The Reaction of α-(Alkylthio)alkyl Radicals with Tetranitromethane. Pulse Radiolysis Evidence for an Intermediate Radical Adduct

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α-(Alkylthio)alkyl radicals, $R^1\dot{C}HSR^2$, which are produced as intermediates in the ·OH radical-induced oxidation of organic sulphides, exhibit reducing properties. The experimental data for their reaction with tetranitromethane are best described in terms of a two-step mechanism *via* an intermediate adduct: $R^1\dot{C}HSR^2 + C(NO_2)_4 \longrightarrow [R^2SCHR^1 \cdots O_2N \cdots C(NO_2)_3]^{\cdot} \longrightarrow (R^1CH{=}SR^2)^+ + NO_2 + C(NO_2)_3^-$. The bimolecular rate constants for formation of the adducts have been found to be in the range $(2–4) \times 10^9$ mol^{-1} dm^3 s^{-1} for all the sulphides investigated and to be independent of temperature. The stability of the adduct depends significantly on the substituent R^1 and also on temperature. The rate constant, k_1, for its decay was found to be *ca.* 10^5 s^{-1} for R^1 = H, and $(1–4) \times 10^6$ s^{-1} for R^1 = alkyl at 21 °C. Values for $\Delta H^‡$ of 55.5 and 54.4 kJ mol^{-1}, and $\Delta S^‡$ of +40.1 and +62.4 J mol^{-1} K^{-1}, have been determined for the activated transition state of the radical adducts derived from $(CH_3)_2S$ and $(C_2H_5)_2S$, respectively. The positive change in activation entropy probably indicates that the final products are already more or less preformed in the activated complex. The reaction of α-(alkylthio)alkyl radicals with tetranitromethane has been used to determine the site and yield of ·OH radical attack on the sulphides. In the particular case of 2-(ethylthio)ethanol the kinetic data on the decay of the radical–tetranitromethane adduct have been used to characterize the identity of the various reducing radicals formed from this sulphide. Possible implications on the ·OH radical-induced oxidation of substituted aliphatic sulphides are discussed.

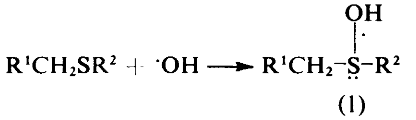
The reduction of tetranitromethane (TNM) is widely used as a reliable probe for reducing radicals, A·, since the reaction product nitroform anion, $C(NO_2)_3^-$, from the general reaction (1) is a stable and, because of its strong colour ($\lambda_{max.}$ 350 nm;

$$C(NO_2)_4 + A^{\cdot} \longrightarrow C(NO_2)_3^- + NO_2 + A^+ \qquad (1)$$

ε 1.5×10^4 mol^{-1} dm^3 cm^{-1}), easily detectable species.[1-6] Most of the reduction reactions of TNM by α-hydroxyalkyl and α-monoalkoxyalkyl radicals have been described as one-step electron-tranfer processes. In some cases, however, evidence could be produced for a two-step mechanism with a radical adduct, $[A \cdots C(NO_2)_4]^{\cdot}$, as an intermediate. Such adducts have been postulated from kinetic arguments for the reaction of TNM with dioxane radicals in dioxane solutions,[4] and $^{\cdot}CH_2OH$ radicals in methanol solutions.[5] Eibenberger *et al.* could even observe this intermediate from the reaction of some α-alkoxyalkyl radicals with TNM in aqueous solution by its optical absorption, $\lambda_{max.}$ = *ca.* 300 nm.[6] From kinetic and thermodynamic data for various substituted species these authors could also obtain information on the selectivity of the attack by the ·OH radical on alkoxyalkanes and on the structure of the intermediate radical–TNM adduct. It was concluded that the final products, *i.e.* $C(NO_2)_3^-$, NO_2, and the cation A^+, were already preformed through charge separation and bond lengthening before the complex decayed *via* an S_N mechanism.

