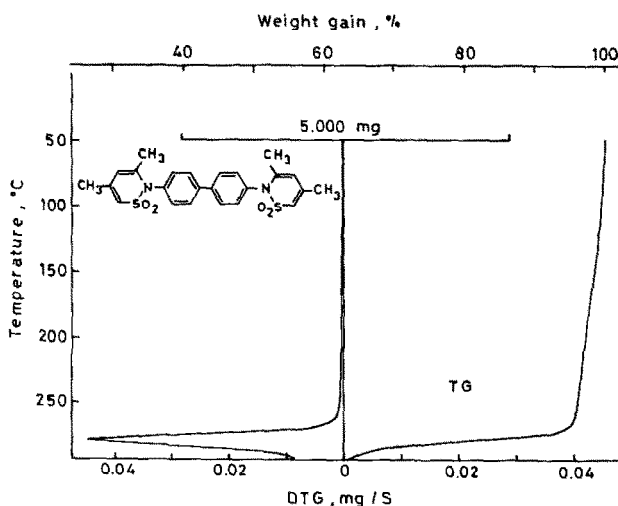


Fig. 4. DTG/TG of compound III.

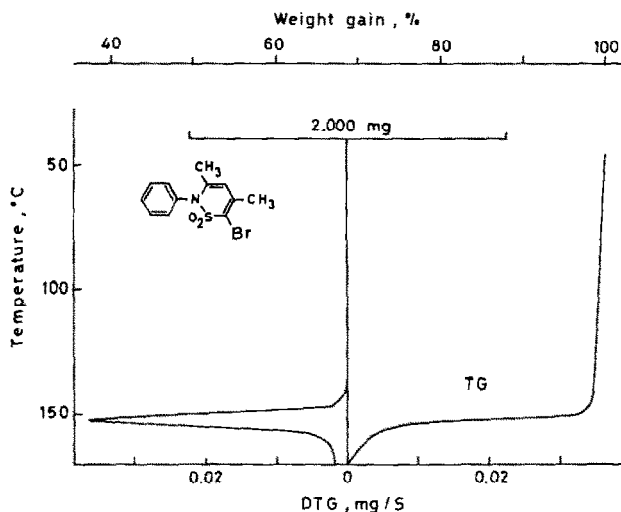


Fig. 5. DTG/TG of compound IV.

The first thermal decomposition follows that of compounds I, II and III and is due to the strengthening of the alkyl sulphur bond by the three electron-donating methyl groups. The remaining sultam moiety will follow the route of the thermal analysis for compound IV, due to the presence of the benzyl ring, eliminating the SO_2 and the methyl groups present. The peak temperature of the first event is 276.7°C , close to those of compounds I, II and III. The peak temperature for the elimination of SO_2 is very high in comparison with that of compound IV (343.3°C), see Fig. 6.

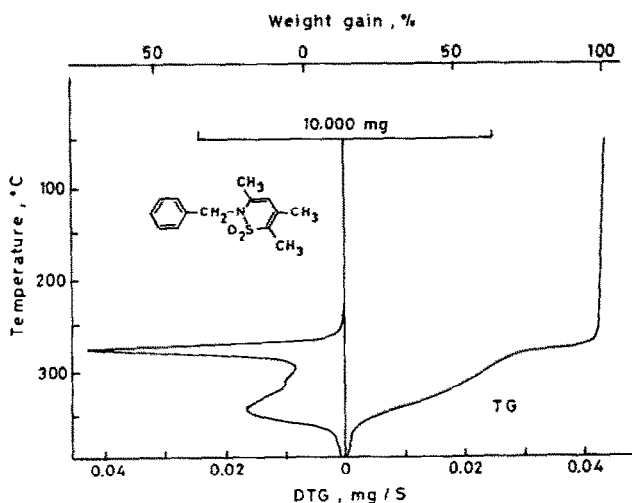


Fig. 6. DTG/TG of compound V.

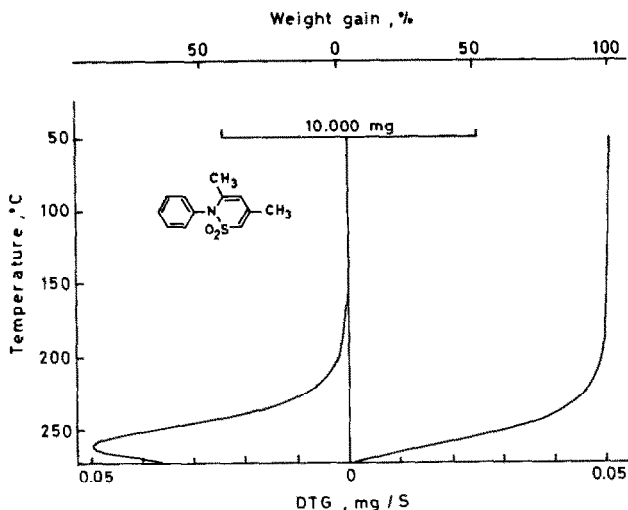


Fig. 7. DTG/TG of compound VI.

Compound VI melted and evaporated normally; SO_2 was not eliminated due to the methyl groups present. The DTG profile has a single peak at 261.7°C which represents the temperature at which the rate of mass change was at a maximum, see Fig. 7 (TG and DTG).

Changing the methyl group to a heptyl group (compound VII) or to an undecyl group (compound VIII) had no effect on the ease of elimination of the SO_2 , provided the electron-donating groups were present. DTG showed that compounds VII and VIII melted and volatilised without decomposition. Specifically, there was no thermal oxidation as the thermal analysis was carried out in a nitrogen atmosphere [10].

Changing the flow rate of nitrogen (20 to >10 to >5 cc min^{-1}) had no effect on the DTG profile.

Compound IX is the starting material for some polymeric sultam derivatives and is used in many industries for this property [11]. Here the initial weight loss is due to the elimination of one molecule of water from two sultone molecules (at 151.7°C). After this, the polymer easily loses SO_2 and the CH_3 group, because of the presence of oxygen in the ring. The 2,4-dimethyl-1,3-butadiene-sultone, compound IX, behaves like a polyarylamide in its weight-loss pattern: loss of water during the first peak, then subsequent ammonia loss, in our case SO_2 , which is partly from polyacrylonitrile structure and partly from the remaining polyacrylamide.

Due to the partial elimination of water from sultone and the polymer, with SO_2 and CH_3 from the starting sultone and the polymer formed, an exact interpretation of the differences between the calculated and found values for weight loss cannot be made as they fall within the range of experimental error.

Finally, compound X was very stable under these thermolytic conditions and its weight loss was negligible. In this saturated sultam ring system, where there are no methyl groups, the electron lone pair on the nitrogen atom attains an acidic nature due to the presence of SO₂, hence the stability of the ring [12].

CONCLUSION

In spite of the complex thermal decomposition of these organic compounds, and the fact that many of the decomposition stages are overlapping and confined to narrow temperature ranges, making precise deductions can be difficult [13]; DTG is a valuable analytical tool, especially if accompanied by mass spectrometry and photolysis [14] of the organic compounds under investigation.

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