

# On the Thermal Decomposition of Thiobenzophenone *S*-Oxide<sup>1</sup>

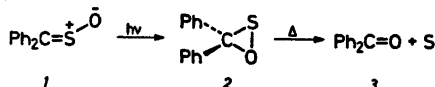
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Dedicated to Professor K. A. Jensen on his 70th birthday

Thiobenzophenone *S*-oxide (1) undergoes thermal decomposition in solution around 130 °C in the absence of oxygen to give benzophenone (3) and sulfur together with small amounts of thiobenzophenone (4) and sulfur dioxide. The reaction was studied by means of differential thermal analysis (DTA) and our results lead us to propose that two initial processes, a ring closure to give 3,3-diphenyl-oxathiirane and a "dimerization", are operating. Some evidence for a consecutive step, partially involving the starting material, was found. Decomposition of thiobenzophenone *S*-oxide in an oxygen atmosphere affords benzophenone and sulfur dioxide in high yields. In agreement with DT-analyses this reaction is formulated as an oxidation of thiobenzophenone *S*-oxide by molecular oxygen. Mass spectrometric evidence for carbene formation in the gas phase at temperatures above 230 °C has been obtained.

A study of the photolytic conversion of thiobenzophenone *S*-oxide (1) into benzophenone (3) and sulfur was reported recently, and evidence for the intermediacy of the thermally labile 3,3-diphenyl-oxathiirane (2) was presented.<sup>2</sup>

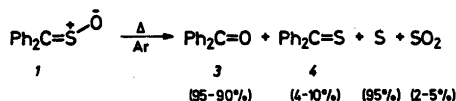


The results of CNDO/B calculations have been interpreted as showing that the electrocyclic ring closure of sulfine giving the three-membered oxathiirane is photochemically as well as thermally allowed.<sup>3</sup> The intermediacy of oxathiiranes has also been proposed for the

thermolysis of thiophosgene *S*-oxide<sup>4</sup> and thio-propanal *S*-oxide.<sup>5</sup> Furthermore, oxathiirane *S*-oxides have been postulated as intermediates in the thermal decomposition of thiocarbonyl *S*-dioxides (sulfenes).<sup>6</sup>

We report here a study of the thermal decomposition of thiobenzophenone *S*-oxide (1) by means of differential thermal analysis (DTA).<sup>7</sup> The analyses were performed and evaluated as described in the experimental section.

The sulfine 1 is stable at room temperature in the absence of light but decomposes in solution (0.15 M) at around 130 °C under an argon atmosphere to give benzophenone (3) (95 %), sulfur (95 %), thiobenzophenone (4) (4 %) and sulfur dioxide (2 %). At higher concentrations (0.5 M) the yields were 90, 95, 10 and 5 %, respectively. Yields were not altered by addition of sulfur or sulfur dioxide, or by continuous removal of sulfur dioxide by means of a stream of argon gas.



The DTA curves show only one peak over a wide range of concentrations and heating rates, excluding consecutive reactions with comparable rates.<sup>8</sup>

In diphenylmethane under argon, variation of the initial activation data and the mechanistic coordinates<sup>8-10</sup> was found by increasing the concentration of 1 from 0.12 to 0.52 M (cf. Table 1).

Table 1. Kinetic and mechanistic data derived from DTA experiments (argon atmosphere) with different concentrations of *I*. Heating rate  $m = 1.58 \pm 0.11$  K/min.

Conc. (M)	Reaction enthalpy $-\Delta H$ (kJ/mol)	Activation energy $E_a$ (kJ/mol)	$\log k$ ( $k$ in $\text{min}^{-1}$ )	Shape index $S_{\text{corr}}$	Reaction type index $M$ (J/mol K)	Specific temperature difference $um$ (K)
0.115	69.7	310.6	35.9	0.63	8.03	5.2
0.180	69.9	263.3	30.7	0.84	13.81	5.9
0.310	59.7	250.7	29.5	0.87	12.97	6.2
0.430	74.1	146.1	16.6	0.97	21.42	11.0
0.520	81.3	140.2	15.8	0.94	29.46	11.4

