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THERMAL BEHAVIOUR OF ISOPERTHIOCYANIC ACID

M.A. UBEDA, E. MARTINEZ-TAMAYO and D. BELTRAN-PORTER *

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Valencia (Spain)

M.D. CLIMENT

Cátedra de Química General y Analítica, Escuela Técnica Superior de Ingenieros Agrónomos, Universidad Politécnica de Valencia (Spain)

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ABSTRACT

Isoperthiocyanic acid (**I**) decomposes at 184°C in two steps. The first endothermic step corresponds to a breaking of the ring with evolution of one mole of CS_2 per mole of **I**. Kinetic analysis of this process has been performed using different methods and a nucleation mechanism is proposed. The best fit corresponds to the Avrami bidimensional diffusion controlled equation. The calculated activation energy value is 54 kcal mol^{-1}. X-ray and IR studies of **I** and thermal intermediates provided information regarding the possible structure of the reaction products.

INTRODUCTION

Solutions of HSCN acid in H_2O–*p*-dioxane mixtures generate yellow precipitates [1]. These yellow solids have variable compositions and are formed by the reaction of SCN^- species with the photochemically produced ether peroxides [2]. However, HSCN, both in the gas phase or in aqueous concentrated solutions, reacts with water to give, as a final product, isoperthiocyanic acid ($C_2H_2N_2S_3$, 5-ammin-1,2,4-dithiazole-3-tione) [2–5].

The oxidation of isoperthiocyanic acid, via solid reaction or in solution with various agents, generates a yellow solid with physical characteristics and chemical behaviour similar to the oxidation products formed by reaction of the alkaline thiocyanates with oxidizing agents such as concentrated sulphuric acid, H_2O_2 in aqueous solution or with potassium persulphate, by solid state reactions at temperatures above 100°C. Isoperthiocyanic acid has been identified as an intermediate in these oxidation reactions.

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* Author to whom all correspondence should be addressed.

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The aim of this paper is to study the thermal behaviour of isoperthiocyanic acid and to give insight into the role of this compound in the above-described complicated phenomena.

EXPERIMENTAL

Isoperthiocyanic acid was prepared by the procedure described in ref. 6. The acidification with aqueous HCl of a concentrated aqueous solution of KSCN gives a crystalline solid that precipitates as yellow needles. The solid was separated by filtration from the solution, washed with cold water and dried in a desiccator over solid $CaCl_2$.

Analysis: found: $C = 16.80\%$; $H = 1.45\%$; $N = 18.48\%$; $S = 63.27$: calcd: $C = 16.00\%$; $H = 1.33\%$; $N = 18.66\%$; $S = 64.00\%$.

The compound was characterized by IR and UV–visible spectroscopy and contrasted against the literature data [7,8]. The X-ray powder diffraction data was perfectly indexed using the single crystal data from the literature [9–11].

Thermal analysis was performed using a Setaram simultaneous thermobalance. The heating rate used for kinetic non-isothermal analysis was 4.42°C min^{-1} and the study was carried out in flowing air and in a static nitrogen atmosphere.

Infrared spectra were taken as KBr pellets on a Pye-Unicam SP 2000 infrared spectrophotometer.

The X-ray powder patterns were recorded using Cu$K\alpha$ radiation on a Siemens Kristalloflex 810 X-ray diffractometer.

RESULTS AND DISCUSSION

Thermal decomposition studies

The TGA, DTG and DTA curves of isoperthiocyanic acid are given in Fig. 1. From them it can be seen that the thermal decomposition begins at 184°C and occurs in two well-defined steps. The first step corresponds to an endothermic process between 184 and 230°C. The observed weight loss is 46.6% and the temperature at the DTA peak (T_M) is 210°C. The thermal character of the process does not depend on the atmosphere and consequently we associate it with a thermal dissociation of the isoperthiocyanic acid molecule accompanied by the evolution of some volatile species.

The second step, which occurs between 230 and 305°C, presents a weight loss of 19.6% in air as well as in a nitrogen atmosphere. Nevertheless, its thermal character is exothermic in air (corresponding to a combustion reaction) but endothermic in nitrogen.

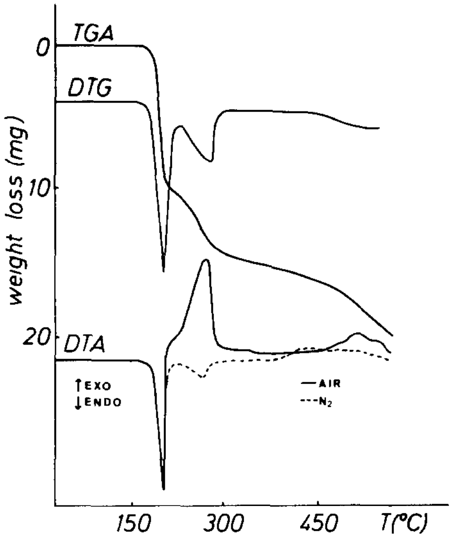


Fig. 1. Thermal decomposition curves of isoperthiocyanic acid. ———, Air; - - - - - -, N_2.

