Study on Thermal Behavior of Some New Azomethines

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In the present paper four new azomethines are characterized by TG-DTG-DTA thermal methods in order to investigate the structure-thermostability-degradation mechanism correlation. The results of thermal analysis are indicative of a complex degradation mechanism which is characteristic of every sample, some similarities reflecting the structure influence being also noticed . The thermostability series of the compounds under study is correlated to their structure. The quantitative analysis by TG-DTG afforded the elucidation of some aspects of the thermal degradation mechanism The melting points of the samples estimated from DTA and by the Boetius method were in good agreement. The initial degradation temperatures resulting from TG-DTG-DTA led to the estimation of the temperature range of using and storing these compounds which is an useful information on their possible practical applications and of some of their derivatives as herbicides , plant growth stimulators , fungicides, acaricides.

Keywords: *azomethines, thermal analysis (TG-DTG-DTA), degradation mechanism, thermo-stability*

Among the various classes of chemical compounds studied lately the aryloxy-alkylcarboxylic acids and their derivatives are particularly important for their herbicidal and auxinic action which has been knowing for a rather long time [1,2].

The introduction of a sulphonamide group into the structures of the phenoxyacetic, chlorophenoxyacetic, crezoxyacetic, xylenoxyacetic and phenoxy-γ-butiric acids results in the improvement of their auxinic properties along with the features of selective herbicides also characterized by a low toxicity towards mammalians and human beings and by the lack of toxic residues[1,5].

By carrying on our studies in this field [6,7] the present paper is aimed to perform the synthesis and characterization by TG/DTG/DTA thermal methods [8-13], under nitrogen atmosphere, of four new azomethines, namely 4-dimethylaminobenzaldehyd{2-[4-(sulphonamido)-2-methylphenoxy]ethyl}hydrazone**(1)**, 4-clorobenzaldehyd{2-[4-(sulphonamido)-2-chlorophenoxy]ethyl}hydrazone**(2)**,4-methoxy benzaldehyd{2-[4-(sulphonamido)-2-chlorophenoxy]propyl}hydrazone**(3)**, 4-nitrobenzaldehyd {2-[2-(sulphonamido)-4-chlorophenoxy] ethyl}hydrazone**(4)** in order to follow the structure-thermostability-degradation mechanism correlation.

The characterization by thermal methods gives indication on the temperature range within which these compounds may be used and stored while the thermostability series is correlated with the chemical structure and confirmed by the values of the apparent activation energies of the first process of thermal degradation.

The quantitative analysis by TG-DTG under nitrogen atmosphere afforded a discussion on the thermal degradation mechanism. The compounds under study were found to be thermally degraded into two stages, the first being the significant one. For the first stage, the DTG curves show a clear inflexion point on the descending part of the curve.

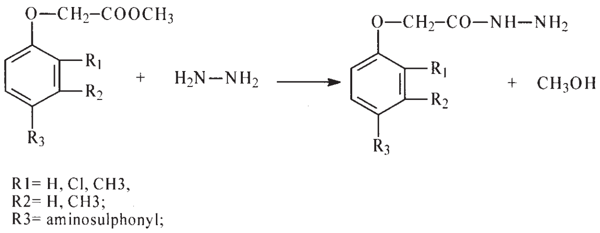
The quantitative TG-DTG analysis shows that the first chemical process of the first stage up to the temperature corresponding to the inflexion consists in the elimination of H_2N-SO- group in the structure of every azomethine under study, followed by processes of specific degradation under the influence of the nature of the substitutes.

The kinetic parameters, *n* and E_a, estimated by two methods [14,15] support the first process to be the splitting of similar bonds since the reaction order is the same, n=1, while the apparent energy of activation is slightly influenced by the substitutes in the close vicinity. The melting points estimated both from DTA under nitrogen atmosphere [16-18] and by the Boetius method were in good agreement .

