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# Thermal behaviour and nonisothermal decomposition kinetics of 2,5-dihydrothiophene-1,1-dioxide and some of its derivatives

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## Abstract

Results concerning the liquid phase nonisothermal decomposition kinetics of 2,5-dihydrothiophene-1,1-dioxide and three of its derivatives are presented.

## INTRODUCTION

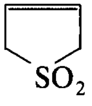
The synthesis and reactivity of 2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide and its derivatives is a subject of interest, owing to their theoretical importance [1] as well as to their practical use as pesticides and pharmaceuticals [2].

Generally investigations concerning such compounds are carried out in solution. This paper deals with some results concerning the thermal behaviour of 2,5-dihydrothiophene-1,1-dioxide and some of its derivatives as individual compounds in the molten state.

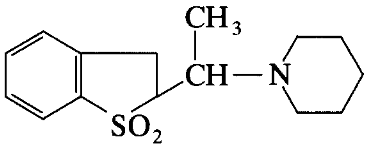
## EXPERIMENTAL

Powders of 2,5-dihydrothiophene-1,1-dioxide (**I**), 2,3-dihydrobenzo[*b*] thiophene-1,1-dioxide (**II**), (piperidinyl-1-ethyl)-2,3-dihydrobenzo[*b*] thiophene-1,1-dioxide (**III**), and 3-(*N*-methyl-1-piperazinyl)-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**IV**) were synthesized according to methods described elsewhere [3].

The thermal decomposition curves have been recorded in static air atmosphere using a-1500D derivatograph type Paulik–Paulik–Erdey in the 20–1000°C temperature range at various heating rates between 2.5 and 10 K $min^{-1}$.



**I**



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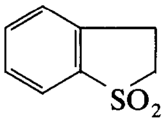

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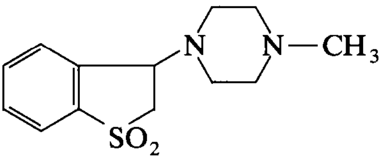

**IV**

In order to evaluate the nonisothermal kinetic parameters, four integral methods worked out by Coats and Redfern [4], Flynn and Wall for constant heating rate [5], Doyle [6a] and Gorbachev [6b] and Urbanovici and Segal [7] have been applied. The last procedure is actually a modified variant of the Coats–Redfern method. In order to process the data automatically, a program written in the language BASIC [8] was used. Besides the computation of the nonisothermal kinetic parameter values with the assistance of the four previously mentioned methods, the program allows us to regenerate the TG curves in coordinates ($\alpha$, $t$°C), where $\alpha$ is the degree of conversion, using these values and subsequently to put on the same plot the experimental ($\alpha$, $t$°C) points. The coincidence between the experimental points and the regenerated ($\alpha$, $t$°C) curve indicates the correctness of the approximations used to derive the applied integral equations as well as the accuracy of the experimental measurements.

## RESULTS AND DISCUSSION

### *Decomposition of 2,5-dihydrothiophene-1,1-dioxide*

According to the derivatographic data recorded at $\beta = 2.5$ K $min^{-1}$, this compound undergoes melting with an associated endothermic peak located at 67°C. At higher temperatures the liquid compound undergoes thermal decomposition according to the reaction whose stoichiometric equation is

$$\mathbf{I}\,(l) \xrightarrow{160^{\circ}C} SO_{2(g)} + H_2C{=}CH{-}CH{=}CH_{2(g)} \qquad (1)$$

TABLE 1

Values of the nonisothermal kinetic parameters of reaction (1)

| $\beta$ (K min$^{-1}$) | Method | $n^{x}$ [a] | $A$ (s$^{-1}$) | $E$ (cal mol$^{-1}$) | $r^{x}$ [a] |
|---|---|---|---|---|---|
| 2.5 | Coats–Redfern [4] | 1.4 | $1.76\times10^{18}$ | 40000 | 0.9980 |
| 2.5 | Flynn–Wall [5] ($\beta$ = const.) | 1.4 | $1.18\times10^{18}$ | 39600 | 0.9982 |
| 2.5 | Doyle–Gorbachev [6] | 1.4 | $1.76\times10^{18}$ | 40000 | 0.9982 |
| 2.5 | Modified Coats–Redfern [7] | 1.2 | $3.46\times10^{18}$ | 38700 | 0.9971 |

[a] $n^{x}$ and $r^{x}$ mean respectively reaction order and correlation coefficient of the linear regression.

where the figure above the arrow indicates the temperature corresponding to the maximum decomposition rate (peak of the DTG curve). The sulphur dioxide has been identified by chemical procedures. Table 1 lists the values of the nonisothermal kinetic parameters of reaction (1) obtained by use of the applied integral methods for $\beta = 2.5$ K min$^{-1}$. This value of the heating rate was chosen to be low enough not to alter the values of the kinetic parameters by heat transfer limitations.

