

Thermogravimetry–infrared evolved gas analysis of the anomalous thermal decomposition of thiophene fulgamic acid

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Abstract

Thermogravimetry with evolved gas analysis by infrared spectrometry was used to study the thermal degradation of thiophene fulgamic acid in an inert atmosphere. Contrary to the expectation that the amic acid would eliminate water to the corresponding imide, anomalous behaviour was observed whereby the compound lost ammonia. Control experiments on the thermal degradation of thiophene fulgide indicated an initial loss of a nitrile containing species. This might be attributed to the degradation of a trace impurity of dicyclohexylurea to form cyclohexylisocyanate. A proposal that dicyclohexylcarbodiimide (DCC) might have been present as an impurity was discounted on the basis of a measurement which showed that the DCC simply sublimed without formation of other decomposition products. Comparison of the results obtained from different experiments showed that the decomposition of thiophene fulgamic acid was more complex than simple ammonia loss followed by sublimation of the anticipated thiophene fulgide residue. Possible reasons for this are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; FT-IR evolved gas analysis; Photochromic materials

1. Introduction

Fulgides, which were discovered by Stobbe and Eckert [1] and developed by Heller [2,3], are a class of organic photochromic compounds. On exposure to ultraviolet radiation they undergo a transformation to a highly coloured form which can be returned to the original, colourless form by irradiation with visible light of the correct wavelength. Suggested uses for such materials include information storage systems and large area display systems [4].

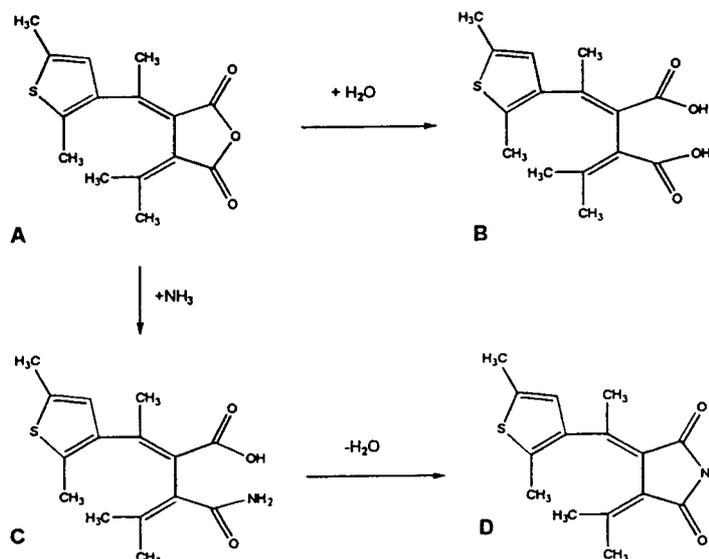
Photochromic fulgides have been synthesised based on thiophene, furan and pyrrole rings [5] – this study is restricted to thiophene fulgide, Z-2-[1-(2,5-dimethylthienyl)ethylidene]-3-(1-methyl-ethylidene)succinic anhydride and its derivatives. This material, which will simply be referred to as thiophene fulgide (**A**), is able to undergo hydrolysis to the diacid (**B**) which is no longer an active photochromic substance. The corresponding imide (**D**), which can be obtained via the amic acid (**C** – one isomer depicted), is less susceptible to hydrolysis and would be the preferred active photochromic. Unfortunately, thermal and/or chemical dehydration of thiophene fulgamic acid too results in a low yield of the imide. Experiments using thermogravimetry combined with infrared analysis of evolved gases were therefore carried out in order to

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investigate the thermal stability of thiophene fulgamic acid (C).

time display of weight loss and post-run analysis such as rate of weight loss determination, etc.



2. Experimental

Thiophene fulgide was prepared according to the method of Glaze et al. [6] and isolated as golden yellow crystals. This was converted to the photochromic E isomer by irradiation with ultraviolet light. Thiophene fulgamic acid was prepared by treatment of thiophene fulgide with ammonia.

