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Thermal analysis of 2-phenyl-3-arylimino-3*H*-indoles using simultaneous TG–DSC

F. Rodante [a], G. Marrosu [a] and G. Catalani [b]

[a] *Dipartimento di Ingegneria Chimica, dei Materiali delle Materie Prime e Metallurgia, Università di Roma "La Sapienza", Via del Castro Laurenziano 7, 00161 Roma (Italy)*
[b] *Istituto Regina Elena, Viale Regina Elena 293, Roma (Italy)*

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Abstract

The thermal stability of some 2-phenyl-3-arylimino-3*H*-indole derivatives was studied by simultaneous TG–DSC measurements and kinetic parameters were determined using the dynamic TG technique.

Gas chromatography–mass spectrometry and UV techniques were used to differentiate the products of the thermal decomposition.

No correlation between the electron-donor and electron-withdrawing power of the substituent groups and the thermal behaviour of the compounds was found. Some compounds undergo decomposition during the liquid–gas transition, which is related to the decreasing influence of the substituent groups on the intermolecular and intramolecular bonds of the molecules.

INTRODUCTION

It is well known that thermal analyses alone cannot identify chemical species: this can be achieved by combining thermal analyses with X-ray, IR, UV, gas chromatography (GC) and mass spectrometry (MS) analyses [1–13]. The combination of gas chromatography and mass spectrometry (GC–MS) is the most useful and sensitive tool in mixture analysis. In a previous work [14], the organic series of 2-phenyl-3-arylimino-3*H*-indoles was studied by an electrochemical technique in some aprotic solvents (dimethylformamide, acetonitrile and dimethylsulphoxide). The entropy and free energy values for the one-electron reduction of the indole derivatives were determined using a non-isothermal cell arrangement. It was observed that in all solvents, from electron-donating to electron-withdrawing substituents, the free energy decreases in the order $NMe_2 > OMe > Me > H > Cl > Br$, corresponding to a decreasing hindrance of the reduction process. The entropy was found to have an absolute value, which was not affected by the solvent, depending only on the net electron density charge of the radical anion and related to

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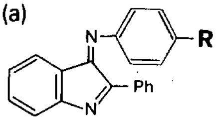
solvent polarisation. In particular, with acetonitrile, the behaviour of the entropy of the radical anions of the above-cited compounds was divided into three pairs as a function of the inductive (*I*) and mesomeric (*M*) effects of the substituent: Cl and Br (electron-withdrawing with $I^- > M^+$); OMe and NMe_2 (electron-donating with $I^- < M^+$); and H and Me (for which I^- and M^+ are very small).

The aim of this work is to study the behaviour of the substituent effects in the solid phase of the 2-phenyl-3-aryl-3*H*-indole derivatives, and to compare it with that of the electro-reduction process in solution. This can be performed by studying the influence of the substituents on the thermal stability, the overall enthalpy and the kinetic activation energy of the decomposition process of compounds [1–6].

(a)



a: R = H
b: R = Me
c: R = OMe
d: R = NMe_2
e: R = Cl
f: R = Br

EXPERIMENTAL

The experimental measurements were carried out by means of a simultaneous TG–DSC Stanton–Redcroft STA 625 connected to a Olivetti 250 computer. Instrumental calibration was achieved using standard indium and tin samples of known melting temperatures and enthalpies of fusion. To study the decomposition of the compounds under dynamic conditions, the TG–DSC apparatus was set up as follows. Samples (5–6 mg) were weighed in alumina pans placed in a nitrogen-filled dry-box. In order to avoid the oxidative decomposition of the samples, the TG–DSC system was flushed with nitrogen gas below (at a flow rate of 50 ml min^{-1}) and above (at a flow rate of 30 ml min^{-1}) the open pan. In this way, the gases evolved during the thermal decomposition experiment are removed continuously. The heating rate was always 10 °C min^{-1}. All the thermodynamic parameters were calculated using the Stanton-Redcroft Data Acquisition System, Trace 2, Version 4.

