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Thermogravimetric studies of alkyl *N*-aryldithiocarbamates

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Abstract

Some alkyl *N*-aryldithiocarbamates were prepared and their thermal behaviour was studied using TG, DTG and GC/MS. Thermogravimetric data were used for calculations of the apparent kinetic parameters of the thermal decomposition. Decomposition proceeds as a reaction with order $n = 1$, except that of butyl *N*-phenyldithiocarbamate which follows order $n = 0$. The apparent activation energies of the processes were found to be above 100 kJ mol^{-1} for almost all compounds studied. The thermally induced decomposition of the compounds occurs as a single-stage process, except that of ethyl *N*-tolyldithiocarbamate where three steps could be distinguished. The products of the decompositions were indentified by gas chromatography–mass spectrometry and used for predictions of the mechanisms involved.

Keywords: Alkyl *N*-aryldithiocarbamates; DTG; GC–MS; TGA

1. Introduction

The pyrolysis products of dithiocarbamic esters are used in the gas chromatographic analysis of amines [1]. Dithiocarbamic acid ester derivatives of primary amines decompose in the injector port of the gas chromatograph to isothiocyanates, whereas derivatives of secondary amines do not decompose. Thus, the method can differentiate between primary and secondary amines. The mass spectra of isothiocyanates are structurally significant, allowing the parent amines to be identified [2]. Dithiocarbamic acid ethyl esters also show characteristic mass spectra of positive and negative ions [3]. These facts prompted us to study the process of thermodecomposition of alkyl *N*-aryldithiocarbamates by TG, DTA, DTG and GC/MS.

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2. Experimental

2.1. Materials

Alkyl *N*-aryldithiocarbamates were prepared according to published methods [4]. The physical properties of the compounds are collected in Table 1.

2.2. Methods

Microanalyses were carried out on a Carlo Erba microanalyser. A derivatograph (MOM, Budapest, Hungary) was used for the thermal decomposition studies, in which 50 mg samples (measured on a scale with 0–100 divisions with ±0.25 mg accuracy) were run against a standard of 50 mg α-Al_2O_3. A platinum semi-micro crucible was used for the thermogravimetry. Linear temperature programming of approx. 5°C min^{-1} was used.

The products of thermolysis were separated with a Varian Aerograph series 1400 chromatograph equipped with a packed column (5% OV-1 on Supelcoport, 100–200 mesh). Quantitative GC analysis of analytical pyrolysis products was carried out on a 1 m stainless steel column packed with Tenax GC (RNCS, R_1SH and RNH_2) or 10% PEG 400 on Chromosorb W (CS_2) with FID or FDP detectors.

Thermolysis of dithiocarbamic acid esters was performed with a Chemical Data Systems pyrolyser connected to the injection port of a gas chromatograph equipped with Porapack Q or OV-1 packed columns. Pyrolysis was carried out for a small amount (about 0.1 mg) of ester placed in the crucible of the pyrolyser. The crucible was heated at a rate of 20°C ms^{-1} to 250°C and kept there for 10 s. The helium flow was adjusted to 20 $cm^3\,min^{-1}$. The mass spectra of GC-separated components were recorded for 70 eV ionization energy with a Varian MAT 711 mass spectrometer, coupled with a Biemann-Watson separator gas chromatograph.

3. Results and discussion

Thermal analysis curves of methyl and ethyl aryldithiocarbamates for heating rates of 5°C min^{-1} are shown in Figs. 1 and 2, respectively. The low-temperature peaks at 97°C (methyl) and 87°C (ethyl) in the DTA curves correspond to the melting points of the compounds.

