# Short Communications

## THERMAL STUDIES ON ARYLSULFINYLAMINES, PART II

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The thermal characteristics of 13 isomeric arylsulfinylamines (iodosulfinylanilines, dichlorosulfinylanilines and dimethylsulfinylanilines) were examined using a Derivatograph. It was found that some of the arylsulfinylamines underwent thermal degradation.

Arylsulfinylamines are finding increasing application in the synthesis of organic chemicals [1–5]. It has lately been found that N-sulfinylamine Ph–N=S=O forms an interesting donor–acceptor system. The Hammett substituent constant has been determined using the NMR method.

A thin-layer chromatography method to analyze arylsulfinylamines [6] was developed and transsulphinylation reaction kinetics were investigated using gas chromatography [7]. The thermal analysis examinations carried out earlier enables us to measure the stabilities of sulfinylaniline, isomeric derivatives of tolylsulfinylaniline and chlorosulfinylaniline, and also α- and β-naphthylsufinylaniline [8].

Thermal investigations of the isomeric iodosulfinylanilines, dichlorosulfinylanilines and dimethylsulfinylanilines are a continuation of the previous ones of the author which can be utilized to develop a GLC method of analyzing these species.

### Experimental

*Materials*

The arylsulfinylamines examined were prepared using the Michaelis and Herz method [9, 10].

The following compounds were used:

2-iodosulfinylaniline
3-iodosulfinylaniline
2,3-dichlorosulfinylaniline
2,4-dichlorosulfinylaniline
2,5-dichlorosulfinylaniline
2,6-dichlorosulfinylaniline
3,5-dichlorosulfinylaniline

2,3-dimethylsulfinylaniline
2,4-dimethylsulfinylaniline
2,5-dimethylsulfinylaniline
2,6-dimethylsulfinylaniline
3,4-dimethylsulfinylaniline
3,5-dimethylsulfinylaniline

These arylsulfinylamines consist of yellow liquids or low-melting solids. They are very susceptible to the action of moisture and in presence of the latter, are easily hydrolysed to the initial amines and $SO_2$. The arylsulfinylamines were kept in sealed glass vials. The purities of the products were checked using NMR, IR methods and GL chromatography [11].

*Apparatus and procedure*

Simultaneous thermogravimetry, derivative thermogravimetry and differential thermal analysis were carried out using a 102 MOM derivatograph. Measurements in the range 20–300° were carried out at an average heating rate of 3 °/min, using 210–370 mg samples in a platinum crucible. Alumina, calcined at 100°, was used as reference material. Determinations were carried out in static air.

Table 1

Thermal properties of arylsulfinylamines in air

| Arylsulfinylamines | m.p. °C | $T^{DTG}$ min, °C | $T^{end}$ °C | $T^{DTA}$ max, °C | $P^{DTA}$ min, cm² | $\frac{P}{g}$ | Weight of sample, g |
|---|---|---|---|---|---|---|---|
| 2-iodosulfinylaniline | 34 | 248 | — | 286 | — | — | 0.300 |
| 3-iodosulfinylaniline | 42 | 250 | 253 | — | 6.0 | 16.2 | 0.370 |
| 2,3-dichlorosulfinylaniline | 46 | 248 | 252 | — | 1.2 | 4.0 | 0.300 |
| 2,4-dichlorosulfinylaniline | 54 | 248 | 248 | — | 1.1 | 3.6 | 0.300 |
| 2,5-dichlorosulfinylaniline | 50 | 246 | 246 | — | 2.8 | 6.5 | 0.300 |
| 2.6-dichlorosulfinylaniline | 24 | 234 | 256 | — | 0.8 | 2.7 | 0.300 |
| 3,5-dichlorosulfinylaniline | 44 | 217 | 236 | — | 0.4 | 1.3 | 0.300 |
| 2,3-dimethylsulfinylaniline | 31 | 221 | 226 | — | 6.0 | 28.6 | 0.210 |
| 2,4-dimethylsulfinylaniline | — | 233 | 239 | — | 8.1 | 27.0 | 0.300 |
| 2,5-dimethylsulfinylaniline | — | 236 | 236 | — | 29.3 | 97.7 | 0.300 |
| 2,6-dimethylsulfinylaniline | — | 213 | 217 | — | 24.9 | 83.0 | 0.300 |
| 3,4-dimethylsulfinylaniline | 27 | 208 | 210 | — | 0.9 | 5.3 | 0.170 |
| 3,5-dimethylsulfinylaniline | — | 238 | 242 | — | 27.0 | 90.0 | 0.300 |

m.p. = melting temperature determined by minimum of DTA curve
$T^{DTG}$ = temperature corresponding to maximum rate of mass loss in DTG curve
$T^{end}$ = end-temperature of conversion
$T^{DTA}$ = temperature corresponding to maximum of DTA curve
$P^{DTA}$ = endothermic peak surface area under DTA curve, obtained by planimetry
$\frac{P}{g}$ = $P$ value for 1 g of arylsulfinylamine

## Results

From the thermal examinations it was evident that not all N-arylsulfinylamines belonging to the benzene group are subject merely to evaporation. It was found that 2-iodosulfinylaniline was unstable at elevated temperatures and was subject to thermal degradation. This is evident from the exothermic maxima in the DTA curves, with a mass loss in the TG curves (Fig. 1).