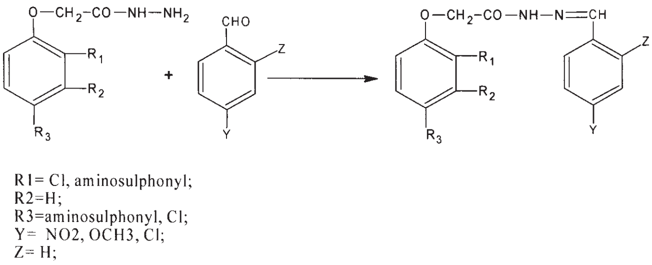
Experimental part

Synthesis of azomethines

The azomethines were synthesized into two stages, beginning with the synthesis of the hydrazides of the sulphonamidated phenoxyacetic acids as shown in scheme 1:



Scheme 1. Syntheses of hydrazides



Scheme 2. Synthesis of azomethines

The azomethines were then obtained by the reaction of the above hydrazides with p-dimethylaminobenzaldehyde, p-chlorobenzaldehyde, anisic aldehyde and p-nitrobenzaldehyde, respectively (scheme 2).

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The optimum synthesis conditions and the characterization of the obtained compounds by elemental analysis data, FTIR and NMR spectral measurements reported in previous papers [6,7] have confirmed the structures of the newly obtained azomethines. The mention has to be made that the compounds were separated with acetone as a solvent.

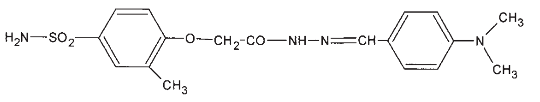
The structures of the obtained azomethines along with their chemical formulae, IUPAC denominations, molecular weights and melting points measured by the Boetius method are given in scheme 3.

Thermal analysis

The thermogravimetric analysis (TG) and the differential thermal analysis (DTA) were performed by means of a Perkin-Elmer-Pyris Diamond TGA/DTA thermobalance function of temperature. The DTG curves were obtained by the numerical differentiation of the TG curves. The working conditions were the following: sample mass -12 mg, heating rate-10 ^{0}C min^{-1}, temperature range 30-900 ^{0}C under nitrogen stream (800 mL min^{-1}).

Results and discussion

The TG, DTG and DTA curves of the azomethines in scheme 3 are depicted in figures 1-4.

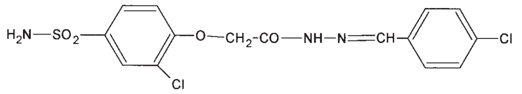


4-dimethylaminobenzaldehyde {2-[4-(sulfonamido)-2-mehtylphenoxy]ethyl}hydrazone) **(1)**

Chemical formula: $C_{18}H_{22}N_4O_4S$

Molecular weight: 390

Melting point: 200-203^{0}C

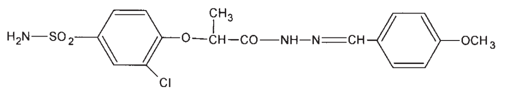


4-chlorobenzaldehyde {2-[4-(sulfonamido)-2-chlorophenoxy]ethyl}hydrazone **(2)**

Chemical formula: $C_{15}H_{13}O_4N_3SCl_2$

Molecular weight: 402

Melting point: 196-203^{0}C

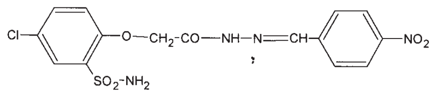


4-methoxybenzaldehyde {2-[4-(sulfonamido)-2-chlorophenoxy]propyl}hydrazone **(3)**

Chemical formula: $C_{17}H_{18}O_5N_3SCl$

Molecular weight: 411,5

Melting point: 215-220^{0}C



4-nitrobenzaldehyde {2-[2-(sulfonamido)-4-chlorophenoxy]ethyl}hydrazone **(4)**

Chemical formula:$C_{15}H_{13}O_6N_4SCl$

Molecular weight: 412,5

Melting point: 230-234^{0}C.

