

THIYL RADICALS

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INTRODUCTION AND SURVEY

The present lecture deals with some characteristics of aliphatic and aromatic thiyl radicals ($\text{RS}\cdot$, $\text{ArS}\cdot$) compared with those of the analogous alkoxy and aryloxy fragments¹.

The usual approach in discussing the reactivity of free radicals is that of bond strength data and heats of reaction, assuming the transition states to resemble the products. As a result of polar, steric or mesomeric factors being often markedly different for these two states, many deviations occur. The merits and pitfalls of the non-crossing rule need not be discussed here.

Since more is known about alkoxy and aryloxy radicals than about thiyl fragments, one is tempted to apply simple rules-of-thumb governing the former to the behaviour of the latter group. This simplification appears to be markedly unsuccessful, though an attempt will be made at suitable adaptations.

In any case, data on bond strengths and other "static" properties are providing an essential background of free radical chemistry, if only for the purpose of eliminating certain alternatives. In this lecture, these data will also be used to interpret many striking differences between thiyl and other radicals. A survey is given in *Table 1*.

Table 1. General characteristics of thiyl radicals

| | |
|------------------------------|--|
| Basic data: | Sulphur bonds and steric accessibility. |
| Formation of thiyl radicals: | Stable thiyl radicals. Formation from thiols and disulphides. Generation from diazothioethers or thionitrites. |
| Chemical properties: | Comments on structure and reactivity. |
| Some special topics: | Thiol catalysis. Non-specific solvent effects. |

BASIC DATA

Dissociation energies of some covalent bonds in sulphur and oxygen compounds^{2,3}

The values of dissociation energies given in *Table 2* indicate that there are important differences between sulphur and oxygen bonds—as well as with well-known data for carbon bonds. Thus, the S—S bond in disulphides is appreciably stronger than the O—O bond in peroxides. The S—H bond in thiols, though relatively strong compared with many carbon—hydrogen bonds (e.g. in allylic or benzylic positions) is weaker than the O—H bond in alcohols. $D_{\text{C-S}}$ is somewhat *lower* than one half the sum of $D_{\text{S-S}}$ and $D_{\text{C-C}}$, in contrast to Pauling's electronegativity rule; this is probably due to the

Table 2. Dissociation energies of some bi-covalent sulphur and oxygen bonds

| Bonding | D | Bonding | D |
|--|----|---------------------------------------|-------|
| CH ₃ S --- SCH ₃ | 73 | —O --- O— | 40-45 |
| CH ₃ S --- CH ₃ | 73 | CH ₃ O --- CH ₃ | 77 |
| CH ₃ S --- H | 89 | CH ₃ O --- H | 100 |
| CH ₃ S --- Benzyl | 51 | Benzyl --- H | 80 |
| C=S minus C—S | 45 | C=O minus C—O | 73 |

fact that the S—S bond is “too strong”, since D_{S-H} is practically equal to $1/2 D_{H-H}$ plus $1/2 D_{S-S}$. On the basis of these data *alone*, one might expect that the S—H and S—S bonds should be quite refractory towards the attack by stabilized radicals such as benzyl. This is, however, not so. The difference between $D_{C=S}$ and D_{C-S} is much smaller than that for the pair $D_{C=O}$ and D_{C-O} . The facile loss of a carbon radical to form a carbonyl compound is one of the most characteristic reactions of alkoxy radicals⁴; it is due to the high energy gain involved in the formation of the carbonyl linkage lowering the C—C bond strength to some 10–15 kcal. For thyl radicals, the corresponding process has not yet been reported; energetically, it should be some 30 kcal less favourable.

Bond lengths and bond angles³

The covalent radius of the sulphur atom is appreciably larger than that of the oxygen atom or carbon atom. Some pertinent data are given in *Table 3*, which indicates that, generally speaking, the bond-lengths involving bi-covalent sulphur are about 0.3 to 0.5 Angstrom units greater.

