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KINETICS OF THE SELF-CONDENSATION OF BENZO[b]THIOPHENE 1,1 DIOXIDE

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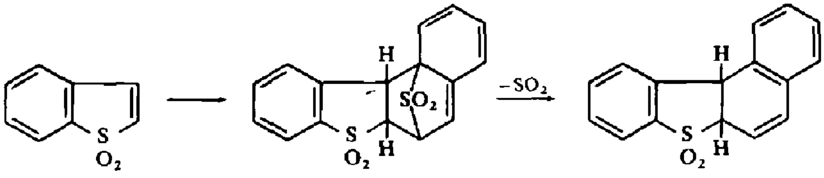
Abstract—The kinetics of the Diels–Alder condensation of benzothiophene 1,1 dioxide (I) with itself in various solvents have been measured at 149 to 191°. The reaction is second order in I, presumably reflecting its bimolecular nature. Depending on the solvent employed, the activation energy varied from approximately 16 to 23 kcal/mole, and the frequency factor from approximately 10^8 to 10^{11} cc/mole/sec. These parameters exhibited a compensation effect in the various solvents so that the rate constant itself only varied by a factor of 6. A negative entropy of activation and low steric factor were observed, which varied with solvent type. These results reflect the highly polar nature of the reaction intermediate.

INTRODUCTION

RECENT studies in this laboratory have been concerned with the chemistry of condensed thiophene monoxides and dioxides.[1,2] In the course of these studies, it became obvious to us that there was a paucity of data available on the kinetics of condensed thiophene dioxide condensation reactions. Bordwell[3] has shown that benzothiophene 1,1 dioxide (I) in the presence of solvent undergoes a Diels–Alder condensation with itself, presumably via intermediate II, to yield 10,11-dihydro-9-thia-3,4-benzofluorene-9,9-dioxide (III).



I II III

Davies subsequently[4] confirmed these results and, in addition, showed that I also undergoes condensation with dienes such as anthracene, cyclopentadiene and 1-vinylnaphthalene.[5] However, no quantitative rate measurements were obtained in either of these studies. In the present work, detailed kinetic data are reported for the self-condensation of benzothiophene dioxide in a variety of solvents over the temperature range of 149 to 191°. The order of reaction and activation energy were measured and, the frequency factors, entropy of activation and steric factors were calculated for the solvents employed. These kinetic parameters have provided some insight on the detailed mechanism of this reaction.

RESULTS

The order of the pyrolysis reaction was determined in a mixed tetradecane/napthalene (32 mole % tetradecane, 68 mole % naphthalene) solvent system by pyrolyzing

I at three concentration levels (0·025, 0·05 and 0·065 moles I per total moles) at 177°. The data were then examined to see if all three concentration runs fit a single second order curve. This was done by plotting (1/A–1/Ao) versus time; where A is the concentration of I (moles per total moles I plus solvent) at time t, and Ao is the concentration of I at time zero (see Ref. (7*a*). As shown in Fig. 1, an excellent correlation results and it can be concluded that the reaction is indeed bimolecular. Thus,

