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THERMAL STUDIES ON SOME REACTIONS IN THE SOLID-STATE

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Abstract

The solid-state thermal reactions of 2,6-diamino-4-chloropyrimidine, 3,3-dimethoxybenzidine and of thiosemicarbazide with each of 2-hydroxy-1-naphthaldehyde and 2,4-dihydroxybenzaldehyde in a mole ratio of 1:1 produced (1+1) condensation products ('half units'). These solid state reactions have been studied by means of differential thermal analysis (DTA). The products of the reactions were identified using elemental analysis and IR spectroscopy. Some kinetic parameters such as orders and activation energies of the reactions were evaluated form the DTA curves.

Keywords: DTA, kinetics, solid-state reaction

Introduction

There are numerous accounts in the literature describing the chemistry of Schiff bases. Schiff bases result from the condensation of two moles of a keto compound with one mole of diamine, even where equimolar amounts of the reactants are used. A few of the Schiff bases that have been reported so far arise from the condensation of the carbonyl group with only one end of diamine. These are referred to as 'half unit' Schiff bases. They have been prepared by template synthesis and isolated as their metal complexes or by partial hydrolysis of symmetrical Schiff bases [1–4]. In a very few cases free 'half unit' Schiff bases have been prepared [5–8]. All the above preparations were performed in solution except a few cases where the reactions were performed in the solid state [9].

The present paper reports the study of some organic reactions induced thermally in the solid state, as well as the measurement of some kinetic parameters of the solid-state reactions.

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Experimental

Materials and apparatus

Reagent grade chemicals were used. Thermal treatments were carried out using a Shimazdu XD-30 thermal analyser. IR spectra were measured in KBr pellets using a Perkin-Elmer 593 (4000–200cm^{-1}) spectrophotometer. Carbon, hydrogen, and nitrogen were determined in the analytical laboratories of the University of Cairo.

Reaction procedures

The solid-state reactions were performed by heating a finely divided mixture of equimolar amounts of diamine and carbonyl compounds in an electric furnace for about 30 min at the temperatures listed in Table 1. The products were recrystallized from ethanol. The kinetic parameters such as orders and activation energies of the reactions were evaluated from the DTA curves of a finely divided mixture of equimolar amounts of diamine and carbonyl compounds using heating rate 15 deg·min^{-1} (Fig. 1).

Table 1 Thermal data of some reactions in the solid state

Compound	t^a / °C	T_p /°C	n	E_o /kJ·mol^{-1}	Transformation
I	117	117	1.4	234.10	210
II	108	108	1.2	415.28	122
IIIa	65.4	65.4	1.3	128.95	122.5
IIIb	110	110	1.3	113.78	200 (change to brown), 230^b
V	–	–	–	–	82
VI	–	–	–	–	220

[a] temperature of preparation in an electric furnace
[b] start of decomposition.

Results and discussion

The solid state thermal reactions of 2,6-diamino-4-chloropyrimidine, 3,3-dimethoxybenzidine and of thiosemicarbazide with 2-hydroxy-1-naphthaldehyde and 2,4-dihydroxybenzaldehyde at a 1:1 mole ratio led to the formation of 'half unit' Schiff bases I–VI respectively. The reaction of III_a with 2,4-dihydroxybenzaldehyde produced the unsymmetric Schiff base III_b.