A dynamic (non-isothermal) TG technique was used in the kinetic study of the decomposition. During heating, all the compounds undergo a solid–liquid phase transition (without molecular decomposition) and a liquid–gas phase transition (with a possible molecular decomposition). This can be verified with UV and GC–MS spectra of the reactants and products of the thermal process. These measurements were carried out, respectively, with a Coleman 575 UV spectrophotometer and a Hewlett–Packard 5890A GC with 5970 A mass-selective detector. Separation was performed on a 30 m OV1 capillary column, with the column temperature-programmed from 120 to 270 °C at a rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The trends in thermal behaviour of the examined compounds are given in Figs. 1–7. The values of the thermodynamic and kinetic quantities related to the TG and DSC measurements are reported in Tables 1–5.

Simultaneous TG–DSC is a very useful tool for investigating organic compounds. In a single run, transformations occurring without mass change (fusion, crystallisation, polymorphism) can be studied together with transformations with mass change (chemical reactions, decomposition, vaporisation, oxidation). Thus consistent TG and DSC values can be obtained even for small samples.

The thermal analysis of the compounds was carried out in order to determine the thermal stability, the overall enthalpy and the kinetic activation energy of the various processes.

Thermal stability

The compound **a** with R = H was chosen as a reference; its thermal decomposition follows a single curve over the temperature range 190–351° C, with a weight percent loss (*W*%) of 97.79% (Fig. 1). The corresponding enthalpy value of 237.18 J g^{-1} occurs between 190 and 337° C, with the temperature peak being at 318.16° C. This compound also shows a fusion process, $\Delta T = 140$–173° C (temperature peak 159.32° C), with $\Delta H = 130.97$ J g^{-1}.

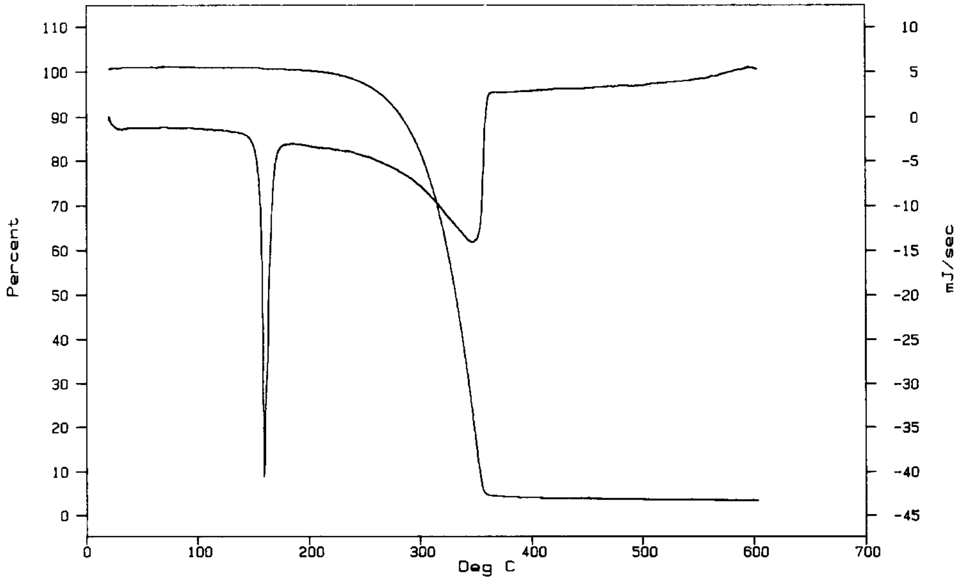


Fig. 1. DSC and TG curves of compound **a**.

