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Thermal behaviour and non-isothermal decomposition kinetics of 2-methyl and 2-ethyl benzo[b]thiophene-1,1-dioxide

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Abstract

The results of a thermoanalytical study and a non-isothermal kinetic analysis of the decomposition of 2-methyl and 2-ethyl benzo[b]thiophene-1,1-dioxide are presented.

Keywords: Decomposition; Kinetics; Non-isothermal

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1. Introduction

The synthesis and reactivity of benzo[b]thiophene-1,1-dioxide and its derivatives are subjects of interest because of their theoretical importance [1] and their practical use [2].

This paper deals with some results concerning the thermal behaviour of 2-methyl and 2-ethyl benzo[b]thiophene-1,1-dioxide.

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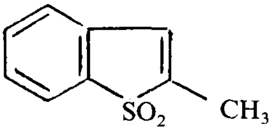
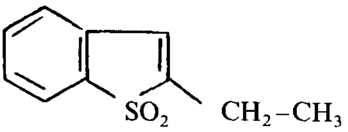
2. Experimental

Powders of the compounds



2-methyl benzo[b]thiophene-1,1-dioxide

and



2-ethyl benzo[b]thiophene-1,1-dioxide

synthesised and characterized (^{1}H NMR, IR and MS data) according to a procedure described elsewhere [3], were used in this study.

The heating curves were recorded in a static atmosphere at two heating rates, 2.5 and 10 K min^{-1}, using a MOM derivatograph, Budapest-type (Paulik–Paulik–Erdey).

In order to obtain information concerning the crystalline state of the studied compounds an X-ray diffractometer (Philips P.W.1400) was used.

Although crystalline, due to the low intensites of the powder diffraction lines, we were not able to list the interplanar distances and the Scherrer mean crystalline sizes of the two compounds investigated.

The values of the non-isothermal kinetic parameters for the workable decomposition steps were estimated using three integral methods: the Coats–Redfern [4], the Flynn–Wall [5] for constant heating rate, and the Urbanovici–Segal [6], a modification of the Coats–Redfern method. The experimental data were processed using a program written in BASIC [7]. The program allows the generation of (α,θ(°C)) curves using the Coats–Redfern-determined values of the kinetic parameters (α is the degree of conversion which is used as a variable in the rate equation) and the plotting of the experimental points. In such a way the correctness of the applied methods, as well as the reliability of the determined values of the non-isothermal kinetic parameters, can be checked.

3. Results

3.1. *The thermal decomposition of 2-methyl benzo[b]thiophene-1,1-dioxide*

Fig. 1 shows the measured curves of this compound recorded at $\beta = 2.5$ K min^{-1}. The DTA curve shows that the first significant change is the melting which occurs with maximum rate at 120°C, followed by the release of some impurity (either

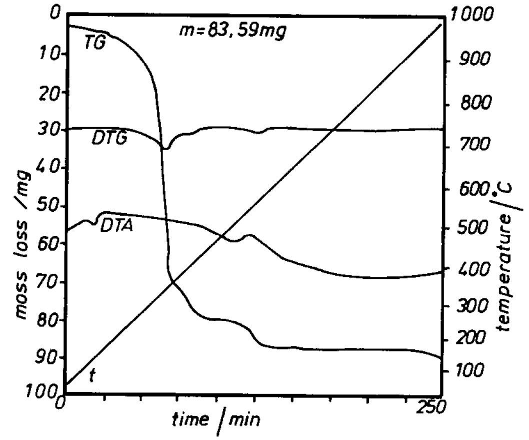


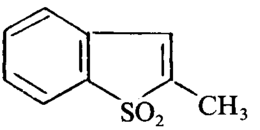
Fig. 1. Measured curves of 2-methyl benzo[b]thiophene-1,1-dioxide, at a heating rate of 2.5 K min^{-1} (sample mass, $m = 83.59$ mg).

Table 1
Values of the non-isothermal kinetic parameters for reaction (1), $\beta = 2.5$ K min^{-1}

Method	n	E in kJ mol^{-1}	A in s^{-1}	r [a]
Coats-Redfern	1.40	95.0	3.40×10^6	0.9985
Flynn-Wall	1.40	98.4	9.50×10^6	0.9987
Modified Coats-Redfern	1.40	94.2	2.90×10^6	0.9987

[a] Correlation coefficient of linear regression.

water or residual solvent) until 140°C. In the temperature range 150-320°C, a main decomposition step corresponding to the reaction



$$(1) \rightarrow C_6H_6(g) + SO_2(g) + \text{solid resin} \qquad (1)$$

is recorded. The reaction products, C_6H_6 and SO_2, were detected using gas chromatography. The temperature corresponding to the maximum reaction rate (at which the peak of DTG curve is located) is 280°C. A new decomposition step can be identified at higher temperatures, in the range 320-380°C, with the maximum rate located at 350°C. The residue of the final decomposition step undergoes exothermic oxidative degradation in the temperature range 380-545°C, the maximum of the DTA peak being located at 520°C.

The only workable step for obtaining the values of the non-isothermal kinetic parameters is the main decomposition step which occurs according to Eq. (1). Table 1 lists the values of the non-isothermal kinetic parameters (reaction order n,

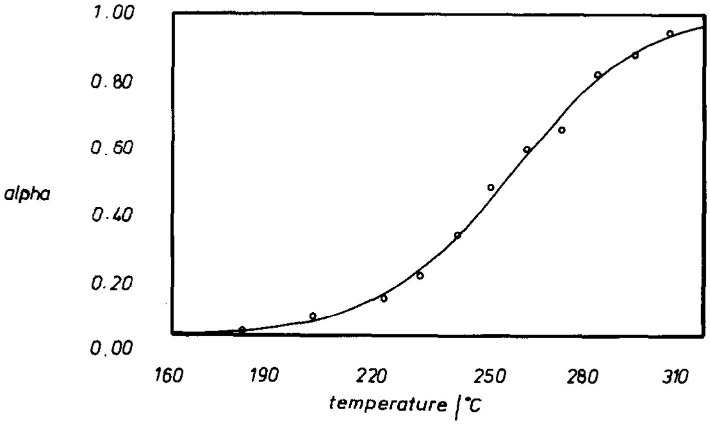


Fig. 2. TG regenerated curve for reaction (1), at a heating rate of 2.5 K min^{-1}, in coordinates (α,θ(°C)): ——, calculated curve; ○, experimental points.