From these results (Table 1) it appears that competing first and second order reactions take place, as indicated by the increase in the shape index from 0.63 to 0.97 on increasing the initial concentration of *I*.<sup>10,11</sup> The shape indices for pure first and second order reactions are 0.55<sup>12</sup> and 1.1,<sup>13</sup> whereas the corresponding reaction type indices are 20.7<sup>12</sup> and 13.0<sup>13</sup> (J/mol K), respectively. However, the pronounced increase in the reaction type index from 8.03 to 29.46 (J/mol K) shows that the initial first and second order reactions are followed by secondary reactions, including reaction of the intermediates with the starting materials.<sup>10</sup>

Two pathways are feasible for the initial unimolecular reaction: (a) Ring closure giving the oxathiirane 2, or (b) CS bond rupture leading to diphenylcarbene and sulfur monoxide, followed by attack of sulfur monoxide on the carbene giving benzophenone and sulfur.

Attempts to trap diphenylcarbene by thermolyzing *I* in 1,1-diphenylethene, which has been found to be an excellent trapping agent for diphenylcarbene,<sup>14</sup> at 150 °C (argon), afforded less than 1 % of 1,1,2,2-tetraphenylcyclopropane (for comparison, 1,1,2,2-tetraphenylcyclopropane could be isolated in 32 % yield when diphenyldiazomethane was thermolyzed in 1,1-diphenylethene<sup>14</sup>). We have also been unable to detect "carbene products", e.g. tetraphenylethene, in the reaction mixtures in which diphenylmethane was used as solvent.

Further evidence against carbene formation was obtained from the thermolysis of *I* in gas phase in the ion source of a mass spectrometer. The intensity of the peak at  $m/e = 166$  ( $M^+ - \text{SO}$ )

relative to that of the peak at  $m/e = 214$  ( $M^+$ ) was almost constant in the temperature range from 50 to 150 °C. However, carbene formation at higher temperature ( $t =$  temperature of ion-source; sample temperature ca. 20 °C) is indicated by increase in the 166:214 ratio ( $r$ ):

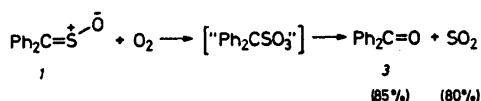
$t$ (°C)	50	120	150	230	250
$10 r$	1.5	1.6	1.8	3.2	6.5

On the basis of the above results we formulate the initial unimolecular reaction as a ring closure of the sulfine *I* to give the oxathiirane 2.

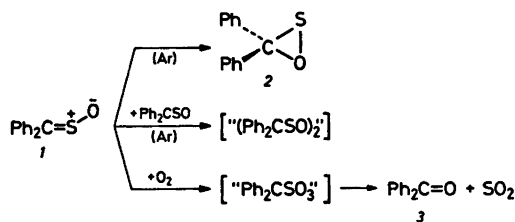
The bimolecular reaction apparently leads to a dimer (" $(\text{Ph}_2\text{CSO})_2$ ") which may decompose further. Walter and Bauer have recently reported a related study of the thermal decomposition of tertiary thioamide *S*-oxides, in which they observed the formation of amide, thioamide and sulfur monoxide.<sup>15</sup> However, independent information concerning the decomposition of the dimer is not available.

Thermolysis of *I* under oxygen was found to proceed ca. 4 times faster than under argon. Benzophenone and sulfur dioxide were detected in 85 and 80 % yield, respectively and DT-analyses revealed nearly first order kinetics [ $E_a = 181.3 \pm 5.4$  kJ/mol,  $\Delta H = -69.5 \pm 9.2$  kJ/mol,  $S_{\text{corr}}: 0.52 - 0.61$  and  $M: 19.50 - 17.91$  (J/mol K)].

The reaction is therefore formulated as an oxidation of the sulfine *I* by molecular oxygen, analogous to the reaction between oxygen and thiobenzophenone.<sup>16</sup>



The initial reactions occurring in the thermal decomposition of thiobenzophenone *S*-oxide in solution are thus summarized in Scheme 1.



Scheme 1.

At higher temperatures in the gas phase CS bond rupture leading to diphenylcarbene and sulfur monoxide is probably dominant.

The above mentioned consecutive reactions may involve either the starting material or secondary products such as sulfur allotropes, but it is not possible to further elucidate this reaction sequence on the basis of present data.

