Short Communications

THERMAL STUDIES OF ARYLSULFINYLAMINES

Z. CZERWIEC and J. PIELICHOWSKI

Department of Chemistry, Pedagogical University, Czestochowa,
Institute of Organic Chemistry and Technology, Technical University, Kraków, Poland

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Thermal examinations of some arylsulfinylamines containing benzene and naphtalene rings were carried out. It was found that the arylsulfinylamines of the benzene series are thermally stable, whereas the naphtalene-type arylsulfinylamines undergo degradation in air.

For some time attention has been paid to the arylsulfinylamines due to their extremely good reactivity. The outstanding reactivity of the sulfinyl group makes them suitable for certain chemical processes [1–3]. Arylsulfinylamines have been successfully used in the synthesis of heterocyclic [4] and polycyclic compounds [5]. They also participate in an interesting transsulfinylation reaction [6]. Very much attention has been given to studies on the structure of arylsulfinylamines, and especially interesting investigations have been made using mass and NMR spectrometry [7, 8]. These compounds are mostly liquids or low-melting solids; they are very sensitive to water and break down under its action with formation of an amine and sulphur dioxide [9, 10]. Due to the high reactivities, analytical work and determinations of the stability of these species often prove troublesome. In the course of studies on arylsulfinylamine determination using GL chromatography [11], it turned out to be necessary to examine the thermal stabilities. A derivatographic method proved most suitable for this. Results of some thermal studies on arylsulfinylamines are presented here. The thermal stabilities of naphthylsulfinylamines provided the basis of a method for quantitative determination of the compounds by GL chromatography [11].

Experimental

Materials

Sulfinylamines were prepared by the method of Michaelis and Herz [9]. The following compounds were investigated: sulfinylaniline, 2-methylsulfinylaniline, 3-methylsulfinylaniline, 4-methylsulfinylaniline, 2-chlorosulfinylaniline, 3-chlorosulfinylaniline, 4-chlorosulfinylaniline, α-naphthylsulfinylamine and β-naphthylsulfinylamine. The purities of the products were checked by using NMR, mass spectrometry and GL chromatography.

Apparatus and procedure

Simultaneous thermogravimetry, derivative thermogravimetry and differential thermal analysis were carried out using a Paulik – Paulik – Erdey, system type OD 102 MOM Derivatograph. Measurements in the range of 20 – 300° were carried out with an average heating rate of 3°/min, using 0.430 to 1000 g samples in a platinum crucible. Alumina, calcined at 1000°, was used as reference material. Determinations were carried out in static air.

Results

The results of the thermal studies are summarized in Table 1 and some TG, DTG and DTA curves are given in Figs 1 – 2. The arylsulfinylamines of the benzene series exhibit deepening minima in the endothermic DTA curves, with a parallel loss of mass, when the temperature rises (Fig. 1). This is reliable evidence that, when heated, this type of compound undergoes only evaporation but does not degrade. This finding has been used to develop a method for the chromatographic determination of these compounds. The results were confirmed by distillation. Phenylsulfinylamine has the highest, and p-toluylsulfinylamine and p-chlorophenylsulfinylamine the lowest latent heat of evaporation. α- and β-naphthyl-N-

Table 1

Thermal properties of arylsulfinylamines in air

Arylsulfinylamines	mp, °C	t^{DTGmin} °C	tend °C	t^{DTAmax} °C	t^{DTAmin} cm²	$\frac{P}{g}$	Weight of sample, g
Sulfinylaniline	—	195	195	—	28.0	32.9	850
2-methylsulfinylaniline	—	220	228	—	26.9	26.9	1000
3-methylsulfinylaniline	—	223	225	—	26.9	26.9	1000
4-methylsulfinylaniline	—	215	217	—	10.5	24.4	430
2-chlorosulfinylaniline	—	240	245	—	26.1	26.1	1000
3-chlorosulfinylaniline	33	233	240	—	27.5	27.5	1000
4-chlorosulfinylaniline	—	235	237	—	23.5	23.5	1000
α-naphthylsulfinylamine	—	275	—	296 decomp.	—	—	700
β-naphthylsulfinylamine	53	237	—	247 decomp.	—	—	500

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
p^{DTAmax} — 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

sulfinylamine exhibit a different behaviour from that of the members of the benzene series, degradation being observed under normal pressure. This is accompanied by pronounced exothermic effects in the DTA curves, as well as the indications of mass loss in the TG curves (Fig. 2). At temperatures above 275°, a considerable increase in rate of loss of mass is revealed by DTG, with a maximum at 296°. For β-naphthylsulfinylamine a minimum is observed in the DTA curve at 53°, corresponding to melting. On further heating, the exothermic degradation of β-naphthylsulfinylamine begins at 185°, with a maximum at 247°. Similar studies in a nitrogen atmosphere showed that β-naphthylsulfinylamine did not undergo degradation so readily as in air. Degradation started only above 247°. This finding provided the possibility of applying GLC for arylsulfinylamine determinations [11].