Table 3. Bond lengths involving bi-covalent sulphur and oxygen

| Bonding | Bond length (Å) | Bonding | Bond length (Å) |
|---------|-----------------|---------|-----------------|
| C—S | 1.82 | C—O | 1.43 |
| S—S | 1.8–2.1 | C—C | 1.53 |
| S—H | 1.33 | O—H | 0.96 |

Since, in most bimolecular free radical reactions, repulsions between non-bonded groups or atoms are probably constituting a large part of the free energy of activation, differences in steric accessibility of the reaction centre should play an important part. *This factor alone* should facilitate reactions of sulphur compounds compared to those of the oxygen analogues; in processes involving the sulphur atom as the reacting centre the distance between the attacking species and that of groups attached to the sulphur atom could well be as much as an Angström larger than in the case of oxygen. The situation is schematically illustrated by *Figure 1*.

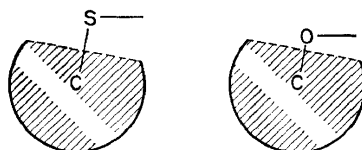


Figure 1. Accessibility of S and O

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Generally, bond angles involving bivalent sulphur are slightly smaller than those of oxygen; this factor would not seem to have much effect on steric accessibility. It may be noted that there are other differences as well; thus, since sulphur is a second row element, stretching force constants will be lower than with oxygen, the same extent of bond-lengthening requiring less energy in the case of the sulphur compound.

A further important, and somewhat unexpected, feature of thiyl radicals is their electrophilicity. Thus, on the basis of the Pauling scale, sulphur is much less electronegative than oxygen; however, the value reported⁵ for the electron affinity of the SH radical (*c.* 53 kcal) is even somewhat higher than that for the hydroxyl radical (*c.* 48 kcal). It seems probable that the same will apply for thiyl as compared with alkoxy radicals, an assumption which is supported by data concerning proton and carbon basicities of mercaptide and alkoxy anions¹. The electrophilicity of thiyl radicals may be further enhanced by the fact that the sulphur atom may use *d*-orbitals to accommodate negative charge, which is impossible for the oxygen atom (*cf.* Table 4).

Table 4. Some differences between bonded sulphur and oxygen

| | |
|--|--|
| 1. Bond strength effects: | S—S 'too strong'; S—H stronger than most C—H bonds; C—S about the same as S—S and C—O; difference C=O and C—O much greater than C=S and C—S. |
| 2. Steric accessibility: | Greater for bivalent S than for oxygen |
| 3. Sulphur atom—electron releasing as well as demanding: | Depending on other groups or reagents present |

FORMATION OF THIYL RADICALS

The isolation of thiyl radicals

At this Symposium, it seems appropriate first to discuss the problem of stable thiyl radicals. In contrast to their carbon and oxygen analogues, thiyl radicals have been isolated as such only recently and then only at temperatures as low as -180°C ⁶. A second example involves the irradiation product of crystalline cystin, the thiyl radical [$\cdot\text{S}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$] being stabilized as a "frozen radical". Probably, several causes exist for the difficulty of preparing stable thiyl fragments. Thus, because of the greater bond length of C—S bond, overlap with an adjacent aromatic ring will be less effective; secondly, the lengths of the S—S bond are so much greater than those of the C—C or O—O bond that even very bulky adjacent groups cannot effectively interfere with bond formation and, finally, the strengths of these bonds are appreciably greater than in the case of the oxygen—oxygen bond. Thus, even "hindered" disulphides⁷ such as dimesityldisulphide are quite stable thermally to temperatures well above 100°C ; spectroscopic changes occurring in solutions of diaryl disulphides at elevated temperatures are undoubtedly due to other causes than free radical dissociation of the hexaphenylethane type^{6,7}.