In the present study we report our findings with α-(alkylthio)-alkyl radicals which are formed from aliphatic sulphides either directly through hydrogen-atom abstraction (2), or indirectly *via* the rather complex scheme of reactions (3)—(7).[7-9]

$$R^1CH_2SR^2 + {}^{\cdot}OH \longrightarrow R^1\dot{C}HSR^2 + H_2O \qquad (2)$$



$$R^1CH_2SR^2 + {}^{\cdot}OH \longrightarrow R^1CH_2{-}\underset{..}{\overset{OH}{\overset{|\cdot}{S}}}{-}R^2 \qquad (3)$$

(1)

$$(1) \longrightarrow R^1CH_2{-}\underset{..}{\overset{+}{\dot{S}}}{-}R^2 + OH^- \qquad (4)$$

$$(1) + R^1CH_2SR^2 \longrightarrow \begin{matrix} R^1CH_2 \\ R^2 \end{matrix}\!\!>\!\underset{..}{S}\overset{+}{\because}\underset{..}{S}\!<\!\!\begin{matrix} CH_2R^1 \\ R^2 \end{matrix} + OH^- \qquad (5)$$

(2)

$$(R^1CH_2SR^2)^{+\cdot} + R^1CH_2SR^2 \rightleftharpoons (2) \qquad (6)$$

$$(R^1CH_2SR^2)^{+\cdot} \longrightarrow R^1\dot{C}HSR^2 + H^+ \qquad (7)$$

A particular difficulty in our system in comparison with the α-alkoxyalkyl system arises from the formation of the strongly absorbing and long-lived 3-electron bonded radical cation (2) which prevents any unambiguous direct observation of a probably much less strongly absorbing radical adduct. The direct action of ·OH radicals will of course also yield (β-ω)-thio radicals. These are, however, not expected to exhibit reducing properties, *e.g.* by analogy with (β-ω)-hydroxy radicals,[2] and therefore are of no relevance for this study. Generally, it seemed of interest to look for additional examples where a radical-induced reduction proceeds *via* an addition–dissociation process rather than direct electron transfer since an increasing number of time-resolved studies have revealed that such a two-step mechanism is probably quite common.

Experimental

All compounds used were of highest commercially available purity. The purity of the sulphides was generally checked by g.c. and h.p.l.c., and if necessary increased to >98% by distillation. Tetranitromethane (TNM) was washed several times with distilled water prior to preparation of a saturated aqueous stock solution ($[TNM]_{sat.} = 6.4 \times 10^{-3}$ mol dm^{-3}). The solvent was deionized, ' Millipore '-filtered water, the quality of which corresponded to water triply distilled in

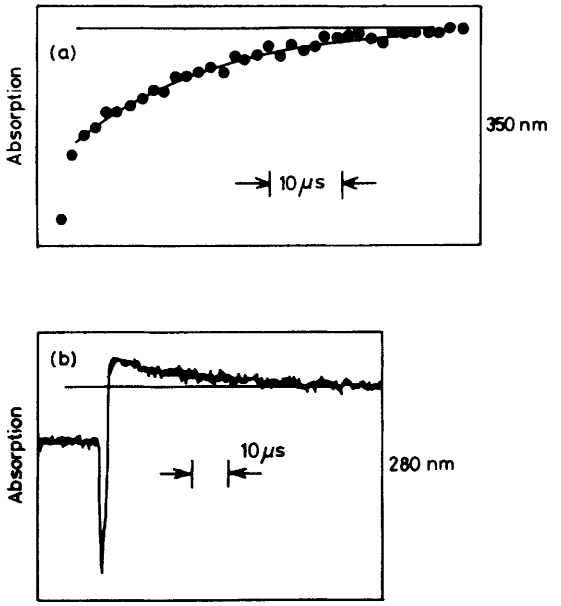


Figure 1. (a) Absorption *vs.* time curve at 350 nm for a pulse-irradiated, N_2O-saturated solution of $(CH_3)_2S$ (5×10^{-4} mol dm^{-3}) and $C(NO_2)_4$ (1×10^{-4} mol dm^{-3}) at pH 3.5. Dose: 2.7 Gy. Solid curve: computer-fitted first-order process; solid straight line: assumed end-level for computer-fitted process. (b) Absorption *vs.* time curve at 280 nm for the same solution

quartz apparatus. The pH was generally adjusted by addition of appropriate amounts of $HClO_4$ or NaOH. The solutions were deoxygenated by bubbling with N_2 (Linde, $[O_2] < 3 \times 10^{-4}$ vol%) and N_2O (Hoechst; traces of O_2 were removed by passing through a column with ' Oxisorb ' catalyst). Volatile solutes, *i.e.* the sulphides and TNM, were always added after deoxygenation of both solute and solvent. Accurate determination of the actual TNM concentrations in the solutions was achieved by treating aliquot samples with alkaline hydrazine solutions and analysis of the $C(NO_2)_3^-$ formed through its absorption at 350 nm using a Varian Superscan 2000 spectrophotometer.

