Free Radical One-electron *versus* Hydroxyl Radical-induced Oxidation. Reaction of Trichloromethylperoxyl Radicals with Simple and Substituted Aliphatic Sulphides in Aqueous Solution

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One-electron oxidation of organic sulphides leading to sulphur-centred radical cations, $R_2S^{+\bullet}$, can conveniently be initiated by $CCl_3O_2^{\bullet}$ radicals. Absolute rate constants have been measured for the reaction of $CCl_3O_2^{\bullet}$ with dimethyl sulphide, 2-(ethylthio)ethanol, and methionine to be 1.8×10^8, 4×10^7, and 2.9×10^7 mol^{-1} dm^3 s^{-1}, respectively. Oxidation of dimethyl sulphide and methionine by the halothane-derived $CF_3CHClO_2^{\bullet}$ radical occurs with absolute rate constants of k 6×10^6 and 1.4×10^6 mol^{-1} dm^3 s^{-1}, respectively. The $R_2S^{+\bullet}$ generally equilibrates according to $R_2S^{+\bullet} + R_2S \rightleftharpoons (R_2S \therefore SR_2)^+$ to yield sulphur-centred three-electron-bonded radical cations. Amino-substituted sulphides such as 3-(methylthio)propylamine, methionine, and methionine ethyl ester also stabilize as intramolecularly formed S $\therefore$ N three-electron-bonded radical cations. This competing reaction route requires a free electron pair at nitrogen, *i.e.* an unprotonated amino group, and steric assistance by five- or six-membered ring structures. The pH profiles of S $\therefore$ S and S $\therefore$ N bond formation are significantly different in the oxidation of the amino-substituted sulphides by one-electron oxidants from those for the $^{\bullet}OH$ radical-induced process. The underlying mechanisms are compared and discussed.

Free radical-induced oxidation mechanisms are commonly and most conveniently initiated by $^{\bullet}OH$ radicals, which can easily be generated by exposing aqueous solutions to high energy radiation or through more conventional metal ion (Ti^{III}, Fe^{II}, *etc.*)–H_2O_2 chemistry. Although $^{\bullet}OH$ radicals exhibit a high oxidation potential of +2.77 V[1] their oxidative action frequently cannot be described by a straightforward one-electron-transfer process. Owing to its high electrophilicity the $^{\bullet}OH$ radical primarily rather tends to add to any centre of high electron density, such as double bonds or free electron pairs at heteroatoms. This addition process may be followed by an OH^- ion elimination, usually proton assisted, the net result of these two consecutive steps being the same as for a simple electron transfer. Many of the intermediate $^{\bullet}OH$ adducts have been identified and characterized particularly by means of time-resolved pulse radiolysis studies, *e.g.* in the $^{\bullet}OH$ radical-induced oxidation of various metal ions[2–6] and organic sulphides.[7–9]

The $^{\bullet}OH$ adducts may, however, also undergo reactions other than OH^- elimination and thus lead into reaction routes which are quite different from those of electron transfer. An instructive example is a comparison of the radical-induced oxidation of alkylthio-substituted amines, amino acids, and derivatives *etc.* The $^{\bullet}OH$ radical-induced processes have been described in the preceding paper;[9] the present investigation is mainly concerned with the oxidation of these compounds and of some simple aliphatic sulphides by a typical one-electron oxidant, namely $CCl_3O_2^{\bullet}$.

This peroxyl radical can conveniently be generated *via* dissociative electron capture (1) of carbon tetrachloride [reduction can also be achieved by other radicals, *e.g.* $(CH_3)_2\dot{C}OH$] followed by oxygen addition to the carbon-centred radicals (2). Both reactions occur with high rate constants, *i.e.* k_1 3.0×10^{10} mol^{-1} dm^3 s^{-1} and k_2 3.3×10^9 mol^{-1} dm^3 s^{-1}, respectively. The high value for the oxygen addition ensures that even low O_2 concentrations are generally sufficient for a quantitative conversion of the $\dot{C}Cl_3$ radicals into the powerful $CCl_3O_2^{\bullet}$[10–14] oxidant.

