The Photochemistry of tetramethyl-3-thio-1,3-cyclobutanedione

Mason Ming-Sun Shen

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THE PHOTOCHEMISTRY OF
TETRAMETHYL-3-S-H10-1,3-CYClOBUTANEDIONE

BY
MASON MING-SUN SHEN

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota
State University
1972
This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Head, Chemistry Department

Date
TO MY PARENTS
THE PHOTOCHEMISTRY OF
TETRAMETHYL-3-THIO-1,3-CYCLOBUTANEDIONE

Abstract

MAISON MING-SUN SHEN

Under the supervision of Professor James J. Worman

The photochemical reaction of tetramethyl-3-thio-1,3-cyclobutanedione in the presence of oxygen and light yields tetramethyl-1,3-cyclobutanedione and sulfur dioxide.

The kinetics and mechanism of the reaction have been studied thoroughly in different solvents and at different concentrations. Results of this study indicate that the mechanism probably involves singlet oxygen and ground state thione although triplet thione and triplet oxygen are not completely eliminated.
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INTRODUCTION

The first law of photochemistry, formulated in the works of Grotthus (1817) and Draper (1843) more than a century ago, states: Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule. The law and its consequences are commonly taken for granted by photochemists today. Until the advent of quantum mechanics, the effect of light on matter was not properly understood. As a result, during the primeval age of photochemistry (-1920) numerous and wondrous photochemical reactions were discovered, but both useful application of these results and formulation of a unifying theory were lacking. From 1920 to 1950, photochemistry was perhaps considered the realm of the physical chemist who studied the details of photoreactions in the gas phase. The availability of new spectroscopic and analytical techniques during the 1950's to the present date and the development of important theories concerning electronically excited states, reduced the difficulty in characterizing the complex products of photoreactions and gave promise of control of photochemistry.

In the last decade the chemical literature was to a very large extent crowded with studies involving the controlled photochemistry of organic compounds, particularly those containing carbon and hydrogen only. More recently many studies have been extended to those compounds containing heteroatoms such as oxygen, nitrogen, and sulfur.
The photochemistry of carbon π bonded to oxygen in unconjugated ketones has been exhaustively studied\textsuperscript{10}. Similar studies on Azo-methines (carbon π bonded to a nitrogen) have also been reported\textsuperscript{15}. Although a certain amount of photochemistry has been done on compounds containing the conjugated thiones\textsuperscript{5}, there are no documented reports on the photochemistry of carbon π bonded to sulfur in molecules containing this system as a simple unconjugated chromophore.

The preparation and reactions of unconjugated thiones are documented elsewhere\textsuperscript{16} and in this work it has also been shown the 1,3-diphenyl-3-prepanthione (1) undergoes an accelerated dimerization in the presence of light\textsuperscript{7} to give the ditheitane (2).

\[
\text{S H}_2 \quad \text{S H}_2
\]
\[
\text{H}_2 \quad \text{H}_2
\]

\[
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C}
\]
\[
\text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\]

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph}
\]

\[
\text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2
\]

\[
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C}
\]
\[
\text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\]

\[
\text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2
\]

The instability of 1 and its ability to dimerize in the dark make it impossible to establish the reaction as a clear cut photochemical phenomenon of the thiocarbonyl chromophore. This accompanied by the fact that cyclohexanethione (3) was known to undergo dimerization by both ionic and free radical mechanisms\textsuperscript{6} prompted us to seek a more stable unconjugated thione.
In 1967 the synthesis of tetramethyl-3-thio-1,3-cyclobutanedione (4) was reported. It is a bright red crystalline solid which, unlike most other unconjugated aliphatic thiones, shows no tendency to dimerize or polymerize at ordinary temperatures, and is very easy to handle. It sublimes readily at room temperature and has characteristic, somewhat camphorous odor. It is a very good compound to use for photochemical studies of the unconjugated thiocarbonyl chromophore because we do not have to worry about the complications of dimerization, hydrolysis, etc.

The photochemistry of tetramethyl-1,3-cyclobutanedione (5) has been investigated thoroughly and therefore represents a base from which to make a comparison. The photolysis of tetramethyl-1,3-cyclo-
butanedione by irradiation with 336 nm light leads to a cleavage and forms tetramethylcyclopropanone, further reaction will produce tetramethylethene$^{11,12}$.

It would seem realistic to expect the photolysis of tetramethyl-3-thio-1,3-cyclobutanedione (4) at a lower wavelength of light at 520 nm (the $n\rightarrow\pi^*$ transition of the $\text{C=S}$ group, compare to the $n\rightarrow\pi^*$ transition of carbonyl group at 320 nm) to give similar results.
Another photochemical study on the carbon sulfur double bond which appeared in the recent literature is the photochemical reaction of sulfines\textsuperscript{13,14}. Sulfines undergo a photodesulfurization in the presence of singlet oxygen. From this reaction we might also expect the photolysis of tetramethyl-3-thio-1,3-cyclobutanedione (4) in the presence of oxygen and sensitizer to undergo a photodesulfurization reaction as follows:

\[
\begin{align*}
\text{C} &= \text{S} + \text{O}_2 \\
\text{hv} & \quad \text{sens.} \\
\text{C} &= \text{C} + \text{SO}_2
\end{align*}
\]

\[
\begin{align*}
o &= \bigcirc \bigcirc \bigcirc &= \text{S} + \text{O}_2 \\
(4) & \quad \rightarrow \\
\bigcirc \bigcirc \bigcirc &= \bigcirc \bigcirc \bigcirc \\
\bigcirc \bigcirc \bigcirc & \quad \bigcirc \bigcirc \bigcirc \\
(5) & \quad \text{O} = \bigcirc \bigcirc = \text{O} + \text{SO}
\end{align*}
\]
One could also expect dimerization of 4 similar to that reported for 1 to give the unusual spiro compound 2.

