Photochemistry of Sulfur Compounds Related to the 1,2-Dithiole System. V. Formation of 1,2-Dithiolyl Radicals and Dithioketonate 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-di-substituted 1,2-dithiolylium salts and un-substituted 1,2-dithiolylium salts that irradiation of these salts in ethanolic solutions gives rise to 1,2-dithiolyl radicals and dithioketonate 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.

$$Ox + Red \rightleftharpoons 2\ Rad \qquad (1)$$

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

$$2\ Rad \rightleftharpoons Dimer \qquad (2)$$

It has been shown by theoretical studies both by PPP methods [1] and by CNDO/2 calculations [2] that both these prerequisites are fullfilled by the dithiolyl radical 1.

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It has previously been shown that 3,5-diphenyl-1,2-dithiolylium perchlorate 2 gives the radical 3 upon irradiation in ethanolic solution.[3]
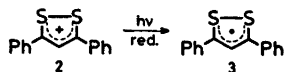
It has now been demonstrated that this is a general reaction for 3,5-disubstituted 1,2-dithiolylium salts in ethanolic solution.

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 5 is a biphotonic 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 an coworkers,[4] that 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 [3] was identical with the visible spectrum of dithiolyl radicals generated by one electron cathodic reduction [5] of 1,2-dithiolylium salts ($\lambda_{max} = 650$ 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 dithiolyl radicals were formed via the following pathway with the solvent acting as reductant.
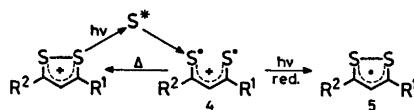
The dithiyl radical *4* was proposed as an intermediate since it is a well established fact that disulfides give thiyl radicals upon irradiation.[6]

$$RS - SR^1 \xrightarrow{h\nu} RS^{\bullet} + {}^{\bullet}SR^1$$
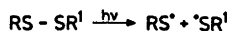
It has further been reported[7] that lipoic acid *6* as well as other 6 and 7 membered cyclic disulfides gives dithiyl radicals upon irradiation at low temperatures. The structure of the diradicals has been established by ESR spectroscopy.[7]
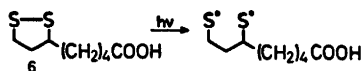
In Table 1 the rate constants are given for the first order decay of the investigated series of 1,2-dithiolyl radicals in absolute ethanol.

The mechanism of the decay was not further studied, but they probably decay by reaction with the solvent under destruction of the dithiol system.[8]

It was observed that the radicals decay faster if water is present. The 3,5-diphenyl-1,2-dithiolyl radical has, *e.g.*, $k_{96\% \text{ ethanol}} = 1500 \text{ s}^{-1}$.

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 a *p*-methoxyphenyl group augments the reactivity of the radical whereas an electron attracting group

such as *p*-bromophenyl diminishes the reactivity.

The extremely low reactivity of the product derived from 3-(*p*-methoxyphenyl)-5-(*p*-dimethylaminophenyl)-1,2-dithiolylium salts is probably due to the fact that the photoproduct is not a dithiolyl radical but an aminyl radical *7* since it is known that nitrogen containing radicals often show high stability.[9]
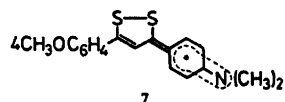
If one phenyl group in *2* is substituted by a methyl group the reactivity augments due to the lower steric hindrance of the methyl group. The di-*tert*-butyl radical is only slightly reactive due to strong steric hindrance.

The unsubstituted 1,2-dithiolyl radical proved to be unusually stable. This has also been observed by thermolytical formation of the dithiolyl radical in the ion source of the mass spectrometer.[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 *8*, *i.e.* the substrate with which it reacts is rather sterically hindered, and different for different dithiolyl 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.
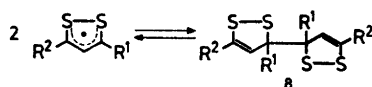
We have in several cases been able to measure the decay rates of radicals where the couple (dithiolylium salt/dithiolyl radical) showed electrochemical irreversibility on a platinum electrode, *i.e.* $E_{pc} - E_{pa} > 60$ mV.[5] This is due to the fact that it is possible to detect radicals with much shorter life time with the method used in this study. 3-Methyl-5-phenyl-1,2-

Table 1. Rate constants for the 1st order decay of 1,2-dithiolyl radicals in absolute ethanol at 25 °C.