Measurements were performed on a TA Instruments model 951 TGA coupled to a heated gas flow cell (maintained at 200°C to prevent condensation of volatile products) housed in the sample compartment of a Nicolet 740 FT-IR spectrometer [7]. Samples were analysed in platinum sample pans and the evolved gases swept into the gas cell in a stream of dry, oxygen-free nitrogen (flow rate 50 ml min⁻¹). Spectra were acquired every 5.8 s (16 co-added interferograms) and stored into sequential scratch files for subsequent processing using the Nicolet GC-FT-IR software. The software allowed real-time stacked display of spectra up to three real-time “chemigram” plots of IR absorbance over specified frequency windows, post-run Gram-Schmidt reconstructs with a choice of basis vectors and additional post-run chemigram reconstructs. The TGA software allowed real-

3. Results and discussion

3.1. Thiophene fulgamic acid

Plots of weight and rate of weight loss for thiophene fulgamic acid are shown in Fig. 1. From the rate of weight loss curve it can be seen that two distinct processes occur. This finding is duplicated in the Gram-Schmidt reconstruct showing the infrared

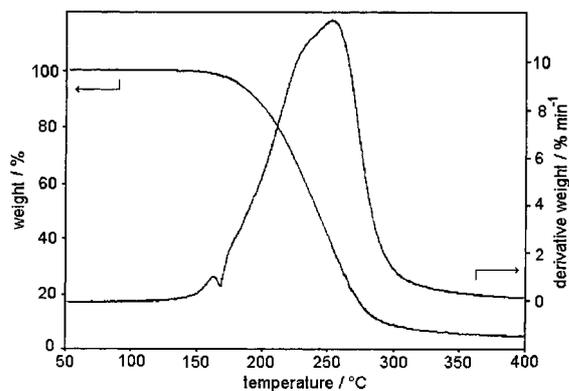


Fig. 1. Weight loss and derivative weight loss plot for thiophene fulgamic acid.

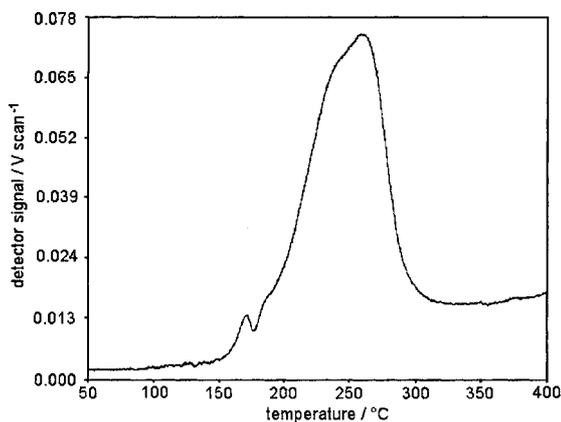


Fig. 2. Gram-Schmidt reconstructed curve for thiophene fulgamic acid.

detector signal vs. temperature (Fig. 2). The infrared spectrum of the evolved gases corresponding to the first (weaker) peak is shown in Fig. 3(a). The main features in the spectrum can readily be assigned to ammonia, although there is evidence for a nitrile containing component as well. From consideration of the thermogravimetric data and structure of the compound, one might speculate that the initial weight loss is due to elimination of water with resultant formation of the corresponding imide. The evolved gas analysis refutes this, suggesting elimination of

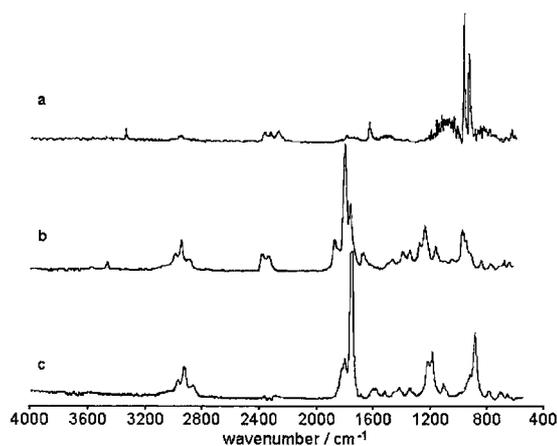


Fig. 3. (a) Infrared spectrum of first peak from the decomposition of thiophene fulgamic acid, (b) infrared spectrum of main peak from the decomposition of thiophene fulgamic acid, (c) infrared spectrum of main decomposition product from thiophene fulgide.

ammonia to give the acid anhydride: thiophene fulgide.