Irradiations were carried out by applying short pulses of high-energy electrons from two different Van de Graaff accelerators (0.5—5 μs pulse duration, 1.55 MeV, and 5—50 ns, 3.8 MeV, respectively). The applied dose per pulse ranged from 1 to 10 Gy (100—1 000 rad, 1—10 J kg^{-1}). Dosimetry was based on the reduction of tetranitromethane in aqueous solutions containing propan-2-ol. Details of this as well as the experimental set-up and the evaluation of data from pulse radiolysis experiments in general have already been published.[10]

Irradiation of an aqueous solution leads primarily to $e_{aq.}^-$, $H^{\cdot}$, and $^{\cdot}OH$ which are formed with yields of $G = 2.8$, 0.6, and 2.8 species per 100 eV at absorbed energy, respectively. Since hydrated electrons can be converted into $^{\cdot}OH$ radicals by the added nitrous oxide *via* the reaction $N_2O + e_{aq.}^- \longrightarrow N_2 + OH^- + {}^{\cdot}OH$, and some electrons are scavenged in the so-called spurs in saturated N_2O solutions ($[N_2O] =$ *ca.* 2.4×10^{-2} mol dm^{-3}) the total yield of $^{\cdot}OH$ radicals in such solutions amounts to $G =$ *ca.* 6, *i.e.* to about 90% of all primary species. The absolute concentrations of $^{\cdot}OH$ radicals produced during a single pulse were in the range $(0.2—5) \times 10^{-6}$ mol dm^{-3}.

Temperature control was achieved by a specially designed flow system connected to a water-bath.[11]

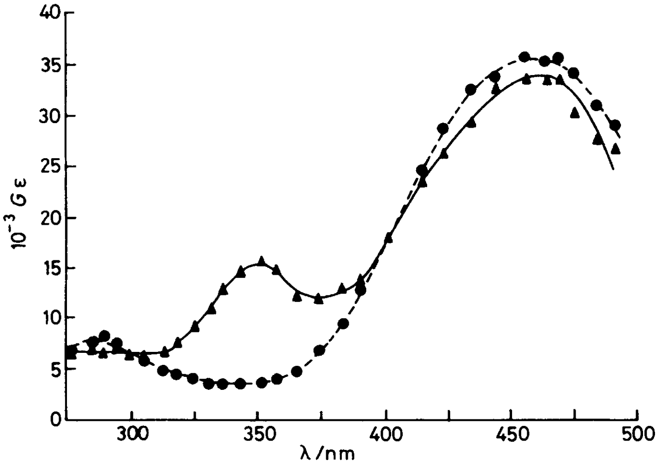


Figure 2. Optical absorption spectra recorded 3 (●) and 36 μs (▲) after the pulse from pulse-irradiated, N_2O-saturated aqueous solutions of $(CH_3)_2S$ (5×10^{-4} mol dm^{-3}) and $C(NO_2)_4$ (5×10^{-5} mol dm^{-3})

Results and Discussion

Kinetics.—α-(Alkylthio)alkyl radicals formed in the $^{\cdot}OH$ radical-induced oxidation of aliphatic sulphides can be monitored through their reaction (8) with tetranitromethane.

$$R^1\dot{C}HSR^2 + C(NO_2)_4 \rightsquigarrow (R^1CH{=}SR^2)^+ + NO_2 + C(NO_2)_3^- \quad (8)$$

Figure 1a shows, for example, the build-up of the absorption at 350 nm as a function of time as it is observable in a pulse radiolysis experiment with a N_2O-saturated aqueous solution of $(CH_3)_2S$ (5×10^{-4} mol dm^{-3}) and $C(NO_2)_4$ (1×10^{-4} mol dm^{-3}) at pH 3.5. At least two kinetically different processes are indicated. The initial step-like increase in absorption which is not time-resolved is due to the formation of $C(NO_2)_3^-$ through direct reaction of a small yield of $e_{aq.}^-$ with TNM (k 6.2×10^{10} mol^{-1} dm^3 s^{-1}[1]) under the experimental conditions, and also to some contributions from the absorptions of the α-(alkylthio)alkyl radical, in this case $^{\cdot}CH_2SCH_3$ ($\lambda_{max.}$ 280 nm), and particularly the sulphur-centred radical cation $(CH_3)_2\overset{+}{S}\therefore S(CH_3)_2$ ($\lambda_{max.}$ 465 nm) at this wavelength of 350 nm.