Thiyl intermediates from disulphides or thiols

Both thiols and disulphides may react with many types of radicals ($\text{X}\cdot$)

to form the corresponding hydride (XH) or thioether (RSX) and a thiyl radical. These reactions occur with great facility, even when the attacking radical is resonance-stabilized, such as the cyano-isopropyl or benzylic radical. Thus, chain transfer constants of these sulphur compounds in most free-radical addition polymerizations are often even greater than unity and many 1 : 1 additions of thiols to double bonds have been reported^{2,3}.

An interesting point in the reactions with thiols is that, in contrast to what is observed in other cases, e.g. in the classical reaction between tetraphenylhydrazine and hexaphenylethane-cross-combination to form thioethers is somewhat *less* important than formation of carbon—carbon dimers and disulphides. Possibly, the better accessibility of the sulphur atom is playing a part; whereas none of the three combination reactions will involve an appreciable activation energy, it is noteworthy that this result is in line with bond strength data indicating the S—S bond to be “too strong”.

The high reactivity of thiols in hydrogen abstraction and, particularly, the direct attack by trivalent carbon on sulphur observed with disulphides can be hardly explained otherwise than by a very favourable steric factor. In the series primary, secondary, tertiary thiols, the hydrogen is abstracted with increasing facility by methyl radicals, as expected from the trend in S—H bond strengths. Bulky radicals, such as cyanoisopropyl fragments and polystyryl radicals, are more reactive towards *primary* thiols, possibly on account of increasing steric hindrance.

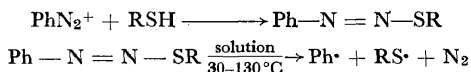
Rapid exchange occurs when thiyl radicals are generated in the presence of disulphides, RS· attacking the sulphur—sulphur bond with formation of a new disulphide and a new thiyl radical. Thus, sulphur-labelled thiols and disulphides in the presence of free radical sources lead to labelled disulphides, a reaction which is also catalyzed by oxygen⁸. The detailed nature of the initiation step has not yet been elucidated; possibly, oxygen oxidizes mercaptide ion rather than thiol to form a thiyl radical.

Photolysis of disulphides or thiols, particularly of aromatic disulphides constitutes a convenient means of generating thiyl fragments. There would seem to be no indications as to formation of “hot” thiyl fragments when using light of suitable wavelengths.

Generation of thiyl radicals by thermolysis of diazothioethers or thionitrites

Whereas the sulphur counterpart of diacylperoxides (e.g. tetramethyl thiuramdisulphide) has found extensive practical applications, generation of thiyl radicals by thermal decomposition of azo compounds has so far received little attention. Very recently, a series of *arylazothioethers* (Ar—N=N—SR) has been synthesized in which R was both aliphatic [e.g. (Ph)₃C—] and aromatic (phenyl, substituted phenyl). Thermolysis in solution led to the generation of phenyl and thiyl radicals, compounds with R = alkyl decomposing at about 120–130°C and with R = aryl in the range 30–60°C. Since diazothioethers can be readily prepared from aryldiazonium ions and thiols, they may constitute a promising new source of thiyl radicals⁹.

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The rates of these reactions decrease in the order ($\text{R} = p\text{-CH}_3\text{O-C}_6\text{H}_4 > \text{C}_6\text{H}_5 > p\text{-O}_2\text{N-C}_6\text{H}_4 > t\text{-butyl}$).

Thionitrites (RS-NO), obtained by treating thiols with nitrosyl chloride, when heated in solution were also found to generate thiyl radicals; in some cases, however, the simultaneous formation of nitrous oxide may cause complications.

The methods used for the formation of thiyl radicals are:

1. From disulphides or thiols by free radical attack, electron transfer or photolysis.
2. From diazothioethers (Ph-N=N-SR) or thionitrites (RS-NO) by homolysis.

CHEMICAL PROPERTIES

Since several comments on the chemistry of thiyl radicals have already been made in the foregoing, only a few special topics will be discussed here.

Both aliphatic and aromatic thiyl radicals display hydrogen abstraction and displacement reactions on sulphur atoms as well as additions to double bonds. Differences among the two classes are, however, less pronounced than with the oxygen analogues; resonance stabilization is less important in the case of thiyl fragments.

