Thermochimica Acta, 159 (1990) 187–191
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF SOME HYDROXY SCHIFF'S BASES

SALMAN R. SALMAN *

Chemistry Department, College of Science, University of Baghdad, Baghdad (Iraq)

S. NOOR

Department of Applied Sciences, University of Technology, Tel Mohammed, Baghdad (Iraq)

(Received 31 July 1989)

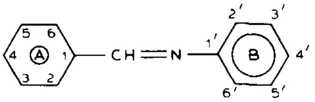
ABSTRACT

The thermal behaviour of six hydroxy Schiff's bases was studied using TG and DTA. It was found that compounds with steric crowding have a thermal behaviour different from those without this effect. The trend of fragmentation for the two groups is discussed.

INTRODUCTION

Hydroxy Schiff's bases have received considerable attention in the past few years [1–15]. It has been found [16,17] that in Schiff's bases (Scheme 1) the aromatic ring (B) is not coplanar with the rest of the molecule. A hydroxy substituent in position 2 will form an intramolecular hydrogen bond [IAMHB] which will fix the CHN group in the plane of ring A.

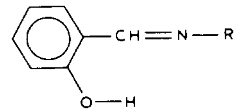
In a study of the thermal decomposition of some Schiff's bases, it was suggested [18] that the weight loss is due to the formation of a C_6H_5O fragment. The aim of this work is to study the thermal behaviour of two groups of Schiff's bases (Scheme 2). The first group (compounds **1**–**3**) has no *ortho* substituent in ring B, while the second group (compounds **4**–**6**) does have an *ortho* substituent in ring B.



Scheme 1.

---

* Author to whom correspondence should be addressed.



Compound	R	Compound	R
1	Benzyl	**4**	2′-Methyl-5′-chlorobenzene
2	Pyridyl	**5**	2′-Trifluoromethyl benzene
3	3′,5′-Ditrifluoromethyl benzene	**6**	2′-Chloro-5′-acetyl benzene

Scheme 2.

EXPERIMENTAL

Compounds **1**–**6** were purchased from Maybridge Chemical Co. Ltd. The TG and differential thermal analysis (DTA) were carried out on a Netzsch Sta 409 under an atmosphere of static air. The heating rate was 10 °C min^{-1}, aluminium oxide was used as reference and the experimental error was ±3 °C. ^{1}HNMR spectra were run on solutions 1 mol% in $CDCl_3$ with TMS as an internal reference, using a Varian FT 80 A instrument.

RESULTS AND DISCUSSION

Table 1 shows the initial decomposition temperature T_{id} and the final decomposition temperature T_{fd} obtained from the TG curves. Figure 1 illustrates TG and DTA for compound **2** which represents the first group (compounds **1**–**3**), while Fig. 2 shows TG and DTA of compound **4** which represents the second group (compounds **4**–**6**). With reference to Table 1 and Figs. 1 and 2, the following remarks can be made:

1. Compounds **1**–**3** decompose to give fragment C_6H_5O (**I**), while compounds **4**–**6** decompose to give fragment C_7H_5NO (**II**).

TABLE 1

Thermal data for compounds **1**–**6**

Compound no.	T_{id} (°C)	T_{fd} (°C)	%wt. loss		Fragment
			Observed	Calculated	
1	260	500	33.2	34.7	**I**
2	218	530	42.0	41.2	**I**
3	225	522	28.0	27.9	**I**
4	50	430	48.0	48.9	**II**
5	130	453	46.0	45.3	**II**
6	50	400	44.8	45.6	**II**

