Photochemistry of Sulfur Compounds Related to the 1,2-Dithiole System. V. Formation of 1,2-Dithioly1 Radicals and Dithioketionate Anions in the Photolysis of 3,5-Disubstituted 1,2-Dithiolylium Salts

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It has been shown in a series of eleven 3,5-disubstituted 1,2-dithiolylium salts and unsubstituted 1,2-dithiolylium salts that irradiation of these salts in ethanolic solutions gives rise to 1,2-dithioly radicals and dithioketionate anions. Rate constants for the first order decay of these radicals and anions are given in absolute and 96 % ethanol respectively.

DITHIOLYL RADICALS

One of the conditions necessary for a radical to be observable is a favourable position of the equilibrium (1) to avoid disproportionation of the radical.

\[ \text{Ox} + \text{Red} \rightleftharpoons 2 \text{Rad} \]  \hspace{1cm} (1)

Further it is necessary, that the equilibrium (2) must be such, that measurable amounts of the radical exist.

\[ 2 \text{Rad} \rightleftharpoons \text{Dimer} \]  \hspace{1cm} (2)

It has been shown by theoretical studies both by PPP methods and by CNDO/2 calculations that both these prerequisites are fulfilled by the dithioly radical 1.

It has now been demonstrated that this is a general reaction for 3,5-disubstituted 1,2-dithiolylium salts in ethanolic solution.

The quantum yield for the reaction was found to be unaffected by the presence of oxygen, which led us to the assumption, that the reaction proceeds via an excited singlet state.

The formation of the radical 3 is a biphptonic process since the quantum yield of 5 was found to be proportional to the square of the light intensities. This means as shown by Porter and coworkers, a photochemically formed intermediate undergoes a further photochemical reaction in competition with a thermal reaction.

The decay of 3 was found to obey first order kinetics.

The visible spectrum of the photoproduct was identical with the visible spectrum of dithioly radicals generated by one electron cathodic reduction of 1,2-dithiolylium salts \( \lambda_{\text{max}} = 650 \) and 450 nm, it was not possible to obtain the absorption spectrum at wavelengths lower than 450 nm due to the strong absorption band of the starting dithiolylium salt in this region.

On the basis of these observations it was proposed that dithioly radicals were formed via the following pathway with the solvent acting as reductant.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

The dithiyl radical \( \mathcal{A} \) was proposed as an intermediate since it is a well-established fact that disulfides give thyl radicals upon irradiation.

\[
\text{RS} + \text{SR}^1 \xrightarrow{\text{hv}} \text{RS}^- + \text{SR}^1
\]

It has further been reported \( \text{7} \) that lipoic acid \( \mathcal{B} \) as well as other \( \text{6} \) and \( \text{7} \) membered cyclic disulfides gives dithiyl radicals upon irradiation at low temperatures. The structure of the di-radicals has been established by ESR spectroscopy.\( \text{7} \)

![Diagram of dithiyl radicals](image)

In Table 1 the rate constants are given for the first order decay of the investigated series of 1,2-dithioly radicals in absolute ethanol.

The mechanism of the decay was not further studied, but they probably decay by reaction with the solvent under destruction of the dithiol system.\( \text{8} \)

It was observed that the radicals decay faster if water is present. The 3,5-diphenyl-1,2-dithioly radical has, e.g., \( k \text{st} = 1500 \text{ s}^{-1} \).

If the variations in rate constants in Table 1 are compared to the variation of the substituent pattern it is observed that the introduction of electron donating groups such as \( \text{p} \)-methoxyphenyl group augments the reactivity of the radical whereas an electron attracting group such as \( \text{p} \)-bromophenyl diminishes the reactivity.

The extremely low reactivity of the product derived from 3-(\( \text{p} \)-methoxyphenyl)-5-(\( \text{p} \)-dimethylanilinophenyl)-1,2-dithiolyium salts is probably due to the fact that the photoproducit is not a dithioly radical but an aminyl radical \( \text{7} \) since it is known that nitrogen containing radicals often show high stability.\( \text{9} \)

![Diagram of radicals](image)

If one phenyl group in \( \text{2} \) is substituted by a methyl group the reactivity augments due to the lower steric hindrance of the methyl group. The di-\text{tert}-butyl radical is only slightly reactive due to strong steric hindrance.

The unsubstituted 1,2-dithioly radical proved to be unusually stable. This has also been observed by thermolitical formation of the dithioly radical in the ion source of the mass spectrometer.\( \text{10} \) No satisfactory explanation can be given for this observation.

If the rate constants in Table 1 are compared to the ratio monomer:dimer given in Ref. 5 the same general trend is found concerning the influence of substitution on the reactivity of the radical. If the radical is generated in acetonitrile it can only decay by formation of dimers \( \delta \), i.e. the substrate with which it reacts is rather sterically hindered, and different for different dithioly radicals. The radicals generated in this study all decay by reaction with the same substrate, ethanol, the rate constants in Table 1 therefore give a more true picture of the reactivity of the radicals.