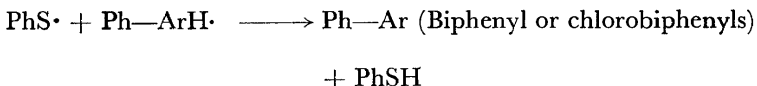
So far, systematic studies on polar effects in hydrogen removal by thiyl radicals have not been made; we may expect these effects to be appreciable. The electron-demanding properties of thiyl radicals are strikingly illustrated in additions to the double bond; thus, octene-1 appears to be more reactive than vinyl acetate in contrast to what is observed for most other radicals.

Hydrogen abstraction by thiyl radicals depends rather strongly on bond strengths, particularly in the case of aromatic thiyl radicals. Here, dihydroanthracene is much more effective as a scavenger than is tetralin.

Generally, thiyl radicals do not add on to aromatic rings other than anthracene. A recent example¹⁰ of homolytic thiylation involves the reaction between thiophene, thiols and Fenton's reagent. As expected, 2- and 2,5-thioalkylated thiophenes are formed. The formation of phenylthio-thiophenol type compounds upon irradiation of diphenyldisulphide may be due to a cage-type interaction. This reaction is not observed for dimesityldisulphide, which is therefore a more convenient source of aromatic thiyls¹¹.

Decomposition of phenylazo-thiophenyl ether (Ph-N=N-S-Ph) in chlorobenzene solution containing a reactive scavenger such as dihydroanthracene yields both benzene and thiophenol. In tetralin, however, no thiol formation was observed; surprisingly, with benzene or chlorobenzene alone, 1-7 per cent thiol was formed. Presumably, (chloro)benzene adds on a phenyl radical, the very loosely bound nuclear hydrogen then being abstracted by a thiyl radical with formation of thiol and (chloro)biphenyls. In the case of tetralin, however, phenyl radicals prefer to abstract a side-chain hydrogen rather than adding to the ring; the resulting labile β -hydrogen is less reactive than that in the case of the phenylchlorobenzene adduct

radical⁹. These reactions are illustrated below:



Before discussing some special topics involving thiyl radicals, let us briefly review some of the main aspects discussed so far. Some characteristics of thiyl radicals are:

1. Dimerization is often highly competitive with H-abstractions. No stable thiyl radicals exist. There is no cracking to thioketones.
2. Rapid (re)generation from thiols and stable radicals. (Favourable geometry.)
3. High reactivity in additions and in many H-abstractions. (Favourable geometry.)
4. Sensitive to bond strength and polar effects.

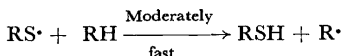
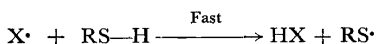
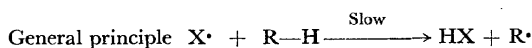
SOME SPECIAL TOPICS

Under this heading, we will briefly discuss two groups of phenomena in an attempt to illustrate the broad scope of thiyl chemistry.

Thiol catalysis

The facility of hydrogen loss from thiols, coupled with the appreciable hydrogen abstracting ability of thiyl fragments, particularly when dimerization probabilities are low on account of low concentrations, is responsible for a number of interesting catalytic phenomena. Generally, small proportions of thiols suffice to effect hydrogen transfer; in this respect, thiols resemble hydrogen bromide, an efficient catalyst in the autoxidation of hydrocarbons. Examples of thiol catalysis are given in *Table 5*^{12a-d}.

Table 5. Homogeneous catalysis by thiols



| | |
|----------|--|
| Examples | <i>Dehydrogenation</i> of dihydroanthracene by cyano-alkyl radicals (Bickel and Kooyman) |
| | <i>Decarbonmonooxylation</i> of aldehydes (Harris and Waters) |
| | <i>Exchange</i> between diphenylmethane and diphenylmethyl radicals (S. G. Cohen) |
| | <i>Dissipation</i> of high-energy radiation (S. G. Cohen) |

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The last example is particularly interesting in view of the fact that even high energy radiation may be effectively dissipated.