Gaseous products evolved during the first step were qualitatively identified as CS_2 by the Viles reaction [12]. The iodometric titration of the CS_2 as xantogenate [13] gives a result of 0.748 g of CS_2 for 1.523 g of isoperthiocyanic acid ($\simeq$ 1 mmol/1 mmol). This result permits us to conclude that this species is the sole gaseous product evolved from the first process of the thermal decomposition.

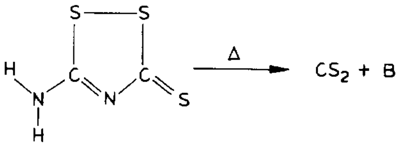
No simple gaseous species were identified as products of the second step.

Kinetic analysis

The kinetic analysis of thermal data for the first step was realized using the Satava integral methods [14]. The best fit of experimental values correspond to a nucleation diffusion controlled mechanism (correlation factor $R = 0.9993$) corresponding to F_1, A_2 and A_3 function models in terms of Sharp nomenclature [15], associated to mono-, bi- or tri-dimensional diffusion controlled mechanisms. The use of the Sharp method [16] frequently requires a choice between the three equally probable models resulting from the above applied method. Consequently an isothermal thermogravimetric experiment was performed at a temperature of 159°C. A plot of $\ln(-\ln(1-\alpha))$ vs. $\ln t^*$ values from this latter experiment results in a straight line with a slope value of 1.45, intermediate between the values corresponding to F_1 and A_2 equations.

However, it is possible to apply the DTG data set to the Abou-Shaaban differential non-isothermal method [17]. In this way it is possible to obtain an independent estimation of activation energy and frequency factor values. The results are listed in Table 1 and from them it seems reasonable to conclude that the most probable equation model corresponds to the Avrami bidimensional diffusion-controlled nucleation equation A_2.

The TGA result and the kinetic conclusions both indicate that all isoperthiocyanic acid molecules decompose in the same way. It means that no reactions occur between the decomposition products and initial species; each molecule of isoperthiocyanic acid breaks down and generates a CS_2 molecule when a high enough energy state is achieved. Thus, the first step of thermal decomposition can be represented as



X-ray and infrared studies

Complementary temperature dependent experiments using X-ray diffraction and IR-spectroscopy techniques have been performed in order to obtain information about the nature of solid product B.

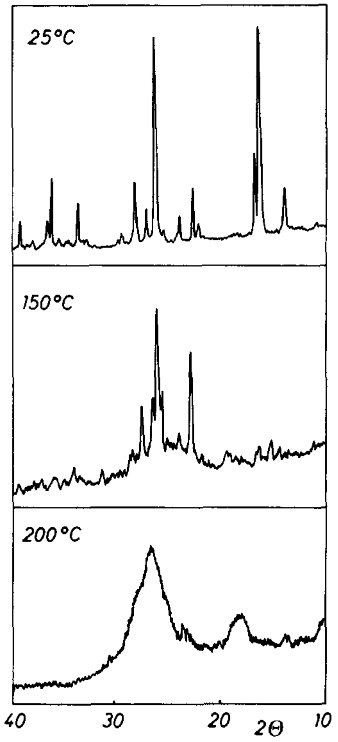
Figure 2 shows the powder X-ray diffraction patterns obtained from samples of **I** at room temperature and after heating at various temperatures. Diffraction peaks corresponding to compound **I** disappear progressively on heating. No new peaks are observed and a broad background signal characteristic of an amorphous phase appears.

Although the amorphous character of B precludes a direct structural approach by X-ray diffraction techniques, the IR spectroscopy can provide information directly related to the nature of chemical bonds broken and formed through the reaction. The IR spectra at various temperatures are shown in Fig. 3. The IR band positions and their assignments are listed in Table 2. The isoperthiocyanic acid IR spectrum was assigned as in the

TABLE 1

Activation energy and frequency factor values obtained by Satava methods ([a]) and Abou-Shaaban

	E_a(kcal mol^{-1})	Z(s^{-1})
F_1 [a]		
$-\ln(1-\alpha)=kt$	144	10^{51}
A_2 [a]		
$\sqrt{-\ln(1-\alpha)}=kt$	54	10^{23}
A_3 [a]		
$\sqrt[3]{-\ln(1-\alpha)}=kt$	34	10^{13}
Abou-Shaaban	60	10^{18}



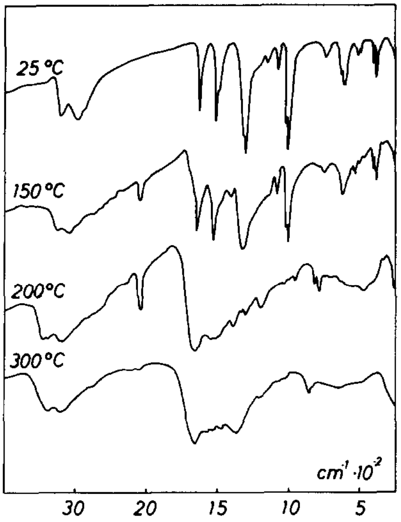


Fig. 2. Powder X-ray diffraction patterns of isoperthiocyanic acid at different temperatures.