From the foregoing discussion it is evident that the photochemistry of the simple unconjugated thiocarbonyl chromophore has avoided investigation. In order to understand more of this system we undertook our investigation.
PURPOSE

This project was undertaken in an attempt to increase our knowledge of photochemical reactions about compounds containing the unconjugated thiocarbonyl chromophore. The main areas of interest and those studied include the reaction mechanisms and kinetic studies of the photochemistry of tetramethyl-3-thio-1,3-cyclobutanedione.
RESULTS AND DISCUSSION

I. THE PREPARATION AND PURIFICATION OF TETRAMETHYL-3-THIO-1,3-CYCLOBUTANEDIONE

The method reported by Elam and Davis for the synthesis of tetramethyl-3-thio-1,3-cyclobutanedione was used. Involved is a reaction of tetramethyl-1,3-cyclobutanedione with phosphorus pentasulfide in pyridine.

\[
0 = \begin{array}{c}
\text{O} \\
\end{array} + P_2S_5 \rightarrow S = \begin{array}{c}
\text{O} \\
\end{array} + S = \begin{array}{c}
\text{O} \\
\end{array}
\]

\[(5) \quad (4) \quad (6)\]

After following the reported method, it was found that washing the products with a solution of 10% sodium hydroxide did not remove tetramethyl-1,3-cyclobutanedithione (6) completely and besides the monothione 4 will react with sodium hydroxide to lower the percentage yield. Instead of following Elam's method completely, a little change was made. If one omits the wash procedure, and chromatographs the products by going through a silicic acid column it will lead to a purer product and the by product dithione 6 can be saved for future use. Another benefit of this revision is that the starting ketone 5 is removed completely. This modified method works mainly because the
characteristic color of the products allows for easy separation on the column. The monothione 4 is red, the dithione 6 is orange-red and the diketone 5 is colorless.

II. THE PHOTOCHEMICAL REACTION OF THE MONOTHIONE (4)

The photochemical reaction of tetramethyl-3-thio-1,3-cyclobutanedione (4) in the presence of oxygen and light yields tetramethyl-1,3-cyclobutanedione (5).

\[
\text{O} \equiv \text{S} + \text{O}_2 \xrightarrow{h\nu} \text{O} \equiv 0 + \text{SO}
\]

The reaction was first run in an isopropyl alcohol solution. The light source was a 250 watt R 40/3 Westinghouse Lamp with no emission below 400 nm. Visible and ultraviolet spectra were taken every twelve hours or twenty-four hours during the reaction. The spectra 1, 2, and 3 in the Appendix show the successive changes in the absorption spectrum of 0.098 M monothione 4 in isopropyl alcohol at twelve hour intervals. One can observe easily the disappearance of the peaks centered at 520 nm and 228 nm, corresponding to the monothione 4 and also the formation of the sulfur dioxide intense peak centered at 270 nm. An isosbestic point was found around 245 to 255
nm and this indicated that the diketone 5 was the only major product formed. Similar phenomena appeared in hexane and carbon tetrachloride solutions. An example of gas liquid chromatographs, nuclear magnetic resonance spectra and infrared spectra following the reaction of a 0.089 M carbon tetrachloride solution are shown in the Appendix. In the gas liquid chromatographs the peak of retention time 770 sec is for the monothione 4 and that of 445 sec is for the diketone 5. The decrease of the peak for 770 sec and increase of the peak for 445 sec indicated the decrease of concentration of monothione (4) and increase of the concentration of diketone 5 respectively. The estimated yield from this chromatograph is around 71%. In nuclear magnetic resonance spectra, the chemical shift changes from 1.33 ppm to 1.20 ppm corresponding to the change from the monothione 4 to diketone 5. The yield is about 75% estimated from these spectra. The infrared spectra shows the disappearance of the 1800 and 1285 cm⁻¹ bands and the increase the intensity of 1740, 1715, 1687 cm⁻¹ as the reaction proceeds from the monothione 4 to the diketone 5.

The reaction was run in the dark and there was no change in the visible absorption spectra of the monothione 4 which establishes the reaction is dependent on light. The reaction was also run in the presence of light but bubbling nitrogen through instead of oxygen, and no change occurred in the visible spectra of 4. The conclusion can be made that this reaction depends on both the presence of oxygen and light.
Using an MPF spectrophotometer the fluorescence spectra of the monothione 4 were taken in various solvents. In the presence and absence of oxygen at room temperature, no measurable amount of fluorescence could be detected by exciting the monothione 4 at 500 nm and observing emission from 500 to 800 nm. If the monothione is going to the singlet state, self-quenching must be taking place since no radiation process was recorded. A similar non-radiative phenomenon was noted by taking the phosphorescent spectrum at 77°K in EPA. The possibility exists that the triplet of the monothione 4 is below 800 nm and therefore would not be detectable with available instrumentation. It would appear that fluorescence and phosphorescent spectra will not establish whether the reaction proceeds via the singlet or triplet state. The low temperature fluorescence did show a very weak emission at 540 nm but this data must be interpreted with some caution. It could mean that there is some singlet monothione 4 being generated under these conditions where self-quenching would be eliminated but small amounts of impurities also cause such low temperature emission.