Scheme 3. Samples under study (structure, molecular weight and melting points)

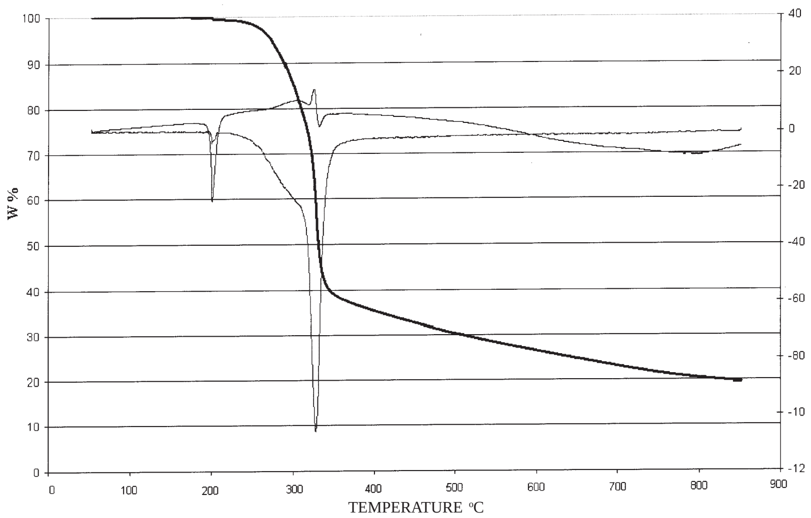


Fig. 1. TG and DTG curves of the compound **(1)**

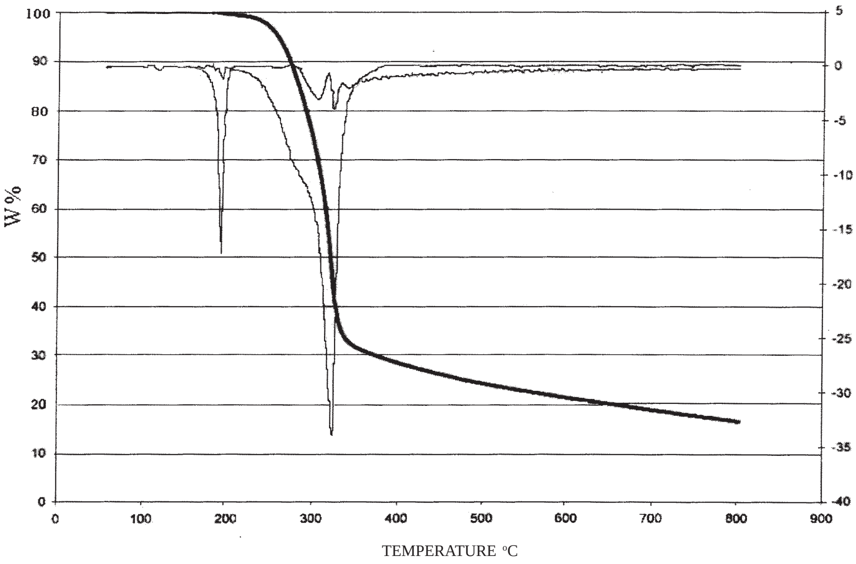


Fig. 2. TG and DTG curves of the compound (**2**)