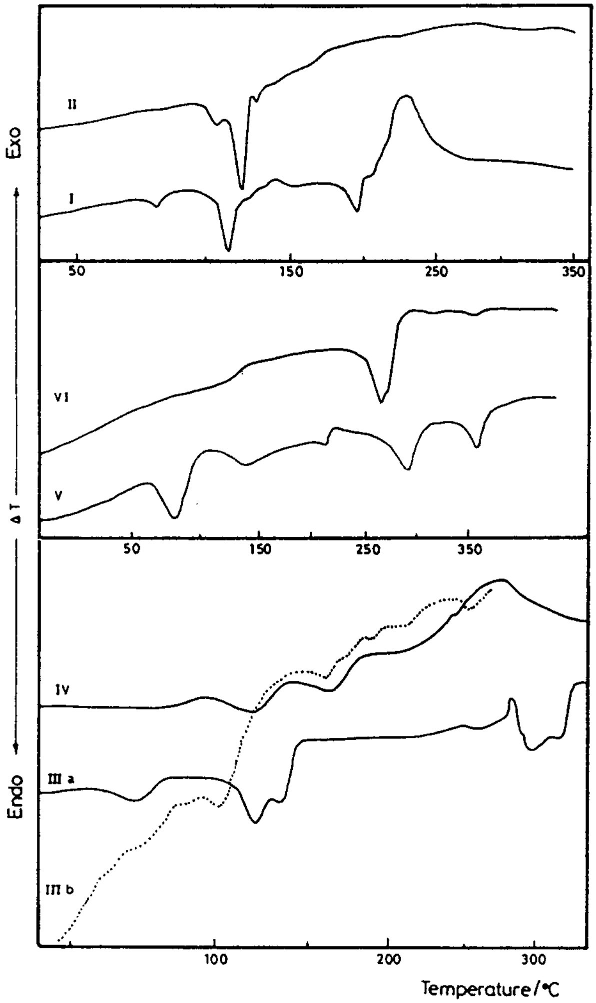
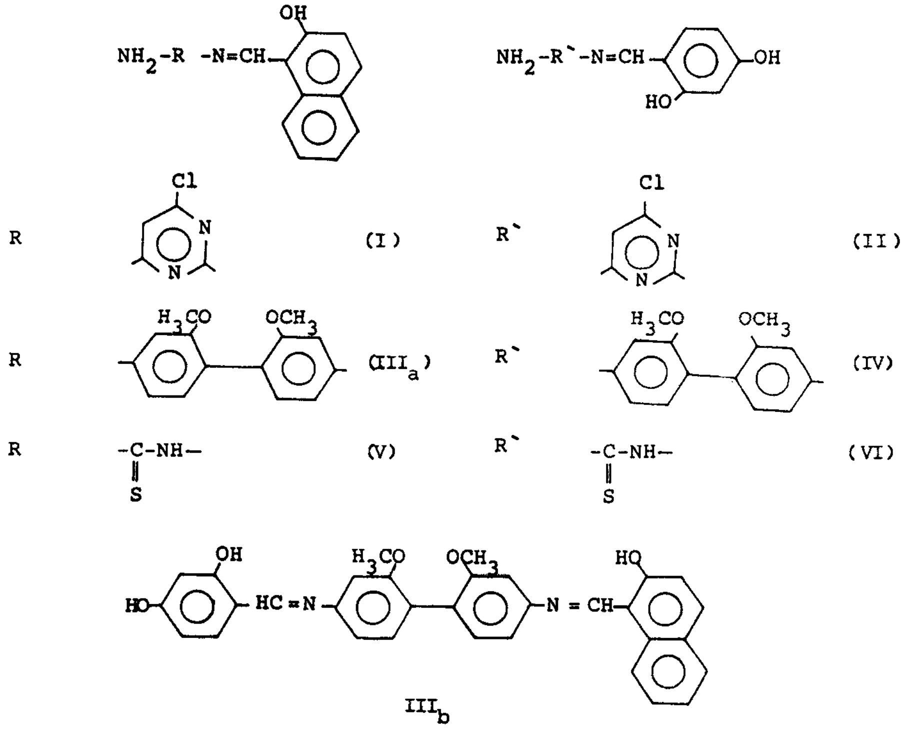


Fig. 1 DTA curves of the solid state thermal reactions leading to the formation of compounds (I–VI)

The products obtained by heating a powdered mixture of equimolar amounts of the reactants at the maximum temperature of the endothermic peak (T_m) (Fig. 1 and Table 1) were investigated by means of elemental analysis and IR spectroscopy.

The analytical and IR spectral results (Tables 2 and 3, respectively) are consistent with the chemical formulations in Fig. 2.