Data obtained from the Turner Fluorometer indicated an emission at 660 nm in the presence of oxygen. No such emission was noted in the absence of oxygen. There is no explanation for this at present.

Using 0.101 M cyclohexadiene, a triplet quencher, triplet energy 52.5 kcal\textsuperscript{18}, in the isopropyl alcohol solution 0.096 M in monothione will increase the reaction rate, and the reaction will be complete in 2.5 days. This is an indication that the reaction probably goes
through the singlet state to some extent. A possibility is that the singlet monothione $\text{4}$ sensitizes cyclohexadiene to the triplet which in turn sensitizes the oxygen to the singlet which will give a larger concentration of singlet oxygen to react with ground state thione and therefore increase the reaction rate.

Singlet oxygen$^{19}$ was generated by reacting hydrogen peroxide and sodium hypochlorite$^{20}$, and was reacted with the monothione. The reaction was complete in five minutes and gave the same product $5$. The monothione $4$ was also shaken separately with hydrogen peroxide and with sodium hypochlorite and no reaction took place. This is strong evidence that the reaction can go via a singlet oxygen mechanism.

Dye-photosensitizer$^{21}$, methylene blue, was added into a solution of monothione $4$ in an attempt to sensitize oxygen to a singlet state, but it reacted with the monothione $4$. No information could be obtained from this reaction.

III. THE RATE OF THE REACTION AND KINETIC STUDIES

The reaction rate varies in different solvents and the presence of sensitizer or quencher. The 0.098 M isopropyl alcohol solution of the monothione $4$ undergoes the photodesulfurization reaction in three days. A similar reaction of 0.101 M monothione $4$ in hexane solution and 0.89 M in carbon tetrachloride solution took five days and one day, respectively. The different rates of the reaction in the different solvents could be due to a solvent effect. The most important factor of the solvent effect however is the solubility of oxygen in the different solvents. The solubility of oxygen$^{17}$ in carbon tetra-
chloride is the largest of the three, isopropyl alcohol is next and hexane is the lowest. This appears to be the main reason why the reaction will go the fastest in carbon tetrachloride, slower in isopropyl alcohol and the slowest in hexane.

A 1.02 M carbon tetrachloride solution of the monothione $4$ under the same conditions, shows no evidence that a reaction takes place even after four days. This probably is also related to the oxygen solubilities. A more detailed explanation will be given in a later section.

The order of the reaction being investigated was based mainly on kinetic studies. Because of the high volatility of hexane and carbon tetrachloride, it is very hard to get a stable decreasing peak in the ultraviolet spectra and so, this reaction was studied only in isopropyl alcohol solution. The main calculation was done by an IBM 360 computer. The program language used is PL/I. A completed program is presented in the Appendix. The data obtained are listed in Table I through VIII, where $T$ is the time in hours from the beginning of the reaction, $A$ is the absorbance, $C_T$ is the concentration of the monothione $4$ in molarity, $C_K$ is the concentration of the diketone $5$ in molarity, and $K$ is the rate constant for a first order reaction or a zero order reaction in reciprocal hour or molarity per hour, respectively.
### TABLE I. KINETIC DATA FOR A FIRST ORDER REACTION

PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPAÑOL IN THE PRESENCE OF OXYGEN

<table>
<thead>
<tr>
<th>T (HR)</th>
<th>A (M)</th>
<th>CT (M)</th>
<th>CK (M)</th>
<th>K (HR-1)</th>
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<tbody>
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<td>0</td>
<td>.938</td>
<td>.097</td>
<td>.018</td>
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<td>.079</td>
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<td>.055</td>
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### TABLE II. KINETIC DATA FOR A FIRST ORDER REACTION

PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPAÑOL IN THE PRESENCE OF OXYGEN

<table>
<thead>
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<th>T (HR)</th>
<th>A (M)</th>
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<th>CK (M)</th>
<th>K (HR-1)</th>
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### TABLE III. KINETIC DATA FOR A FIRST ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROpanol IN THE PRESENCE OF OXYGEN**

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<th>T (HR)</th>
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### TABLE IV. KINETIC DATA FOR A FIRST ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROpanol IN THE PRESENCE OF OXYGEN AND CYCLOHEXADIENE**

<table>
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### TABLE V. KINETIC DATA FOR A ZERO ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPA NOL IN THE PRESENCE OF OXYGEN**

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<th>Time (HR)</th>
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### TABLE VI. KINETIC DATA FOR A ZERO ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPA NOL IN THE PRESENCE OF OXYGEN**

<table>
<thead>
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### TABLE VII. KINETIC DATA FOR A ZERO ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPANOL IN THE PRESENCE OF OXYGEN**

The concentration of the solution is $0.0104663 \text{ M}$

<table>
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### TABLE VIII. KINETIC DATA FOR A ZERO ORDER REACTION

