ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2008, Vol. 82, No. 9, pp. 1601–1604. © Pleiades Publishing, Ltd., 2008.

SHORT COMMUNICATIONS

A Thermal Study of Some Schiff Bases Derivative of α-Napthylamine[1]

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Received September 3, 2007

Abstract—Thermal analyses of some Schiff bases, derivative of α-napthylamine, were performed by the DSC, TG and DTA techniques. The thermograms were used to determine various kinetic parameters, such as the order of degradation (*n*), energy of activation (*E*), frequency factor (*A*), and entropy change (Δ*S*), by the Freeman-Carroll method.

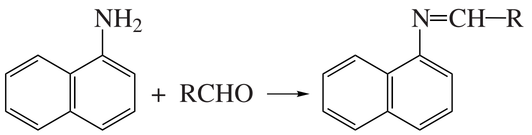
DOI: 10.1134/S0036024408090355

INTRODUCTION

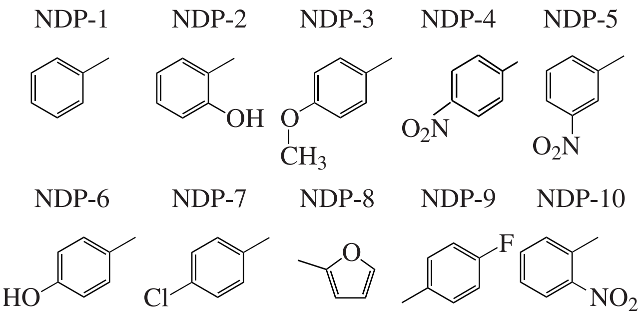
Thermal analysis has become an established method in studies of the thermal behavior of materials and finds wide applications in diverse industrial and research fields [1–5]. Thermal analysis of a number of materials such as drugs, ceramics, composites, geologic materials, biological materials, polymers, polyurethanes, and other organic and inorganic compounds has been reported [6–12]. Varied kinetic information can also be obtained from differential thermal analysis [13, 14]. In the present paper, the thermal properties of some Schiff bases of α-naphthylamine are reported.

EXPERIMENTAL

Various Schiff bases were synthesized by the condensation of α-napthylamine with aldehydes,



where R =



All these compounds were characterized by their IR, NMR, and mass spectra.

The differential scanning calorimetry (DSC), thermogravimetric analysis (TG), and differential thermal analysis (DTA) measurements of all the Schiff bases were taken on a Universal V 2.6D TA Instrument unit at a heating rate of 10 K/min in the nitrogen atmosphere.

RESULTS AND DISCUSSION

The figure shows the TG/DTA and DSC thermograms for NDP-1. Various thermal properties such as the initial decomposition temperature (IDT), the decomposition temperature range, and maximum degradation along with the percentage weight loss and exothermic/endothermic transitions of all the synthesized Schiff bases are reported in Table 1. The experimental melting points are also given for comparison.

It follows from Table 1 that the initial decomposition temperature is minimum for NDP-1 and maximum for NDP-8. However, weight loss is minimum for NDP-3 and NDP-7. Maximum weight loss is observed for NDP-8. Only NDP-8 decomposes in two steps. The weight loss values decrease in the series NDP-8 > NDP-6 > NDP-10 > NDP-1 > NDP-5 > NDP-9 > NDP-2 > NDP-4 > NDP-3, NDP-7. Thus, NDP-8, which appears to be thermally stable, loses maximum weight when decomposes. The temperature of maximum degradation is highest for NDP-5 followed by NDP-8. NDP-7 and NDP-9 have the lowest maximum degradation temperatures. On the whole, all Schiff bases show maximum degradation between 274.7 and 342.2°C. The thermal stability of a compound depends on the type of groups and structure. In the Schiff bases studied, the central moiety is the same, but side chains are different. In NDP-8, side chain is furfuraldehyde, whereas it is benzaldehyde in NDP-1. Hence, the presence of benzaldehyde decreases stability.