$$CCl_4 + e_{aq}^- \longrightarrow \dot{C}Cl_3 + Cl^- \qquad (1)$$

$$\dot{C}Cl_3 + O_2 \longrightarrow CCl_3O_2^{\bullet} \qquad (2)$$

Another typical one-electron oxidant is the corresponding peroxyl radical from halothane formed in reactions (3) and (4) with

$$CF_3CHClBr + e_{aq}^- \longrightarrow CF_3\dot{C}HCl + Br^- \qquad (3)$$

$$CF_3\dot{C}HCl + O_2 \longrightarrow CF_3CHClO_2^{\bullet} \qquad (4)$$

rate constants of k_3 1.4×10^{10} mol^{-1} dm^3 s^{-1} and k_4 1.3×10^9 mol^{-1} dm^3 s^{-1}, respectively.[15,16] The $CF_3CHClO_2^{\bullet}$ radical is not quite as good an oxidant as $CCl_3O_2^{\bullet}$. Investigations with the halothane-derived radical have therefore been restricted to some rate constant measurements.

Experimental

Most experimental details are identical with those described in the preceding paper on $^{\bullet}OH$ radical-induced oxidations,[9] the only difference being that in the present study solutions were air-saturated, *i.e.* $[O_2]$ *ca.* 2.8×10^{-4} mol dm^{-3}.

Results and Discussion

(1) *Oxidation of Simple Aliphatic Sulphides.*—Oxidation reactions initiated by $CCl_3O_2^{\bullet}$ radicals were generally investigated by pulse radiolysis of air-saturated solutions containing 30% v/v propan-2-ol, 3×10^{-2} mol dm^{-3} CCl_4, and 10^{-4}—10^{-2} mol dm^{-3} of the sulphide to be oxidized. In such solutions about half of the $CCl_3O_2^{\bullet}$ radicals are formed *via* reactions (1) and (2). The remainder results from reduction of carbon tetrachloride by $(CH_3)_2\dot{C}OH$ radicals in the reaction sequence (5) and (6) (k_6 1.0×10^8 mol^{-1} dm^3 s^{-1} [17]) and O_2

$$^{\bullet}OH/H^{\bullet} + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O/H_2 \qquad (5)$$

$$(CH_3)_2\dot{C}OH + CCl_4 \longrightarrow \dot{C}Cl_3 + Cl^- + H^+ + (CH_3)_2CO \qquad (6)$$

addition *via* reaction (2). Since reaction (5) accounts for only 85% of the $^{\bullet}OH$ radicals and $H^{\bullet}$ atoms[18] and since *ca.* 30% of

Table. Absolute rate constants for the reactions of various sulphides with $CCl_3O_2^{\bullet}$ and $CF_3CHClO_2^{\bullet}$ radicals, respectively (error limit ± 20%)

Radical	Substrate	k/mol^{-1} dm^3 s^{-1}
$CCl_3O_2^{\bullet}$	CH_3SCH_3	1.3×10^8
	$C_2H_5SCH_2CH_2OH$	4.0×10^7
	Methionine	2.9×10^7 *
$CF_3CHClO_2^{\bullet}$	CH_3SCH_3	6.0×10^6
	Methionine	1.4×10^6 *

* Measured at pH 10 *via* ABTS competitive method.

the $(CH_3)_2\dot{C}OH$ formed will be scavenged by O_2 (k 4×10^9 mol^{-1} dm^3 s^{-1} [19]) rather than undergo reaction (6), the total yield of $CCl_3O_2^{\bullet}$ radicals can be estimated to G 4.8 ± 0.3 (G species per 100 eV absorbed radiation energy). [The $(CH_3)_2C(OH)OO^{\bullet}$ formed upon O_2 addition to $(CH_3)_2\dot{C}OH$ does not lead to an optically absorbing species.]