The IR spectra of the products were compared with those of the reactants. The IR spectral data indicate that all compounds have intramolecular hydrogen bonding (O–H----N), shown by absorption bands in the range 3480–3425 cm^{-1}



Scheme 1 Suggested chemical formulations of the 'half unit' Schiff bases

[10]. The IR spectra of all the compounds except III_b show absorption bands in the range 3360–3170 cm^{-1}, assigned as ν_{NH_2}. The spectra of compounds V and VI display a band near 3160 cm^{-1}, assigned as ν_{NH}. The spectra of all the compounds show a strong band near the region 1630–1600 cm^{-1}, attributed to $\nu_{C=N}$. δ_{NH_2}, δ_{OH} and ν_{C-OH} bands appear in the regions 1666–1623 cm^{-1}, 1235–1210 cm^{-1} and 1140–1080 cm^{-1} respectively. The spectra of compounds I, III_a, III_b and V show two strong bands near 840–820 cm^{-1} and 780–750 cm^{-1}, attributed to oc- and β- substituted naphthyl rings, whilst compounds II, III_b, IV and VI show a strong to medium band near 745 cm^{-1}, due to the out of the plane vibration of C–H in the phenyl ring. The spectra of compounds I and II show three bands near 625, 595 and 480 cm^{-1}, assigned as deformation bands of the pyrimidine ring.

The formation of the 'half unit' Schiff bases is explained as follows

$$H_2N{-}R{-}NH_{2(solid)} + R_1R_2C{=}O_{(solid)} \xrightarrow{heat} R_1R_2C{=}N{-}R{-}NH_2 + H_2O$$

Table 2 Elemental analysis and colours of the prepared products

Compound	[a]C / %	[a]H / %	Colour
I	58.9 (60.3)	3.5 (3.7)	Canary yellow
II	49.3 (49.9)	3.2 (3.4)	Yellow
III_a	75.1 (75.4)	5.3 (5.5)	Scarlet red
III_b	74.3 (74.1)	4.9 (5.0)	Deep red
IV	69.5 (69.2)	5.3 (5.5)	Reddish brown
V	58.9 (58.8)	4.6 (4.5)	Canary yellow
VI	45.7 (45.5)	4.3 (4.3)	Yellow