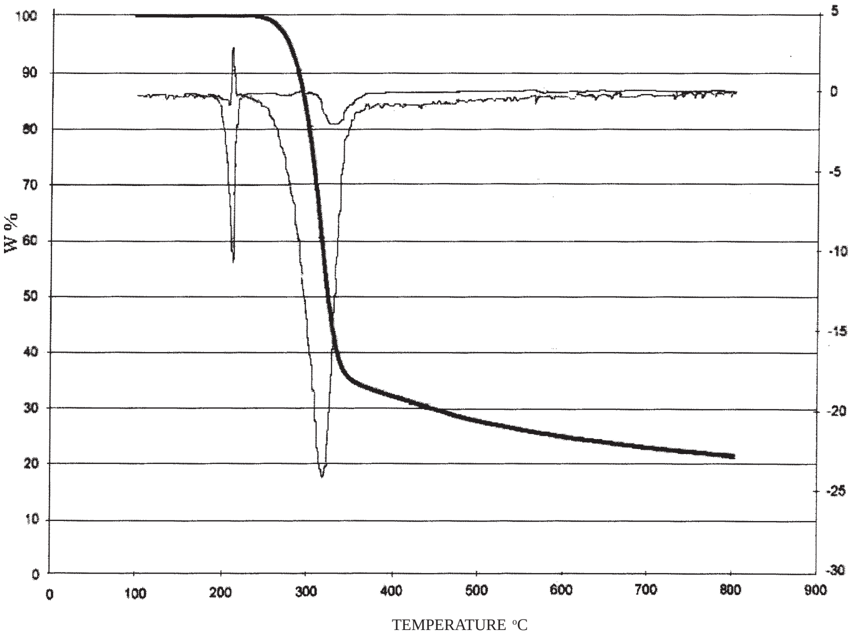


Fig. 3. TG and DTG curves of the compound (**3**)

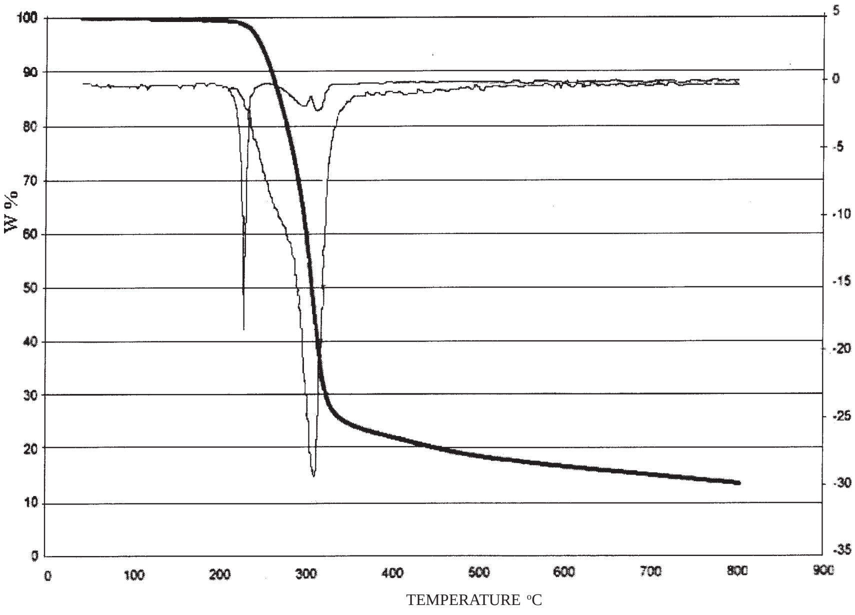


Fig. 4. TG and DTG curves of the compound (**4**)

Table 1
CHARACTERISTIC AMOUNTS FROM TG-DTG CURVES

Sample	Stage I						Stage II			Residue %
	T_i ^{0}C	T_{inf} ^{0}C	$W_{\infty inf}$ %	T_m ^{0}C	T_f ^{0}C	W_∞ %	T_i ^{0}C	T_m ^{0}C	W_∞ %	
1.	222,72	311,0	20,03	330,24	376,32	42,56	376,32	900	19,82	17,5
2.	214,24	307,8	23,52	328,64	391,04	39,28	391,04	900	22,68	14,52
3.	241,28	297,44	17,22	322,4	380,64	49,17	380,64	900	14,47	19,14
4.	220,32	280,38	18,68	306,0	357,0	42,83	357,0	900	26,78	11,71

The analysis of the TG and DTG curves affords the conclusion that the thermal degradation mechanism of the compounds under study under the mentioned working conditions is complex and specific, a similarity between the samples under consideration being noticed. They were also found to decompose into two stages among which the first is the significant one. For this stage, the DTG curves show a clear inflexion point on the descending part.

The characteristic amounts resulting from the TG-DTG analysis are given in table 1.