**PHOTODESULFURIZATION OF MONOTHIONE IN 2-PROPANOL IN THE PRESENCE OF OXYGEN AND CYCLOHEXADIENE**

The concentration of the solution is $0.0957513 \text{ M}$

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<td>0.523</td>
<td>0.054</td>
<td>0.042</td>
<td>0.00350000</td>
</tr>
<tr>
<td>24</td>
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<td>0.035</td>
<td>0.061</td>
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</tr>
<tr>
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<td>0.082</td>
<td>0.00170833</td>
</tr>
<tr>
<td>60</td>
<td>0.005</td>
<td>0.001</td>
<td>0.095</td>
<td>0.00158333</td>
</tr>
</tbody>
</table>
FIG I
Photodesulfurization of Monothione (1)

FIG II
Photodesulfurization of Monothione (2)
FIG III
Photodesulfurization of Monothione (3)

FIG IV
Photodesulfurization of Monothione (4)
The calculation is based on the ultraviolet spectra. The \( n \rightarrow \pi^* \) transition of carbon sulfur double bond has an absorption at 520 nm with a \( \varepsilon \) equal to 9.65 and the calculation is based on the decrease of this peak as a function of decrease the concentration of monothione \( \text{M} \). The expression is as follows:

\[
CT = \frac{A_t}{\varepsilon_T \times l}
\]

where \( CT \) is the concentration of monothione

\( A_t \) is the absorption at 520 nm at time \( t \)

\( \varepsilon_T \) is the molar absorptivity of monothione

\( l \) is the path length through the sample and is equal to 1.

The concentration of diketone \( D \) can be expressed by the formula below:

\[
CK = \frac{A_o - A_t}{\varepsilon_T - \varepsilon_K}
\]

where \( CK \) is the concentration of diketone

\( A_o \) and \( A_t \) are the absorption at time \( o \) and \( t \) respectively

\( \varepsilon_T \) and \( \varepsilon_K \) are the molar absorptivities of monothione and diketone, respectively.

The first order rate constant and zero order rate constant are calculated based on the following equations:

\[
K_1 = \frac{1}{t} \log \frac{A_o}{A_t}
\]

\[
K_0 = \frac{1}{t} \cdot \frac{A_o - A_t}{\varepsilon_T}
\]
The plots of time vs concentration (FIG. I and II) show that the reaction of 0.098 M and 0.075 M monothione solution in the presence of oxygen are zero order in monothione \( \frac{1}{2} \). And the plots of time vs log concentration show that the reaction of 0.010 M monothione solution and 0.097 M monothione solution in the presence of cyclohexadiene are first order in monothione \( \frac{1}{2} \). The detailed explanation of this data will be in the reaction mechanism section.

IV. THE IDENTIFICATION OF THE PRODUCTS

The identification has been done by infrared spectroscopy, nuclear magnetic resonance spectroscopy, gas liquid chromatography and by mixed melting point. The identification of the sulfur dioxide, however, was a problem. The first indication of the formation of sulfur dioxide was found in the condensate which resulted from the evaporation of the isopropyl alcohol from the reaction of \( \frac{1}{2} \) in isopropyl alcohol in the presence of oxygen and light. The ultraviolet spectrum of the condensate is shown in FIG. V (b). The ultraviolet absorption maximum at 270 nm resembled the spectral properties of an authentic sample of \( \text{SO}_2 \), FIG. V (a), which had an absorption maximum at 276 nm. The 6 nm blue shift in the reaction sample probably is due to the slight difference in polarity of the two solutions. The other evidence for the production of sulfur dioxide came from wet chemical techniques. The gas coming out of the reaction during the reaction interval was trapped by a 1% sodium hydroxide and this solution gave much information. After neutralization by hydrochloric acid, the solution
FIG V  Ultraviolet spectra of products (b) and authentic sulfur dioxide (a).
was tested by using an iodine solution and it decolorized the iodine. The reaction must be as follows:

\[ \text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \]

\[ \text{Na}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HI} \]

This is additional evidence for the presence of sulfur dioxide.

The sodium hydroxide used to trap the gas coming out of the reaction was also tested by using barium hydroxide and a white precipitate formed. This white precipitate dissolved when the solution was acidified using hydrochloric acid. The reaction is as follows:

\[ \text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \]

\[ \text{Na}_2\text{SO}_3 + \text{Ba(OH)}_2 \rightarrow \text{BaSO}_3 \downarrow + 2\text{NaOH} \]

The barium sulfite is known to be soluble in acid solution. This data strongly supports the presence of sulfur dioxide as a reaction product.

V. THE MECHANISM OF THE REACTION

Two possible mechanisms are summarized in Scheme 1 and in Scheme 2.

In Scheme 1, the thione 4 is first excited to the singlet state. The singlet state thione can act as a sensitizer to excite triplet oxygen to the singlet state and the singlet thione will go to the triplet state. The singlet oxygen will then react with ground state thione and could form a reaction intermediate 8. This intermediate 8 could decompose immediately to form the products diketone 5 and sulfur
\[ \text{Scheme 1} \]
\[ \begin{align*}
O &= \text{hv} \rightarrow O^+ \\
O^+ + 10-0^+ &\rightarrow O^+ \\
S + 10-0^+ &\rightarrow S + O^+ \\
SO + \frac{1}{2} O_2 &\rightarrow SO_2
\end{align*} \]

Scheme 2
monoxide. The sulfur monoxide can then react with the oxygen stream and form sulfur dioxide.