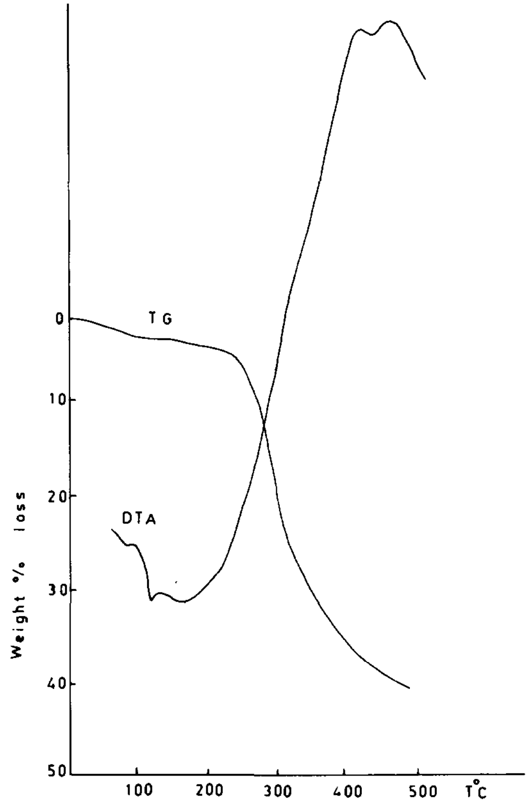


Fig 1. TG and DTA in static air for compound **2**.

2. The rate of weight loss for compounds **1–3** is much slower than for compounds **4–6**; for example, compound **2** lost 38% of its weight in 2.5 h while compound **4** lost the same percentage in about 1.5 h.
3. The DTA for compounds **1–6** indicates that the decomposition begins with an endothermic process and ends with an exothermic one.
4. The T_{id} and T_{fd} values for compounds **1–3** are much higher than those for compounds **4–6**. It has been suggested [19] that Schiff's bases similar to compounds **4–6** decompose to give a C_6H_5O fragment. From the results obtained from the TG curves of compounds **1–6**, one could suggest that the weight loss in compounds **1–3** is due to the formation of a C_6H_5O fragment (**I**), while the weight loss in compounds **4–6** is due to the formation of a C_7H_5NO fragment (**II**). These results are supported by the fact that the percentage weight loss calculated for compounds **1–3** using the assumption that they form fragment **I** agree quite well with the observed results (Table 1), while for compounds **4–6**, only the assumption that the weight loss is due to fragment **II** will give correct results. Those results may be explained on the basis that an *ortho* substituent in ring B will make this ring perpendicular to the plane of the molecule and this will inhibit resonance between this

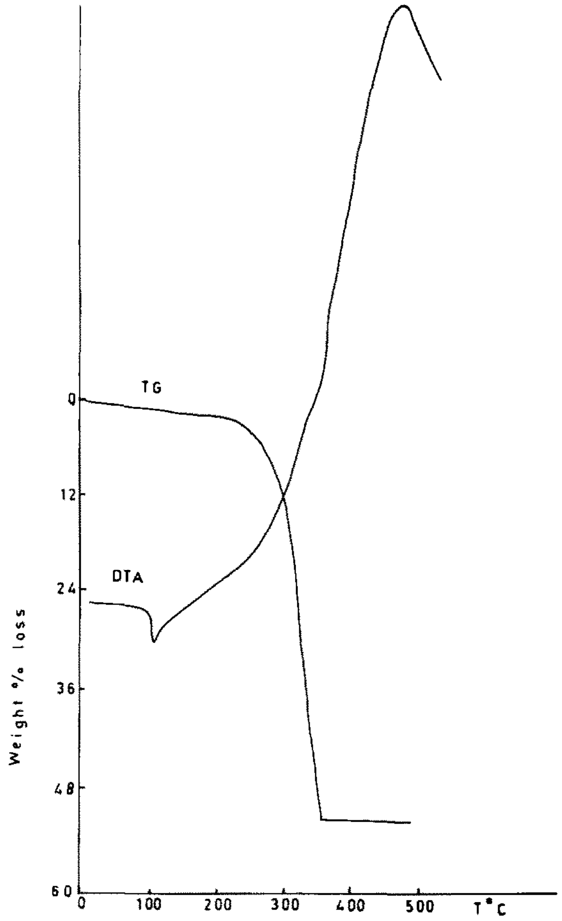


Fig 2. TG and DTA in static air for compound **4**.