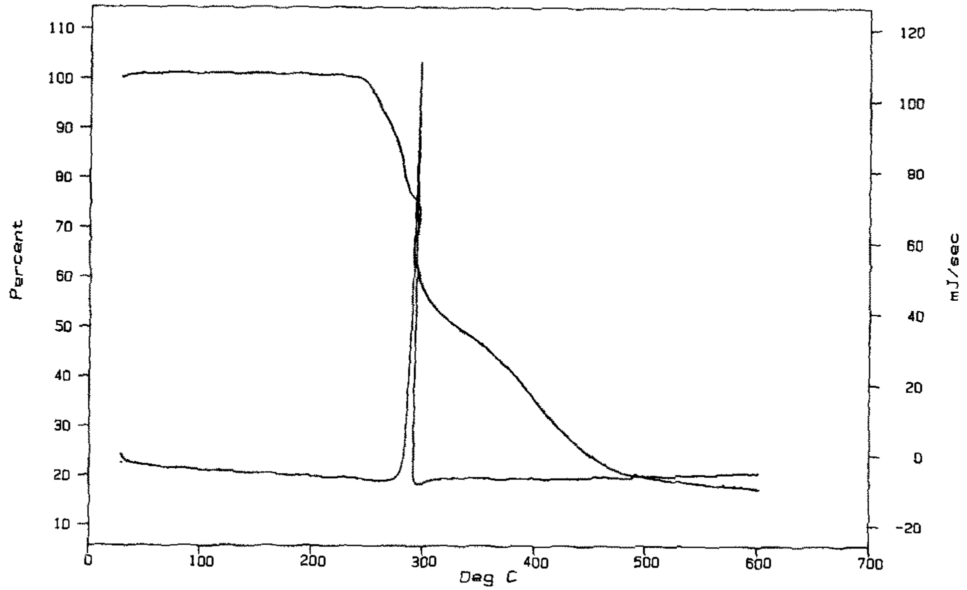
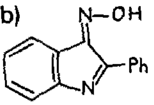


Fig. 2. DSC and TG curves of compound **2a**.

Another compound, **2a**, was also studied in order to provide further data for the understanding of the decomposition mechanism of the reference compound.

(b)



For compound **2a** (Fig. 2), there is no fusion process and the decomposition proceeds in three steps in the temperature ranges 217–285 °C, 285–296 °C and 296–590 °C, with weight percent losses of 22.08%, 18.26% and 42.21% (total 83.55%). There is also an exothermic reaction, $\Delta T = 272$–299 °C, $\Delta H = -388.93$ J g^{-1}, with the temperature peak at 297 °C.

The presence of a hydroxyl group instead of the phenyl group destabilises **2a**, favouring the thermal decomposition from the enthalpic point of view, and making the decomposition process more complicated. The absence of the fusion process in **2a** may be a result of the hydrogen bonds of the hydroxyl groups which raise the fusion temperature above the initial decomposition temperature.

As regards the thermal effects of the substituent groups in the *para*-position of the 3-phenyl, two different kinds of behaviour have been found for the substituents OMe and Cl, and for the substituents Me, NMe_2 and Br. The compounds with substituent groups OMe and Cl both show a behaviour similar to that of reference compound **a**. For R = Cl (Fig. 3), the decomposition occurs in the temperature range $\Delta T = 195$–371 °C, with a percent