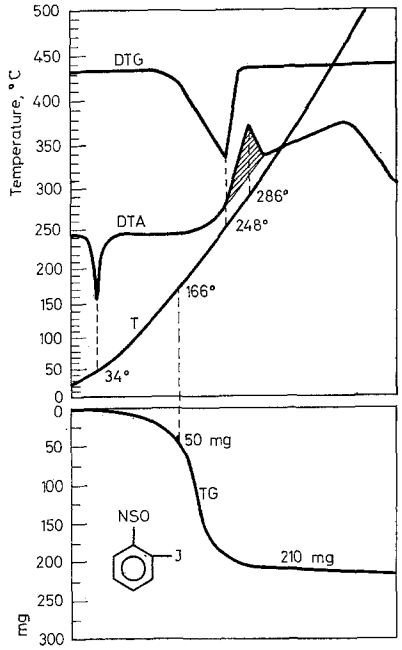


Fig. 1. TG, DTG and DTA curves of 2-iodosulfinylaniline

The results of the thermal studies are summarized in Table 1 and some TG, DTG and DTA curves are given in Figs 1–3. For 2-iodosulfinylaniline an endothermic minimum is observed which corresponds to the melting point at 34°. During further heating an exothermic degradation occurs at 225°. This degradation reaches its maximum at 286° (Fig. 1). The ether isomers of iodosulfinylaniline, dichlorosulfinylaniline and dimethylsulfinylaniline examined evaporate. This is evidenced by the deepening endothermic DTA curves with simultaneous loss of mass when the temperature rises (Table 1, Figs 2–3). Sulfinylaniline and various monochlorosulfinylanilines and tolylsulfinylanilines behave similarly.

The evaporation heat of monochlorosulfinylaniline is about 23.5–27.5 unit much higher than for the isomers of dichlorosulfinylaniline, about 0.4–2.8 unit.

On the other hand, the dimethylsulfinylaniline isomers behave differently, their evaporation heats being more diversified, ranging from 6.0 up to 29.3 unit.

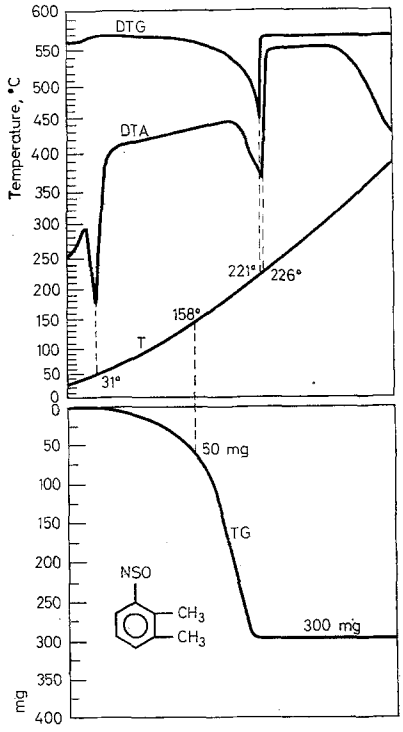


Fig. 2. TG, DTG and DTA curves of 2,3-dimethylsulfinylaniline

Most of the N-arylsulfinylamines examined are solids having low melting temperatures in the range 24–54°.

Thermal investigations provide precise characteristics of N-arylsulfinylamine. This will be of practical importance in both synthesis and chemical analysis.

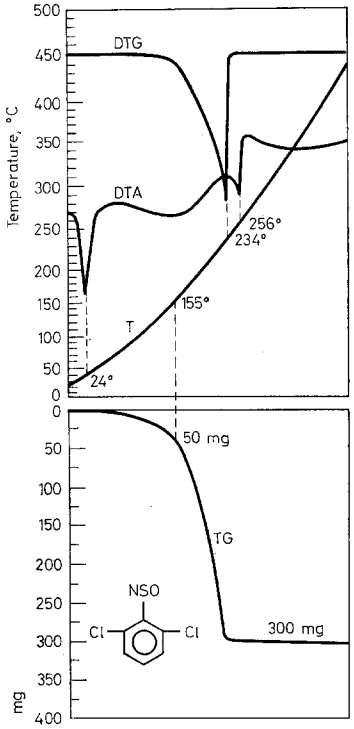


Fig. 3. TG, DTG and DTA curves of 2,6-dichlorosulfinylaniline

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