

Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)

KINETIC STUDY OF THE THERMAL DECOMPOSITION OF SOME AROMATIC *ORTHO*-CHLORINATED AZOMONOETHERS. 1

DECOMPOSITION OF 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene

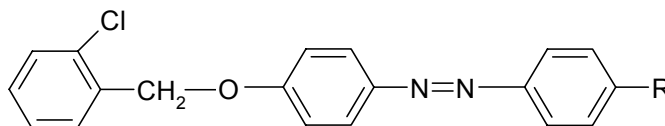
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Received February 23, 2006

New synthesized aromatic azomonoethers, exhibiting dyeing properties and liquid crystalline nature, generate interest as materials for non-linear optical applications. The thermal stability of the *ortho*-chlorinated derivatives, with the general formula:



where R is a nematogenic group CF₃, CN, Cl, or a highly polarizable group NO₂, is proposed to be investigated under non-isothermal conditions. In this investigation, the thermal stability and the decomposition kinetics of 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene were carried out. The activation energy of the first decomposition step was evaluated by means of different multi-heating methods.

INTRODUCTION

The investigated compounds, potential materials for non-linear optical applications and also exhibiting dyeing properties, generate increasing interest and attention. Aromatic azomonoethers can be obtained, in alkaline medium, by the condensation of some 4-(phenylazo)phenols with chloromethylated derivatives of chlorobenzene. The synthesis, also known as the “Williamson ether synthesis”, as well as the spectral characterization were described elsewhere.^{1,2} Also some of their liquid crystalline properties were investigated and reported.^{1,3-5}

The *ortho*-chlorinated isomers determine lower melting temperatures with respect to the *para*-chlorinated ones. On the other hand, for the *ortho*-chlorinated derivatives, the melting point increases following this order of R: CF₃, Cl, CN, NO₂. CF₃ terminal group favors smectic A mesophase formation and the melting temperature is the lowest one: 105^oC.⁶

This note aims to investigate the thermal stability and to evaluate the decomposition kinetic parameters of 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene. Recent studies dealing with the decomposition kinetics of this aromatic azomonoethers were carried out.⁷

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In order to evaluate the activation energy from thermogravimetric data, without knowing the kinetic model of the thermoanalytical curve, isoconversional methods are recommended to be used.⁸⁻¹⁰

EXPERIMENTAL

The thermoanalytical curves (TG,DTA) of the powders obtained by synthesis were recorded on a MOM Budapest Q-1500 D type Paulik-Paulik-Erdey derivatograph, in the temperature range 23-500°C, at the heating rates of 1.5 K min⁻¹, 5.9 K min⁻¹ and 12.7 K min⁻¹, in static air atmosphere. DTG curve was obtained from the numerical derivation of the TG curve. Sample weights ranging from 49 mg to 83 mg were used.

RESULTS AND DISCUSSION

Isoconversional kinetic parameters evaluation methods, known as the “model-free kinetics” methods, are based on the following reaction rate equation:

$$\beta \frac{d\alpha}{dT} = Af(\alpha)e^{-\frac{E}{RT}} \quad (1)$$

for differential methods such as Friedman,¹¹ or

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} e^{-\frac{E}{RT}} dT \equiv \frac{A}{\beta} I(E_\alpha, T_\alpha) \quad (2)$$

for integral methods such as Kissinger-Akahira-Sunose¹² and Flynn-Wall-Ozawa,¹³ where: β is the heating rate, A is the preexponential factor, $f(\alpha)$ is the differential conversion function, $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ is the temperature integral.

This differential and integral “model-free” methods are linear, the activation energy being calculated straight from the slope specific to the method, by considering $\alpha = \text{const}$.

Friedman Method:

$$\ln \beta \frac{d\alpha}{dT} = \ln Af(\alpha) - \frac{E}{RT} \quad (3)$$

KAS Method:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (4)$$

FWO Method:

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (5)$$

Relation (3) can be obtained directly from the reaction rate equation (1).