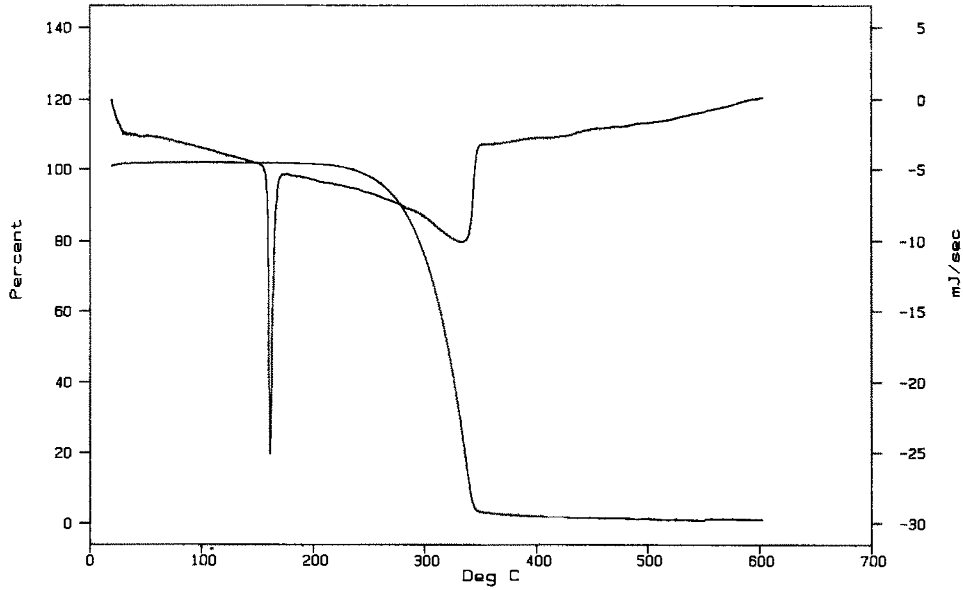


Fig. 3. DSC and TG curves of compound **e**.

weight loss of 98.96%. The fusion process (151–177 ° C) with peak temperature at 161.64 ° C shows an enthalpic value equal to 120.11 J g^{-1}. For R = OMe (Fig. 4), the decomposition shows ΔT = 206–401 ° C with a percent weight loss of 26.34%; for the fusion process, ΔT = 162–191 ° C, with peak temperature at 173.94 ° C and ΔH = 135.64 J g^{-1}. Because these two

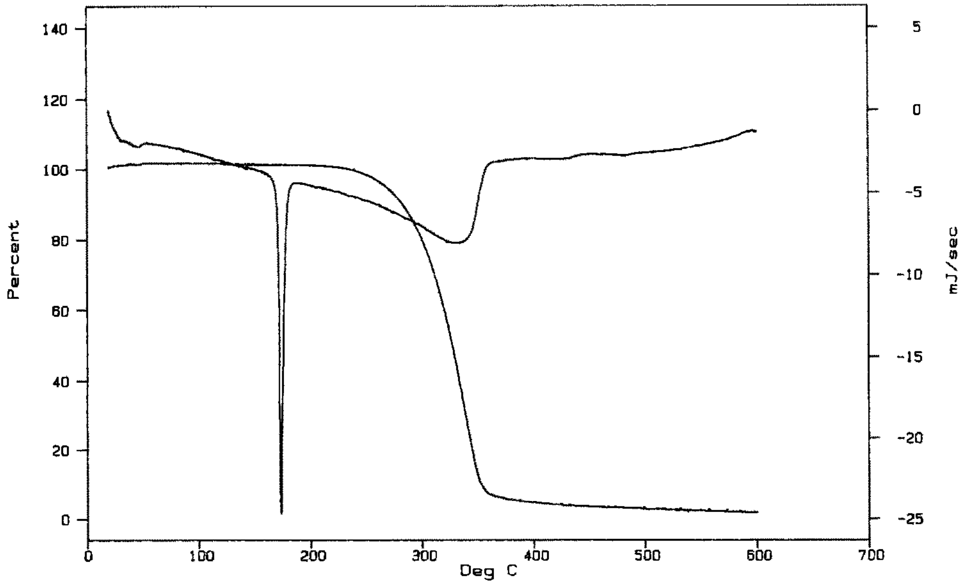


Fig. 4. DSC and TG curves of compound **c**.