Pulse radiolysis of such solutions containing simple aliphatic sulphides, *e.g.* CH_3SCH_3, $C_2H_5SC_2H_5$, $(CH_3)_2CHSCH(CH_3)_2$, *etc.* lead to transient optical absorptions in the visible region. The latter are identical with those absorption bands assigned to the $(R_2S \therefore SR_2)^+$ three-electron-bonded radical cation in the $^{\bullet}OH$ radical-induced processes.[7,8,20,21] Since $CCl_3O_2^{\bullet}$ is known to be a one-electron oxidant, which acts *via* direct electron transfer,[10-15] the underlying reactions are formulated as (7) followed by (8).

$$CCl_3O_2^{\bullet} + R_2S \longrightarrow R_2S^{+\bullet} + CCl_3O_2^{-} \qquad (7)$$

$$R_2S^{+\bullet} + R_2S \rightleftharpoons (R_2S \therefore SR_2)^{+} \qquad (8)$$

Absolute rate constants for reaction (7) and the corresponding process (9) for the halothane-derived radical have been

$$CF_3CHClO_2^{\bullet} + R_2S \longrightarrow R_2S^{+\bullet} + CF_3CHClO_2^{-} \quad (9)$$

evaluated for dimethyl sulphide as substrate (the halothane solutions contained t-butyl alcohol instead of propan-2-ol). For this sulphide the conditions of equilibrium (8) and the long lifetime of the $(R_2S \therefore SR_2)^+$ radical cation[7] permit evaluation of k_7 and k_9 (1.3×10^8 and 6×10^6 mol^{-1} dm^3 s^{-1}, respectively), from the pseudo-first-order build-up kinetics of the $(Me_2S \therefore SMe_2)^+$ absorption at $\lambda_{max.}$ 465 nm (concentration range 10^{-4}—3×10^{-3} mol dm^{-3} dimethyl sulphide) (see Table).

Equilibrium (8) is indicated in the dependence of the $(R_2S \therefore SR_2)^+$ yield on the dimethyl sulphide concentration. Corresponding plots for the $CCl_3O_2^{\bullet}$-induced formation of $(Me_2S \therefore SMe_2)^+$ and $(Et_2S \therefore SEt_2)^+$, respectively, are shown in Figure 1 (the radical cation yields are expressed in terms of $G\varepsilon$ measured at the respective $\lambda_{max.}$ 465 nm for the all-methylated, and 480 nm for the all-ethylated species). These concentration dependences exhibit the same characteristics as in the $^{\bullet}OH$ radical-induced oxidations.[7] For diethyl sulphide, the absolute $(Et_2S \therefore SEt_2)^+$ yields from the $CCl_3O_2^{\bullet}$ reaction are, however, considerably lower than in the $^{\bullet}OH$ system. This finds a plausible explanation in the relatively slow formation of the $(Et_2S \therefore SEt_2)^+$ radical cation and its much shorter lifetime compared with the methylated species. No attempt is therefore made in this paper to evaluate the rate constant for the $CCl_3O_2^{\bullet}$ reaction with diethyl sulphide. It can, however, be estimated to be similar to that of the corresponding dimethyl sulphide oxidation. It should further be noted that the turning points of the curves in Figure 1 cannot numerically be identified with the equilibrium constant K_8. Evaluation of the latter requires consideration of the kinetics of all associated processes.

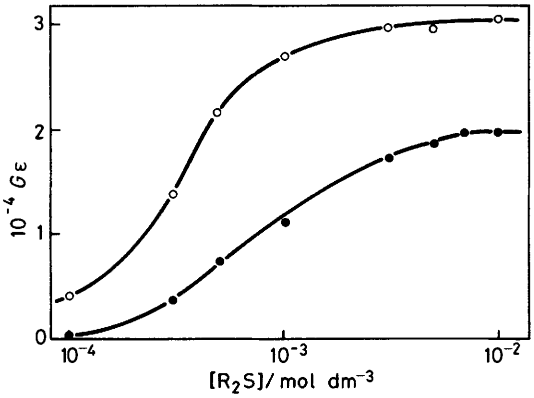
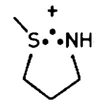