T_i ^{0}C= initial degradation temperature;

T_{inf} ^{0}C= temperature corresponding to the inflexion point of the descending branch of the DTG curve;

T_m ^{0}C= temperature corresponding to the maximum degradation rate;

T_f ^{0}C= final degradation temperature;

$W_{\infty inf}\%$, W'_{inf}, %, $W_{\infty}\%$ = weight losses at the inflexion temperature, in the first stage and in the second stage.

As revealed by the data in table 1, the first and the second degradation stages develop within the 210-392^0 C and 392-900°C temperature ranges, respectively.

The theromostabilities of the samples expressed by the initial temperature of thermal degradation under nitrogen stream (T_i) lead to the following series: **3 >1>4 ≥ 2**

By taking the influence of the electronic effects on the stabilities of the four azomethines into account the following conclusions can be drawn.

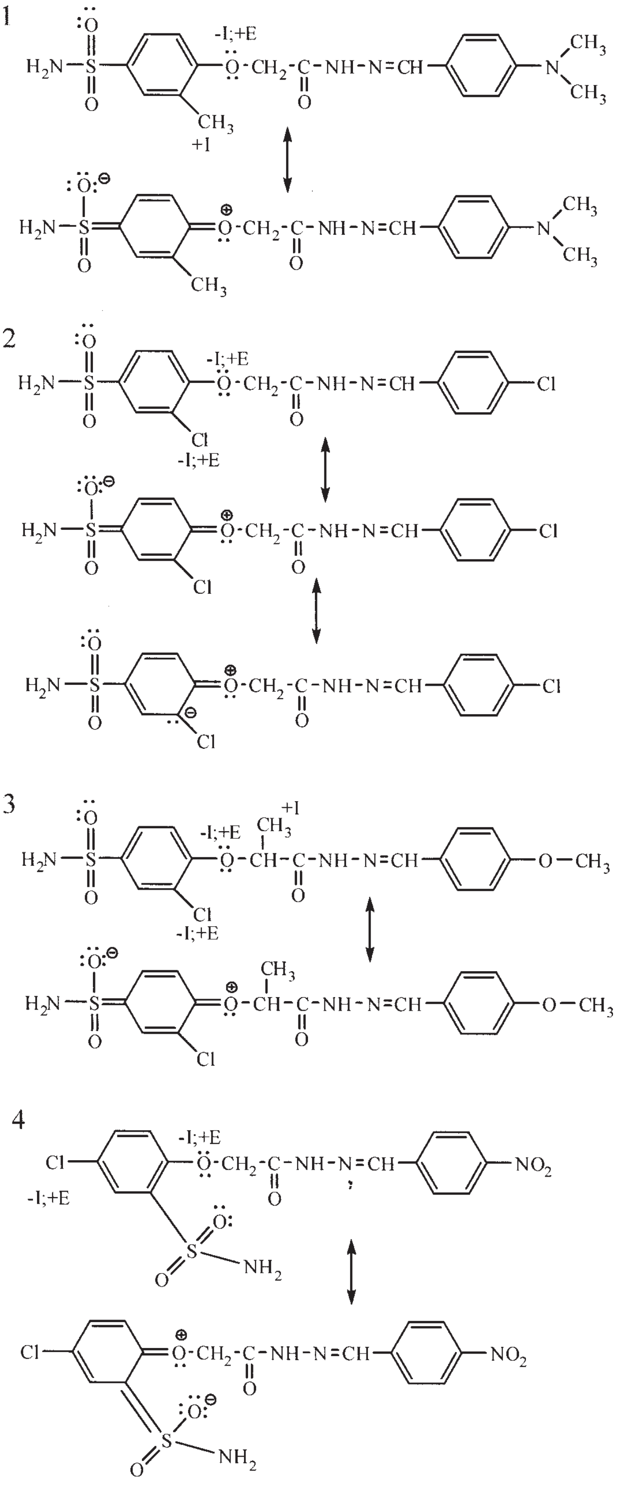
The main factor determining the stabilities of the four compounds is the electron-releasing effect (+E) of the ethereal oxygen.

This effect is responsible for the delocalization of the electrons in the aromatic ring which results in the double bond character of the (C-S) bond and consequently, the stronger the (+E) effect of the ethereal oxygen is the higher the (C-S) bond order and, hence, the compound stability are.