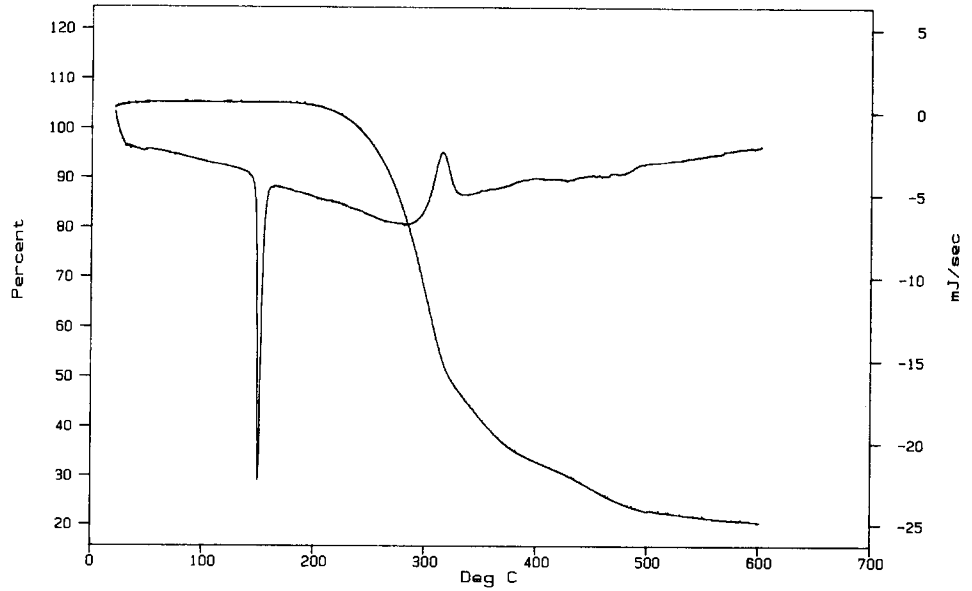


Fig. 5. DSC and TG curves of compound **b**.

compounds show peak temperatures and total enthalpies higher than those of the reference compound, it can be hypothesised that the substituents stabilise the compounds, thus strengthening the intermolecular and intramolecular bonds.

The thermal processes of the compounds with R = Me and R = NMe_2 show a fusion process followed by two stages of decomposition, the first stage in both compounds being characterised by an exothermic reaction. For R = Me (Fig. 5), the ranges of temperature and weight changes are 180–320 °C, percent weight loss 53.55%, and 320–576 °C, percent weight loss 29.76% (total 83.31%). The fusion process occurs in the range of temperature ΔT = 140–167 °C (temperature peak, 150.66 °C; $\Delta H = 117.53$ J g^{-1}). The exothermic process occurs in the range ΔT = 291–334 °C (peak temperature, 315.32° C; $\Delta H = -73.68$ J g^{-1}).

The solid–liquid phase transition shows the same peak temperature but a smaller enthalpy compared to the reference compound. The liquid–gas transition also begins at a lower temperature and has an exothermic enthalpy. The methyl group could destabilise the structure by weakening the intermolecular and intramolecular bonds.

The compound with R = $N(Me)_2$ (Fig. 6) also undergoes an initial fusion process (ΔT = 189–223° C; $\Delta H = 130.78$ J g^{-1}; temperature peak 207.64 °C) followed by two decomposition stages in the temperature ranges (with weight changes) 235–308 °C (5.32%) and 308–600 °C (77.58%) respectively. The enthalpic process related to the decomposition shows ΔT = 234–297 °C, with a peak temperature of 282° C and $\Delta H = -167.05$ J g^{-1}.