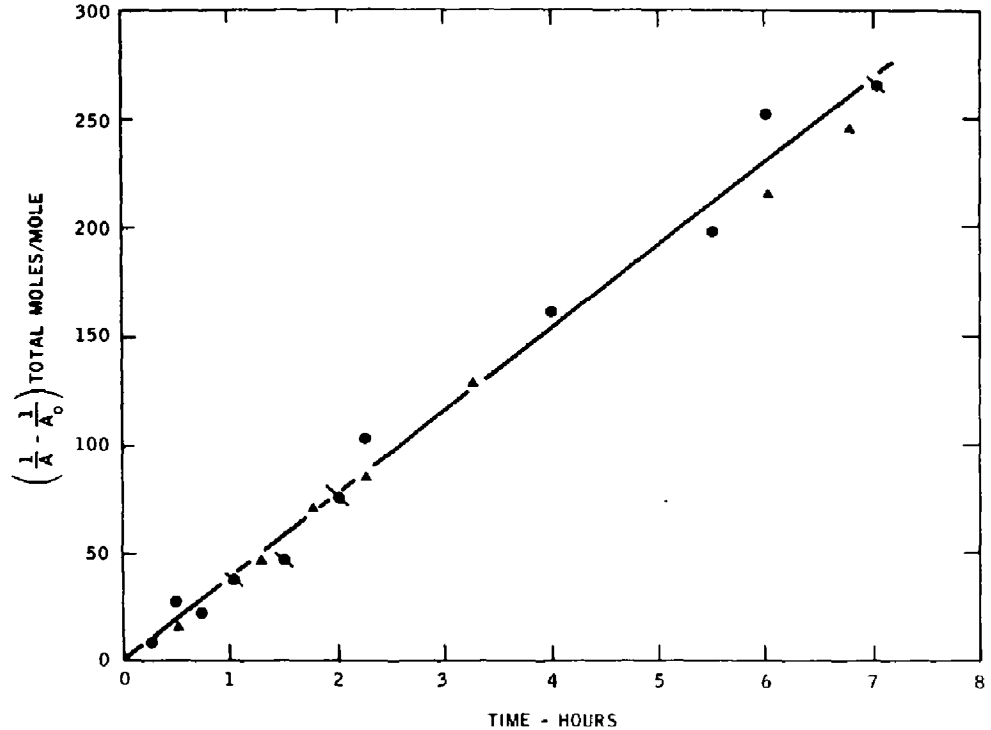


FIG. 1 Second order plot of benzothiophene 1,1 dioxide (I) concentration versus time at 177° at various initial concentrations in mixed hydrocarbon solvent (TN): ●, 0·065 mole (I) per total moles; ▲, 0·050 mole (I) per total moles; ◉, 0·025 mole (I) per total moles.

all subsequent pyrolysis data were treated as second order kinetics and second order rate constants were calculated in units of total moles per mole of I per unit time. Runs were next carried out in three solvent systems over the temperature range of 149 to 191°. The solvents employed were a mixture of tetradecane/naphthalene (TN), benzotrichloride (BTC) and diethylene glycol monobutyl ether (DGMBE). Some typical data is shown in Fig. 2 for the pyrolysis of I in DGMBE at various temperatures. An Arrhenius plot of the second-order rate constants obtained in the various solvent systems is shown in Fig. 3. Activation energies obtained from the slope of the Arrhenius plots are summarized in Table 1, along with the second-order rate constants that were measured at 177°. From these data, the frequency factor, entropy of activation and steric factor were calculated[6] for the various solvent systems. These values are also listed in Table 1. As shown, A varied from 1·72 × 10^8

TABLE 1. SUMMARY OF KINETIC PARAMETERS

Solvent	Rate constant, k, at 177° moles per mole per second	Activation energy, E_a, kcal/mole	Frequency factor, A, cc per mole per sec[a,b]	Entropy of activation, $\Delta S^{\ddagger}$, cal/mole/°K[a,c]	Steric factor[a,d]
Tetradecane/naphthalene blend (TN)	$10{\cdot}78 \times 10^{-3}$	16·5	$1{\cdot}72 \times 10^{8}$	−21·7	10^{-5}
Benzotrichloride (α,α,α trichlorotoluene) (BTC)	$3{\cdot}67 \times 10^{-3}$	19·4	$1{\cdot}37 \times 10^{9}$	−17·7	10^{-4}
Diethylene glycol monobutyl ether (DGMBE)	$1{\cdot}75 \times 10^{-3}$	23·6	$8{\cdot}40 \times 10^{10}$	−9·4	10^{-2}

[a] For a general discussion of the calculations used see reference.[7]

[b] Determined from relationship $k = A \exp E_a/RT$.

[c] Standard state for $\Delta S^{\ddagger}$ is 1 mole per cc. kT/h evaluated at 177°.

[d] Approximate.

to $8{\cdot}40 \times 10^{10}$ cc/mole/sec, $\Delta S^{\ddagger}$ varied from −21·7 to −9·4 E.U. and the steric factor varied from 10^{-5} to 10^{-2}.

DISCUSSION

The self-condensation of benzothiophene 1,1 dioxide is clearly second order. A similar conclusion has been previously observed[10] for Diels–Alder reactions in the vapor phase. This presumably reflects the bimolecular nature of the reaction.

