Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 783–787

SUBLIMATION/VOLATILISATION KINETICS OF 8-HYDROXYQUINOLINES AND THEIR NITRO-DERIVATIVES

M. S. Crespi[*], *H. E. Zorel Jr., C. A. Ribeiro, A. G. C. Costalonga and C. Torres*

Instituto de Química – Unesp, C.P. 355, CEP 14801-970, Araraquara – SP – Brazil

Abstract

5-Nitro-8-hydroxyquinoline (B) and 5,7-dinitro-8-hydroxyquinoline (C) were obtained from nitration of 8-hydroxyquinoline (A) and purified in acetone medium and under heating in which the formation of (B) or (C) depends on the amount of HNO_3 added. TG curves present mass loss in only one step before and after the melting point (T_m=76°C (A) and 180°C (B)) in different proportions as a function of the heating rate, characterising the sublimation and the volatilisation processes, respectively. The thermal stability of the compounds follow the order: A (77°C)<B (121°C)<C (222°C). Kinetic parameters through TG curves, dynamic process, using heating rates of 1, 2.5, 5, 10 and 20°C min^{-1}, enabled to obtain the following increasing order to the activation energy values of the compounds: 80.4 (A), 102.0 (B) and 153.9 kJ mol^{-1} (C). Other kinetic parameters as pre-exponential and half-lifetime were also estimated.

Keywords: 8-hydroxyquinoline, kinetic parameters, sublimation, thermogravimetry, volatilisation

Introduction

8-Hydroxyquinoline and their derivatives are strong complexing agents to metallic ions and they have been widely used in analytical chemistry [1]. Besides, they act as bactericides and fungicides just due to their ability in forming chelate of inactive metallic ions even in small quantities [2]. In spite of their importance in analytical and applied chemistry, what is known about the thermal behaviour of these ligands is either incomplete or paradoxical information.

Silva *et al.* [3] determined the standard enthalpies of sublimation of 8-hydroxyquinoline and 5-nitro-8-hydroxyquinoline by the Knudsen technique and by using the vacuum sublimation microcalorimetric method [4].

Structures were proposed having in mind a correlation between the obtained results through mass spectra and thermal analysis of 5,7-dinitro-8-hydroxyquinoline chelant and their complexes with uranium. Activation energies were calculated for each step of the thermal degradation of the ligands and chelates [5].

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[*] Author for correspondence: E-mail: crespims@helio.iq.unesp.br

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Zorel *et al.* [6] synthesised and characterised the ligands 8-hydroxyquinoline, 5-nitro-8-hydroxyquinoline and 5,7-dinitro-8-hydroxyquinoline. Studies of the thermal behaviour of these compounds indicate the occurrence of consecutive processes of sublimation, fusion and volatilisation and also that the amount of sublimated material depends on the heating rate.

Experimental

The nitro-derivatives of oxine were obtained by nitration and purified in acetone medium and under heating and, depending on the quantity of HNO_3 added, the entrance of one or two nitro group takes place.

The compounds present the composition that follows C_9H_7NO (M=145.08; T_m=76°C), $C_9H_6N_2O_3$ (M=190.07; T_m=180°C) and $C_9H_5N_3O_5$ (M=235.07) [6].

TG curves of the compounds were obtained with DST 2960 equipment, from TA Instruments, under dynamic atmosphere of N_2 (100 mL min^{-1}), heating rate of 1, 2.5, 5, 10 and 20°C min^{-1}, α-Al_2O_3 crucible and sample mass around 3.5 mg. Data were evaluated by using software of TA Instruments based on kinetic methods proposed by Ozawa [7] and Flynn and Wall [8].

Results and discussion

The contents of sublimated material observed in TG curves based on the fusion of the compounds obtained under different heating rates are shown in Table 1 [6].

Table 1 Sublimated material (%) content observed through TG curves, based on the fusion of the compounds

Compounds	Heating rate/°C min^{-1}				
	1	2.5	5	10	20
8-hydroxyquinoline	2.20	1.21	0.51	0.23	0.14
5-nitro-8-hydroxyquinoline	54.73	19.76	11.27	4.95	2.31
5,7-dinitro-8-hydroxyquinoline	28.52	14.65	6.40	3.21	1.49

Through these results the same behaviour was verified for all the ligands studied. The major quantity of mass loss sublimation is found to the slower heating rate and so the volatilisation process increases in an opposite way. The amount of volatilised compound couldn’t be calculated due to the thermal decomposition which occurred along with the end of this process [6].

The kinetic parameters were determined after the appropriate choice of the conversion degree to the event.

The activation energy, E_a, was determined by relating the heating rate to the temperature, according to the expression:

$$E_a = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right]$$

where: E_a – activation energy (J mol^{-1}); R – gas constant (8.314 J mol^{-1} K^{-1}); T – temperature at constant conversion (K); β – heating rate (°C min^{-1}); b – constant (0.457).

The value of the derivative term $d\log\beta/d(1/T)$ is the slope of the line. The value of the constant b varies depending upon the value of E_a/RT. The value of E_a is first estimated and a corresponding value for b is chosen until the value of calculated E_a no longer changes with successive iterations.