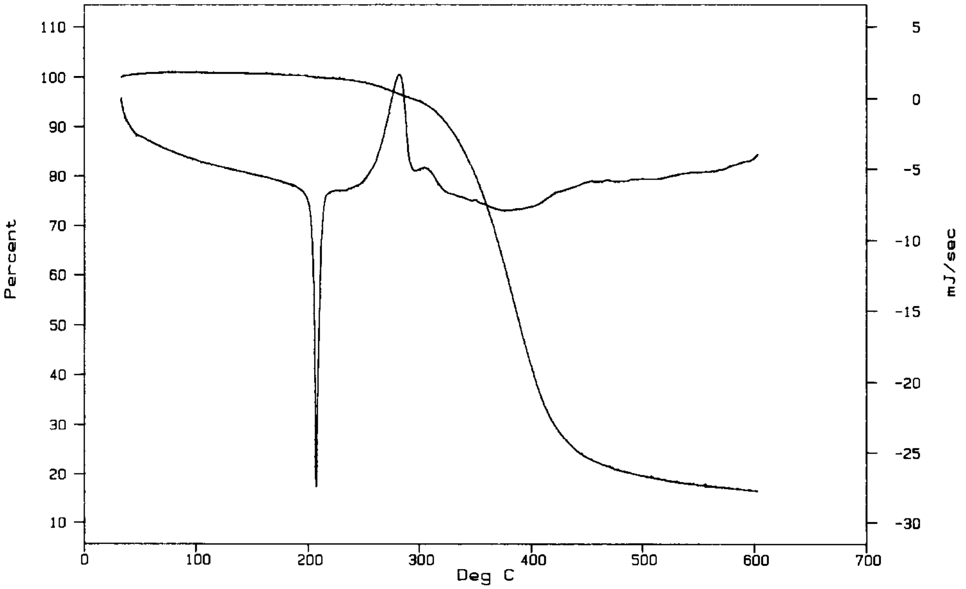


Fig. 6. DSC and TG curves of compound **d**.

Compound **d** ($R = NMe_2$) has a peak temperature of fusion and a decomposition temperature higher than those of the reference compound, but an exothermic decomposition process. In the liquid–gas phase transition, the substituent group has a destabilising influence.

Finally, the compound with R = Br (Fig. 7) undergoes an unusual process with fusion followed by three stages of decomposition, one of which may be characterised as exothermic. The first stage of decomposition has a temperature interval $\Delta T = 195–303°C$ and a percent weight loss of 19.32%; the second has $\Delta T = 303–313°C$, percent weight loss 10.42%; and the third, $\Delta T = 313–600°C$, percent weight loss 35.31% (total 65.05%). The fusion process, $\Delta T = 144–169°C$, has a peak temperature of 157.69°C and $\Delta H = 86.63\ J\ g^{-1}$, which is a small value. Thus, the peak temperature and the enthalpy of the fusion process are smaller than those of the reference compound and the decomposition process is exothermic. It can therefore be hypothesised that the bromine atom weakens the intermolecular bonds and leaves the molecule structure. A complete scale of thermal stability referring to the initial temperature of decomposition can be written: $NMe_2 > OMe > Br = Cl > H > Me$.

Enthalpy

The enthalpy values for the fusion process are in the order (Table 2) $OMe > H = NMe_2 > Cl > Me > Br$, while for the decomposition process, the enthalpy order is $Cl > OMe > H > Me > NMe_2 > Br$ (Table 2).

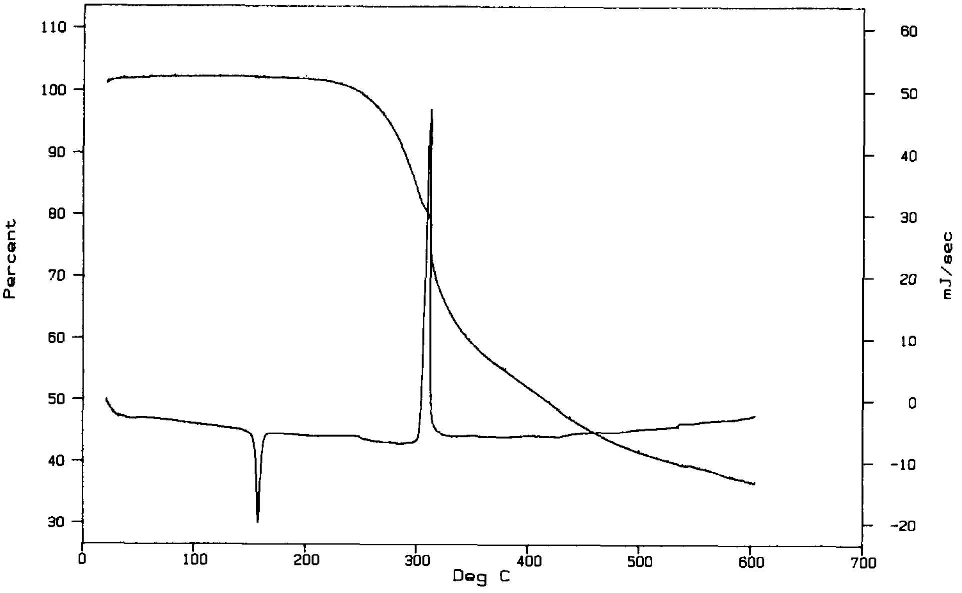


Fig. 7. DSC and TG curves of compound **f**.