In Scheme 2, the monothione 4 is excited to the singlet state and then after an intersystem crossing produces the triplet state. The triplet thione can react with the oxygen stream which is in a triplet state and give the intermediate 8. This will collapse to produce the diketone 5 and sulfur monoxide which leads to sulfur dioxide.

The reaction of singlet oxygen\textsuperscript{20} in the presence of monothione 4 both in the dark and under light is completed in five minutes and gives diketone 5. This means that the thione will react with singlet oxygen readily even in the ground state.

An increase in the concentration of the thione will slow down the reaction and this is probably due to the limited solubility of oxygen in the solvent. This would give a certain insignificant amount of singlet oxygen to react with excess thione and no detectable amount of products would be found. Self-quenching of the thione at large concentration could also inhibit the reaction. The kinetic data indicated that the reaction is a zero order reaction in monothione 4, but from the mechanisms it should be a bimolecular reaction by reacting monothione 4 with singlet oxygen (Scheme 1) or by reacting triplet monothione with triplet oxygen (Scheme 2). An explanation of this apparent anomalous behavior could be as follows: the low
Intensity lamp only produces a limited amount of photons and, therefore, the rate determining step could be the first step, that is, to excite ground state monothione $\frac{4}{4}$ to the first excited singlet. The comparatively large excess amount of monothione $\frac{4}{4}$ makes the reaction rate only dependent on the number of photons and this is a constant throughout the reaction. This makes the reaction a pseudozero order in monothione $\frac{4}{4}$. Only at the very end of the reaction does it appear to be first order in monothione $\frac{4}{4}$ or in other words at a very low monothione $\frac{4}{4}$ concentration. (See FIG. I through IV). At this time, the third step is the rate determining step.

The fact that the presence of cyclohexadiene will increase the reaction rate is seen at first somewhat anomalous. If it were quenching the triplet of the thione, it must certainly slow down the reaction and this is definitely not observed. The kinetic data suggest that in the presence of cyclohexadiene the reaction is first order. This could be interpreted to mean that cyclohexadiene is helping to generate more singlet oxygen. A plausible scheme is shown below:

\[
\begin{align*}
on\rightarrow \square = S \xrightarrow{\text{hv}} & \quad \quad o
\end{align*}
\]

\[
\begin{align*}
on\rightarrow \square = S + C & \quad \quad o = \square = S
\end{align*}
\]

\[
\begin{align*}
C + O_2 & \quad \quad \quad \quad O_2 + C
\end{align*}
\]
Sufficient singlet oxygen would then be available to allow for first order kinetics.

The oxygen solubility dependent rate of the reaction also supports the singlet oxygen mechanism. If the reaction goes through triplet thione reacting with triplet oxygen (Scheme 2), the comparatively large excess amount of oxygen (as we suggested to explain the kinetic data) should not affect the reaction rate. This is contrary to what we observed.

It is impossible from the present data to completely eliminate the reaction of triplet thione with triplet oxygen but most of the data suggests a singlet oxygen mechanism.

In order to eliminate triplet oxygen, we must determine the triplet energy of the thione and then choose a quencher with slightly lower energy. Cyclohexadiene has a triplet energy of 52.5 kcal (550 nm) and this is too high for the triplet of the thione.

An experiment which would establish that excited thione is definitely generating singlet oxygen would be to coat the inside of a glass tube with a thin layer of thione and then pass oxygen gas through the tube while exciting the thione at 520 nm. The effluent oxygen could then be passed into a singlet oxygen acceptor such as anthracene to form a well known addition product.

Detailed work on the dithione 6 will also give some interesting information. Some preliminary work indicated a hexane solution of dithione 6 in the presence of oxygen and light will react twice as
fast as the monothione under similar conditions. This suggests that the two thiocarbonyl groups could excite twice the amount of singlet oxygen and this would increase the reaction rate.
CONCLUSIONS

The photodesulfurization of tetramethyl-3-thio-1,3-cyclobutanedione has been thoroughly studied. The products were identified as tetramethyl-1,3-cyclobutanedione and sulfur dioxide. The kinetic studies indicated that the reaction in isopropyl alcohol in the presence of oxygen is zero order in monothione and this is probably due to the limited amount of singlet oxygen generated by the singlet thione. A first order reaction in monothione is obtained in the presence of cyclohexadiene. The mechanism of the reaction probably involves singlet oxygen although a triplet oxygen mechanism is not completely eliminated. The photochemistry of diketone has also been studied and shows that a similar reaction takes place to give the diketone, but more detailed studies must be done before photodesulfurization of thione can be defined as a general reaction.
EXPERIMENTAL

DESCRIPTION OF INSTRUMENTATION:

Visible and ultraviolet spectra were run on a Beckman DK-2A ratio recording spectrophotometer. Samples were run in silica cells as dilute solutions in various solvents.

Infrared spectra were run on either the Perkin-Elmer 700 Infrared Spectrophotometer or the Perkin-Elmer 521 grating Infrared Spectrophotometer. Samples were run neat, as nujol mulls, or as KBr pellets. KBr pellets were prepared on a Carver Laboratory Press Model B.