The thermolysis of the compounds occurs as endothermic processes with negative peaks in the DTA curves. Methyl derivatives collapse in a single-stage process although a multi-step process is observed for for ethyl *N*-tolylodithiocarbamic ester. Let us assume that a compound decomposes into gaseous components

$$A \rightarrow B + C \qquad (1)$$

There are many approaches to the calculation of the kinetic parameters. Some of them are based on the peak temperature–program rate relations [5–7], the shape of the heat

Table 1
The physical properties of *N*-aryldithiocarbamic acid esters

Aryl	R	Yield %	%N		M.p./°C	Partial EI (70 eV) mass spectra [*m*/*z*][a]					
			Calc.	Found		$M^{+\cdot}$	$M\text{-}CH_2CH_2^{\rceil+\cdot}$	$ArNCS^{+\cdot}$	$C_6H_5S^{\rceil+}$	$C_6H_5NH_2^{\rceil+\cdot}$	$RSH^{\rceil+\cdot}$
C_6H_5	CH_3	87	7.65	7.41	94–95	183(34)		135(100)	109(14)	93(28)	48(11)
p-$CH_3C_6H_4$	CH_2CH_3	83	6.63	6.71	74–77	211(5)	183(3)	149(100)			62(15)
o-$CH_3C_6H_4$	CH_2CH_3	90	6.63	6.57	73–74	211(1)	183(3)	149(100)			62(19)
C_6H_5	$(CH_2)_3CH_3$	78	6.22	6.17	58–59	225(4)	169(4)	135(100)	109(2)	93(2)	90(21)
C_6H_5	$CH_2C_6H_5$	73	5.40	5.35	84	259(3)		135(100)		93(7)	124(26)

[a] Figures in parentheses refer to relative intensities.