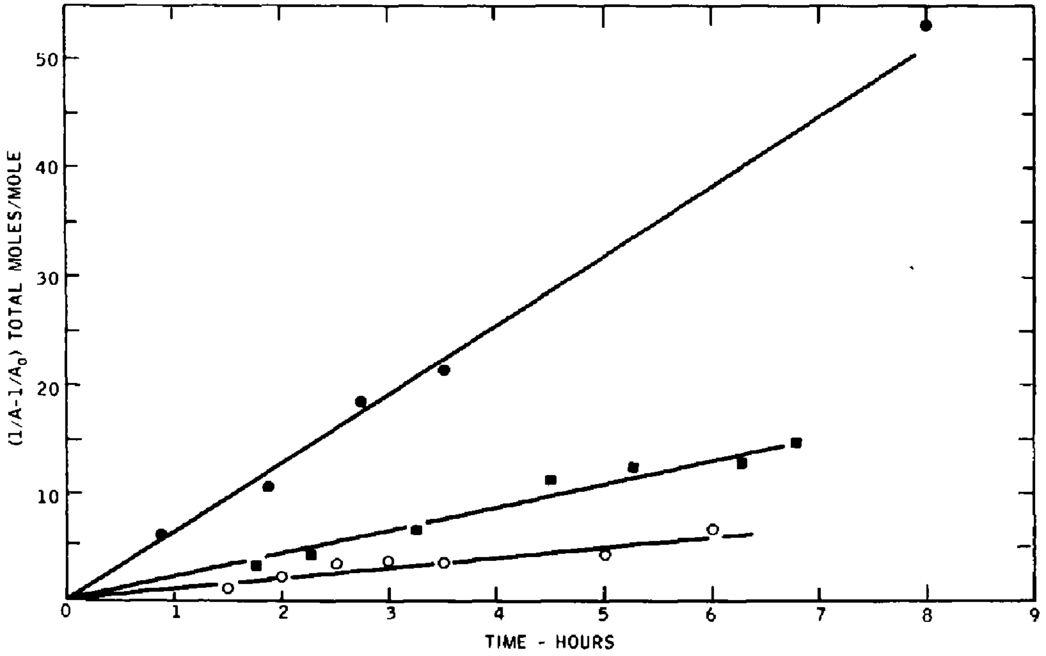


FIG. 2 Second order plot of concentration of I versus time DGMBE solvent at initial concentrations 0·050 ml (I) per total moles with various temperatures: ○, 149°; ■, 163°; ●, 177°.