By substituting in relation (2) $I(E_\alpha, T_\alpha)$ with the Coats-Redfern approximation:¹⁴

$I(E_\alpha, T_\alpha) = \frac{RT_\alpha^2}{E_\alpha} e^{-\frac{E_\alpha}{RT_\alpha}}$, one obtains equation (4) – KAS method, and by substituting with the Doyle

approximation:¹⁵ $I(E_\alpha, T_\alpha) = \frac{E_\alpha}{R} e^{(-5.331 - 1.052 \frac{E_\alpha}{RT_\alpha})}$, one obtains equation (5) – FWO method.

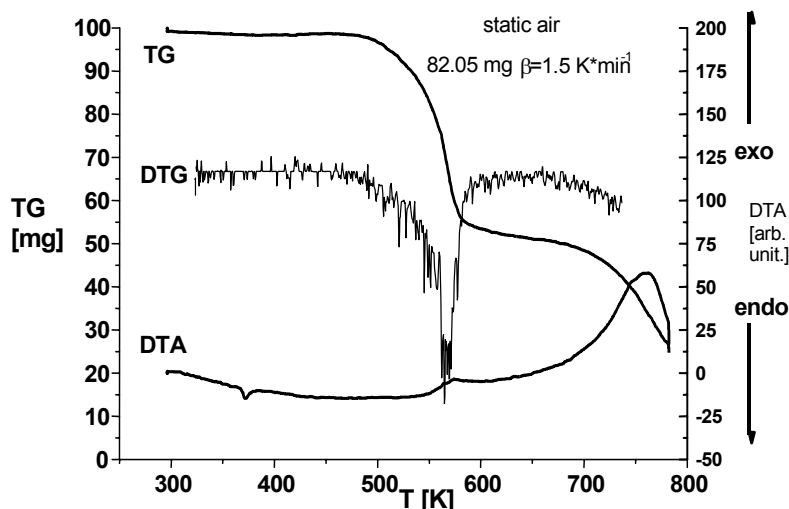
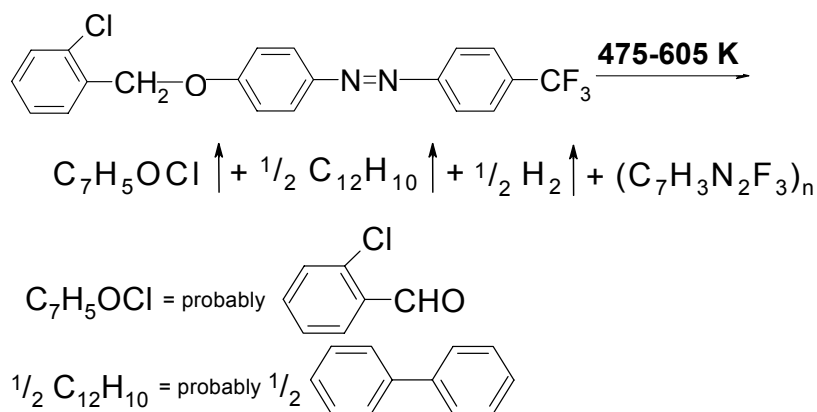


Fig. 1 – The thermal curves of 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene for $\beta = 1.5 \text{ K min}^{-1}$.

Fig. 1 shows the TG, DTG and DTA curves of 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene corresponding to $\beta = 1.5 \text{ K min}^{-1}$. After melting at 105°C (378 K), as can be seen from these curves, in the first step, it undergoes decomposition in the temperature range 475-605 K. The second step indicates the burning of the solid residue.

For the first step, the experimental loss of weight ($\Delta m_{\text{exp}} = 55.50\%$) is in good agreement with the theoretical loss of weight ($\Delta m_{\text{theor}} = 55.77\%$), leading to the most probable mechanism:



The first step corresponds to a simple decomposition process characterized by a weak exothermal effect, which does not affect the linearity of the heating program. The heating rate remains thus constant during the entire kinetic analysis.