The infrared spectrum obtained at the maximum of the main peak in Fig. 2 is shown in Fig. 3(b). The basic pattern of bands can be assigned to thiophene fulgide. Absorptions in the 1780 cm^{-1} region can be attributed to the C=O stretching of an anhydride and the band at 1222 cm^{-1} to the C–O–C anhydride linkage. The band at 956 cm^{-1} is presumably the C=C–H out-of-plane deformation of the thiophene ring. Closer examination of the spectrum, however, reveals a more complex picture. The high frequency region shows evidence for NH and/or OH groups, and a band at 1653 cm^{-1} , not easily assigned to a thiophene fulgide type of molecule, may well be connected with nitrogen in some way, possibly as an amine or amide. It might be argued that thiophene fulgamic acid is itself subliming to produce these additional features, although such a proposal is necessarily speculative at this stage.

An obvious suggestion is that the species responsible for the main peak is principally thiophene fulgide. After all, one would expect a residue of thiophene fulgide following loss of ammonia from thiophene fulgamic acid. Such a proposal, however, is found to be at best an oversimplification and at worst, totally invalid. Fig. 3(c) shows the infrared spectrum of the main decomposition product of thiophene fulgide. Although the spectra in Fig. 3(b) and (c) are similar, there are significant differences which suggest that two distinct but structurally related compounds are produced. An attractive explanation of the above observations is that, in the case of thiophene fulgamic acid, secondary gas-phase reactions lead to the formation of further decomposition products. It is not unreasonable to propose that at elevated temperatures thiophene fulgide is attacked by ammonia to form an amine derivative. This would clearly explain both the thiophene fulgide and the NH features in the infrared spectrum of Fig. 3(b). Such secondary reactions of evolved gases from thermogravimetry are not altogether uncommon and have been invoked in several other systems.

In spite of these complications, it is worth stressing that the thermal decomposition of thiophene fulgamic acid results in loss of ammonia with no evidence for loss of water. It is likely that the thiophene fulgide residue undergoes gas-phase decomposition in the

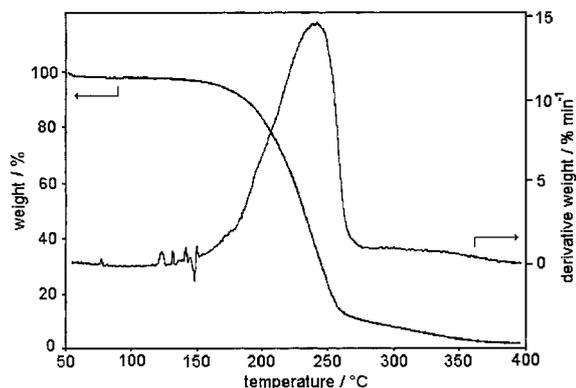


Fig. 4. Weight loss and derivative weight loss plot for thiophene fulgide.

presence of ammonia to form a simple thiophene fulgide derivative.

3.2. Thiophene fulgide

As a control experiment, the thermal decomposition of thiophene fulgide was investigated. Plots of weight (%) and rate of weight loss ($\% \text{ min}^{-1}$) vs. temperature are shown in Fig. 4. The corresponding Gram–Schmidt reconstruct is shown in Fig. 5. Immediately, it can be seen that there is an apparent discrepancy between the plots; with two peaks being observed in the Gram–Schmidt reconstruct and only one peak in the rate of weight loss curve. This suggests that the

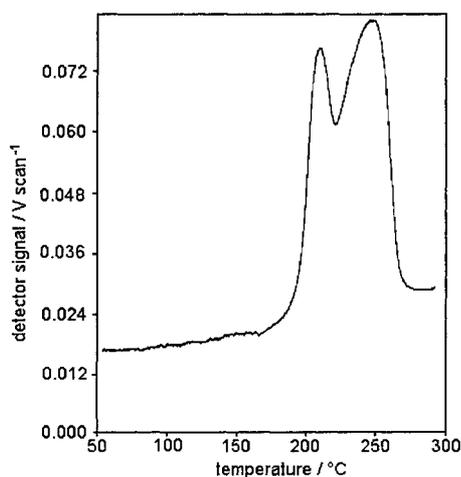


Fig. 5. Gram–Schmidt reconstructed curve for thiophene fulgide.