The process of concern is the second slower step which comes to completion after about 50 μs. It is attributable to the reduction of TNM by the $^{\cdot}CH_2SCH_3$ radicals formed through either the direct abstraction process [reaction (2)] or fast deprotonation of the radical cation $(CH_3)_2S^{+\cdot}$ [reaction (7)] before complexation to the 3-electron-bonded species could take place [reaction (6)]. A possible contribution from radicals formed through the indirect route [reactions (3), (5), back reaction (6), and (7)] is expected not to play any significant role on this time-scale owing to the long lifetime of $(CH_3)_2\overset{+}{S}\therefore S(CH_3)_2$ ($t_{\frac{1}{2}} > 70$ μs) under these conditions. In fact, $^{\cdot}CH_2SCH_3$ radical formation through this indirect pathway is likely to be responsible for and compatible with a very slow increase in 350 nm absorption which can be detected beyond the time-scale shown in Figure 1a.

The foregoing facts are also illustrated in Figure 2 which shows the absorption spectra recorded in pulse-irradiated, N_2O-saturated aqueous solutions of $(CH_3)_2S$ (5×10^{-4} mol dm^{-3}) and $C(NO_2)_4$ (5×10^{-5} mol dm^{-3}) at 3 and 36 μs after the pulse, respectively. During this time the $(CH_3)_2\overset{+}{S}\therefore S(CH_3)_2$ peak at 465 nm hardly decreases while, on the other hand, a pronounced absorption maximum develops at 350 nm where the $C(NO_2)_3^-$ absorbs. A small decrease in absorption is also observed over this period at 280 nm where $\cdot CH_2SCH_3$ and also $C(NO_2)_3^-$ and $(CH_3)_2S\overset{+}{\therefore}S(CH_3)_2$ contribute to the overall absorption. The optical spectra shown in Figure 2 do not indicate the possible presence of a $\cdot CH_2SCH_3$ adduct to TNM. It can be appreciated, however, from Figure 2 that it would hardly be possible to detect such a short-lived adduct in the 300 nm range without ambiguity underneath all the other absorptions.

Kinetic analysis of the slow second increase in absorption at 350 nm (Figure 1a) reveals that this process occurs exponentially. The half-life amounts to 11.6 μs under the above-mentioned conditions. A corresponding absorption–time curve recorded at 280 nm is shown in Figure 1b. The small overall decay exhibits the same kinetic characteristics with a practically identical half-life of 11.8 μs. At both wavelengths the experimental traces were fitted by a computer-processed least-mean-square calculation (shown as the solid curve in Figure 1a; the straight lines indicate the assumed t_∞ levels for the respective processes).

The half-lives of the two absorption–time curves decrease with increasing TNM concentration. At high TNM concentrations, however, they approach a constant value of *ca.* 7.8 μs [measurable within reasonable limits of error only at 350 nm, *i.e.* for $C(NO_2)_3^-$ formation]. Similar results are obtained also for the reaction of TNM with a number of other α-(alkylthio)alkyl radicals investigated in this study. Figures 3a and 3b show two typical plots of the measured first-order rate constants $k' = \ln 2/t_{\frac{1}{2}}$ from the analysis of the 350 nm traces *vs.* TNM concentration for solutions containing 5×10^{-4} mol dm^{-3} of $(CH_3)_2S$ and $(C_2H_5)_2S$, respectively.

This kind of kinetic behaviour is, in principle, indicative of a process for $C(NO_2)_3^-$ formation occurring *via* a mechanism with at least two steps, with a TNM-independent reaction becoming rate determining at high TNM concentrations. Two reasonable possibilities must be considered on the basis of the experimental information available so far, and both will be discussed now.

Mechanism I is based on the analogy with the TNM reduction by α-alkoxyalkyl radicals [6] and includes the formation of a radical–TNM adduct. In this case the data in Figure 3a and 3b would pertain to the reaction sequence (9a) and (9b) with

$$R^1\dot{C}HSR^2 + C(NO_2)_4 \xrightarrow{k_2} [R^1CHSR^2 \cdots C(NO_2)_4]^{\cdot} \quad (9a)$$

$$\xrightarrow{k_1} (R^1CH{=}SR^2)^+ + NO_2 + C(NO_2)_3^- \quad (9b)$$

$R^1\dot{C}HSR^2$ being formed in a comparatively faster reaction (2) and/or a fast sequence of reactions (3), (4), and (7). The bimolecular rate constants k_2 for the formation of the radical–TNM adduct can be obtained from the initial slope of the curves, while the respective plateau values refer to the first-order decay of the adduct.