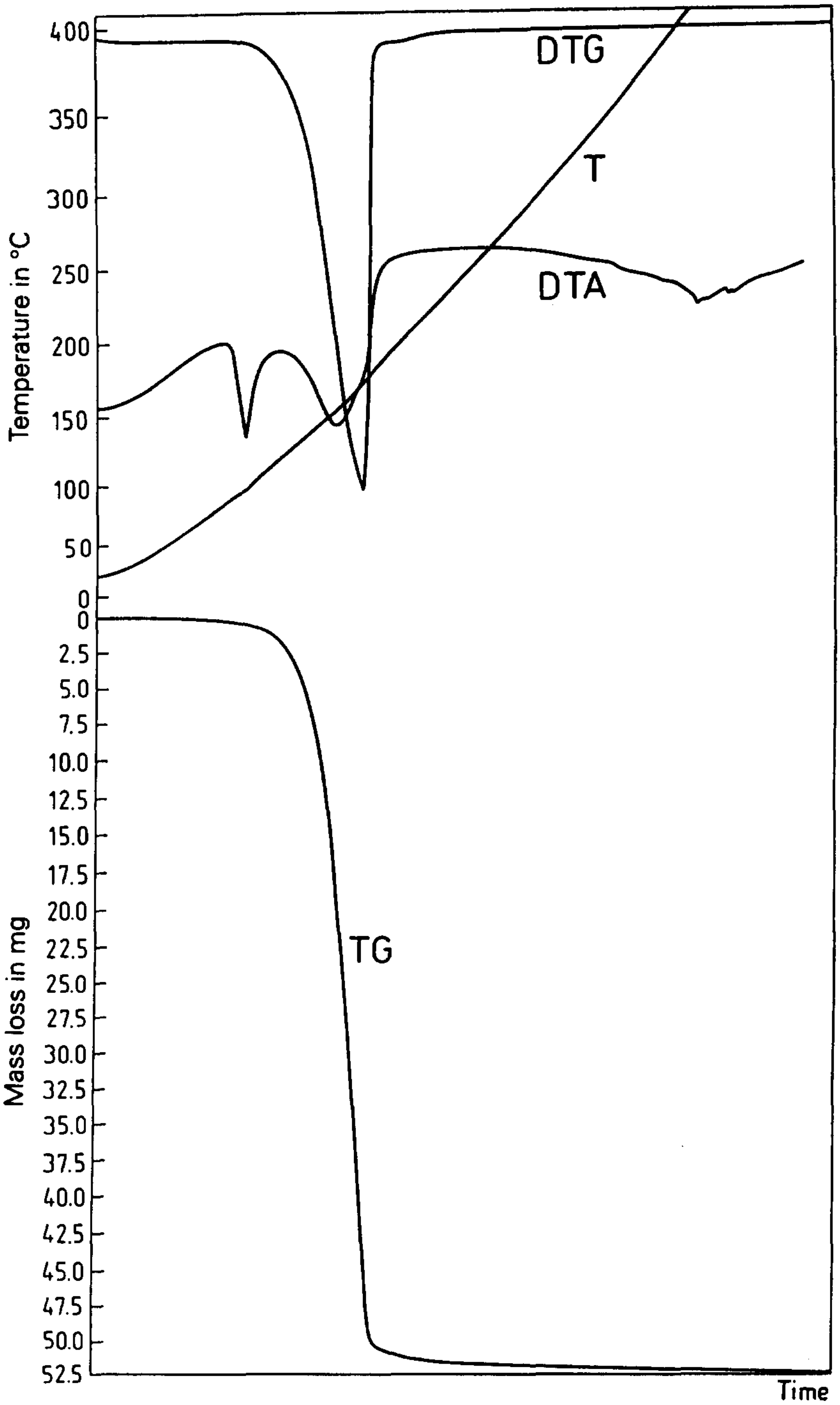


Fig. 1. Thermal curves of methyl phenyldithiocarbamate. Average heating rate $\Phi = 5°C\,min^{-1}$.