The estimation of the conversion degree for each temperature, $\alpha(T)$, depends on the TG value considered for the end of the decomposition process. For our curves, Fig. 2, the end of the decomposition process can not be accurately determined. In order to avoid this error source, we considered instead of $\alpha(T)$ the use of the weight loss (in percents) which is not dependent on the TG value for the end of the process. Accordingly, for our three heating rates, the temperatures corresponding to the same conversion degree are estimated as the temperatures corresponding to the same weight loss (in percents).

However, the equations of KAS and FWO integral isoconversional methods do not use the conversion degree or the form of the conversion function to evaluate the activation energy.

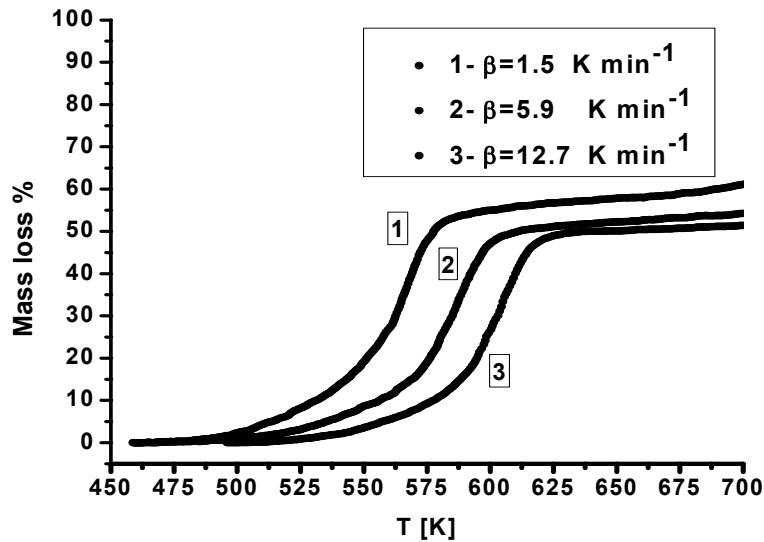


Fig. 2 – Mass loss % vs. temperature, at three constant heating rates.

Table 1

Activation energy evaluation using the KAS and FWO methods

Mass loss %	KAS E/kJ mol ⁻¹	KAS (%) kJ mol ⁻¹	KAS -r	FWO E/kJ mol ⁻¹	FWO (%) kJ mol ⁻¹	FWO -r
5	107.7	16.6	0.9882	110.8	15.7	0.9900
6	108.8	17.7	0.9873	111.9	16.5	0.9893
7	106.2	16.6	0.9879	109.5	15.7	0.9898
8	106.0	14.8	0.9903	109.4	13.9	0.9919
9	108.2	12.8	0.9929	111.5	12.1	0.9941
10	109.2	10.9	0.9950	112.6	10.2	0.9958
11	111.6	8.9	0.9968	114.8	8.3	0.9973
12	113.3	8.7	0.9970	116.5	8.1	0.9975
13	113.7	10.2	0.9960	116.9	9.6	0.9966
14	114.7	7.8	0.9976	117.9	7.3	0.9980
15	118.3	7.5	0.9979	121.4	7.0	0.9983
16	119.2	6.2	0.9986	122.2	5.8	0.9988
17	120.5	6.6	0.9985	123.5	6.1	0.9987
18	123.0	7.0	0.9983	125.9	6.5	0.9986
19	123.6	7.0	0.9983	126.5	6.5	0.9986
20	125.0	7.4	0.9982	127.8	7.0	0.9985
21	128.1	8.2	0.9979	130.8	7.7	0.9982
22	131.1	7.4	0.9984	133.7	6.9	0.9986
23	132.9	8.9	0.9977	135.4	8.4	0.9980
24	137.5	9.4	0.9976	139.8	8.8	0.9980
25	137.1	10.0	0.9973	139.4	9.4	0.9977
26	137.9	11.0	0.9968	140.2	10.3	0.9973
27	140.1	11.2	0.9968	142.3	10.5	0.9972
28	142.6	12.5	0.9961	144.7	11.8	0.9966
29	142.9	11.4	0.9968	145.0	10.8	0.9972
30	141.3	11.6	0.9966	143.5	10.9	0.9971
31	140.8	12.3	0.9962	143.1	11.5	0.9967
32	141.4	11.9	0.9964	143.6	11.2	0.9969

