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Thermal decomposition kinetics of naphthoquinoneoxime and its complexes with iron(III), silver(I) and lead(II)

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Abstract

Thermogravimetric (TG), derivative thermogravimetric (DTG), and differential scanning calorimetry (DSC) studies of naphthoquinoneoxime metal complexes in static air and nitrogen flow have been performed. The kinetics of the thermal decomposition processes have been investigated. It has been found that the random nucleation mechanism operates consistently with the Mampel equation. A solid state reaction is proposed for the decomposition of complexes, since they decompose without melting. The procedure of thermal decomposition depends on the nature of the metal in the complexes.

Keywords: Complexes; Decomposition kinetics; α-Nitroso-β-naphthol;TG–DSC–DTG

1. Introduction

α-Nitroso-β-naphthol is widely used in analytical chemistry as a reagent for the determination of many metal ions [1]. It chelates to these ions through its quinoneoxime form [2–4]. There are only a few papers published on the thermal decomposition of oxime metal complexes [5,6], and a search of the available literature revealed that no attention has been paid to the thermal decomposition of naphthoquinoneoxime metal complexes. Therefore, it was thought worthwhile to analyse the thermal decomposition of naphthoquinoneoxime and its Fe(III), Co(III), Ni(II), Pd(II), Ag(I) and Pb(II) complexes. The aim of this study is to show the influence of the surrounding atmosphere and of the nature of the metal on the thermal decomposition.

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2. Experimental

Analytical grade chemicals were used. The complexes were prepared according to a recommended procedure [2,4]. The identities of the compounds were confirmed through satisfactory comparisons of their physical and spectroscopic properties with reported data (in static air). The thermal studies were carried out on a Mettler TA 3000 thermal analyser, the heating rate being adjusted to 10°C min^{-1}.

3. Results and discussion

The TG, DTG and DSC results are summarised in Table 1. The ligand α-nitroso-β-naphthol and its complexes were subjected to TG analysis from 50 to 700°C in static air and in flowing nitrogen.

The thermal curve of naphthoquinoneoxime (nqo), α-nitroso-β-naphthol, in static air indicates a three-stage thermal decomposition (Fig. 1a). The mass loss associated with the first step corresponds to the loss of NO (calulated, 17.3%; found, 16.2%). For this weight loss, an exothermic DSC peak is recorded at 158°C (Fig. 1b). The DSC curve also exhibits an endothermic peak at 112°C due to melting of the compound. The second and third steps are indicated on the DSC trace as two small exothermic peaks. In nitrogen atmosphere, three steps are also observed, but the second and third strongly overlap. The endothermic peak at 113°C is clearly connected with melting of the compound. The DSC curve shows an exotherm for the first step and a broad exothermic peak for the second and third steps.

The pyrolysis curve (Fig. 2) of $\mathrm{Fe(nqo)_3}$ reveals that in static air the complex is stable up to 185°C. Then, the compound decomposes in three steps corresponding to three exothermic peaks in the DSC trace; the weight loss in the first step is 44.4%. A similar behaviour is recorded in nitrogen atmosphere. The final residue is $\mathrm{Fe_2O_3}$, as indicated from the TG thermogram and IR spectra.

The TG thermogram of the silver complex, Ag(nqo), in static air exhibits two decomposition steps representing two exothermic reactions. The first mass loss (56.9%) leads to the formation of $\mathrm{Ag_2O}$, which decomposes in the second step. The thermolysis curve in nitrogen also shows two decomposition steps accompanied by two exothermic peaks.

In static air, the lead complex, $\mathrm{Pb(nqo)_2}$, yields a TG thermogram consisting of a major step at 211°C (57.8%). $\mathrm{PbO_2}$ is formed at the end of this step, which further decomposes in the second step at 430°C. Two exothermic peaks are shown in the DSC trace for the two steps. A similar pattern is also recorded in nitrogen flow.

The study was extended to include other complexes of naphthoquinoneoxime, which either have similar behaviour to the previous complexes or have strongly overlapping decomposition steps, i.e. those of Co(III), Ni(II), Cu(II) and Pd(II). In the following, a short report about each is made. Table 1 contains the TG temperature range, $\mathrm{DTG_{max}}$ and DSC temperature maximum.

In both static air and nitrogen flow, the cobalt complex, $\mathrm{Co(nqo)_3}$, yields two steps (TG curve) corresponding to two exotherms in the DSC trace.