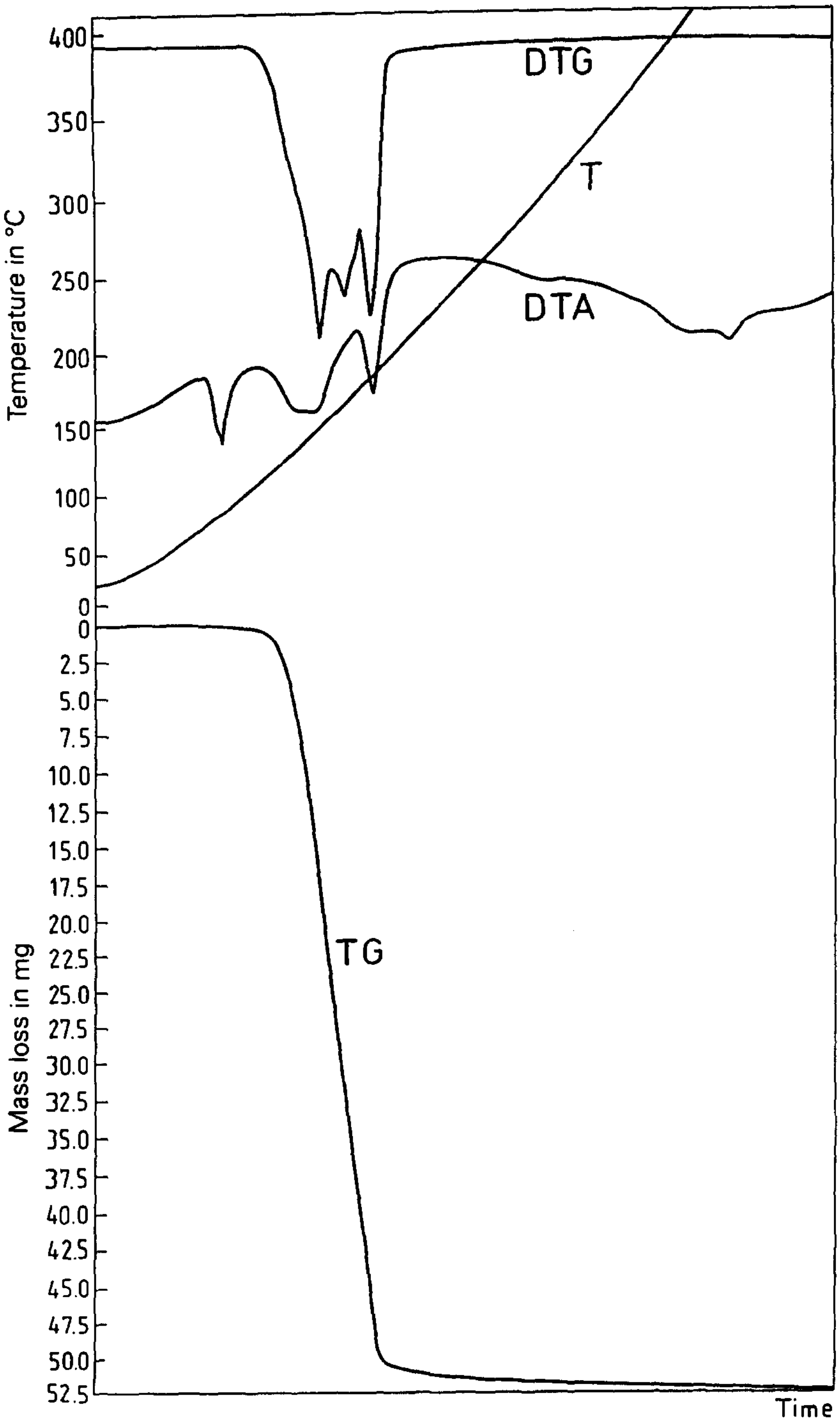


Fig. 2. Thermal curves of ethyl *p*-tolyldithiocarbamate. Average heating rate $\Phi = 5°\mathrm{C\,min^{-1}}$.

flow curve obtained [8] or the derivative of the peak [9]. Here a method which allows us to calculate directly the reaction order was applied.

The kinetics of the process can be described by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

where α is the fractional conversion and

$$k(T) = A\exp(-E/RT) \tag{3}$$

with A the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

Assuming constant heating rates, $\Phi = \mathrm{d}T/\mathrm{d}t$ and separating the variables, one obtains

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\Phi}\int_0^T \mathrm{e}^{-E/RT}\mathrm{d}T \tag{4}$$

Coats and Redfern [10], applying the function

$$f(\alpha) = (1-\alpha)^n \tag{5}$$

derived for $n \neq 1$

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\Phi E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \tag{6}$$

and for $n = 1$

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{AR}{\Phi E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \tag{7}$$

When $E \gg 2RT$, calculation of the activation energy E and the frequency factor A is possible as an appropriately chosen value for n will give a straight-line relation [10] for the experimental points of the TG curve.

The thermogravimetric parameters of the pyrolysis processes of the compounds (calculated according to Eqs. (6) and (7)) are given in Table 2. The decompositions of the compounds follow first-order kinetics except that of ethyl *N*-*p*-tolyldithiocarbamate which has zero order.

Activation energies of thermolysis of the compounds were found to be in the range 90–140 kJ mol^{-1} (Table 3). The energies were computed for α in the range 0.2–0.8; those calculated for distinct stages of the process of ethyl *N*-*p*-tolyldithiocarbamate were 112, 65 and 112 kJ mol^{-1} (Table 4).

The analytical pyrolysis of dithiocarbamic acid esters was performed with a pyrolyser connected to a gas chromatograph. The following pyrolysis products of ethyl *N*-*p*-tolyldithiocarbamate were separated and identified by GC/MS: carbon disulphide, thioethanol, *p*-tolylamine and tolyl isothiocyanate. These identifications were confirmed by coinjection of the standard compounds. Another product of

Table 2
Thermogravimetric properties of alkyl *N*-aryldithiocarbamates

Compound	Temperature of thermolysis/°C	Maximum of DTG/°C	Maximum of DTA/°C
C_6H_5–NH–CS_2–CH_3	60–230	172	97 153
p-CH_3–C_6H_4–NH–CS_2–Et	70–240	148	86
		166	139
		183	183
o-CH_3–C_6H_4–NH–CS_2–Et	50–220	174	78 148
C_6H_5–NH–CS_2–*n*-But	50–220	168	69 167
C_6H_5–NH–CS_2–Bnz	70–270	173	90 172

Table 3
Apparent kinetic parameters of thermal decomposition of alkyl *N*-aryldithiocarbamates