Nuclear magnetic resonance spectra were obtained by use of a Varian A-60 analytical nuclear magnetic resonance spectrometer. Samples were run neat or as solutions in carbon tetrachloride.

Gas liquid chromatography was run on a Beckman GC-2A. Either nitrogen or helium was used as the carrier gas at a gas pressure 15 psi. The temperature was 160°C. The column used was a 1/4 inch by 10 feet aluminum column packed with 15% SE-30 on 42-60 mesh chromosorb P.

Melting points were obtained using a Thiele tube containing paraffin oil, and are uncorrected.

Fluorescence and phosphorescence spectra were run on a Perkin-Elmer MPP-2A spectrophotometer, at the University of Wyoming, Laramie, Wyoming.

The experimental work was performed at South Dakota State University, Brookings, South Dakota.
THE PREPARATION OF TETRAMETHYL-3-THIO-1,3-CYCLOBUTANEDIONE (4):

The procedure used here was a modification of the one used by Elam and Davis.

A solution of 150 g (0.67 mole) of phosphorus pentasulfide (Fisher Scientific Co.) and 210 g (1.5 mole) of tetramethyl-1,3-cyclobutanedione (Aldrich Chemical Co.) in 500 ml of pyridine was refluxed with stirring. The reaction was stopped after 40 minutes. The hot solution was allowed to settle. The settled solution was deanted. The solid was heated to boiling with 125 ml of fresh pyridine, then cooled and decanted. The combined pyridine solutions were distilled rapidly without fractionating at 35 to 50 mm (Hg) in order to remove the last of the inorganic material. The pyridine was removed in vacuo (30 mm Hg) by fractional distillation (FIG. VI) until the temperature reached 60°C. The distillation residue was taken up in 150 ml of warm hexane, and the solution was decanted from a small amount of tar and cooled to 20°C. The crystals of diketone 5 were removed by filtration and washed with a small amount of hexane until all the red color had been removed. The filtrate was distilled and a fraction collected between 160-170°C.

THE PURIFICATION OF TETRAMETHYL-3-THIO-1,3-CYCLOBUTANEDIONE (4):

The products obtained above are not very pure and usually are a mixture of the monothione 4, dithione 6 and diketone 5, because of the similarity of the boiling points. The best way to separate them is to
1. Heating Mantle
2. 250 ml Distillation Flask
3. Distillation Head (40 cm 2.5 cm) glass packed
4. 5 mm 7 mm glass tubings
5. Thermometer
6. Cooling water intake
7. Cooling water outlet
8. Vacuum pump
9. Cooling jacket
10. 250 ml Distillation Flask

FIG VI The Column Distillation Equipment for Pyridine in preparation of tetramethyl-3-thio-1,3-cyclobutanedione.
use column chromatography. A column, 80 cm long with a 3 cm diameter, was packed half full with silicic acid (Matheson Coleman & Bell) and hexane used as the eluting solvent. The crude products were dissolved in a minimum amount of hexane. The hexane solution was poured into the column. After the red solution was all run onto the silicic acid column, the sample was eluted with hexane. About one hour later, the solution was separated into three layers. The first lower orange layer is the dithione 6, the second red layer is the monothione 4 and the last light yellow layer is the diketone 5. To separate 10 g of the products usually takes elution with 5 liters of hexane over a three day period. The purified solutions were then evaporated under vacuum and in the case of the monothione a red solid was obtained, yield 50%. A 10% yield of the dithione 6 was also obtained. The remaining material was mainly unreacted starting material. The products were checked by gas chromatography and NMR. If the samples showed contamination, a second run through the column was necessary.

The purified monothione 4 melted at 157-158°C; infrared absorptions at 1800, 1770, 1450, 1290 and 1125 cm$^{-1}$; nmr spectrum in CCl$_4$, singlet at 1.33 ppm; visible and ultraviolet absorptions in hexane, $\lambda_{\text{max}}$ 228 nm ($\varepsilon = 8700$), 270 nm (300), 318 nm (100), and 520 nm (9.65).

A purified dithione 6 melted at 123.5-125°C; infrared absorptions at 1460, 1265 and 1075 cm$^{-1}$; nmr spectrum in CCl$_4$, singlet at 1.40 ppm; visible and ultraviolet absorptions in hexane $\lambda_{\text{max}}$ 227 nm ($\varepsilon = 21600$), 298 nm (409), and 500 nm (22.4).
PHOTODESULFURIZATION OF TETRAMETHYL-3-THIO-1,3-CYCLOBUTANEDIONE (4):

A method was devised for our purposes where irradiation of the solution could take place through a Kimax filter and in the presence of a stream of oxygen (FIG. VII). Oxygen (Linde), was first passed through a reducing valve at 5 lbs. per square inch of pressure. Then it was forced through a calcium chloride drying tube to remove any trace of water, finally it was bubbled through the reaction tube shown in Figure VII.

The reaction tube contains two parts, one is a L tube with a glass frit (Pyrex 20 M) and 19/22 female glass joint in one end and another part is a 19/22 Kimax reflux condenser where the glass frit acted as a support. The reaction solution was supported by the oxygen stream to prevent its dropping. The oxygen stream was passed through another reflux condenser containing glass beads in order to condense the solution which was being carried out by the oxygen stream. The gas coming out was conducted by glass tubing into a flask which contained 100 ml of 1% Na OH solution.