Table 1
Thermal decomposition data of naphthoquinoneoxime and its complexes of Fe(III), Ag(I) and Pb(II)

Compound	TG temp.range/°C	DTG$_{max}$/°C	DSC temp.max/°C
	Static air		
α-Nitroso-β-naphthol (nqo)	82–137	133	158(exo)
	280–400	375	220(exo)
	500–580	550	452(exo)
Fe(nqo)$_3$	185–227	220	235(exo)
	230–348	338	–
	348–430	361	432(exo)
Co(nqo)$_3$	235–329	327	320(exo)
	329–372	350	360(exo)
Ni(nqo)$_2$	100–120	110	50(exo)broad
	120–150	130	Unresolved peak
	237–315	305	330(exo)
Cu(nqo)$_2$	218–237	234	239(exo)
	350–450	380	390(exo)
Pd(nqo)$_2$	329–352	335	330(exo)
	352–550	370	360(exo)
	425–550	500	520(exo)
Ag(nqo)	100–165	150	157(exo)
	320–460	390	414(exo)
Pb(nqo)$_2$	205–213	211	241(exo)
	300–480	430	510(exo)
	Nitrogen flow		
α-Nitroso-β-naphthol (nqo)	140–164	150	154(exo)
	250–400	375	220(exo)
	500–350	300	
	350–500	–	350(exo) (broad)
Fe(nqo)$_3$	211–256	242	245(exo)
	300–350	325	270(exo)
Co(nqo)$_3$	322–349	332	338(exo)
	349–420	380	–
Ni(nqo)$_2$	144–151	145	146(endo)
	333–347	342	345(exo)
	449–457	451	440(exo)
Cu(nqo)$_2$	238–259	249	251(exo)
	380–450	410	360(exo)
Pd(nqo)$_2$	300–370	350	341(exo)
	Unresolved	–	–
	Tg steps	–	–
Ag(nqo)	126–170	150	153(exo)
	310–450	375	380(exo)
Pb(nqo)$_2$	174–271	220	236(exo)
	500–600	550	500(exo)

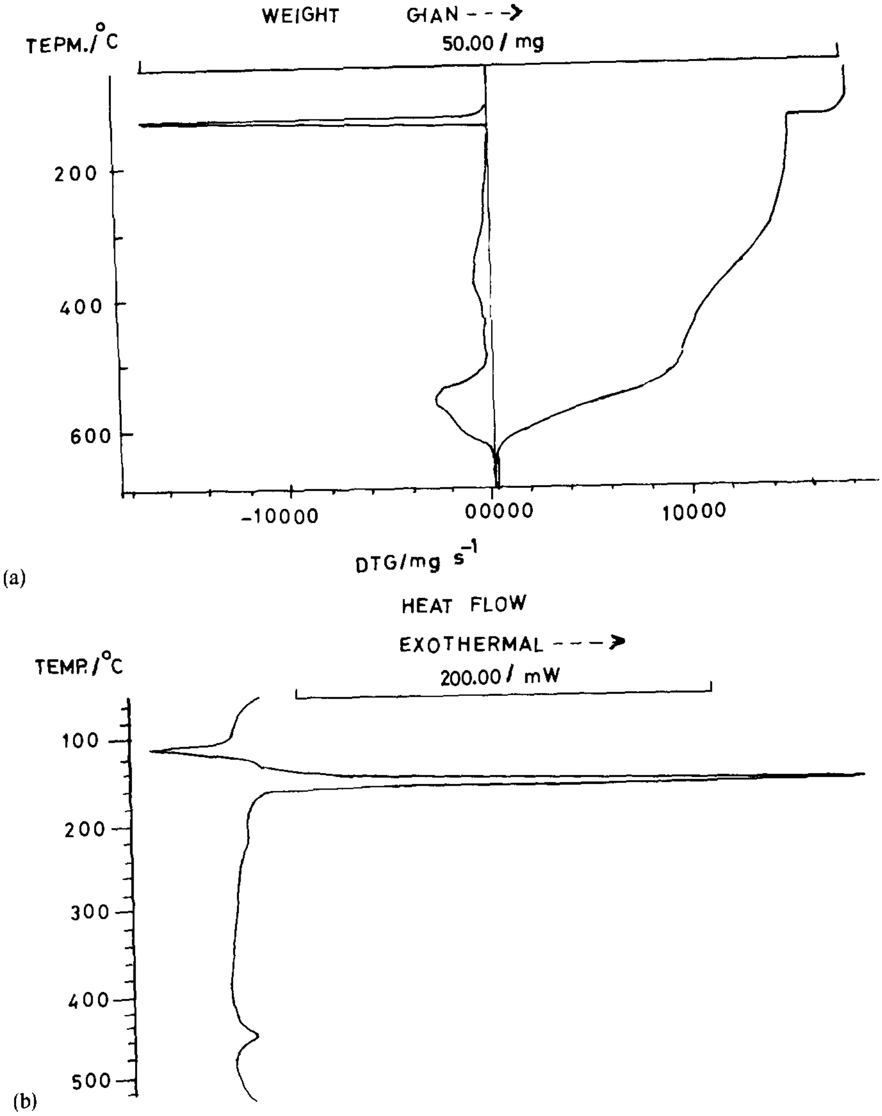

Fig. 1. (a) TG and DTG thermograms of α-nitroso-β-naphthal, (b) DSC trace of α-nitroso-β-naphthol.