Figure 1. Yield of $(R_2S \therefore SR_2)^+$ radical cations, expressed in terms of $G\varepsilon$ at $\lambda_{max.}$, as a function of sulphide concentration in pulse-irradiated, air-saturated aqueous solutions of 30% (v/v) propan-2-ol, 3×10^{-2} mol dm^{-3} CCl_4 at pH 4: ○, $CCl_3O_2^{\bullet}$-induced oxidation of CH_3SCH_3; ●, *ditto* for $C_2H_5SC_2H_5$

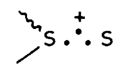
Finally, the pH dependence of the $(R_2S \therefore SR_2)^+$ formation in the $CCl_3O_2^{\bullet}$-induced processes is also the same as in the $^{\bullet}OH$ system, *i.e.* the radical cation yield is practically unchanged up to pH *ca.* 10. At higher pH it then decreases owing to increasing neutralization by OH^- ions.

In summary, for simple aliphatic sulphides no differences are apparent with respect to $(R_2S \therefore SR_2)^+$ formation and consecutive processes irrespective of the nature of the oxidant radical.

(2) *Oxidation of Substituted Sulphides.*—A significantly different picture is obtained, however, in the radical-induced oxidation of sulphides which carry additional functional groups such as NH_2, COOH, OH, *etc.* As shown later, completely different pH profiles are found in the reaction mechanism depending upon whether $^{\bullet}OH$ radicals are used as oxidants or one of the typical one-electron oxidants.



(I)



(II)

It has been found, for example, that the $^{\bullet}OH$ radical-induced oxidation of 3-(methylthio)propylamine (3-MTPA) leads to either the transient, intramolecularly S $\therefore$ N three-electron-bonded radical cation (I) which is stabilized at pH $\gtrsim$ 2, or to the intermolecularly formed S $\therefore$ S-bonded radical cation (II) at pH $\lesssim$ 2. As described in the preceding paper,[9] the formation of these two species is complementary and essentially reflects the mode of a proton-assisted dehydroxylation of the primary $^{\bullet}OH$ adduct at the sulphur function. Thus (I) and (II) are formed from $>S \therefore OH$ *via* intramolecular proton transfer from the $-NH_3^+$ group or *via* reaction with external protons, the rates of these two competitive processes being equal at *ca.* 10^{-2} mol dm^{-3} H_{aq}^{+}.

The same species (I) and (II), which are characterized by optical absorptions with $\lambda_{max.}$ 385 and 465 nm, respectively, are also produced as transient intermediates if 3-MTPA is oxidized by $CCl_3O_2^{\bullet}$ instead of $^{\bullet}OH$. The respective pH dependences of their formation are, however, remarkably different. This is illustrated in Figure 2. It shows the optical absorptions measured at 400 and 480 nm in terms of $G\varepsilon$ immediately after

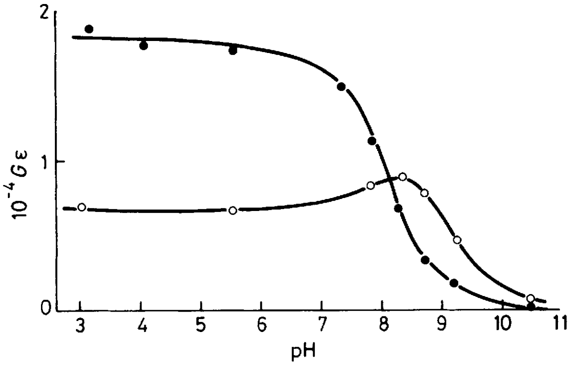


Figure 2. Yield of optical absorption, expressed in terms of $G\varepsilon$, measured at 480 (●) and 400 nm (○) as a function of pH in pulse-irradiated, air-saturated aqueous solutions of 30% (v/v) propan-2-ol, 3×10^{-2} mol dm^{-3} CCl_4, and 5×10^{-3} mol dm^{-3} 3-(methylthio)propylamine