R^1	R^2	$k \text{ s}^{-1}$
C_6H_5	C_6H_5	903
C_6H_5	$4\text{-}CH_3OC_6H_4$	2020
C_6H_5	$4\text{-}CH_3C_6H_4$	895
C_6H_5	$4\text{-}BrC_6H_4$	735
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	880
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	2300
$4\text{-}CH_3OC_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	49
C_6H_5	CH_3	2040
C_6H_5	SCH_3	2480
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	252
CH_3	CH_3	4270
H	H	754

dithiolylium perchlorate, *e.g.*, displays irreversible electrochemistry at room temperature on a platinum electrode in acetonitrile solution, but the electrochemistry became reversible at $-70\,^{\circ}C.$[11] In the photolysis experiment it was possible to determine the decay rate of the corresponding radical at room temperature.
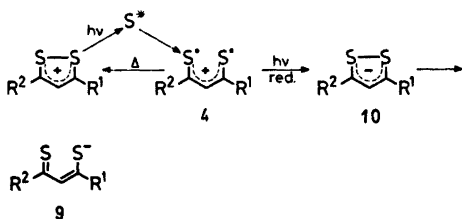
DITHIOKETONATE ANIONS

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

The absorption spectrum of the compound derived from 3,5-diphenyl-1,2-dithiolylium salts [3] was found to be indentical to the absorption spectrum of the dithioketonate anion prepared electrochemically by two electron reduction of the same salt; [5] $\lambda_{max} = 490$ nm. It has been reported that dithioketonate anions in, *e.g.*, Ni chelates have an absorption band near 480 nm.[12]

The first product formed is probably the anion *10*, which on the basis of CNDO/2 calculations [2] and the irreversibility of the electrochemical reduction of dithiolyl radicals [5] has been shown to be less stable than its valence tautomer the dithioketonate anion.

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


Thermally the dithioketonate 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 dithioketonate anions in 96 % ethanol at 25 °C.

R^1	R^3	$k\ s^{-1}$
C_6H_5	C_6H_5	0.774
C_6H_5	$4\text{-}CH_3OC_6H_4$	1.56
C_6H_5	$4\text{-}CH_3C_6H_4$	0.941
C_6H_5	$4\text{-}BrC_6H_4$	0.781
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	1.17
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	7.35
$4\text{-}CH_3OC_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	not observable
C_6H_5	CH_3	41.4
C_6H_5	SCH_3	4.81
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	282
CH_3	CH_3	40.4

It was observed that the amount of dithioketonate anion formed as well as the decay rate of the dithioketonate 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 dithioketonate anion after the photolysis, this may be due to a neutralization of the fairly basic anion.
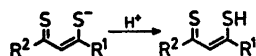
As the formation and decay of dithiolyl radicals are only slightly dependent on the presence of acid, it is probably not the formation of the dithiyl radical which is hindered by acid nor is this biradical destroyed by acid.

It can be noticed from Table 2, that the decay of the dithioketonate 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 dithiolyl radicals as well as dithioketonate 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.[13] The flash lamps were filled with air, and flash energies were reproducible to ± 2 %. The decay rates were constant to ± 5 %. The concentration of dithiolylium salts was 10^{-4} M. The measurements were always carried out on freshly prepared solutions which were only used for one flash.

REFERENCES

1. Zahradnik, R., Cársky, P., Hünig, S., Kiesslich, G. and Scheutzow, D. *Int. J. Sulfur Chem. Part C* (1971) 109.
2. Guimon, C., Conbeau, D., Pfister-Guillouzo, G., Bechgaard, K., Parker, V. D. and Pedersen, C. Th. *Tetrahedron 29* (1973) 3695.
3. Pedersen, C. Th. and Lohse, C. *Tetrahedron Lett.* (1972) 5213.
4. Brocklehurst, B., Gibbons, W. A., Lang, F. T., Porter, G. and Savadatti, M. I. *Trans. Faraday Soc. 62* (1966) 1793.
5. Bechgaard, K., Parker, V. D. and Pedersen, C. Th. *J. Amer. Chem. Soc. 95* (1973) 4373.
6. Rao, P. M., Copeck, J. A. and Knight, A. R. *Can. J. Chem. 45* (1967) 1369.
7. Smissman, E. E. and Sorenson, J. R. J. *J. Org. Chem. 30* (1965) 4008.
8. Prinzbach, H. and Futterer, E. *Advan. Heterocycl. Chem. 7* (1966) 39.
9. Forrester, A. R., Hay, J. M. and Thomson, R. H. *Organic Chemistry of Stable Free Radicals*, Academic, New York 1968.
10. Pedersen, C. Th. and Møller, J. *Tetrahedron 30* (1974) 553.
11. Pedersen, C. Th. and Parker, V. D. *Unpublished results.*
12. Ouchi, A., Nakatani, M. and Takahashi, Y. *Bull. Chem. Soc. Jap. 41* (1968) 2044.
13. Porter, G. In Weissberger, A., Ed., *Technique of Organic Chemistry*, Interscience, New York 1963, Vol. 8, Part II, p. 1055.