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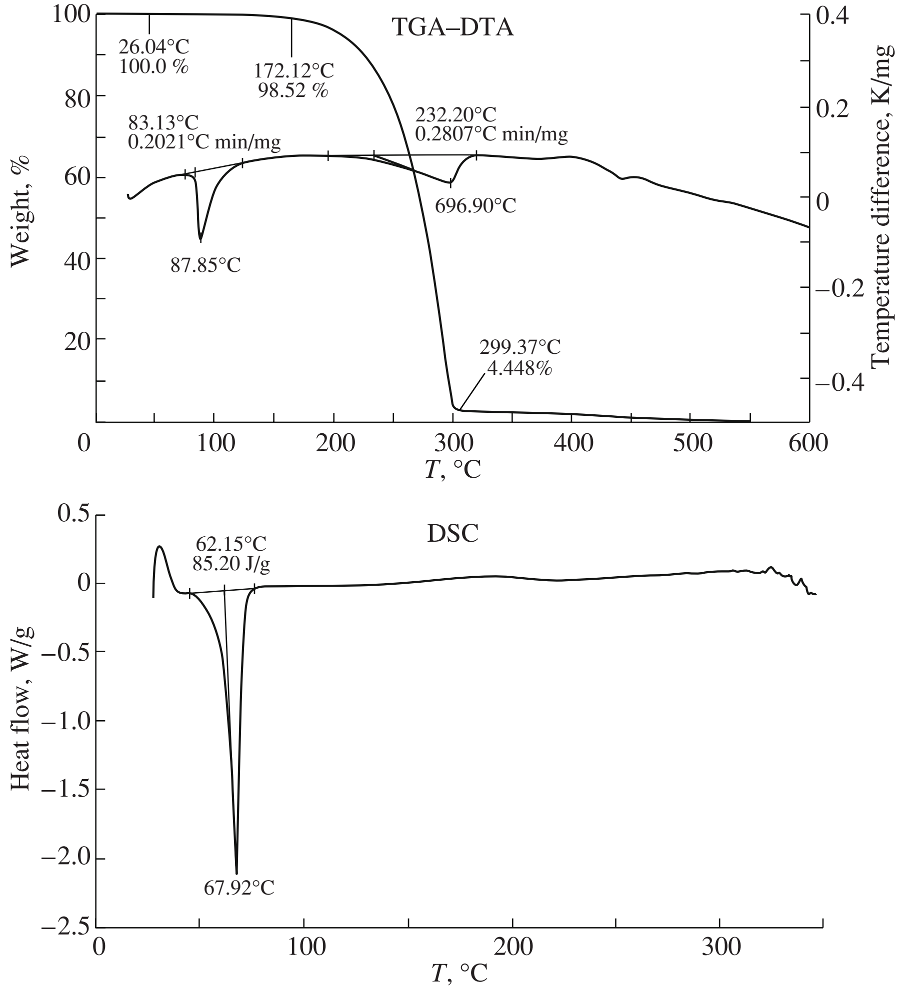
[1] The text was submitted by the authors in English.



TGA/DTA and DSC graph for NDP-1.

The experimental melting points are also compared with those observed by the DSC and DTA methods. It was found that, for some Schiff bases, the experimental values were in close agreement with the results of DSC and DTA measurements.

The following Freeman–Carroll equation [15] was used to determine the kinetic parameters:

$$\ln(dC/dt)/\ln(1 - C) = n - E/R[(1/T)/(\Delta\ln(1 - C)], \quad (1)$$

where dC/dT is the rate of conversion of the initial material, C is the degree of conversion, n is the order of degradation reaction, E is the activation energy, and T is the absolute temperature. A plot of the left-hand side of (1) against $\Delta(1/T)/[\Delta\ln(1 - C)]$ gives a straight line with a slope of $-E/R$, and the intercept gives n.

The frequency factor (A) and entropy change (ΔS) are determined by the equations

$$\ln E - \ln(RT_s^2) = \ln A - \ln\beta - E/RT_s^2, \quad (2)$$

where T_s is the temperature of maximum decomposition and β is the rate of heating;

$$A = (k_B T/h)e^{\Delta S/R}, \quad (3)$$

where k_B is the Boltzmann constant and h is the Planck constant. Other symbols have their usual meanings.