To calculate the estimated time to failure (t_f), the value of the temperature (T_c) at a constant conversion point is first selected for a slow heating rate (β). This value, along with the activation energy (E_a), is used to calculate the quantity E_a/RT and $\log P(E_a/RT)$ from the numeric integration table [9]. The numeric value of $P(E_a/RT)$ can be calculated by taking the antilogarithm and the selection of a value of failure temperature (T_f) allows the calculation of t_f from the equation bellow:

$$\ln t_f = \frac{E_a}{RT_f} + \ln\left[\frac{E_a}{\beta R}P\left(\frac{E_a}{RT_c}\right)\right]$$

where: t_f – estimated time to failure (min); T_f – failure temperature (K); $P(E_a/RT)$ – value from a numerical integration; T_c – temperature for 5% mass loss at β (K).

Rearrangement of the equation above yields a form which may be used to calculate the maximum use temperature (T_f) for a given lifetime (t_f), by relating the kinetic parameters.

Figure 1 shows the behaviour of 5,7-dinitro-8-hydroxyquinoline as the representative of the ligands. The activation energy, the pre-exponential factor and the half-lifetime were calculated to different conversion degrees, where it was verified compatible values from 2.5 up to 35% of conversion to the ligands.

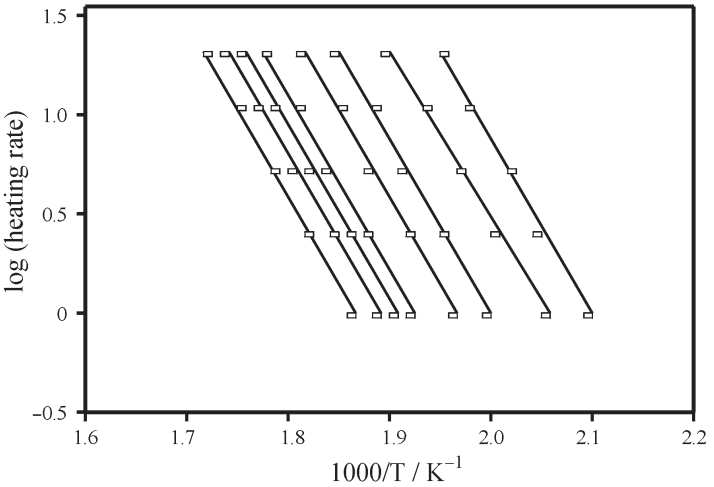

Fig. 1 log heating rate *vs.* temperature of constant conversion to 5,7-dinitro-8-hydroxyquinoline

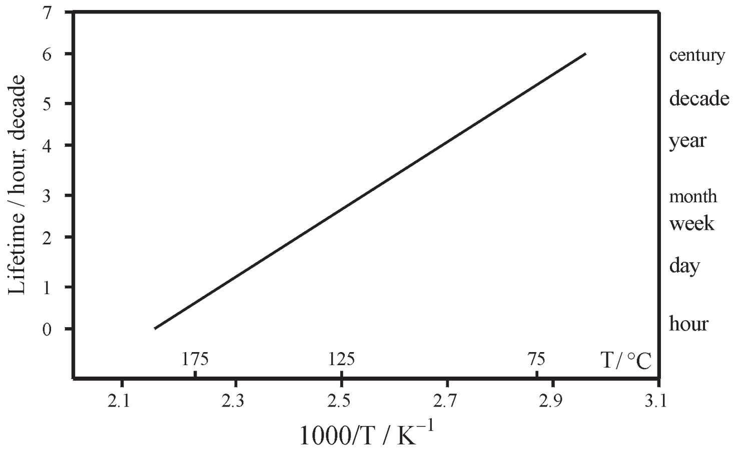

Fig. 2 Estimated lifetime-temperature dependent to 5,7-dinitro-8-hydroxyquinoline

Figure 2 presents the relationship between logt_f is related with the reciprocal of the failure temperature (T_f), where the drastic increase in the estimated lifetime with a small decrease in temperature is verified as indicated to 5,7-dinitro-8-hydroxyquinoline.

Table 2 presents the average values of the kinetic parameters.

Table 2 Kinetic parameters of the compounds

Compounds	E_a/ kJ mol^{-1}	A/min^{-1}	T/°C	Half-time/ min	Rate constant/ $\frac{10^{-2}}{\text{min}^{-1}}$
8-hydroyquinoline	80.4	9.23	103.3	64.2	1.07
5-nitro-8-hydroxyquinoline	102.0	10.32	161.6	67.4	1.03
5,7-dinitro-8-hydroxyquinoline	153.9	13.36	252.1	61.3	1.13

Through these results it was verified that the thermal stability and the activation energy are related to the presence of nitro groups in the ring of 8-hydroxyquinoline where the values increase according to the number of nitro groups present. This is also verified to both the pre-exponential and temperature corresponding to the half-lifetime of these ligands.

Conclusions

Kinetic parameters as half-lifetime are determined quickly by using results from thermogravimetry, as well as by comparing them to other techniques.

The first reaction order can be seen to the three ligands although variable processes of sublimation and volatilisation, which can be higher or lower, are involved depending on the heating rate. The values of E_a (kJ mol^{-1}) and A (min^{-1}) increase the same way when there is an increase in the number of the nitro groups. This fact is important because the presence of the nitro group increases the thermal stability of the ligand.

The values of half-lifetime and rate constant indicate that the reactions follow the multiple heating rate kinetic method used [10] and that the sublimation is an independent process of the nucleation [11].

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The authors acknowledge the financial support received from FAPESP (97/05613-6).

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