Some of the possible limiting structures of the four compounds as well as the electronic effects involved into their stabilities are presented in scheme 4.

With the compound 4-methoxybenzaldehyd{2-[4-(sulphonamido)-2-chloro-phenoxy] propyl}hydrazone**(3)**, the presence of the -CH_3 group in the α position with respect to the ethereal oxygen causes, due to the electron-releasing effect (+I), an enhancement of the (+E) effect of the ethereal oxygen and hence a higher C-S bond order and thus a higher stability of the compound.

The compound 4-dimethylaminobenzaldehyd{2-[4-(sulphon-amido)-2-methylphenoxy]ethyl}hydrazone **(1)** has a –CH_3 group in the aromatic ring exerting an (+I) inductive effect which contributes to the increase in the C-S bond order and thus to the higher stability of the compound. Since the -CH_3 group in the compound 4-dimethylaminobenzaldehyd 2,4-(sulphonamido)-2,2-methylphenoxy-ethyl hydrazone**(1)** does not influence on the (+E) effect of the ethereal oxygen the stability is lower



Scheme 4. The possible limiting structures of the four compounds and the electronic effects involved into their stabilities

Table 2
KINETIC PARAMETERS (n, E_a) OF THE INITIAL REACTION OF THERMAL DEGRADATION

Sample	Chan-Balke method			Coats-Redfern method		
	Reaction order (n)	Energy of activation Ea (Kj/mol)	Error R^2	Reaction order (n)	Energy of activation Ea (Kj/mol)	Error R^2
1.	1	122,96	0,991	1	120,0	0,985
2.	1	106,30	0,997	1	116,30	0,962
3.	1	188,59	0,957	1	190,60	0,997
4.	1	110,88	0,980	1	117	0,992

Table 3
CHARACTERISTIC TEMPERATURES FROM DTA

Sample	Melting			Stage I			Stage II		Thermal nature
	T_i ⁰C	T_m⁰C	T_f⁰C	T_i ⁰C	T_m⁰C	T_f⁰C	T_i ⁰C	T_f⁰C	
1.	184,32	201,6	230,4	230,4	322,56 334,08	345,56	345,56	900	endo
2.	166,4	195,52	218,4	218,4	312 330,72	391,04	391,04	900	endo
3.	195,52	220,48	232,96	232,96	334,88 343,2	374,4	374,4	900	endo
4.	208,08	228,48	248,88	248,88	297,84 314,16	332,52	332,52	900	endo

Table 4
MELTING TEMPERATURES

Sample	Melting point (T_m),⁰C (DTA)	Melting point(T), ⁰C Boetius Method
1.	201,6	200-203
2.	195,52	196-203
3.	220,48	215-220
4.	228,48	230-234

Table 5
EXPERIMENTAL AND THEORETICAL WEIGHT LOSSES FOR (NH_2-SO_2-) GROUP

Sample	Molecular weight	Temperature range T_i ⁰C - T_{inf} ⁰C	$W_{\infty inf}$ %, experimental (NH_2-SO_2-)	W_∞ %, theoretical (NH_2-SO_2-)
1.	390	222,72 – 311,0	20,03	20,51
2.	412,5	214,24 -307,8	23,52	19,39
3.	402	241,28- 297,44	17,22	19,44
4.	411,5	220,32-280,38	18,68	19,39

than that of the compound 4-methoxy-benzaldehyd{2-[4-(sulphonamido)-2-chloro-phenoxy]propyl}hydrazone**(3).**

The compounds 4-clorobenzaldehyd{2-[4-(sulphonamido)-2-chlorophenoxy]ethyl}hydrazone**(2)** and 4-nitrobenzaldehyd {2-[2-(sulphonamido)-4-chlorophenoxy] ethyl}hydra-zone**(4)** contain a chlorine atom in the aromatic ring situated at different positions with respect to the sulphonamidic group (S-C). The chlorine atom shows a strong (-I) effect which causes the stopping of the electron delocalization at the carbon atom where the chlorine is bound which determines the decrease in the (C-S) bond order and thus a lower thermal stability of these compounds.