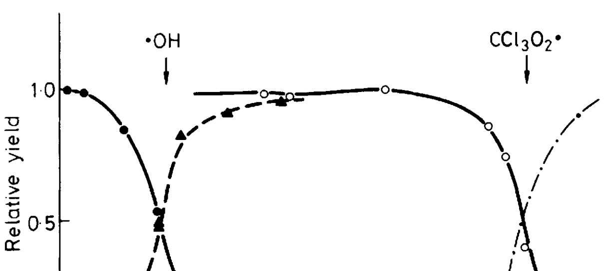
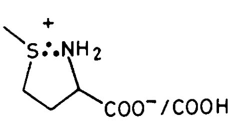


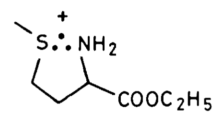
Figure 3. Normalized yields of $(R_2S \therefore SR_2)^+$ and S ∴ N-bonded radical cations from the $^{\bullet}OH$ radical- (● and ▲, respectively) and $CCl_3O_2^{\bullet}$ (○ and – • – • – • –, respectively)-induced oxidation of methionine

the *ca.* 1 μs pulse in an air-saturated aqueous solution of 30% (v/v) propan-2-ol, 3×10^{-2} mol dm^{-3} CCl_4, and 5×10^{-3} mol dm^{-3} 3-MTPA as a function of pH. From consideration of the $\lambda_{max.}$ values of (I) and (II), the 400 nm curve essentially reflects the yield of the S ∴ N-bonded radical cation, while the 480 nm curve can be associated with the S ∴ S-bonded species. The experimental data clearly indicate that in contrast to the $^{\bullet}OH$ system the S ∴ S-bonded radical cation (II) is stabilized over the entire acid and neutral pH range before it is replaced by the S ∴ N-bonded radical cation (I) at pH $\gtrsim$ 8. The latter can be detected only in a very small pH range (*ca.* 8.5—9.5) owing to neutralization by OH^- at higher pH. From the consideration that the apparent change in reaction mechanism occurs in slightly basic solution, *i.e.* near the p*K* of the amino group, the experimental results suggest that formation of the S ∴ N three-electron bond in the $CCl_3O_2^{\bullet}$ systems requires availability of the free electron pair of the unprotonated amino function.

Corresponding differences with respect to pH are found for the oxidation of methionine by either $^{\bullet}OH$ or $CCl_3O_2^{\bullet}$ radicals. Figure 3 shows, for example, normalized plots for the formation of the $(R_2S \therefore SR_2)^+$-type radical cation and the S ∴ N-bonded species from the oxidation of methionine, which are known to exhibit optical absorptions with $\lambda_{max.}$ 480 and 400 nm, respectively.[9,21] The stability range of the S ∴ S-bonded species is again shifted to higher pH by *ca.* 5 units* near to the p*K* 9.2 of the amino group at the expense of (III) if $CCl_3O_2^{\bullet}$ is used



(III)



(IV)

as oxidant instead of $^{\bullet}OH$. This has also significant chemical consequences, since radical cation (III) suffers fast decarboxylation (*k* 3.2×10^6 s^{-1})[9,21] to yield the strongly reducing α-amino radical $CH_3SCH_2CH_2\dot{C}HNH_2/NH_3^+$, while the S ∴ S-bonded radical cation does not suffer fast decarboxylation.[9,21,22] The S ∴ S curves would therefore represent the respective yields of radical-induced decarboxylation of methionine. It is interesting to note that oxidation of methionine by Tl^{2+} ions also leads to $(R_2S \therefore SR_2)^+$ radical cations (at high enough solute concentrations) rather than formation of (III) over the entire acid pH range.[23] Tl^{2+} like other oxidizing metal ions is also known to be a one-electron oxidant as are the halogenated peroxyl radicals.[4,6,23,24]

Absolute rate constants of 2.9×10^7 and 1.4×10^6 mol^{-1} dm^3 s^{-1} could be measured for the reaction of methionine with $CCl_3O_2^{\bullet}$ and $CF_3CHClO_2^{\bullet}$, respectively, by using a competitive method (see also Table). The latter involves oxidation of 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonate)(ABTS) by these peroxyl radicals to the strongly absorbing $ABTS^{\bullet +}$ radical cation [$\lambda_{max.}$ 415 nm (ε 3.6×10^4 mol^{-1} dm^3 cm^{-1})] as a reference reaction.[25,†]

