

Abdallah Abd El-Azeem Abdallah* (1) and Hind Mostafa El Nahas

Chemistry Department, Faculty of Science,
Alexandria University, Alexandria, Egypt
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Isomerisation of 2,4,6-triphenyl-4*H*-thiopyran into 2,4,6-triphenyl-2*H*-thiopyran has been studied kinetically and the rate of the reaction was determined in dimethylformamide. The first order rate constant could be expressed in terms of the Arrhenius parameters by the equation $k_1 = 2.85 \times 10^7 e^{-15820 \pm 110 / RT}$.

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The interconversions of 2*H*- and 4*H*-pyran derivatives have been studied in hydrogen chloride/acetic acid, perchloric acid/acetic acid and trifluoroacetic acid (2-5) where a very fast disproportionation reaction has taken place and resulted in the formation of pyrylium salts in high yields. However, the kinetics and mechanism of such an interconversion has not been reported. In the present communication, we are reporting this isomerisation under other conditions, particularly with different catalysts. Furthermore, the kinetics of the reaction have been studied by ¹H nmr spectroscopy.

2,4,6-Triphenyl-4*H*-thiopyran (**1**) was quantitatively converted to 2,4,6-triphenyl-2*H*-thiopyran (**2**) in the presence of 2,4,6-triphenylthiopyrylium perchlorate (**3**) in dimethylformamide. The ¹H nmr spectrum of 4*H*-thiopyran (**1**) in deuterated dimethylformamide (DMF-d₇) showed a triplet at δ 4.5 which is attributed to the H-4 proton, a doublet at δ 6.0 due to H-3 and H-5 proton and a multiplet at δ 7.3 for the aromatic protons. Upon isomerisation the 2*H*-thiopyran isomer **2** showed in its ¹H nmr spectrum a sharp singlet at δ 6.93 due to H-3 proton and two doublets at δ 4.97 and δ 6.0 assigned to H-5 and H-6 proton, respectively, in addition to aromatic protons at δ 7.3. A comparative study of both spectra, indicated that the triplet at δ 4.5 has disappeared from the spectrum of 4*H*-thiopyran (**1**), whereas a new doublet appeared at δ 4.97 in spectrum of 2*H*-thiopyran (**2**). Moreover, the doublet at δ 6.0 for 4*H*-thiopyran (**1**) became a singlet at δ 6.93 upon isomerisation. The difference in the spectra of both compounds attracted our attention to follow the rate of reaction by ¹H nmr spectroscopy.

Thus, the reaction of 4*H*-thiopyran (**1**) (0.01 mole) in (DMF-d₇) (0.4 ml) with thiopyrylium perchlorate **3** (0.01 mole) was conducted in a ¹H nmr tube at constant temperature. The ¹H nmr spectra were recorded immediately after mixing up the reactants mixture and at various intervals of time. The intensity of the triplet at δ 4.5 ppm belonging to 4*H*-thiopyran (**1**) has been decreased with

time and became very weak at the end of the reaction. Meanwhile the doublet at δ 4.97 ppm belonging to 2*H*-thiopyran (**2**) started to appear and became stronger with time. The change in intensities of the triplet and doublet were recorded and from which the % conversion was calculated and recorded in (Table I). The same reaction was carried out at different temperatures and with different concentrations of the thiopyrylium perchlorate **3**. The calculated rate constants, energy and entropy of activation are compiled in (Table II).

The results obtained from the kinetic data were found to follow a first-order kinetics according to the equation

$$\log(a - x) = \log a - (k_1/2.303)t$$

where *a* denotes the initial concentration of [4*H*-thiopyran (**2**)], *x* the amount of 4*H*-thiopyran (**2**) reacted in time *t* and *k*₁ the first-order rate constant. The value of *k*₁ was evaluated from the slope of the linear plots of log *a*/(*a*-*x*) against *t* (Figure 1). Linear plots showing first-order kinetics were also obtained at 50, 60 and 70° and at each temperature the runs were reproducible.

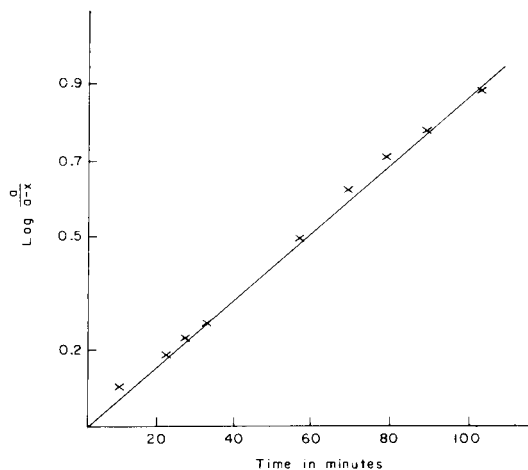


Figure 1. Reaction between **1** and **3** at 60°.