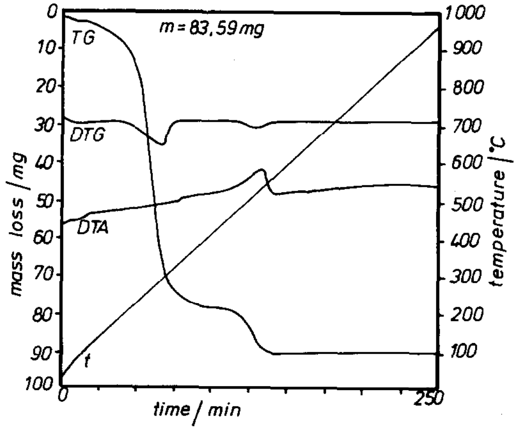


Fig. 3. Measured curves of 2-ethyl benzo[b]thiophene-1,1-dioxide, at a heating rate of 2.5 K min^{-1} (sample mass, m = 83.59 mg).

activation energy E and pre-exponential factor A) for this reaction. As may be seen from this table, there is quite a good agreement among the non-isothermal kinetic parameters determined using the three applied methods. Using the values of the non-isothermal kinetic parameters determined using the Coats–Redfern method, the regenerated (α,θ(°C)) curve in Fig. 2 was obtained.

Inspection of this figure shows that the experimental points lie very close to the regenerated curve, thus confirming the reliability of the determined values of the non-isothermal kinetic parameters.

3.2. The thermal decomposition of 2-ethyl benzo[b]thiophene-1,1-dioxide

As seen from the thermogram recorded for this compound at $\beta = 2.5$ K min^{-1} (Fig. 3), after a slight loss of weight and an endothermic peak, located at 90°C

Table 2
Values of the non-isothermal kinetic parameters for reaction (2), $\beta = 2.5$ K min^{-1}

Method	n	E in kJ mol^{-1}	A in s^{-1}	r
Coats–Redfern	1.40	95.3	3.90×10^6	0.9975
Flynn–Wall	1.40	98.6	1.09×10^7	0.9979
Modified Coats–Redfern	1.40	97.4	7.15×10^6	0.9979

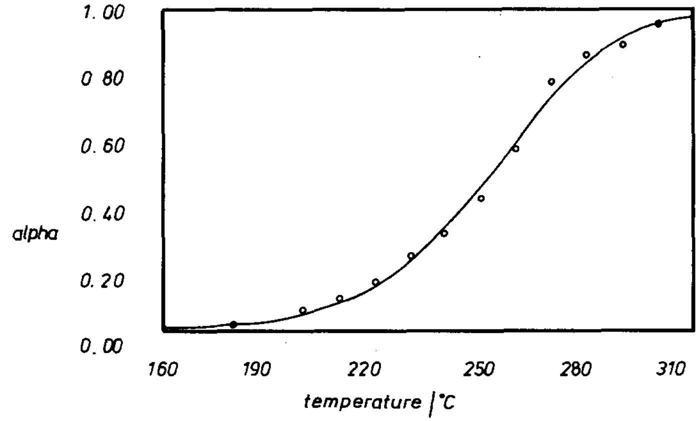
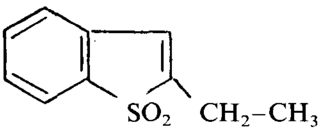


Fig. 4. TG regenerated curve for reaction (2), at a heating rate of 2.5 K min^{-1}, in coordinates (α,θ(°C)): ——, calculated curve; ○, experimental points.

corresponding to the melting, a main decomposition step in the temperature range 100–320°C occurs corresponding to a reaction described by the equation



$$(\text{l}) \rightarrow C_6H_6(\text{l}) + SO_2(\text{l}) + \text{solid resin} \qquad (2)$$

This is the only kinetically workable reaction, the products of which, C_6H_6 and SO_2, were confirmed using gas chromatography. The maximum decomposition rate (the peak of the DTG curve) is recorded at 280°C. The decomposition is followed at higher temperatures (in the range 320–540°C) by the exothermic oxidative degradation, which occurs with maximum rate at 520°C.

Table 2 lists the values of the non-isothermal kinetic parameters for reaction (2). As in the former case, we can notice a more than satisfactory agreement between the values of the non-isothermal kinetic parameters obtained via the three methods used.

As shown in Fig. 4 the experimental points lie practically on the regenerated curve in (α,θ(°C)) coordinates.

A comparison between the results listed in Tables 1 and 2 shows that the values of the non-isothermal kinetic parameters for reactions (1) and (2) are very close (practically equal). This shows that the supplementary methylene group does not introduce any change in the decomposition rate.

The fractionary value of the reaction order ($n = 1.40$) is probably due to the possible contribution to the decomposition of structural units consisting of various numbers of molecules.

4. Conclusions

A comparative non-isothermal kinetic investigation of the decompositions of 2-methyl and 2-ethyl benzo[b]thiophene-1,1-dioxide was performed.

The values of the non-isothermal kinetic parameters for the main decomposition step of the two investigated compounds are practically equal.

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