Another example of the same pH shift in reaction mechanism is the radical-induced oxidation of methionine ethyl ester. As demonstrated in the preceding paper,[9] the $^{\bullet}OH$-induced process leads to the S ∴ N-bonded radical cation (IV) at pH $\gtrsim$ 2, while the corresponding $(R_2S \therefore SR_2)^+$ radical cation is again only stabilized in very acid solutions. Species (IV) shows an absorption with $\lambda_{max.}$ 385 nm. It also exhibits considerable stability with a lifetime of >1 ms since in contrast to (III) it cannot be decarboxylated.

Pulse radiolysis of an air-saturated aqueous solution of 30% (v/v) propan-2-ol, 3×10^{-2} mol dm^{-3} CCl_4, and 5×10^{-3} mol dm^{-3} methionine ethyl ester now indicates stabilization of the $(R_2S \therefore SR_2)^+$-type radical cation over the entire acid and neutral pH range as well. Figure 4a shows, for example, the transient optical absorption spectrum obtained from such solutions at pH 3, *i.e.* at a pH where in the $^{\bullet}OH$ system the 385 nm absorption of the S ∴ N-bonded species (IV) is observed. In the $CCl_3O_2^{\bullet}$ system the band clearly peaks, however, at *ca.* 460 nm which in analogy to all other examples is indicative of the formation of the S ∴ S-bonded radical cation.[7,8,9,20,21,26]

The $(R_2S \therefore SR_2)^+$ radical cation of methionine ethyl ester decays exponentially with $t_{\frac{1}{2}}$ 23 μs. Most interesting is that this decay is accompanied by a blue-shift of the absorption. At

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* A 480 nm absorption from the reaction $CCl_3O_2^{\bullet}$ + methionine in neutral solutions was first observed by R. L. Willson, personal communication.

† Measurements were made at pH 10 to avoid possible oxidation of ABTS by the S ∴ S-bonded radical cation. Direct determination of the rate constants by the build-up kinetics of the $(R_2S \therefore SR_2)^+$ absorption at lower pH was not feasible owing to the short lifetime of this radical cation.

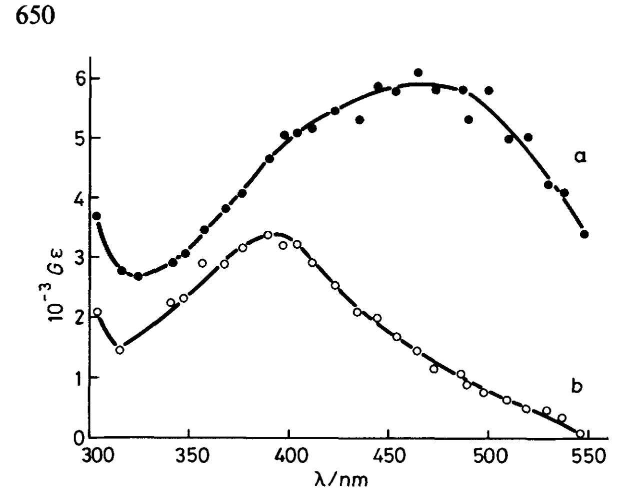
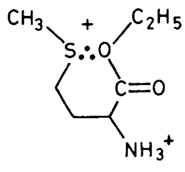


Figure 4. Transient absorption spectra measured 20 μs (●) and 100 μs (○) after the *ca.* 1 μs pulse in irradiated, air-saturated aqueous solutions of 30% (v/v) propan-2-ol, 3 × 10^{-2} mol dm^{-3} CCl_4, and 5 × 10^{-3} mol dm^{-3} methionine ethyl ester