![Diagram of radicals](image)

We have in several cases been able to measure the decay rates of radicals where the couple (dithiolyium salt/dithioly radical) showed electrochemical irreversibility on a platinum electrode, i.e. \( E_{\text{pc}} - E_{\text{pa}} > 60 \text{ mV} \). This is due to the fact that it is possible to detect radicals with much shorter life time with the method used in this study.

dithiolylium perchlorate, e.g., displays irreversible electrochemistry at room temperature on a platinum electrode in acetonitrile solution, but the electrochemistry became reversible at -70 °C. In the photolysis experiment it was possible to determine the decay rate of the corresponding radical at room temperature.

**DITHIOKETONATE ANIONS**

During the photolysis of 1,2-dithiolylium salts another species with a longer life time than dithioly radicals was observed. We have ascribed the dithioketone anion structure 9 to these compounds.

\[
\begin{align*}
R^2 & \quad S^- \quad S^- \\
& \quad R^1
\end{align*}
\]

The absorption spectrum of the compound derived from 3,5-diphenyl-1,2-dithiolylium salts was found to be identical to the absorption spectrum of the dithioketone anion prepared electrochemically by two electron reduction of the same salt; \( \lambda_{\text{max}} = 490 \text{ nm} \). It has been reported that dithioketone anions in, e.g., Ni chelates have an absorption band near 480 nm.

The first product formed is probably the anion 10, which on the basis of CNDO/2 calculations and the irreversibility of the electrochemical reduction of dithioly radicals has been shown to be less stable than its valence tautomer the dithioketone anion.

The formation of 9 is found to be a biphotonic process (cf. p. 831). As the decay of the dithioly radical is thermal we assume that the anion 10 and the dithioketone anion is formed directly from the dithioly radical 4.

\[
\begin{align*}
R^2 & \quad S^- \quad S^- \\
& \quad R^1
\end{align*}
\]

Thermally the dithioketone anions decay in a first order reaction. The rate constants for the decay are given in Table 2.

**Table 2. Rate constants for the 1st order decay of dithioketone anions in 96 % ethanol at 25 °C.**

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>( k \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_6H_5</td>
<td>C_6H_5</td>
<td>0.774</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>4-CH_3OC_6H_4</td>
<td>1.56</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>4-CH_3C_6H_4</td>
<td>0.941</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>4-BrC_6H_4</td>
<td>0.781</td>
</tr>
<tr>
<td>4-CH_3C_6H_4</td>
<td>4-CH_3C_6H_4</td>
<td>1.17</td>
</tr>
<tr>
<td>4-CH_3OC_6H_4</td>
<td>4-CH_3OC_6H_4</td>
<td>7.35</td>
</tr>
<tr>
<td>4-CH_3OC_6H_4</td>
<td>4-(CH_3)_2NC_6H_4</td>
<td>not observable</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>CH_3</td>
<td>41.4</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>SCH_3</td>
<td>4.81</td>
</tr>
<tr>
<td>t-C_6H_5</td>
<td>t-C_6H_5</td>
<td>282</td>
</tr>
<tr>
<td>CH_3</td>
<td>CH_3</td>
<td>40.4</td>
</tr>
</tbody>
</table>

It was observed that the amount of dithioketone anion formed as well as the decay rate of the dithioketone anions were augmented by the presence of water in the alcohol. It was further noticed that both these factors were strongly influenced by the presence of acid. In 10^{-4} M ethanolic hydrogen chloride it was not possible to detect any dithioketone anion after the photolysis, this may be due to a neutralization of the fairly basic anion.

\[
\begin{align*}
\begin{array}{c}
R^2 \\
\quad \text{S}^- \\
\quad \text{S}^-
\end{array} \quad \text{hv} \quad \begin{array}{c}
R^2 \\
\quad \text{S}^- \\
\quad \text{S}^-
\end{array} \quad \text{hv} \quad \begin{array}{c}
R^2 \\
\quad \text{S}^- \\
\quad \text{S}^-
\end{array} \\
\text{n} \quad \frac{\text{red}}{} \quad \text{n} \quad \frac{\text{red}}{}
\end{align*}
\]

As the formation and decay of dithioly radicals are only slightly dependent on the presence of acid, it is probably not the formation of the dithiyl radical which is hindered by acid nor is this biradical destroyed by acid.

It can be noticed from Table 2, that the decay of the dithioketone anions is only slightly dependent on the nature of the substituents present, the aliphatic ones being a little less stable than the aromatic ones.

Both the formation of dithioly radicals as well as dithioketone anions were independent of the nature of the anion in the starting dithiolylium salt.

**EXPERIMENTAL**

1,2-Dithiolylium salts. For the preparations of these salts, cf. Ref. 5 and references given there.
Equipment. Conventional flash kinetic equipment was used. The flash lamps were filled with air, and flash energies were reproducible to \( \pm 2 \% \). The decay rates were constant to \( \pm 5 \% \). The concentration of dithioliulium salts was \( 10^{-4} \) M. The measurements were always carried out on freshly prepared solutions which were only used for one flash.

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REFERENCES


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