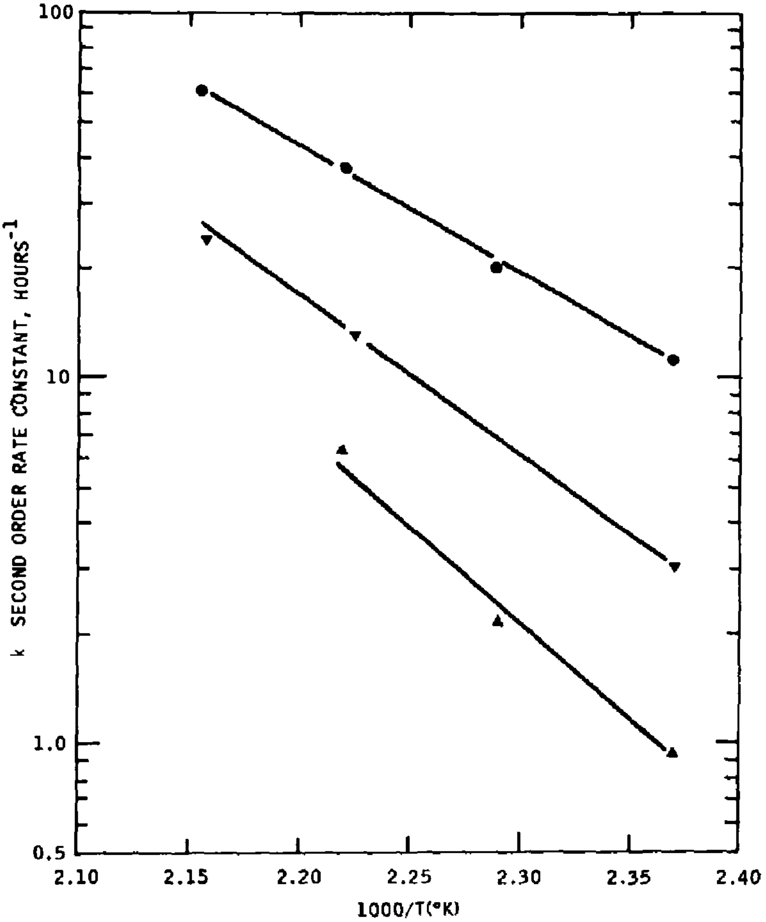


Fig. 3 Arrhenius plot of the effect of temperature on second order rate constant in different solvents: ●, TN; ■, BTC; ▲, DGMBE.

As shown in Table 1, the solvent exerts a strong influence on the kinetic parameters. The frequency factor for the reaction varied by a factor of approximately 500 and the activation energy varied from 16 to 23 kcal/mole. As shown in Fig. 4, these parameters exhibit a compensation effect in the various solvent systems, i.e. a high frequency factor is partially offset by a high activation energy. Therefore, the rate constant, k, only changes by a factor of approximately 6 at 177° in spite of a much wider change in frequency factor. These results are in contrast to the effects found with the Diels–Alder dimerization of cyclopentadiene where, with a wide variety of solvents, a relatively small change in activation energy and frequency factor was observed.[7] An approximate 16 kcal/mole activation energy was observed for the dimerization of cyclopentadiene in various solvents. The solvent induced compensation effect observed in the benzothiophene 1,1 dioxide condensation presumable reflects the strong polar nature of the intermediate formed. This would not be the case for the cyclopentadiene dimerization. However, our results are analogous to

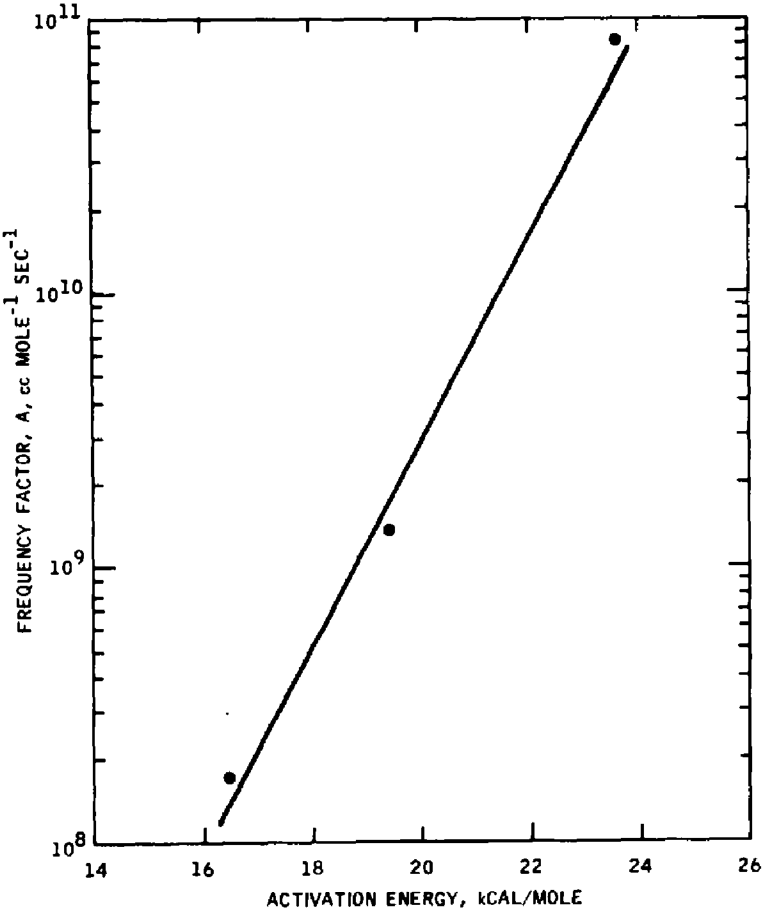


FIG. 4 Frequency factor versus activation energy for the three solvent systems employed.

those observed in the Diels–Alder addition of benzoquinone to cyclopentadiene.[8] This reaction was influenced by solvent type and changes were observed both in the frequency factors and energies of activation. However, the energies of activation observed for the benzoquinone–cyclopentadiene condensation were considerably lower than those observed in the present study, i.e. they ranged from approximately 8 to 12 kcal/mole. This is most likely due to the loss in resonance energy which occurs during the dimerization step.