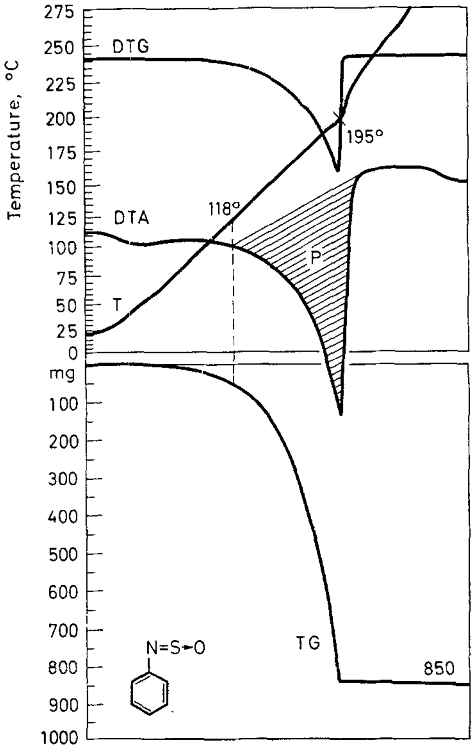

Fig. 1. TG, DTG and DTA curves of sulfinylaniline

Derivatography provided a means of studying the precise thermal characteristics of the arylsulfinylamines. It also enabled the starting point of thermal degradation to be found, this being of importance as regards synthesis and analytical determination.

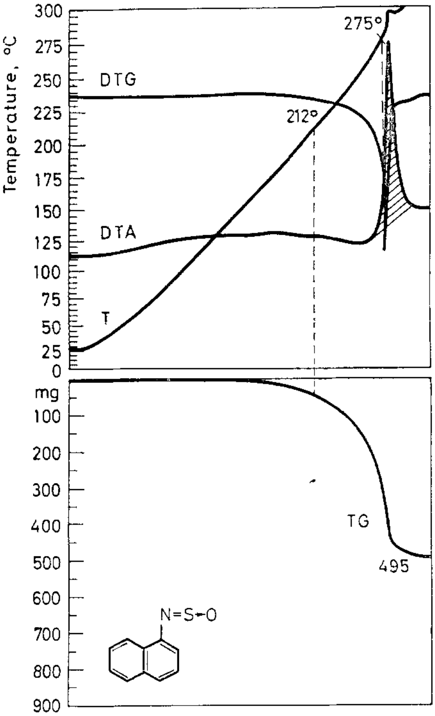

Fig. 2. TG, DTG and DTA curves of α-naphtylsulfinylaniline

References

1. H. Szmant and Z. Vidant, Rev. Soc. Quim. Mex. 6 (1962) 121.
2. J. Blatter and Lukaszewski, Tetrahedron Letters, 1964, 855.
3. G. Kresze, Ch. Scyfried and A. Trede, Tetrahedron Letters, 1965, 3933.
4. L. S. Samaraj, F. Gondar and J. Derkacz, M. Op. X. 1 (1965) 2004.
5. A. Macaluso and J. Hamer, J. Org. Chem., 32 (1967) 506.
6. W. T. Smith, N. K. Plucknett and T. L. Dawson, U. S. Dept. Com. Office, Techn. Serv. PB Rept. 153451, 16 pp, (1962).
7. J. H. Bowie, FCV. Larson, G. Schroll, S. O. Lawesson and R. G. Cooks, Tetrahedron Letters, 23 (1967) 3743.
8. Z. Czerwiec and J. Mirek, Zeszyty Nauk Uniw. Jagiel., Ser. Chem., 18 (1973) 183.
9. A. Michaelis and R. Herz, Ber., 23 (1880) 3481.
10. O. Wichterle and J. Rocek, Chem. Listy, 47 (1953) 1768.
11. Z. Czerwiec and J. Mirek, Zeszyty Nauk Uniw. Jagiel, Ser. Chem. 14 (1969) 103.