The pyrolysis curve of Ni(nqo)$_2$ consists of three decomposition steps in both atmospheres (the second and third steps strongly overlap in nitrogen flow). In static air, the DSC trace reveals an endotherm for the first step and two exotherms for the second and third ones. In nitrogen flow the trace exhibits an endotherm and two exotherms for the first, second and third steps, respectively.

The TG curve for Cu(nqo)$_2$ in static air and nitrogen flow displays the same profile, i.e. the complex decomposes in two steps corresponding to two exotherms in the DSC curve.

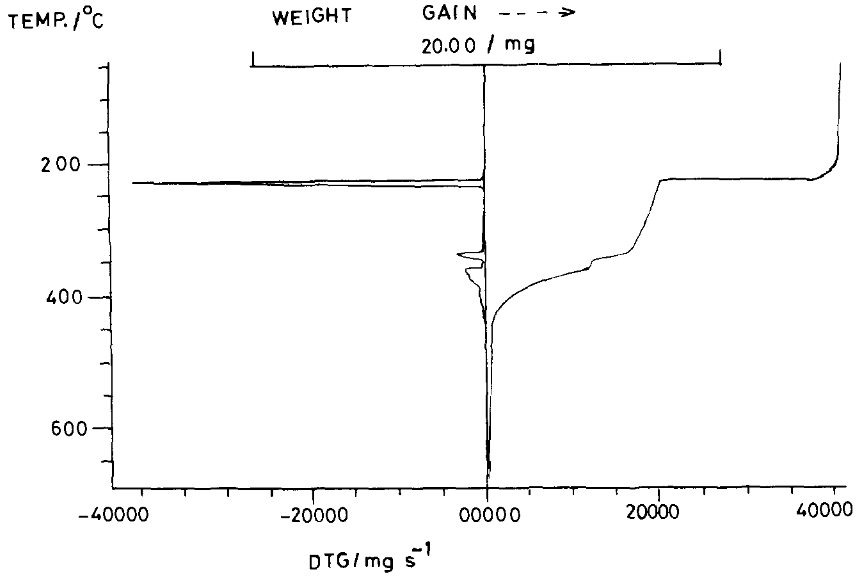

Fig. 2. TG and DTG thermogram of Fe(nqo)$_3$.

The decomposition of Pd(nqo)$_2$ in static air proceeds in three steps, but the steps overlap to a great extent; these are associated with three exothermic peaks in the DSC curve. In nitrogen atmosphere, the initial weight loss (exothermic reation) is followed by a progressive mass loss with poorly resolved peaks, which correspond to unresolved peaks in the DSC curve.

4. Evaluation of kinetic parameters

The ligand and complexes of Fe(III), Ag(I) and Pb(II) exhibit a well-defined and non-overlapping first-stage pattern; this stage is chosen for detailed study.

The present work applies the Coats–Redfern [7] and Horowitz–Metzger [8] equations for the evaluation of the kinetic parameters. The methods of calculation based on the two equations are summarized below.

(i) The Coats–Redfern equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = M/T + B \qquad \text{for } n \mp 1 \tag{1}$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = M/T + B \qquad \text{for } n = 1 \tag{2}$$

where $M = -E/R$ and $B = \ln ZR/\Phi E$; Z, R, Φ and E are the pre-exponential factor, gas constant, heating rate and activation energy, respectively. Eq. (2) represents a first-order reaction. The correlation coefficient r is computed using the least-squares method for the two equations with $n = 0, 0.33, 0.66, 1$ and 2, and a maximum value for the equation with $n = 1$ is obtained. The slope M and intercept B of Eq. (2) are obtained from the plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$. Values of E and Z are calculated from the slope and intercept, respectively.