The stabilities of the compounds, 4-clorobenzaldehyd{2-[4-(sulphonamido)-2-chlorophenoxy]ethyl}hydrazone**(2)** and 4-nitrobenzaldehyd {2-[2-(sulphonamido)-4-chlorophenoxy] ethyl}hydrazone**(4)** would be rather similar, the compound 4-cloro-benzaldehyd{2-[4-(sulphonamido)-2-chlorophenoxy]ethyl}hydrazone**(2)** being somehow less stable due to the *ortho* position of the chlorine atom toward the ethereal oxygen.

It follows that the thermostabilities of the four azomethines are in the same order as found by the TG-DTG-DTA thermal analysis.

$$\mathbf{3 > 1 > 4 \geq 2}$$

The thermostability series of the compounds under study is also confirmed by the values of the apparent energies of activation estimated by two methods for the first chemical process corresponding to the elimination of the H_2N-SO_2- group by the splitting of the (S-C) sulphonamidic bond: the Chan-Balke differential method[14] and the Coats-Redfern integral method [15] (table 2).

The data in table 2 are indicative of the following series: $\mathbf{E_{a3} > E_{a1} > E_{a4} \geq E_{a2}}$.

The values thus obtained are close to the theoretical ones for this bond type.

The DTA curves also confirm the complex and specific degradation mechanism resulting by the TG-DTG analysis, the same endothermal and well-defined degradation stages being found again.

Prior to the thermal degradation stages the azomethines under study show an endothermal peak within the 160-250⁰C temperature range corresponding to the melting peak, where the sample weights (TG-DTG) are constant.

The characteristic temperatures from DTA are given in table 3.

As made evident by the data in table 3, the thermal degradation takes place within the same temperature range as found by the TG-DTG analysis, 215-900⁰C. The development of two processes in the first stage is made evident in DTA by two endothermal peaks, among which the first corresponds to the elimination of the H_2N-SO_2-group, since the inflexion temperatures from the TG-DTG correspond to the temperatures at the maximum of the first peak of the DTA curve.

For the second degradation process of the first stage the temperatures at the maximum of the DTA peak coincide with those from DTG at the maximum degradation rate which also supports the two chemical processes developing in the first stage.

The melting points (table 3) were estimated from the temperatures corresponding to the maximum of the DTA peak-melting [16].

The melting points in table 4 estimated by the both Boetius and DTA method are seen to be in good agreement.

The weight losses corresponding to the inflexion points in TG-DTG correlated with the structure and thermostability of the azomethines affords a discussion on the degradation mechanism. Thus, the weight loss (%) corresponding to the inflexion point in TG-DTG within the 220-311⁰C temperature range corresponds to the H_2N-SO_2- group elimination by the (C-S) bond splitting (table 5).

The values of the kinetic parameters (n and Ea) estimated for this process (table 3) confirm this reaction to be a degradation one since the reaction order n=1 is characteristic of such a reaction and also the values of the activation energies are close to the energy of the C-S bond.

It follows that the degradation mechanism begins with the elimination of the H_2N-SO_2- group followed by chemical processes of specific degradation influenced subsequently by the substitute natures, the whole complex mechanism consisting in successive reactions.

Conclusions

The analysis of the TG-DTG-DTA curves of the compounds under study is indicative of complex and specific mechanisms of thermal degradation influenced by the chemical structure.

The thermostabilities of the compounds estimated from the initial degradation temperatures from DTG and DTA obey the following series: **3 >1>4 ≥ 2**

The thermostability is correlated with the chemical structure and apparent energy of activation of the first degradation chemical process which enables the assessment of the temperature range where these compounds might be used and stored.

The melting points of the compounds under study estimated from DTA and by the Boetius method are in good agreement.

The results of the thermal analysis correlated with the kinetic parameters of the first chemical process of the degradation afforded some assertions on the reaction mechanism, when the first reaction of the complex mechanism developing by successive reactions was ascertained.

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