## EXPERIMENTAL

All reactions were carried out in the absence of light to prevent the known photolytic decomposition<sup>2</sup> of *I*.

**Thermolysis of thiobenzophenone *S*-oxide (1).** Argon or oxygen was bubbled through 10 ml solutions of *I* (0.15–0.50 M) in diphenylmethane for 20 min at 30 °C. The solution was then heated to 150 °C (while maintaining the gas flow) for 30 min. After cooling to room temperature, 10 ml of dichloromethane containing octadecanol (as internal GLC standard) was added and the mixture was submitted to GLC analysis (Pye Unicam 104 chromatograph with dual flame-ionization detector, in conjunction with a Varian Aerograph 477 electronic integrator; 2 m × 6 mm column of 3 % OV1 on Gaschrom Q (100–120 mesh); nitrogen as carrier gas). From the chromatograms the amounts of unconverted *I*, benzophenone (3), and thiobenzophenone (4) could be calculated (calibration curves). The yields of sulfur dioxide were determined by iodine/thiosulfate titration<sup>17</sup> (average of several experiments). The sulfur formed was isolated by filtration of the final mixture, washed with ether and dried *in vacuo*.

The relative rates of benzophenone formation during the thermolyses under argon or oxygen atmosphere, respectively (equal concentrations of *I*) were calculated on the basis of the benzophenone yields found by GLC.

**Differential thermal analysis (DTA).** (a) **Equipment.** A modified version of the solution DTA apparatus<sup>18</sup> developed in Mülheim/Ruhr<sup>19</sup>

was employed. The instrument has Teflon stirring disks, copper/constantan thermocouples and 5 ml test tubes installed in an alumina heating block for the sample and reference solutions. Temperatures and temperature differences were monitored with a two-channel recorder (model BD 6, Kipp and Zonen, Delft, The Netherlands; voltage measurement range 0.02–5 mV).

(b) **Procedure.** A solution of thiobenzophenone *S*-oxide (*I*) and the pure solvent (diphenylmethane, reference glass) were thermostated at 350 K. Constant heating rates between 0.75 and 1.5 K/min could be employed, and 1.5 K/min was adopted as standard heating rate.

(c) **Evaluation.** The DTA curves were analyzed using a FORTRAN IV program and a PDP 10 computer (Digital Equipment Corp., Maynard, Mass., U.S.A.).<sup>19</sup> The algorithm is based on the Borchardt-Daniels equation<sup>7</sup> and the Arrhenius law, and yields both initial and overall activation parameters. The program takes account of temperature dependence of the cell constant, *c*, and the decreasing significance of the rate constants as a function of increasing extent of reaction. Furthermore, the half-width, *h*, and the shape index, *S*, of the DTA curves are extrapolated to *c* → ∞ and zero temperature change, corresponding to a reaction without temperature feedback and with the same activation parameters.<sup>12</sup>

The reaction type index, *M*, is calculated from eqn. 1:

$$M = \frac{mRu (\ln 10)^2}{h_{\infty} n^{0.52}} \quad (1)$$

where *n* = reaction order, *h*<sub>∞</sub> = corrected half width, *m* = heating rate, and *u* = specific time.<sup>12,13</sup>

Non-compatibility of a reaction with an elementary first- or second order process is indicated:

1. By the mechanistic data, since *S* = 0.55 and *M* = 20.7 J/mol K for a first and *S* = 1.10 and *M* = 13.0 J/mol K for a second order curve.

2. By correlation coefficients for the straight lines over the entire range of < 0.97. For elementary reactions a value of 0.99–1.00 is usual.

3. By a dependence of the specific time, *u*, on the reactant concentration.

4. By differences in the *u* values for the initial and the complete reaction range.

For complex processes the interpretation is based on comparison with the results of model calculations.

The enthalpies were obtained from the integrated curve areas:

$$\Delta H = \frac{cC_p}{n_0} \int_0^{\infty} \theta dt \quad (2)$$

$\Delta H$  = reaction enthalpy, *C*<sub>p</sub> = heat capacity, *n*<sub>0</sub> = amount of reactant,  $\theta$  = measured temperature difference.

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