From the inspection of these results a satisfactory agreement between the values of the nonisothermal kinetic parameters obtained by using the four applied methods can be noticed.

The regenerated ($\alpha$, $t$°C) curve for reaction (1) at $\beta = 2.5$ K min$^{-1}$, using the Coats–Redfern values of the nonisothermal kinetic parameters is given in Fig. 1. The experimental points which lie practically on it, indicate the accuracy of the obtained nonisothermal kinetic parameter values.

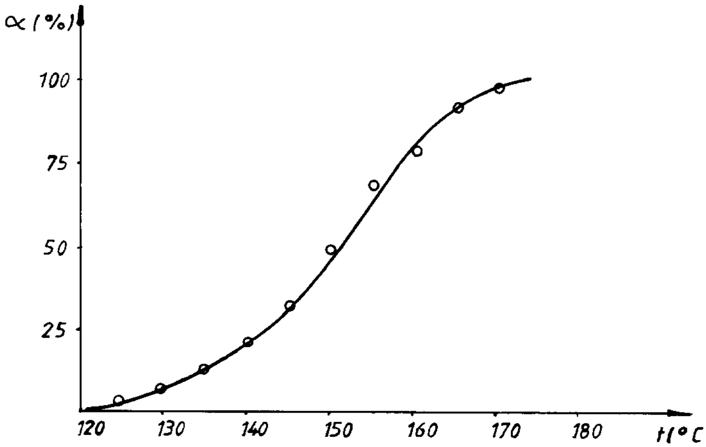

Fig. 1. Regenerated TG curve of reaction (1) in ($\alpha$, $t$°C) coordinates at $\beta = 2.5$ K min$^{-1}$: ——, regenerated curve; ○, experimental points.

TABLE 2

Values of the nonisothermal kinetic parameters of reaction (2)

| $\beta$ (K min$^{-1}$) | Method | $n$ | $A$ (s$^{-1}$) | $E$ cal mol$^{-1}$) | $r$ |
|---|---|---|---|---|---|
| 5 | Coats–Redfern [4] | 0.5 | $1.35\times10^4$ | 18072 | 0.9966 |
| 5 | Flynn–Wall [5] ($\beta$ = const.) | 0.4 | $4.74\times10^4$ | 18849 | 0.9973 |
| 5 | Doyle–Gorbachev [6] | 0.5 | $1.37\times10^4$ | 18072 | 0.9966 |
| 5 | Modified Coats–Redfern [7] | 0.5 | $2.36\times10^4$ | 18533 | 0.9965 |

### *Decomposition of 2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide*

The derivatogram of this compound recorded at $\beta = 5$ K min$^{-1}$ shows an endothermic peak corresponding to melting at 110°C. The liquid compound undergoes subsequent decomposition which occurs according to the chemical equation

$$\mathbf{II}\ (l) \xrightarrow{330°C} SO_{2(g)} + C_6H_{6(g)} + H_2C{=}CH_{2(g)} \qquad (2)$$

In this case also gaseous sulphur dioxide was identified by chemical analysis.

Table 2 lists the nonisothermal kinetic parameter values for reaction (2) at $\beta = 5$ K min$^{-1}$ (the lowest heating rate at which the derivatogram of this compound has been recorded).

As seen from Table 2, the values of the nonisothermal kinetic parameters obtained by the four applied methods agree satisfactorily in this case also.

Figure 2 shows the regenerated TG curve in coordinates ($\alpha$, $t$°C) using the Coats–Redfern values of the nonisothermal kinetic parameters. In this case also the experimental points practically lie on the curve.