The solutions used in this experiment were: isopropyl alcohol solutions, hexane solutions and carbon tetrachloride solutions, a summary of these reactions is shown in Table IX.
FI G VII  The Photodesulfurization Apparatus
TABLE IX: Summary of photodesulfurization of tetramethyl-3-thiol-1,3-cyclobutanedione

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (M)</th>
<th>Sensitizer</th>
<th>Completion Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl alcohol</td>
<td>0.098</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.075</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.011</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.096</td>
<td>0.101 M cyclohexadiene</td>
<td>2.5</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.101</td>
<td>0.099 M methylene blue</td>
<td>-</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.101</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.010</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.089</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.009</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>
All these reactions were run in the presence and absence of light and in the presence and absence of oxygen except for the carbon tetrachloride solution.

The reaction was followed by ultraviolet and visible spectroscopy and gas liquid chromatography. Samples for analysis were taken every twelve or twenty-four hours.

THE ISOLATION OF THE TETRAMETHYL-1,3-CYCLOBUTANEDIONE (5):

After the reaction was completed as determined by ultraviolet and visible spectroscopy, that is the disappearance of the absorption at 520 nm and at 228 nm was complete, the solution was evaporated at room temperature in vacuo and the concentrated solution was left in the cold room for twenty-four hours. A yellowish product crystalized out. The compound was then recrystallized from warm hexane. The infrared, nuclear magnetic resonance spectra and gas liquid chromatographic retention time were recorded and all of them indicated the product to be identical with an authentic sample of the diketone (5), yield 75%.

The mixed melting point also was taken. The pure diketone 5 melted at 113-114.5°C; the product melted at 107-111°C. The mixed melting point was 110-113°C.

THE IDENTIFICATION OF SULFUR DIOXIDE:

The identification of one of the products "sulfur dioxide" from
the photolysis of tetramethyl-l-thio-1,3-cyclobutanedione (4) was
done by two different methods:

I. The condensate from the evaporation of the completed
reaction solution was first used for identification of sulfur
dioxide. The ultraviolet spectrum of the condensated isopropyl
alcohol solution had an absorption at 270 nm. This was compared
to the 276 nm absorption of an authentic sample of sulfur dioxide
(Matheson Co.).

II. The oxygen stream evolving from the photolysis (FIG. II)
was trapped by 100 ml 1% sodium hydroxide solution during the
reaction period. The sodium hydroxide solution was analyzed for
the presence of sulfite. After the excess sodium hydroxide was
neutralized with hydrochloric acid, the presence of sodium sulfite
can be proven by titration and decolorization of iodine.¹³

III. The presence of sulfur dioxide also can be proven by the
precipitation with barium hydroxide. The trapped gas in sodium
hydroxide solution can form a white precipitate with barium hy-
droxide, this indicates the presence of sulfate or sulfite ion.
This precipitate will dissolve after acidification with hydro-
chloric acid, and this proves it must be sulfite.

DELSULFURIZATION BY SINGLET OXYGEN:

The preparation of singlet oxygen has been reported by Foote
and his co-workers²⁰. This involves a reaction of sodium hypo-
chlorite with hydrogen peroxide. The sodium hypochlorite (5.25%)
used was provided by the Hilex Company. The hydrogen peroxide (30%) was supplied by J. T. Baker Chemical Company. The procedure used was as follows:

A 50 ml isopropyl alcohol solution of 0.102 M tetramethyl-3-thio-1,3-cyclobutanedione (4) was placed in a 250 ml separatory funnel and 50 ml of 5.25% sodium hypochlorite solution was placed in another separatory funnel. Both funnels were attached to a 250 ml 3 neck flask containing 50 ml of 30% hydrogen peroxide which was being stirred magnetically. The sodium hypochlorite solution was added dropwise into the reaction flask and a large amount of gas formed immediately. The red monothione 4 solution was introduced next into the reaction flask, and the reaction started. The gas evolving from the reaction was trapped by 100 ml 1% sodium hydroxide solution. A positive analysis for sulfur dioxide was obtained as previously described. This reaction both in the dark and exposed to light was completed in five minutes. Tetramethyl-1,3-cyclobutanedione (5) was isolated by evaporating the isopropyl alcohol and water mixture. It was identical in all respects with that of an authentic sample.

There were no apparent reactions when the red monothione 4 was shaken with hydrogen peroxide only or with sodium hypochlorite.

**FLUORESCENCE AND PHOSPHORESCENCE SPECTROSCOPY:**

The fluorescence of the monothione 4 was done both in the presence and absence of oxygen. Irradiation of the monothione 4
in isopropyl alcohol solution in the absence of oxygen does not have any fluorescence if the light source has a wavelength longer than 400 nm. In the presence of oxygen, there is a fluorescence at 660 nm if the monothione 4 solution is irradiated at 620 nm. This work was done on the Turner Model B Fluorometer.

Using the Perkin-Elmer MPF spectrophotometer no detectable room temperature fluorescence could be detected when the sample was irradiated at 500 nm.