Fig. 3. Infrared spectra of isoperthiocyanic acid samples heated at various temperatures.

literature [7]. In agreement with X-ray and TGA results, it can be observed that most of the characteristic bands of I disappear on heating. Thus, the bands associated with ring-skeleton vibrations in the range 450–300 cm^{-1} suffer first a broadening and finally disappear at $T > 200°C$. This observation probably indicates that the decomposition takes place with ring breaking. However, the band associated with the C=S stretching vibration at 1006 cm^{-1} is also absent at $T \simeq 200°C$. Moreover, the absorptions corresponding to C=N and C–N frequencies overlap at higher temperatures between them generating the broad band observed between 1700 and 1100 cm^{-1}; this band also includes the $\delta(NH_2)$ (1630 cm^{-1}) and rocking NH_2 (1082 cm^{-1}) vibrations. These are accompanied by a shift and a splitting of the stretching bands of the NH_2 groups (3100–3400 cm^{-1}).

The solid product B generated by the thermal decomposition conserves the $-NH_2$ groups and also bonds such as C–N and C=N. Hydrogen bonds of $-NH_2$ entities are weaker than in the parent molecule, corresponding to the shift to higher wavenumbers. The splitting of their stretching vibrations may be due to the existence of inequivalent $-NH_2$ groups in compound B.

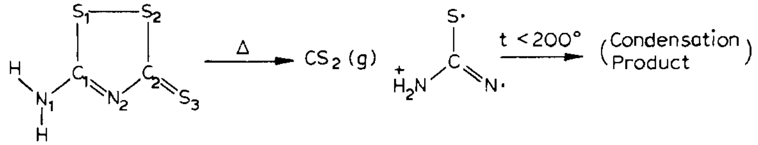
All these results seem to indicate that the decomposition of product I

TABLE 2

Frequencies (cm^{-1}) and band assignments of isoperthiocyanic acid and transformation solid products at different temperatures: b, broad band; d, doublet

Isoperthiocyanic acid	Temperature (°C)			Band assignment
	150	200	305	
3190	3250	3425	3400	$\nu_a NH_2$
	3200	3350		
3030	3100	3200	3200	$\nu_s NH_2$
	3030	3150	3100	
–	2060	2060	–	νC≡N or νS–C≡N
1630	1635	1640 b	1640 b	δNH_2
1510	1510	1520 b	1529 b	νC=N
1310	1305	1305 b	1305 b	νC–N coupled
1082	1082	1180 d	1180 d	NH_2 rocking
1006	1006	–	–	νC=S
–	810	810	810	νS–N
–	760	760	–	νC–S
620	620	630	630	NH_2 wagging
–	–	550 ~ 450	–	νS–S
410	410	–	–	Ring-skeleton vibrations
390	390	–	–	

generates a CS_2 molecule by the breaking of C_2–N_2 and S_1–S_2* bonds in the ring. A homolytic bond breaking should lead to the formation of a biradical species (**II**) besides CS_2, as indicated by the equation



(I) (II) (B)

The highly reactive species **II** must quickly lead to the formation of condensation products. The nature of these products, which probably form a heterogeneous mixture, is difficult to establish. Indeed, insolubility of B in all solvents often used for molecular weight determination precludes the identification of size and degree of condensation of this substance.

Other interesting features of the spectra in Fig. 3 are the presence of new absorption bands at 2060 cm^{-1} and a doublet at about 800 cm^{-1} for samples heated to temperatures lower than 200°C. These bands disappear at higher temperatures and should be associated with bond vibrations of the product

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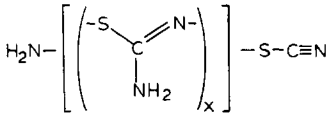
* The S_1–S_2 bond energy calculated by application of the CNDO method to **I** is one of the smallest values of this species [1].

B. The higher frequency band is characteristic of stretching vibrations of –C≡N groups [18] in cyanide and thiocyanate derivatives. The lower frequency doublet may be associated with S–C and S–N stretching vibrations [19].

Obviously the cyanide or thiocyanates must act as terminal groups, stopping condensation of radicals. The high relative intensity of IR bands associated with them in the spectra studied indicates that the mean degree of condensation of radical **II** giving the product B is relatively low. However, the broad band at 450–550 cm^{-1} indicates the possible existence of S–S bonds.

Based on the above considerations a possible structure of product(s) B can be proposed as



where a random linkage of $-SC(NH_2)N-$ entities is possible. Moreover, two kinds of $-NH_2$ group are present, in good accord with the IR results.

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