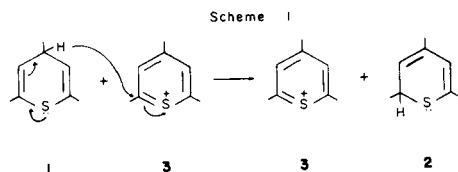
Table I

Action of Thiopyrylium Perchlorate (3) (0.01 mole)
on 4*H*-thiopyran (1) (0.01 mole) in DMF-d, at 60°C

t (minutes)	8	20	25	30	54	66	75	87	100
% conversion	17.69	34.64	41.93	47.05	69.15	77.05	81.60	84.18	84.77
10 ⁴ k ₁ , sec ⁻¹	4.05	3.54	3.62	3.53	3.66	3.71	3.76	3.53	3.50

In a series of runs at constant temperature, when the [4*H*-thiopyran (1)] was maintained constant; in large excess but [thiopyrylium perchlorate (3)] was varied, the rate constants were found to be constant. This clearly shows that the reaction is zero-order in thiopyrylium perchlorate (3) and is in good agreement with the overall first order reaction. No change in the rate of the isomerisation by changing the concentration of the added thiopyrylium perchlorate (3) was observed.

Furthermore, the isomerisation of 4*H*-thiopyran (1) to 2*H*-thiopyran (2) was not achieved in boiling DMF alone. However, addition of the thiopyrylium perchlorate (3) resulted in complete isomerisation. This shows that the isomerisation has taken place through an intermolecular hydride transfer reaction (Scheme I).



Calculation of the Arrhenius parameters by the method of least square using at least two concordant values of k_1 at 50, 60 and 70° showed that the rate constant could be expressed by the following equation.

$$k_1 = 2.85 \times 10^7 e^{-15820 \pm 110 / RT}$$

During the course of this investigation, it became interesting to find out other conditions for the isomerisation of 4*H*-thiopyran (1) to 2*H*-thiopyran (2). Thus, the latter reaction was carried out by treating 4*H*-thiopyran (1) with trifluoroacetic acid. The rate of the isomerisation was found to increase with addition of small amounts of thiopyrylium perchlorate (3). However, it was difficult to measure the rate of isomerisation by ¹H nmr due to the turbidity of the solution as a result of the formation of thiopyrylium cation (3) (2).

Table II

Rate Constants, E_a and ΔS‡ Values for the Reaction of 4*H*-Thiopyran (1) and Thiopyrylium Perchlorate (3) in DMF-d,

Reactants [1]:[3]	Temperature °C	10 ⁴ k ₁ , sec ⁻¹
0.01 <i>M</i> :0.01 <i>M</i>	50	1.81
0.01 <i>M</i> :0.01 <i>M</i>	60	3.76
0.01 <i>M</i> :0.01 <i>M</i>	70	7.96
0.01 <i>M</i> :0.002 <i>M</i>	60	3.64
0.01 <i>M</i> :0.004 <i>M</i>	60	3.83
0.01 <i>M</i> :0.006 <i>M</i>	60	3.74

EXPERIMENTAL

The ¹H nmr spectra were recorded on Jeol 100 Spectrometer with TMS as an internal standard.

2,4,6-Triphenyl-4*H*-thiopyran (1).

This compound was prepared by the reduction of 2,4,6-triphenylthiopyrylium perchlorate (6,7) with sodium borohydride (2). Repeated crystallisation from methanol gave yellow needles mp 112° dec [lit (8) mp 100-102.5° dec]; ¹H nmr (deuteriochloroform): (9) or (DMF-d₇): δ 4.5 (t, H-4, 1 H), 6.0 (d, H-3 and H-5, 2 H), 7.3 (m, aromatic, 15 H).

2,4,6-Triphenyl-2*H*-thiopyran (2).

This compound was quantitatively obtained from the action of 2,4,6-triphenylpyrylium perchlorate on 2,4,6-triphenyl-4*H*-thiopyran in dry dimethylformamide. The product was obtained as an oil and identified from its spectroscopic measurements (9); ¹H nmr (deuteriodimethylformamide): δ 4.97 (d, H-5, 1 H), 6.0 (d, H-6, 1 H), 6.93 (s, H-3, 1 H), 7.3 (m, aromatic, 15 H).

REFERENCES AND NOTES

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