A low temperature fluorescence spectrum did indicate a very weak emission at 540 nm.

The phosphorescence spectrum was taken at 77°K in EPA exciting the monothione 4 at 500 nm. No phosphorescence was detected from 500 to 800 nm.

PHOTOCHEMISTRY OF TETRAMETHYL-1,3-CYCLOBUTANEDITHIONE (6):

A similar reaction, photodesulfurization of the dithione 6 has also been done. A 0.099 M hexane solution of the dithione (6) was irradiated by visible light in the presence of an oxygen stream. The orange-red solution was decolorized after three days irradiation. The gas liquid chromatograph indicated the presence of the diketone 5 and some other undefined products. Further studies should be done before a complete report can be written.

THE PURIFICATION OF SOLVENTS:

Four liters of hexane was stirred with one liter of concentrated sulfuric acid for seventy-two hours after which the sulfuric acid was changed with a fresh one and the mixture was stirred another
forty-eight hours. The upper layer was removed and washed with two liters of water three times. After the water was separated, the hexane was dried over anhydrous magnesium sulfate with swirling for two hours. The hexane was then filtered, passed through a silica gel and then through an aluminum column (80 cm x 3 cm) prior to distillation.

Carbon tetrachloride was mixed with anhydrous phosphorus pentoxide. The mixture was distilled into a vessel with anhydrous potassium carbonate powder in it for storage. The solution samples were taken from this vessel.
APPENDIX

This section contains the ultraviolet and visible spectra, infrared spectra, nuclear magnetic resonance spectra and gas liquid chromatographs which describe the photochemical reaction of tetramethyl-3-thio-1,3-cyclobutanedione (4) as it proceeds. In the Results and Discussion Section these spectra are referred to in order to verify conclusions made on the reaction mechanism.

A PL/I computer program is also attached for the documented kinetic calculations.
ULTRAVIOLET SPECTRA
Ultraviolet spectra follow the photodesulfurization reaction of tetraethyl-3-thio-1,3-cyclobutanedione in isopropyl alcohol solution in the presence of oxygen.

Curves:
1 : Beginning of the reaction
2-8: Taken every 12 hours
9 : Reaction complete

SPECTRUM 1. Visible spectra of the reaction taken every twelve hours.
SPECTRUM 2. Ultraviolet spectra of the reaction taken every twelve hours.

SPECTRUM 3. Ultraviolet spectra of the reaction taken every twelve hours. (Ten times dilution of spectrum 2)
GLC SPECTRA

Gas liquid chromatographs of the photodesulfurization reaction of tetramethyl-3-thio-1,3-cyclobutane dine in carbon tetrachloride solution in the presence of oxygen.

SPECTRUM 4
At the beginning of the reaction.

SPECTRUM 5
After the reaction has proceeded 12 hours.

SPECTRUM 6
Reaction complete after 24 hours.
SPECTRUM 7: Infrared spectrum follow the photodesulfurization reaction of tetraethyl-3-thio-1,3-cyclobutanedione in carbon tetrachloride solution.

Start of the reaction
After 12 hours irradiation
After 24 hours irradiation
NMR SPECTRA:
Nuclear magnetic resonance spectra following the reaction in carbon tetrachloride solution every twelve hours.

SPECTRUM 8. NMR spectrum of 4 at the start of the reaction \( \left( 1.35 \text{, s, CH}_3 \right) \).
SPECTRUM 9. NMR spectrum of 4 after irradiation for 12 hours in the presence of O₂ (1.35, s, CH₃ and 1.25, s, CH₃).

SPECTRUM 10. NMR spectrum of 4 after irradiation for 24 hours in the presence of O₂ (1.25, s, CH₃).
START.. PROCEDURE OPTIONS (MAIN),
DECLARE A(999) FLOAT, CT(999) FLOAT, CK(999) FLOAT, R(999) FLOAT,
NAME(999) CHARACTER(4),
LCCP., DO L=1 TO 4,
GET EDIT((NAME(I) DO I=1 TO 13)) (13A(4)),
GET EDIT(N,A1,F(1),F(5,3)),
PUT PAGE LIST(' PHOTODECAORIZATION OF MONOTHIONE IN 2-PROPANOL '),
PUT EDIT((NAME)(SKIP(1),13A(4)),
PUT EDIT(' THE CONCENTRATION OF THE SOLUTION IS ' ,A1/9.65,' M')(SKIP,
A,F(10,7),A),
PUT SKIP LIST(' T A CTCK 1'),
PUT SKIP LIST( ' (HR) (M) (M) (HR-1)'),
PUT EDIT(T,A1,A1/9.65)(SKIP(2),X(2),F(3),X(5),F(5,3),X(5),F(5,3)),
A(1)=A1.,
DO J=2 TO N BY 1.,
GET EDIT(A(J)) (F(5,3)),
R(J)=1/T*LOG(A(1)/A(J)),
PUT EDIT(T,A(J),A(J)/9.65,CK(J),R(J)) (SKIP,X(2),F(3),X(5),F(5,3),
X(5),F(5,3),X(5),F(5,3),X(5),F(10,8)),. END LOOP.,
FINISH.. END START.,

PROGRAM: Computer program to calculate the kinetic data for a first order reaction.
REFERENCES


22. Bubbling nitrogen gas through the solution to remove oxygen.