(ii) The Horowitz–Metzger equation

For first-order reactions, the Horowitz–Metzger equation can be written as

$$\ln[-\ln(1-\alpha)] = \frac{E\theta}{R\,T_s^2} \tag{3}$$

where $\theta = T - T_s$; T_s is the temperature at the DTG peak. The plot of $\ln[-\ln(1-\alpha)]$ vs. θ is linear; from its slope the activation energy is calculated. The value of Z is calculated from the equation

$$\frac{E}{R\,T_s^2} = \frac{Z}{\Phi} e^{-E/R\,T_s} \tag{4}$$

In order to deduce the proper kinetic rate equation, which describes the decomposition reaction, the following equation is used

$$\log\frac{g(\alpha)}{T^2} = \log\frac{ZR}{\Phi E}\left(1 - \frac{2R\,T}{E}\right) - \frac{E}{2.303\,R}\frac{1}{T} \tag{5}$$

The $g(\alpha)$ assumes different forms depending on the model put forward to describe the rate process. Eq. (5) is based on the proposed reation mechanisms given by Satava [9] together with the Coats–Redfern equation. For the correct kinetic rate equation, the plot of $\log(g(\alpha)/T^2)$ against $1/T$should be a straight line, with a slope of $-E/2.303R\,T$; the frequency factor Z can be obtained from the intercept. The values of E, Z and r (Table 2) were computed using the least - squares method for various rate processes.

The F_1 model is found to give the maximum value of r in all cases. This indicates that the thermal decomposition of these complexes follows the Mampel equation [10], i.e. $-\ln(1-\alpha)$ for $g(\alpha)$, and that the rate -controlling process is random nucleation with the formation of a single nucleus on every particle. It is to be noted that no evidence for melting was found in the DSC curves of the complexes. Therefore, this can be regarded as a solid state reaction.

The kinetic parameters n, E, and Z for the first decomposition step of the ligand and its complexes of Fe(III), Ag(I) and Pb(II) have been determined (Table 2) using the Coats–Redfern and Horowitz–Metzger equations. The values obtained from the two methods are quite comparable.

The order of the reaction in all cases was found to be $n = 1$,with high correlation coefficient, r, values. The values of E for the above Coats–Redfern and Horowitz–Metzger equations, as well as for the kinetic rate equations are lower for the silver complex than for the iron and lead complexes, which may be attributed to a higher autocatalytic effect of silver in the decomposition reaction.

Furthermore, there are no appreciable differences in the decomposition pattern and activation energies of the ligand and its complexes in static air and flowing nitrogen,

Table 2
Kinetic parameters for F_1 model calculated according to the Coats–Redfern and Horowitz–Metzger equations

Compound		Rate equation	Coats–Redfern equation	Horowitz–Metzger equation n
		Static air		
nqo	n		1	1
	E	153.8	149.1	146.3
	Z	2.9×10^{13}	9.2×10^{15}	1.2×10^{17}
	r	0.9952	0.9936	0.9933
$Fe(nqo)_3$	n		1	1
	E	268.7	268.7	260.1
	Z	5.1×10^{24}	5.2×10^{24}	1.0×10^{25}
	r	0.9973	0.9978	0.9972
Ag(nqo)	n		1	1
	E	101.1	101.2	116.6
	Z	10.9×10^{10}	3.1×10^{9}	3.0×10^{12}
	r	0.9854	0.9874	0.9883
$Pb(nqo)_2$	n		1	1
	E	307.2	301.1	295.3
	Z	5.4×10^{28}	6.2×10^{28}	2.5×10^{30}
	r	0.9857	0.9887	0.9897
		Nitrogen flow		
nqo	n		1	1
	E	187.6	188.9	187.8
	Z	7.2×10^{20}	9.0×10^{20}	1.6×10^{21}
	r	0.9788	0.9750	0.9899
$Fe(nqo)_3$	n		1	1
	E	259.2	260.4	269.2
	Z	5.0×10^{24}	5.0×10^{23}	5.0×10^{25}
	r	0.9509	0.9545	0.9572
Ag(nqo)	n		1	1
	E	113.7	117.4	111.2
	Z	2.2×10^{11}	2.8×10^{11}	6.3×10^{10}
	r	0.9623	0.9647	0.9693
$Pb(nqo)_2$	n		1	1
	E	296.8	290.1	282.8
	Z	5.7×10^{28}	5.6×10^{27}	2.5×10^{28}
	r	0.9931	0.9946	0.9953

E in kJ mol^{-1}, A in s^{-1}.

which indicates that the decomposition steps are not significantly influenced by the surrounding gaseous atmosphere employed.

Taking the activation energy as a criterion for the thermal stability of the complexes, the following sequence can be deduced: $Pb(nqo)_2 > Fe(nqo)_3 > Ag(nqo)$. This means that the thermal decomposition of the complexes greatly depends on the nature of the metal involved in the complex.

Finally, the decomposition products of α-nitroso-β- naphthol and the complexes could not be established, except for the evolution of NO from the ligand and the residues at the end of the decomposition for the complexes. Decompositions of the silver and lead complexes yield residual oxides (Ag_2O or PbO_2respectively) although the organic products volatilised were not characterised. The reaction of the iron(III) complex was more complicated.

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