Table 1 (continues)

Table 1 (continued)

33	143.2	11.3	0.9969	145.4	10.6	0.9973
34	143.3	11.1	0.9970	145.4	10.4	0.9974
35	143.9	10.5	0.9973	146.0	9.8	0.9977
36	143.0	10.5	0.9973	145.2	9.9	0.9976
37	142.7	11.3	0.9968	144.9	10.7	0.9973
38	142.1	11.2	0.9969	144.3	10.5	0.9973
39	141.5	10.0	0.9974	143.8	9.4	0.9978
40	142.7	8.8	0.9980	144.9	8.2	0.9983
41	142.1	8.6	0.9981	144.4	8.0	0.9984
42	142.4	8.0	0.9984	144.7	7.5	0.9986
43	141.3	7.4	0.9986	143.6	6.9	0.9988
44	140.9	6.3	0.9990	143.2	5.8	0.9991
45	140.1	6.2	0.9990	142.6	5.8	0.9991
46	138.9	6.8	0.9987	141.5	6.4	0.9989
47	135.1	5.7	0.9991	137.8	5.3	0.9992
48	131.6	5.0	0.9992	134.5	4.6	0.9994
49	123.0	5.5	0.9990	126.4	5.1	0.9991
50	100.9	6.2	0.9981	105.5	5.8	0.9984

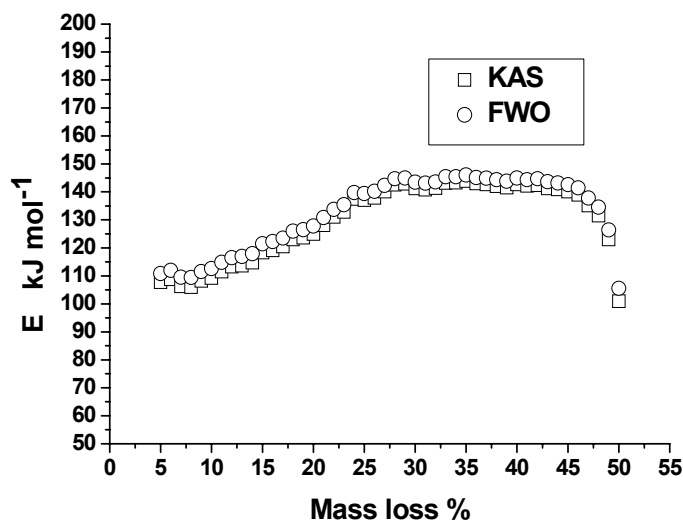


Fig. 3 – Activation energy vs. mass loss (%).

As can be seen in Fig. 3, the calculated values remain practically constant (errors less than 7%) from 21% to 48% of the entire lost weight (corresponding to approximate values of alpha between: 0.4-0.8).

The average values of the activation energy calculated in the 21% – 48% weight loss range are:

$$\bar{E}_{KAS} = 140.0 \text{ kJ mol}^{-1} \quad \bar{E}_{FWO} = 141.9 \text{ kJ mol}^{-1}$$

The obtained values of the activation energy through the KAS method are in good agreement with those obtained with the FWO method.

CONCLUSIONS

A kinetic study of the thermal decomposition of 4-[(2-chlorobenzyl)oxi]-4'-trifluoromethyl-azobenzene was performed. The chemical processes were established for each decomposition step. Activation energy of the first decomposition step was calculated using two integral isoconversional methods. The obtained results are in satisfactory agreement.

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