### *Decomposition of 2-(piperidinyl-1-ethyl)-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide*

As shown by the derivatogram of this compound recorded at $\beta = 10$ K min$^{-1}$ the endothermic peak of melting is located at 180°C (at lower heating rates the accuracy of the melting point measurement is lowered). At higher temperatures a first decomposition step occurs with maximum rate at 280°C ($\beta = 2.5$ K min$^{-1}$). This step corresponds to the reaction

$$\mathbf{III}\ (l) \xrightarrow{280°C} SO_{2(g)} + C_6H_{6(g)} + C_9H_{17}N_{(l)} \qquad (3)$$

The evolved sulphur dioxide was identified by chemical analysis. The compound $C_9H_{17}N$ is a yellow liquid with basic character. The presence of nitrogen was revealed by chemical analysis.

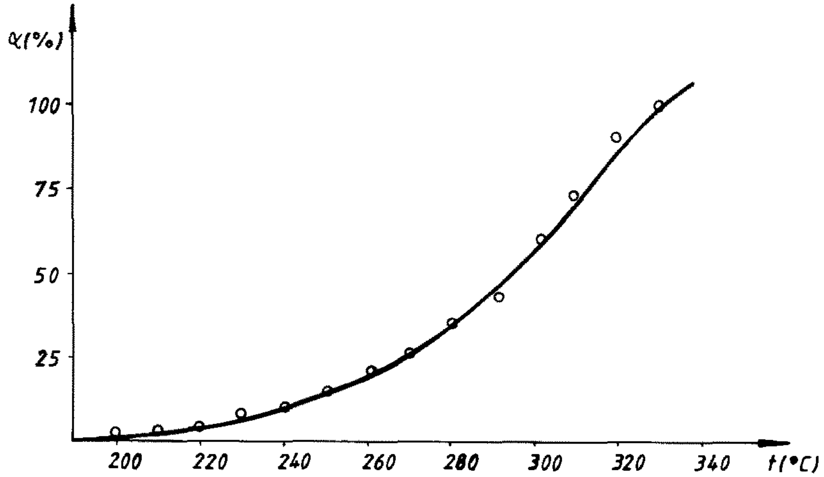

Fig. 2. Regenerated TG curve of reaction (2) in ($\alpha$, $t$°C) coordinates at $\beta = 5$ K min$^{-1}$: ——, regenerated curve; ○, experimental points.

In the temperature range 400–600°C the compound $C_9H_{17}N_{(l)}$ undergoes oxidative degradation in a multistep overall reaction which is not workable kinetically.

The values of the nonisothermal kinetic parameters of reaction (3) are listed in Table 3.

Again a satisfactory agreement among the values of the nonisothermal kinetic parameters obtained by the applied methods should be noticed.

Figure 3 shows the regenerated ($\alpha$, $t$°C) curve and the experimental points which lie on it.

### *Decomposition of 3-(*N*-methyl-1-piperazinyl)-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide*

At $\beta = 2.5$ K min$^{-1}$ this compound undergoes melting with an endothermic peak at 125°C followed at higher temperatures by decomposition

TABLE 3

Values of the nonisothermal kinetic parameters of reaction (3)

| $\beta$ (K min$^{-1}$) | Method | $n$ | $A$ (s$^{-1}$) | $E$ (cal mol$^{-1}$) | $r$ |
|---|---|---|---|---|---|
| 2.5 | Coats–Redfern [4] | 0.8 | $1.01 \times 10^{11}$ | 34800 | 0.997 |
| 2.5 | Flynn–Wall [5]<br>($\beta$ = const.) | 0.8 | $1.41 \times 10^{11}$ | 35100 | 0.998 |
| 2.5 | Modified Coats–Redfern [7] | 0.8 | $1.08 \times 10^{11}$ | 34800 | 0.997 |

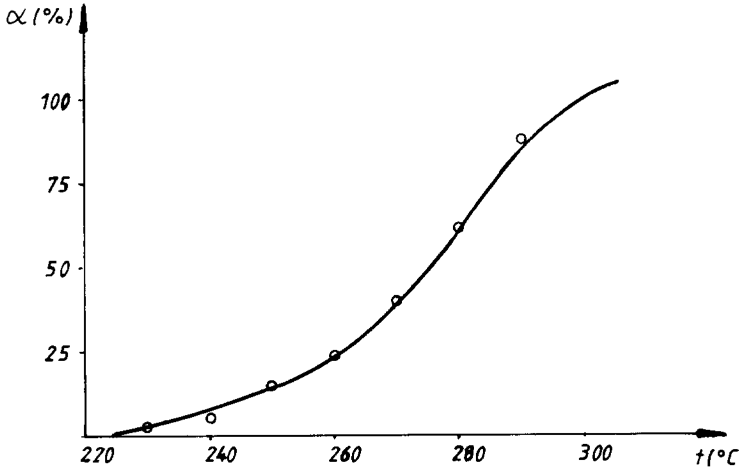

Fig. 3. Regenerated TG curve of reaction (3) in ($\alpha$, $t$°C) coordinates at $\beta = 2.5$ K min$^{-1}$: ——, regenerated curve; ○, experimental points.