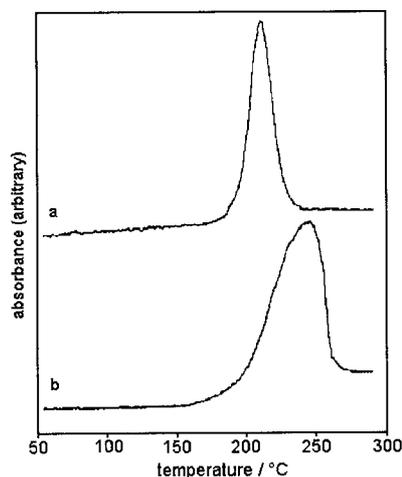


Fig. 6. “Chemigrams” for thiophene fulgide: (a) $2306\text{--}2206 \text{ cm}^{-1}$ window, (b) $1797\text{--}1759 \text{ cm}^{-1}$ window.

first peak is caused by the evolution of a relatively small amount of material which has a particularly high infrared extinction coefficient. The evidence for two distinct components is illustrated in curves (a) and (b) of Fig. 6. Curve (a), which can be equated to the first peak in Fig. 5, is indicative of a nitrile species using a $2306\text{--}2206 \text{ cm}^{-1}$ window for the reconstruction procedure. Curve (b), which corresponds to the second peak in the Gram–Schmidt reconstruct, is set up for a high frequency carbonyl stretch ($1797\text{--}1759 \text{ cm}^{-1}$), e.g. an anhydride.

The infrared spectra obtained at the positions for the two peaks are shown in Fig. 7(a) and (b). The spectrum from the second peak (Fig. 7(a)) is reasonably assigned to thiophene fulgide generated by sublimation of the sample. The spectrum of the first peak (Fig. 7(b)) is found to be a composite peak of a nitrile species and thiophene fulgide. (Note the similarity of the two spectra below 2000 cm^{-1} .) A scaled computer subtraction of curves (a) and (b) can be used to remove the contribution of thiophene fulgide. The resultant spectrum (Fig. 7(c)) contains only absorptions belonging to the nitrile species. The spectrum is dominated by a strong nitrile band at 2264 cm^{-1} with features in the aliphatic C–H stretching region characteristic of methylene groups. A more detailed discussion of the origin of this species will be deferred until the next section.

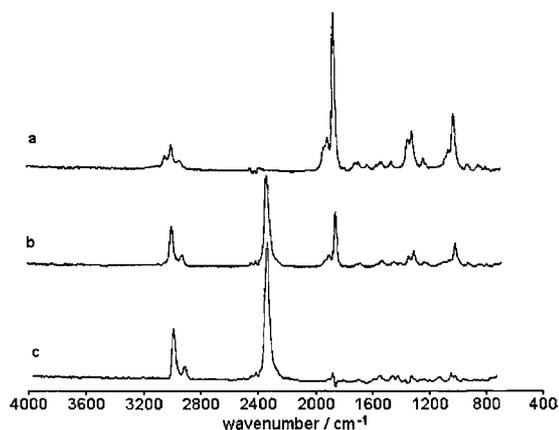


Fig. 7. (a) Infrared spectrum of second peak from the decomposition of thiophene fulgide, (b) infrared spectrum of first composite peak from the decomposition of thiophene fulgide, (c) scaled computer subtraction of (b) minus (a) showing absorptions of nitrile species only.