Non-specific solvent effects

Photolysis of dimesityldisulphide in the presence of an excess of dihydroanthracene leads to mesitylene thiol and dehydrogenation products of the scavenger. Variation of the solvent under otherwise identical conditions was found to produce changes in rates of thiol formation in a manner apparently unrelated to the chemical properties of the solvent, its dielectric constants, molecular weight or bulk viscosity. In all cases, thiol formation occurred by a first order process with respect to disulphide, suggesting that all thiyl radicals escaping the solvent cage had been trapped by the scavenger. Rates, however, varied by a factor of 8 from the "fast" solvents carbon disulphide and pentane to the slow solvents dimethyl and dioctyl phthalate. Some data are given in *Table 6*¹¹. In this table solvents were ordered

Table 6. Solvent effects on photolysis rates of dimesityldisulphide (Apparent rate constants in arbitrary units—Schaafsma, Bickel, and Kooyman)

| <i>Solvent</i> | k_{ph}^{25} | <i>Solvent</i> | k_{ph}^{25} |
|-------------------|---------------|---|---------------|
| CS ₂ | 195 | PhCl + 5% polystyrene | 95 |
| <i>n</i> -Pentane | 181 | <i>n</i> -C ₁₆ H ₃₄ | 85 |
| Acetone | 154 | Et- <i>p</i> -Et-benzoate | 67 |
| PhCl | 122 | Dioctyl phthalate | 25 |
| Toluene | 143 | | |

according to increasing *activation energies of viscous flow*. The satisfactory inverse correlation with rate constants, even for a polystyrene solution as the solvent, may indicate that the "microviscosity" of the solvent molecules rather than bulk viscosity should be the dominating factor. Following Gomberg's discovery of triphenylmethyl free radicals, many arylated ethanes have been studied, both with regard to rates and dissociation constants. Both constants appear to be governed by essentially the same solvent properties and, indeed, plots of log rate or log dissociation constants versus our log rates for disulphide dissociation are showing straight lines.

References

- ¹ E. C. Kooyman. *IInd Organosulfur Symposium Handbook*, Introductory Lecture.
- ² Ch. Walling. *Free Radicals in Solution*, Ch. 2, Wiley, New York, 1957.
- ³ W. A. Pryor. *Mechanisms of Sulfur Reactions*, (Ch. 3), McGraw-Hill, New York, 1962.
- ⁴ Ch. Walling. *This Symposium Handbook*.
- ⁵ R. S. Neale. *J. Phys. Chem.* **68**, 143 (1964).
- ⁶ U. Schmidt. *Angew. Chem.* **76**, 629 (1964).
- ⁷ W. Rundel. *Z. Naturforsch.* **15b**, 546 (1960);
O. Dimroth. *Angew. Chem.* **70**, 165 (1958).
- ⁸ A. Fava. Personal Communication.
- ⁹ H. van Zwet and E. C. Kooyman. *Chem. Comm.*, No. 14 (1965).
cf. H. van Zwet. Thesis, Leiden 1966. (Detailed papers to be published).
- ¹⁰ L. I. Belenkii. Communicated at the IInd Organosulfur Symposium, Groningen, May 1966.

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- ¹¹ A. Schaafsma, A. F. Bickel, and E. C. Kooyman. *Tetrahedron* **10**, 76 (1960).
cf. Y. Schaafsma. Thesis, Leiden 1961 (In English).
- ^{12a} A. F. Bickel and E. C. Kooyman. *Nature* **170**, 211 (1952).
- ^b E. F. P. Harris and W. A. Waters. *Nature* **170**, 212 (1952).
- ^c S. G. Cohen and C. H. Wang. *J. Am. Chem. Soc.* **77**, 4435 (1955).
- ^d S. G. Cohen. Review Lecture at the IInd Organosulfur Symposium, Groningen, May 1966.