If the enthalpy values related to different ranges of temperatures are added, an overall enthalpy, considered as the heat that the compound has exchanged with the external system at constant pressure up to its complete decomposition, can be deduced. These enthalpy data are given in Table 4. The heat scale of stability shows the order Cl > OMe > H > Me > NMe_2 > Br.

From this experimental evidence it can be seen that the liquid–gas transition is prevailing in the enthalpic behaviour.

TABLE 1

Thermodynamic parameters of the thermal degradation of 2-phenyl-3-arilymino-3*H*-indole derivatives (**a**–**f**) from TG measurements

Compound		Stage of degradation					
		I		II		III	
		T (°C)	*W* (%)	*T* (°C)	*W* (%)	*T* (°C)	*W* (%)
a	R = H	190–351	97.79				
b	R = Me	180–320	53.55	320–576	29.76		
c	R = OMe	206–401	96.34				
d	R = Cl	195–371	98.96				
e	R = Br	195–303	19.32	303–313	10.42	313–600	35.31
f	R = NMe_2	235–308	5.32	308–600	77.58		
2a	R = OH	217–285	22.08	285–296	18.26	296–590	42.21

TABLE 2

Thermodynamic parameters of thermal degradation of 2-phenyl-3-arylimino-3*H*-indole derivatives (**a**–**f**) from DSC measurements

Compounds		Fusion			Degradation		
		T (°C)	ΔH (J g^{-1})	Peak	T (°C)	ΔH (J g^{-1})	Peak
a	R = H	140–173	130.97	159.32	190–337	237.18	318.59
b	R = Me	140–167	117.53	150.66	291–334	−73.68	315.32
c	R = OMe	162–191	135.64	173.94	234–368	388.85	333.82
d	R = Cl	151–177	120.11	161.64	205–352	523.24	333.00
e	R = Br	144–169	86.63	157.69	296–329	-306.00	312.13
f	R = NMe_2	189–223	130.78	207.64	234–297	−167.05	282.00
2a	R = OH	272–289	−388.93	297.00			

TABLE 3

Degree of decomposition expressed as a percent weight loss of indole derivatives (**a**–**f**) at high temperatures

Compound		T (°C)	W (%)
a	R = H	351°C	97.79
b	R = Me	576°C	83.30
c	R = OMe	401°C	96.32
d	R = Cl	371°C	98.96
e	R = Br	600°C	65.05
f	R = NMe_2	600°C	82.90

TABLE 4

Overall enthalpy values of complete decomposition of indole derivatives (**a**–**f**)

Compound	ΔH (J g^{-1})
a R = H	368.15
b R = Me	43.85
c R = OMe	524.49
d R = Cl	643.35
e R = Br	−219.37
f R = NMe_2	−36.27

Kinetics

A kinetic TG-dynamic study of the decomposition processes for the compounds has been carried out using the method of McCarthy and Green [14]. The activation energy values, together with the frequency factors ln A and reaction order, are reported in Table 5.

TABLE 5

Kinetic parameters of thermal degradation of indole derivatives (**a**–**f**) from TG measurements, assuming first-order reaction, E_a (kcal mol^{-1})

Compound	T (°C)	E_{a_1}	ln A_1	T	E_{a_2}	ln A_2	T	E_{a_3}
a R = H	190–362	71.27	12.55					
b R = Me	180–320	46.45	8.34	320–576	34.29	3.68		
c R = OMe	206–401	71.57	12.76					
d R = Cl	195–371	74.64	13.59					
e R = Br	195–303	79.07	18.71	303–340	240.34	48.39	340–600	31.85
f R = NMe_2	250–300	107.81	22.44	300–450	70.05	11.07		

From the kinetic point of view, the compounds with R = H, R = OMe and R = Cl show an identical thermal stability. For the other compounds the kinetics values are different in the various stages. For the compound with R = Br, the activation energy of the second stage is greater than the first by virtue of the bromine release. For R = NMe_2, the first stage shows a greater activation energy value, while for the compound with R = Me the value of the two stages are similar.