The kinetic parameters, such as the order of degradation (n), activation energy (E), frequency factor (A), and entropy change (ΔS), are reported in Table 2 along with the correlation coefficients (γ). Table 2 shows that, for all the Schiff bases, the order of the reaction (n) is larger than one and is maximum for NDP-2. The activation energy decreases in the series NDP-3 > NDP-7 > NDP-9 > NDP-10 > NDP-2 > NDP-5 > NDP-8 (first step) > NDP-6 > NDP-4 > NDP-1. The frequency factor A is also maximum for NDP-3 and NDP-7 and minimum for NDP-1. On the whole, A varies over a wide range. It decreases in the same order as activation energy. Entropy changes (ΔS) are positive for all the Schiff bases, which indicates that the transition state is a less ordered state. The entropy of Schiff bases decreases in the series NDP-7 > NDP-3 > NDP-9 > NDP-10 > NDP-2 > NDP-5 > NDP-8 (first step) > NDP-6 > NDP-4 > NDP-1.

Table 1. Thermal data for the Schiff bases

Comp. code	Amt., mg	IDT, °C	Decomp. range, °C	% wt loss	Residual Wt. loss, mg	Temp. of max. degradation	Transition	DSC temp., °C	DTA temp., °C	Exp. I.M.P, °C
NDP-1	11.84	139.81	139.81–279.06	13.29	1.5736	279.06	Endo Endo	67.92	68.19 270.97	85
NDP-2	13.04	172.12	172.12–299.37	4.45	0.5799	299.37	Endo Endo	85.94	87.85 296.90	89
NDP-3	10.77	186.41	186.41–298.07	0.83	0.0890	298.07	Endo Endo	148.37	148.93 296.77	144
NDP-4	10.38	207.40	207.40–321.82	0.90	0.0931	321.82	Endo Endo	82.10	85.20 320.11	80
NDP-5	13.02	192.90	192.90–342.22	12.58	1.6374	342.22	Endo Endo	138.88	141.20 334.65	130
NDP-6	10.48	212.38	212.38–295.48	64.94	6.8088	295.48	Endo	214.77	217.70	204
NDP-7	10.36	163.04	163.04–274.70	0.83	0.0860	274.70	Endo Endo	126.69	127.50 273.81	122
NDP-8	10.13	220.17	220.17–333.13	76.76	7.7776	333.13	Endo	179.73	215.08	193
NDP-9	12.04	173.42	173.42–274.70	8.94	1.0757	274.70	Endo Endo	89.85	98.71 269.26	85
NDP-10	13.18	179.91	179.91–311.06	22.32	2.9421	311.06	Exo Endo	78.10	83.48 82.21	104

Table 2. Kinetic parameters for Schiff bases

Compound	n	E, kJ	A, s^{-1}	ΔS	γ
NDP-1	2.44	8.85	0.11	231.92	0.95
NDP-2	5.57	266.26	9.07×10^{23}	708.97	0.98
NDP-3	3.64	494.78	1.52×10^{45}	1115.26	1.00
NDP-4	3.41	14.23	0.40	243.15	0.97
NDP-5	3.25	233.30	2.23×10^{19}	621.32	0.98
NDP-6	3.11	36.09	131.05	290.82	0.99
NDP-7	1.56	486.83	2.41×10^{46}	1137.90	1.00
NDP-8	Step-I 3.72 Step-II 2.31	105.24 33.47	1.9×10^{8} 5.06	409.29 266.48	0.99 0.98
NDP-9	1.25	423.32	1.85×10^{40}	1020.82	1.00
NDP-10	3.16	288.66	3.1×10^{25}	738.51	0.99

Thus, the thermal properties suggest that thermal stability depends on the type of substituents present. The presence of benzaldehyde as a side chain decreases stability, whereas the presence of 4-hydroxybenzaldehyde increases it.

ACKNOWLEDGMENTS

The authors are thankful to Head of Chemistry Department for providing the necessary facilities.

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