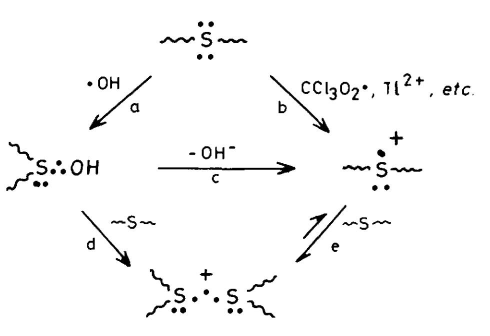
(V)

much longer times then a long-lived transient with $\lambda_{max.}$ *ca.* 385 nm remains, as can be seen in Figure 4b. It may be anticipated that this latter absorption was due to the S ∴ N-bonded radical cation (IV). This assignment can, however, be excluded, since ring closure of the dication formed in reaction (10) cannot

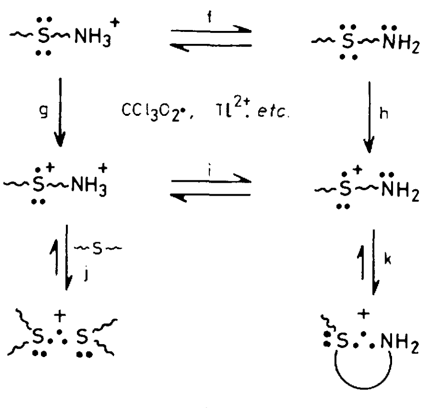
$$CCl_3O_2\cdot + CH_3SCH_2CH_2CH(COOC_2H_5)NH_3^+ \longrightarrow -\underset{\cdot\cdot}{\overset{+\cdot}{S}}\sim\sim NH_3^+ + CCl_3O_2^- \quad (10)$$

compete with association of the molecular sulphur-centred radical cation with a second molecule to yield the $(R_2S \therefore SR_2)^+$-type radical cation at this pH so far from the p*K* of the amino group (see also preceding paper). Furthermore, its half-life of *ca.* 200 μs is much shorter than that of (IV) under comparable conditions.[9] We therefore suggest this new 385 nm absorption to be attributable to an S ∴ O-bonded radical cation, *e.g.* in view of similar S ∴ O three-electron-bonded species found in the oxidation of *S*-methylcysteine,[9] 4-(methylthio)butyric acid,[9] and 6-*endo*-(methylthio)bicyclo-[2.2.1]heptane-2-*endo*-carboxylic acid.[27] (An S ∴ O bond with the other oxygen atom may also be envisaged.) The particular stability of (V) would arise from the sterically favourable six-membered ring configuration, the lack of fast consecutive reactions, and the fact that the thermodynamically more stable S ∴ N three-electron bond cannot be established at low pH.

A final example of a changed product-pH profile is the oxidation of 2-(ethylthio)ethanol. In the •OH radical-induced process the $(R_2S \therefore SR_2)^+$ radical cation of this compound could only be observed in very acid (pH $\lesssim$ 3) solutions.[28] Oxidation by $CCl_3O_2^\cdot$ reveals that the stability range of this S ∴ S-bonded species is also shifted to much higher pH. The rate constant for the reaction of $CCl_3O_2^\cdot$ with 2-(ethylthio)ethanol is determined to 4 × 10^7 mol^{-1} dm^3 s^{-1} from the formation kinetics of the $(R_2S \therefore SR_2)^+$ species at 480 nm (see Table). It may of course be asked why no S ∴ O-bonded species is observed whenever the S ∴ S-bonded radical cation is not stabilized. An S ∴ O bond is, however, generally very weak[9] and also, in the case of 2-(ethylthio)ethanol, could not be supported by a sterically favourable intramolecular ring structure. It is therefore assumed that fast, consecutive reactions, such as deprotonation, *etc.*, prevent formation of any detectable concentration of such species.



Scheme 1.



Scheme 2.

(3) *Reaction Mechanism.*—The experimental results presented in this and the preceding paper serve as a very instructive example of how different the mode of oxidative action of •OH and other radicals could be. It becomes particularly apparent for the oxidation of organic sulphides, which carry certain functional groups.