A negative entropy of activation and a low steric factor was obtained in all solvents tested. Such values have been found previously for a variety of Diels–Alder reactions in the gas phase.[9, 10] This reflects the increase in orientation and, of course, the decrease in entropy which takes place in the transition state during condensation. The most negative entropy of activation and lowest steric factor were observed in the least polar solvent. This also reflects the influence of a polar transition state. The molecules of the least polar solvent possess less orientation initially. Thus, such a solvent system will show the greatest increase in orientation and a corresponding decrease in entropy. These considerations are consistent with the formation of the polar adduct (II) which has been postulated for the condensation of benzothiophene 1,1-dioxide.[3]

EXPERIMENTAL

Reagents and materials. Benzothiophene was obtained from Wateree Chemical Co., Lugoff, South Carolina and used as received. Benzotrichloride (Matheson, Coleman and Bell), tetradecane (Matheson, Coleman and Bell) and Naphthalene (Eastman Organic Chemicals) were obtained as ultra pure materials and used as received. Diethyleneglycol monobutylether (Matheson, Coleman and Bell) was purified by distillation on a spinning band column. VPC indicated that the center cut material was better than 99% pure.

Benzothiophene 1,1 dioxide was prepared by the method of Mustafa and Zayed[11] which is a modification of the method of Bordwell *et al.*[12] Benzothiophene (20·0 g) was added to a mixture of glacial AcOH, (50 cc) $(Ac)_2O$ (50 cc) and 30% H_2O (80 cc). The mixture was heated on a steam bath for 1 hr, poured over crushed ice, allowed to stand for 1 hr, filtered, washed several times with distilled water and dried. This procedure yielded 21·0 g of white crystalline product; m.p. 142–143° (reported m.p. 142–143°).

Preparation of reaction mixtures and pyrolysis experiments. All reaction mixtures were thoroughly degassed in a vacuum apparatus prior to use by repeated freeze–thaw cycles. After degassing, the mixtures were transferred to the reaction flask in a N_2-dry-box. The reaction flask was a 2-necked 25 ml Erlenmeyer flask sealed with Neoprene caps. To allow for gas volume above the liquid pyrolysis mixture, an Orsat gas expansion bag containing N_2 was attached to the reaction flask via a hypodermic needle which was inserted through one of the Neoprene caps. The other sealed neck was used to remove aliquots from the reaction mixture. Pyrolysis runs were carried out by placing the reaction flask (up to its neck) in a temp controlled (±0·3°) heating bath. The bath consisted of a Dow Corning 21OH fluid contained in a 3 l. stainless steel beaker wrapped with a heating element. The heating element was controlled by a thermoregulator which was inserted into the bath and attached to a Bath Control System. The temp control was maintained even at the highest temps employed. The progress of each pyrolysis reaction was determined by removing an aliquot from the mixture by a hypodermic syringe, dissolving the aliquot in acetone and analyzing the mixture on an F & M 500 temp-programmed gas chromatograph which was equipped with either a 2 ft or 4 ft Silicone Gum Rubber column (10% on 60/80 mesh Chromosorb White). The unit was operated at a 100 to 275° range. The helium flow through the column was 50 cc/min and the injection part temp was maintained at approximately 150°. Gas chromatographic analyses indicated the presence of a single reaction product from the pyrolysis runs carried out in the present study. The product was identified as III. A neat sample recrystallized from acetone yielded a product m.p. 183° (reported m.p.,[3] 181–182°). A mass spectrometric analysis indicated a mol wt of 268 (theoretical mol wt, 268). A microanalysis of the product agreed with the values previously reported for III.[3]

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