[a]Calculated values in parentheses

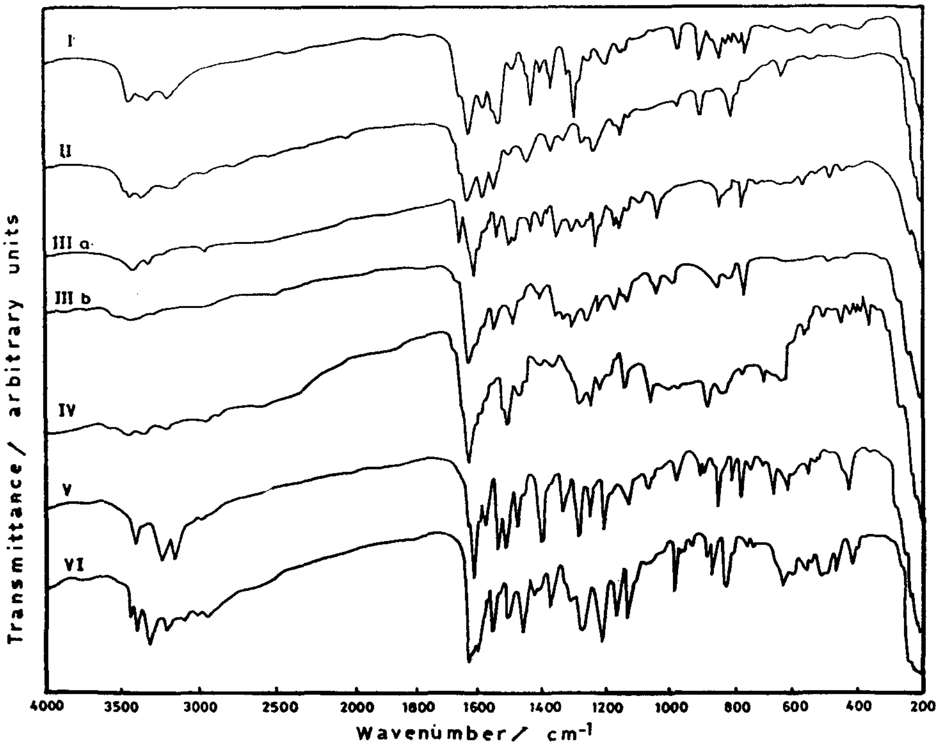


Fig. 2 IR spectra of compounds (I–VI)

Solid state thermal reactions of 'half unit' Schiff bases with the same or with a different carbonyl compound to produce (1+2) condensation Schiff base products (symmetrical or unsymmetrical) did not proceed, except for compound III_a which reacted with 2,4-dihydroxybenzaldehyde and produced III_b. The forma-

Table 3 Infrared spectra[a]

Band assignation	Compound						
	I	II	III$_a$	III$_b$	IV	V	VI
ν_{OH}	3450 m	3480 sh 3460 s	3430 w,br	3440 br	3425 br	3440 s	3480 s 3440 s
ν_{NH_2}	3330 m 3180 m,br	3360 s,br 3180 br	3340 w 3310 sh	–	3340 w 3170 vw	3360 w 3250 s	3360 s 3340 s 3240 m
ν_{NH}	–	–	–	–	–	3160 s	3130 w, br
δ_{NH_2}	1655 sh	1660 sh	1666 s	–	1640 sh	1640 sh 1623 m	1630 s
$\nu_{C=N}$	1623 s	1630 s	1615 s	1620 s	1620 s	1605 s	1600 s
δ_{OH}	1215 sh	1230 s	1220 s	1210 s	1225 s	1235 s	1213 s
ν_{C-OH}	1140 m	1130 m	1080 br	1080 br	1080 sh	1115 s	1130 s
oc, β-substituted naphthyl ring	840 s 750 s	–	830 s 760 s	830 s 780 s	–	820 s 750 s	
benzene ring (out of plane)	–	755 s	–	745 s	740 m	–	745 s
substituted pyrimidine ring (deformation bands)	625 w,br 595 s 480 sh	635 m,br 600 s 470 sh					

[a]m = medium, sh = shoulder, br = broad, s = strong, w = weak

tion of this compound is evidenced by the this appearance of the band characteristic of ν_{NH_2} and δ_{NH_2} in the IR spectrum of compound III$_a$.

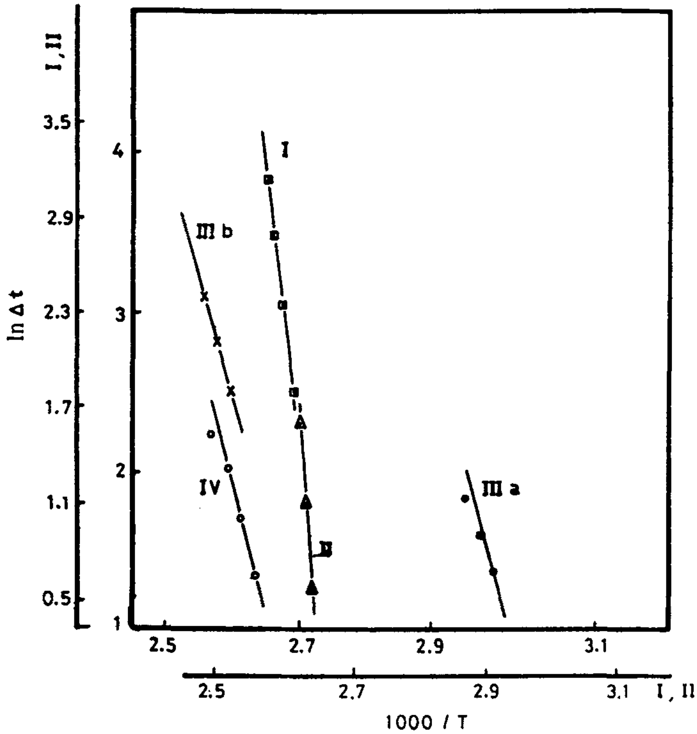


Fig. 3 Plot of lnΔ*t* *vs.* 1000/*T* (K) for compounds (I–IV)

The formation of the obtained products was also supported by the disappearance of the endothermic peak corresponding to the formation of the products prepared in an electric furnace at the maximum temperature T_p (Fig. 1 and Table 1).