For unsubstituted sulphides only the initial step is different. As outlined in Scheme 1 the •OH radical always adds to sulphur (route a) before it is converted into the $(R_2S \therefore SR_2)^+$ radical cation either *via* consecutive reaction with a second sulphide (d) or by proton-assisted ionization (c) and complexation (e). Oxidation by $CCl_3O_2^\cdot$ or any other oxidants that undergo straightforward electron transfer leads directly to the molecular sulphur-centred radical (b) before equilibration to the S ∴ S-bonded radical cation occurs (e).

Oxidation of substituted sulphides by $CCl_3O_2^\cdot$, *etc.*, is exemplified in Scheme 2 for alkylthio-amines. The parameter which essentially controls whether the S ∴ S- or S ∴ N-bonded species is formed is the equilibrium constant K_i, which generally should be close to K_f, *i.e.* the protonation constant of the amino group in the original sulphide.* Since S ∴ N formation requires interaction of the unpaired electron at sulphur with the free electron pair at nitrogen, Scheme 2 explains why this species is only formed beyond and near the pK of the amino group. The

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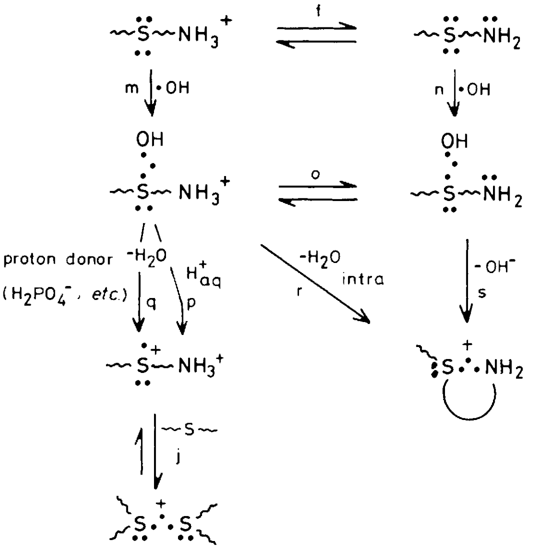
* K_i would differ from K_f only if through-bond resonance could be established between the unpaired electron at the oxidized sulphur atom and the free electron pair at nitrogen.



Scheme 3.

actual titration curves (Figures 2 and 3) reflect, of course, not only K_i but also the kinetics of associated processes.

The mechanism underlying the $^{\bullet}OH$-induced oxidation of substituted sulphides has already been described in previous papers,[9,28] and briefly outlined in the Introduction. The essential point is the formation of an intermediate $^{\bullet}OH$ radical adduct, >S ∴ OH, which is subject to proton-assisted dehydroxylation. The latter process leads to different reaction products depending on the origin of the protons, as is summarized in Scheme 3 for the amino-substituted compounds.

Accordingly, the S ∴ S-bonded radical cation is formed *via* reaction routes p and q, *i.e.* when high enough concentrations of external protons are available for dehydroxylation of the >S ∴ OH adduct. This can be achieved by free protons, *i.e.* at low pH, but also by high concentrations of potent proton donors such as $H_2PO_4^-$, CH_3COOH, *etc.* An example of the latter has been described in the $^{\bullet}OH$ radical-induced oxidation of methionine.[21] A competing alternative to these two processes which involve external proton sources for the dehydroxylation of >S ∴ OH is an intramolecular process where protons are provided by the NH_3^+ group (r). The associated S ∴ N bond formation should then, however, be assisted by a suitable steric arrangement (five- or six-membered rings). Finally, if the amino group is already deprotonated the corresponding process is considered to occur *via* OH^- elimination. Energetically, this is quite feasible, since S ∴ N bonds are generally more stable than S ∴ O bonds, from the thermodynamic point of view, particularly in sterically favourable arrangements.[9] Intermolecular S ∴ N formation has not been observed in our systems, but in principle cannot be excluded. The stability of such a species is in any case expected to be much lower than that of a sterically assisted intramolecular species.

The same considerations apply in principle also to sulphides carrying COOH, COOR, OH, *etc.* instead of an amino group, provided that this functional group contains a heteroatom, X, which can provide a free electron pair for establishment of an S ∴ X bond and which is not too different in electronegativity from sulphur.

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