according to the chemical equation

$$\text{IV (l)} \xrightarrow{240^\circ\text{C}} SO_{2(g)} + C_6H_{6(g)} + C_7H_{14}N_{2(l)} \qquad (4)$$

As in the other reactions investigated in this paper the sulphur dioxide was identified by chemical analysis. The compound $C_7H_{14}N_2$ has basic character. The presence of nitrogen was shown by chemical analysis.

As in the previous case, in the temperature range 420–650°C this compound undergoes oxidative degradation in a multiple step overall reaction which is not workable kinetically.

Table 4 lists the nonisothermal kinetic parameter values for reaction (4). A satisfactory agreement among the values of the nonisothermal kinetic parameters obtained by the three applied integral methods can be noticed. The regenerated TG curve in coordinates ($\alpha$, $t$°C) and the corresponding experimental points are given in Fig. 4.

An analysis of the presented results in the framework of the "reaction order" model shows that the values of this parameter oscillate between

TABLE 4

Values of the nonisothermal kinetic parameters of reaction (4)

| $\beta$ (K min$^{-1}$) | Method | $n$ | $A$ (s$^{-1}$) | $E$ (cal mol$^{-1}$) | $r$ |
|---|---|---|---|---|---|
| 2.5 | Coats–Redfern [4] | 2 | $8.67 \times 10^{26}$ | 69241 | 0.9976 |
| 2.5 | Flynn–Wall [5] ($\beta$ = const.) | 2 | $2.98 \times 10^{26}$ | 67773 | 0.9977 |
| 2.5 | Doyle–Gorbachev [6] | 2 | $8.67 \times 10^{26}$ | 69241 | 0.9976 |

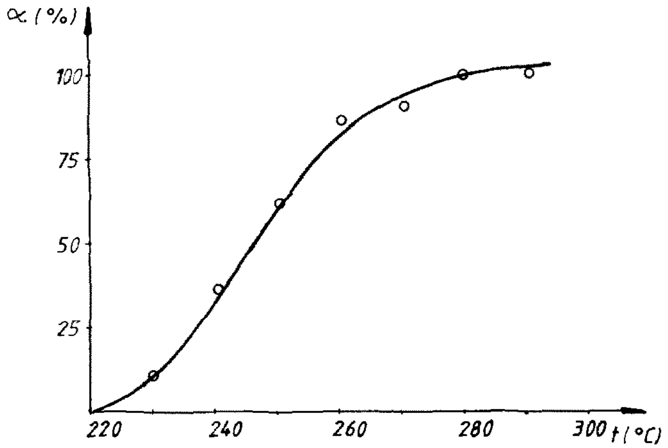

Fig. 4. Regenerated TG curve of reaction (4) in ($\alpha$, $t$°C) coordinates at $\beta = 2.5$ K min$^{-1}$: ———, regenerated curve; o, experimental points.

zero and two. The fractionary and subunitary values of $n$ could be assigned to mixed diffusional and kinetic regimes of decomposition occurrence. Concerning the supraunitary values of the reaction order, these could be due to the decomposition of structural units which consist of more than one molecule and coexist in various ratios in the molten state compounds submitted to decomposition.

As far as the apparent low value of the preexponential factor of reaction (2) and high value of the same parameter of reaction (4) one can notice equally a low value of the activation energy of reaction (2) and a high value of the same parameter for reaction (4). Such compensation effects keep the rate constant or the Gibbs free energy of activation within reasonable limits.

## CONCLUSIONS

Investigation of the thermal behaviour of four derivatives of dihydrothiophene-1,1-dioxide showed that they all decomposed in the liquid phase. Nonisothermal kinetic parameter values of the decomposition reactions have been determined using four integral methods; values so obtained agree satisfactorily.

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