Compound	n	E/kJ mol^{-1}	A/s^{-1}	r
C_6H_5–NH–CS_2–CH_3	0.7	102.8 ± 0.7	$(1.02 \pm 0.05) \times 10^{10}$	−0.9997
p-CH_3–C_6H_4–NH–CS_2–Et	1.9	116.8 ± 3.2	$(9.00 \pm 2.02) \times 10^{11}$	−0.9953
o-$CH_3C_6H_4$–NH–CS_2–Et	0.8	94.0 ± 1.8	$(8.42 \pm 1.12) \times 10^{8}$	−0.9974
C_6H_5–NH–CS_2–*n*-But	0.1	111.7 ± 2.8	$(7.33 \pm 1.45) \times 10^{10}$	−0.9971
C_6H_5–NH–CS_2–Bnz	1.1	156.4 ± 5.6	$(2.99 \pm 0.47) \times 10^{16}$	−0.9976

Table 4
Apparent kinetic parameters of distinguished steps of thermal decomposition of *p*-CH_3–C_6H_4–NH–CS_2–Et

Temperature range	n	E/kJ mol^{-1}	A/s^{-1}	r
125–157°C	4.5	169.2 ± 4.3	$(8.77 \pm 2.01) \times 10^{18}$	−0.9981
157–175°C	1.4	81.4 ± 3.2	$(2.60 \pm 0.58) \times 10^{7}$	−0.9976

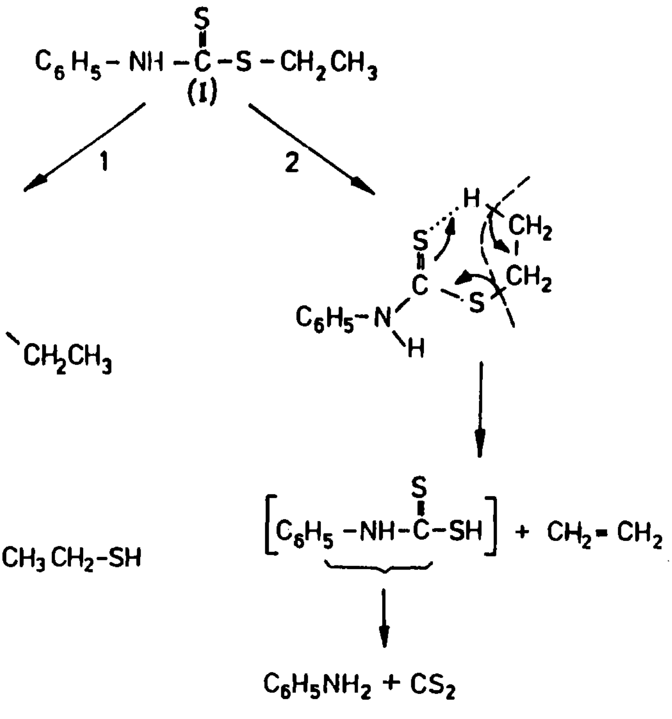
pyrolysis identified only by GC/MS was diethyl disulphide which was generated by dehydrogenation of thioethanol in a Biemann–Watson molecular separator. The compounds identified allowed us to draw up the mechanisms involved (Scheme 1). The transfer of the nitrogen-bonded hydrogen atom to the thiol sulphur atom causes

Table 5
Quantitative GC analysis of pyrolysis products (mol%)

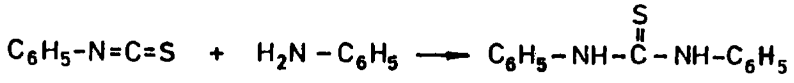
Compound	ArNCS	RSH	$ArNH_2$	CS_2
$C_6H_5NHCS_2CH_3$	69	94	2	2
p-$CH_3C_6H_4NHCS_2CH_2CH_3$	95	96	5	5.8
o-$CH_3C_6H_4NHCS_2CH_2CH_3$	89	71	9	7.5
$C_6H_5NHCS_2(CH_2)_3CH_3$	72	55	12	20
$C_6H_5NHCS_2CH_2C_6H_5$	71	35	4.5	29

simultaneous cleavage of the carbon–sulphur bond. The process leads directly to isothiocyanates according to the mechanism of Ottenbrite [11].