3.3. *N,N'*-dicyclohexylcarbodiimide

N,N'-dicyclohexylcarbodiimide (DCC) is a dehydrating agent used in the preparation of thiophene fulgide and may have been present as an impurity in the final product. A further control experiment was therefore carried out using this compound as it could have been responsible for the evolved nitrile product detected above.

The weight loss curve and corresponding Gram–Schmidt reconstruct are shown in Fig. 8. The shape of the weight loss curve is characteristic of a sublimation process and the spectrum of the evolved material (Fig. 9(a)) can be readily assigned to that of DCC. The spectrum of the nitrile species detected during the decomposition of thiophene fulgide is reproduced for comparison in Fig. 9(b). Note that the frequency of the nitrile band of the latter compound at 2129 cm^{-1} indicates that it is most certainly not DCC. Apart from this difference, the spectra of both substances are similar suggesting that, apart from the nitrile linkage, DCC and the nitrile species are structurally related.

This observation can be reconciled quite easily if we propose that the thiophene fulgide sample was contaminated with a trace impurity of dicyclohexyl urea (DCU) rather than DCC. DCU is produced from DCC by the addition of water. Thermal decomposition

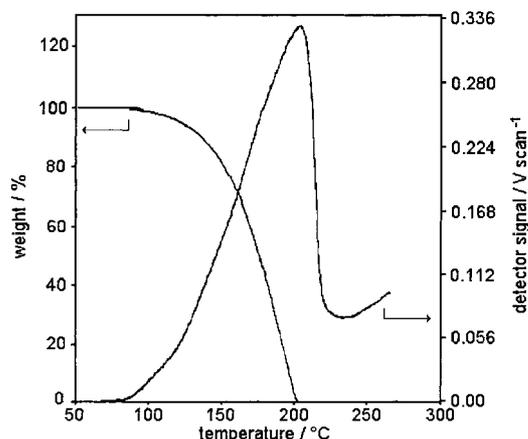


Fig. 8. Weight loss and Gram–Schmidt reconstruct for *N,N'*-dicyclohexylcarbodiimide.

of DCU results in the formation of cyclohexylisocyanate, a proposal which is fully consistent with the spectrum of the unknown nitrile species. Moreover, isocyanates are known to have very high infrared extinction coefficients for the asymmetric $\text{O}=\text{C}=\text{N}$ stretch. This is in accord with the observed differences between the rate of weight loss and Gram–Schmidt reconstruct in Figs. 4 and 5. Thus, although only a very small amount of DCU is probably present in the thiophene fulgide sample, its detection (in the form of its decomposition product, cyclohexylisocyanate) is exaggerated by a particularly high infrared extinction coefficient. Unfortunately, time did not permit a confirmatory experiment on a pure sample of DCU.

With regard to the thermal decomposition of thiophene fulgamic acid, it is likely that the nitrile band

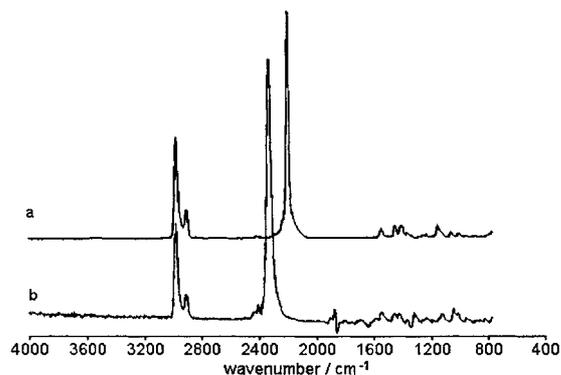


Fig. 9. (a) Infrared spectrum of *N,N'*-dicyclohexylcarbodiimide vapour, (b) infrared spectrum of nitrile species, cf. Fig. 7(c).

observed in the first weight loss peak is also due to cyclohexylisocyanate.

4. Conclusions

The value of coupling thermogravimetry with infrared detection and identification of the evolved gases has been clearly demonstrated. This study shows that thermal decomposition mechanisms are often complex, and that interpretation may be further complicated by secondary gas phase reactions of volatile decomposition products. This technique provides a unique insight into the thermal behaviour of thiophene fulgamic acid and related compounds.

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