It can be noted that the largest activation energies belong to the stages which show exothermic processes with decomposition.

GC–MS and UV measurements

GC–MS and UV analyses show that the behaviour of the compounds **a**–**f** can be differentiated in the following manner.

The UV and GC–MS spectra of the reference compound **a** and of the gaseous products of the thermal process deposited as crystals on the water-cooled finger hangdown surround of the STA 625, are identical. Moreover, in the GC–MS analysis, only one chromatographic peak appears, with the same mass fragmentation in the MS spectra, for both the gaseous products and the reference compound **a**. This implies that after fusion, the reference compound undergoes the liquid–gas phase transition without molecular decomposition and with intermolecular bond-breakage.

Methoxy- and chloro-substituted compounds show gas-chromatographic peaks with retention times equal to those of their thermal products. The MS spectra of these compounds and of the products have the same fragmentation and base peaks ($m/e = 312$ for methoxy and $m/e = 310$ for the chloro derivative). Furthermore, the UV spectra of these compounds and their products are identical.

As regards the Me-substituted compound, **b**, the GC–MS spectra show that it decomposes by losing the PhCN group and, in part, the substituent group (Table 6). Indeed, gas chromatography of the thermal decomposition products of compound **b** indicated three peaks with retention times of 18.5,

TABLE 6

Fragment ions for compound **b** and for its thermal decomposition products A, B and C [a]

b		A		B		C	
m/e	Abundance (%)	m/e	Abundance (%)	m/e	Abundance (%)	m/e	Abundance (%)
296	100	296	100	282	100	193	100
281	10	281	10	205	9	165	21
205	8	205	8	179	57	89	8
193	42	193	42	77	26		
65	13	65	13	51	16		

[a] A, B, C: chromatographic peaks with retention time 18.5, 17.4 and 12.4 min respectively.

17.4 and 12.4 min respectively, and with relative abundances of 72%, 7% and 21%. The MS spectra related to each gas-chromatographic peak show: for the first, the same base peak ($m/e = 296$) and fragmentation as the original compound (**b**); for the second, a base peak with $m/e = 282$ (loss of a radical CH_2); and, finally, for the third, a base peak $m/e = 193$, probably obtained by loss of a PhCN group from the undissociated compound.

The derivative with R = Br shows four decomposition products, represented by chromatographic peaks. From the first peak, it can be calculated that 9% of the compound remains undissociated. The corresponding MS spectrum shows the same base peak and fragmentation as the undissociated compound. The fragmentations in the MS spectra of the other chromatographic peaks show how a part of the substituent group leaves the molecule, as seen previously on the exothermic DSC curve. Accordingly, the UV spectra of the compound and products are very different.

Finally, the seven chromatographic peaks of the products of the NMe_2-substituted compound and the complex fragmentations of their MS spectra, together with the remarkable difference between the UV spectra of the compound and its products, suggest that this compound undergoes a full decomposition.

CONCLUSIONS

The thermal analysis and GC–MS techniques agree substantially with the fact that some of the compounds partially decompose at the liquid–gas transition, while others remain undissociated. This is because some substituent groups strengthen intermolecular and intramolecular bonds while others weaken them.

Finally, it can be noted that in the various solvents [14], the electrochemical behaviour of compounds **a**–**f** is affected by their substituents as a function of their electron-donor and electron-withdrawing power, which in the solid phase show no correlation with the thermal behaviour of the compounds. Further studies on the reduction processes in the solid state are in progress.

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