ring and the rest of the molecule, which will make the N–aromatic bond easier to break than the C–aromatic bond. However, it has been suggested [19,20] that the hydrogen bond strength between the hydroxy proton and the nitrogen atom could be calculated using the hydroxy chemical shift δ_{OH} and eqn. (1):

$$\Delta\delta_{OH} = -0.4 + E \tag{1}$$

In general this equation will give low energy values for compounds **5** and **6** (Table 2) compared with those of compounds **1** and **2**. This will make the IAMHB in compounds **4**–**6** easier to break compared with that in compounds **1**–**3** (cf. T_{id} and T_{fd}).

One could conclude that in sterically hindered hydroxy Schiff's bases, less energy is needed to break the intramolecular hydrogen bond and that the decomposition of these groups of compounds will result in the formation of

TABLE 2

^1H chemical shift (ppm) of the hydroxy proton $\Delta\delta_{OH}$ and the calculated hydrogen-bond energy E for compounds **1–6**

Compound no.	δ_{OH}	E (kcal mol^{-1})
1	13.1	8.847
2	15.3	11.077
3	12.4	8.097
4	12.6	8.397
5	12.1	7.885
6	11.2	6.961

a C_7H_5NO fragment, while with less sterically hindered hydroxy Schiff's bases, the decomposition process will result in the formation of a C_6H_5O fragment.

REFERENCES

1 J. Csaszar, J. Balog and A. Makary, Acta Phys. Chem., 24(4) (1978) 473.
2 J. Balog and J. Csaszar, Acta Chim. (Budapest), 88 (1976) 53.
3 D. Mago, J.S. Sandhu and B.J. Wakefield, J. Chem. Soc. Perkin Trans. 2, (1979) 715.
4 M. El-Kersh, M. Caber, M.R. Issa and A.I. Mansour, Kolor. Ert., 26(6) (1984) 1215.
5 S. Mal and J.L. Norula, J. Indian Chem. Soc., 58 (1981) 652.
6 G.O. Dudek and E.P. Dudek, J. Am. Chem. Soc., 88 (1966) 2407.
7 S.A. Suleimanov and K.A. Ibad-Zade, (U.S.S.R.) Prisadkismaz. Maslam, 5 (1978) (Chem. Abstr., 91 (1979) 192333j).
8 J.J. Charette, Spectrochim. Acta, 22 (1963) 1275.
9 S.R. Salman and J. Al-Rawi, Org. Magn. Reson., 22 (8) (1984) 535.
10 J. Klicnar, F. Kristek, V. Bekarek and M. Vecera, Collect. Czech. Chem. Commun., 34 (1969) 553.
11 N.Y. Ibragimov, A.S. Mirmovsumova and A.M. Bilalov, (U.S.S.R.) Prisadkismaz. Maslam, 5 (1978) 91 (Chem. Abstr. 91 (1979) 192332h).
12 T. Hedley, Tetrahedron, 18 (1962) 299.
13 F. Kristek, J. Klincnar and P. Vetesnik, Collect. Czech. Chem. Commun., 36 (1971) 3608.
14 V.I. Minkin and M.I. Gorelor, Opt. Spectrosk., 18 (1965) 328.
15 J. Charette, G. Falthans and P.H. Teyssic, Spectrochim. Acta, 20 (1964) 597.
16 K. Tabel and E. Saitou, Bull. Chem. Soc. Jpn., 42 (1969) 1440.
17 M.A. El-Bayoumi, M.E. El-Aasser and F. Abdel-Halim, J. Am. Chem. Soc., 93 (1971) 586.
18 A.A.H. Saeed, E.K. Ebraheem and A.A. Tossonian, Thermochim. Acta, 97 (1986) 337.
19 M. Takasuka and Y. Matsui, J. Chem. Soc. Perkin Trans. 2, (1979) 1743.
20 T. Schaefer, J. Phys. Chem., 79 (17) (1975) 1888.