Additional support of the mechanism was obtained from quantitative studies of the analytical pyrolysis of the compounds (Table 5). Two components, ArNCS and RSH, are the main products with a molar ratio, more or less, close to 1:1; $ArNH_2$ and CS_2 are



Scheme 1



$$C_6H_5\text{-}N{=}C{=}S \;+\; H_2N-C_6H_5 \longrightarrow C_6H_5-NH-\overset{\displaystyle S}{\overset{\|}{C}}-NH-C_6H_5$$

Scheme 2

Table 6

Specific rate constants and half-life times of alkyl *N*-aryl dithicoarbamate thermal decompositions

Temp.	C_6H_5–NH–CS_2–CH_3		*p*-CH_3–C_6H_4–NH–CS_2–Et		*o*-CH_3–C_6H_4–NH–CS_2–Et		C_6H_5–NH–CS_2–*n*-But		C_6H_5–NH–CS_2–Bnz	
°C	k/s^{-1}	$\tau_{1/2}$	k/s^{-1}	$\tau_{1/2}$	k/s^{-1}	$\tau_{1/2}$	k/s^{-1}	$\tau_{1/2}$	k/s^{-1}	$\tau_{1/2}$
120	2.2×10^{-4}	51.9 min	1.5×10^{-4}	42.9 min	2.7×10^{-4}	42.7 min	1.0×10^{-4}	111.9 min	4.9×10^{-5}	236.4 min
140	1.0×10^{-3}	11.3 min	2.7×10^{-3}	7.6 min	1.1×10^{-3}	10.6 min	5.4×10^{-4}	21.3 min	4.9×10^{-4}	23.3 min
160	4.1×10^{-3}	2.8 min	7.3×10^{-3}	1.6 min	3.8×10^{-3}	2.9 min	2.4×10^{-3}	4.7 min	4.1×10^{-3}	2.8 min
180	1.4×10^{-2}	0.8 min	3.1×10^{-2}	0.4 min	1.2×10^{-2}	0.9 min	9.6×10^{-3}	1.2 min	2.7×10^{-2}	0.4 min
200	4.5×10^{-2}	15.2 s	1.1×10^{-1}	3.8 s	3.5×10^{-2}	19.8 s	3.3×10^{-2}	20.6 s	1.6×10^{-1}	4.3 s
250	5.5×10^{-1}	1.2 s	1.9×10^{0}	0.3 s	3.4×10^{-1}	2.0 s	5.1×10^{-1}	1.4 s	7.2×10^{0}	0.09 s
300	4.3×10^{0}	0.1 s	2.0×10^{1}	0.03 s	2.3×10^{0}	0.3 s	4.8×10^{0}	0.1 s	1.6×10^{2}	0.004 s

minor products. More amines in the pyrolysis products are accompanied by more carbon disulphide. Both products are generated in a process (Scheme 1), where an unstable intermediate, *N*-aryldithiocarbamic acid, breaks down to amine and carbon disulphide.

The process mentioned above is clearly demonstrated in the TG curve of ethyl *N*-tolyldithiocarbamic ester where three stages could be distinguished. The sample size used in the thermal analysis (50 mg) was not comparable with analytical thermolysis. A preparative-scale experiment was also performed at 250°C, yielding not only the products mentioned above, but also symmetrical arylthiourea, which was isolated and identified by mass spectrometry. This compound was formed by an intermolecular reaction of ester (or isothiocyanate) with amine (Scheme 2). It seems that this side reaction disturbs the TG curve of ethyl *N*-tolyldithiocarbamic ester.

The average values of the pre-exponential factor A were used to calculate the specific rate constants k and half-life times $t_{1/2}$ for the series of temperatures of chromatographic interest (Table 6). It can be concluded that the injection port of the gas chromatograph should be kept above 250°C for proper analysis conditions.

Our results clearly indicate that the thermolysis of alkyl *N*-aryldithiocarbamic esters is a complicated process. Therefore, the compounds can be applied in gas chromatography analysis with some precautions.

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