It is worth noting that these solid-solid reactions took place without any heat treatment. But the formation reaction takes a long time for completion. This leads to the conclusion that the heat only assists the loss of water molecules from the reaction medium and causes the reaction to be shifted greatly towards the formation of products.

$$\text{Amine} + \text{Aldehyde} \rightleftharpoons \text{Schiff's base} + H_2O$$

Kinetic studies

The orders (n) and activation energies (E_a) of the condensation reactions were determined from DTA curves (Fig. 1). The orders of the reaction were evaluated using Reich's empirical relation [11]

$$n = 1.26\ S^{1/2} \qquad \text{and} \qquad S = \frac{a}{b}$$

where n is the reaction order and S is the peak shape factor. The values of a and b were calculated as shown in Fig. 1. The calculated values of n (Table 1) range between 1.2 and 1.4 which indicates that the reaction order is more than one.

The activation energies listed in Table 1 were calculated using the formula of Piloyan *et al.* [12].

$$\ln \Delta t = C - \frac{E_a}{RT}$$

where Δt is the deviation from the baseline, its values being taken directly from the DTA curve in units of length (cm or mm), as shown in Fig. 1, C is a constant, E_a is the activation energy, R is the universal gas constant (equal to $8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) and T is the absolute temperature. The plot of $\ln\Delta t$ *vs.* $1000/T$ gave a straight line (Fig. 3), with a slope of $-E_a/R$.

References

1 R. O. Elder, Aust. J. Chem., 31 (1978) 35.
2 H. A. Goodwin and F. Lions, J. Am. Chem. Soc., 82 (1960) 5013.
3 W. N. Wallis and S. C. Cummings, Inorg. Chem., 13 (1974) 991.
4 A. C. Braithwaite, C. E. F. Rickard and T. N. Waters, J. Chem. Soc., Dalton Trans., (1975) 2149.
5 A. P. Summerton, A. A. Diamantis and M. R. Snow, Inorg. Chim. Acta, 27 (1978) 123.
6 P. G. Beckingsale, A. T. Morcom, C. E. F. Rickard and T. N. Waters, J. Chem. Soc., Dalton Trans., (1977) 2135.
7 J. P. Costes and G. Cros, C. R. Acad. Sci., 294–II (1982) 173.
8 H. Adams, N. A. Bailey, J. P. Costes, D. E. Fenton and J. R. Tate, International Conference on Inorganic Stereochemistry, Reading England, (1982) poster A-25.
9 F. A. El-Saied, Thermochim. Acta, 141 (1989) 245.
10 K. Morishige, J. Inorg. Nucl. Chem., 40 (1978) 843.
11 T. Reich, J. Inorg. Nucl. Chem., 28 (1966) 1329.
12 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, 5067 (1966) 1229.

Zusammenfassung — Die thermische Feststoffreaktion von 2,6-Diamino-4-chloropyrimidin, 3,3-Dimethoxybenzidin und von Thiosemikarbazid mit 2-Hydroxy-1-Naphthaldehyd bzw. 2,4-

Dihydroxybenzaldehyd im Molverhältnis 1:1 ergab (1+1) Kondensationsprodukte ('Halbeinheiten'). Diese Feststoffreaktionen wurden mittels DTA untersucht. Die Reaktionsprodukte wurden mittels Elementaranalyse und IR-Spektroskopie identifiziert. Anhand der DTA-Kurven wurden einige kinetische Parameter ermittelt, wie z.B. Reaktionsordnung und Aktivierungsenergie.