The alternative mechanism II is also based on $R^1\dot{C}HSR^2$ formation *via* the reaction sequence (3), (4), and (7) with, however, the deprotonation (7) of the molecular radical cation

$$(R^1CH_2SR^2)^{+\cdot} \xrightarrow{k_1} R^1\dot{C}HSR^2 + H^+ \quad (7)$$

being a relatively slow and rate-determining step at high TNM concentrations. The bimolecular rate constant would then refer to a simple electron-transfer reaction (10). Such a

$$R^1\dot{C}HSR^2 + C(NO_2)_4 \xrightarrow{k_2} (R^1CH{=}SR^2)^+ + NO_2 + C(NO_2)_3^- \quad (10)$$

mechanism would, of course, render an intermediate radical–TNM adduct unnecessary without, however, excluding it as an intermediate which is kinetically not observable.

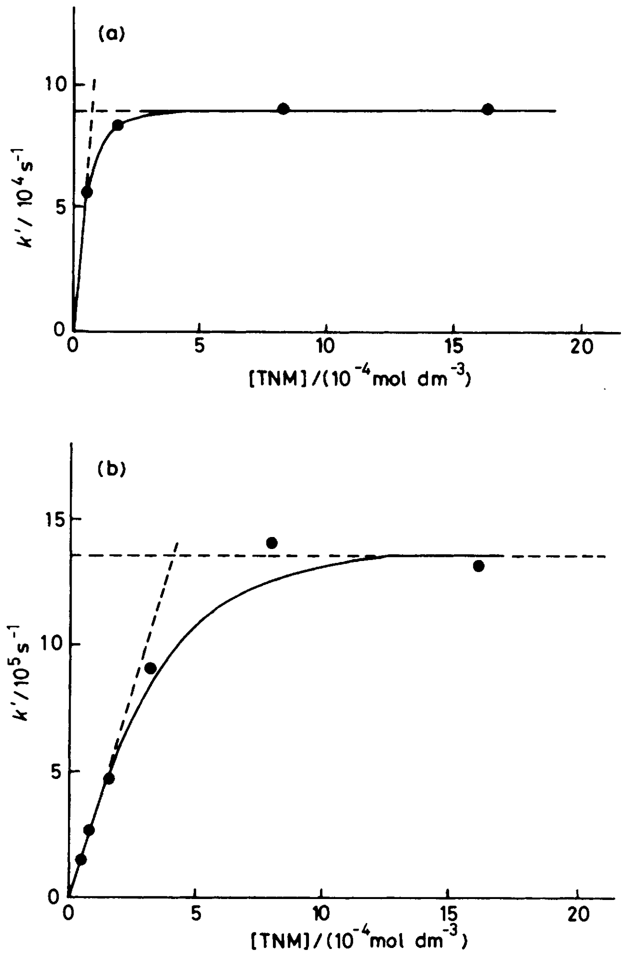


Figure 3. Plots of observed first-order rate constants $k' = \ln 2/t_{\frac{1}{2}}$ for the formation of $C(NO_2)_3^-$ from reactions (9a/b) *vs.* TNM concentrations; N_2O-saturated solutions at pH 3.5 containing 5×10^{-4} mol dm^{-3} of (a) CH_3SCH_3 and (b) $C_2H_5SC_2H_5$

Both mechanisms are described by the same differential equation (11) for the formation of $C(NO_2)_3^-$ (NF^-),[11] with

$$\frac{d[NF^-]}{dt} = k_2\left\{[A]_0 - \frac{1}{k_1}\cdot\frac{d[NF^-]}{dt} - [NF^-]\right\}[TNM] \quad (11)$$

$[A]_0$ being the maximum (initial) concentration of either $R^1\dot{C}HSR^2$ (mechanism I) or $(R^1CH_2SR^2)^{+\cdot}$ (mechanism II). Solution of equation (11) yields equation (12) and predicts the

$$[NF^-]_t = [A]_0\left\{1 + \frac{k_1}{k_2[TNM] - k_1}\exp(-k_2[TNM]) + \frac{k_2[TNM]}{k_1 - k_2[TNM]}\exp(-k_1t)\right\} \quad (12)$$

curve for $C(NO_2)_3^-$ formation to include an induction period and a point of inflexion. Qualitatively this is shown as an example in Figure 4 for solutions containing $CH_3SCH_2CH_2CH_3$ (5×10^{-4} mol dm^{-3}) and TNM (1×10^{-4} mol dm^{-3})

Table 1. Rate constants for the formation (k_2) and decay (k_1) of the radical-TNM adduct, and α-(alkylthio)alkyl radical yields from direct abstraction *via* reaction (2) for various sulphides at 21 °C

Sulphide	$\frac{k_2}{\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}}$	$\frac{k_1}{\text{s}^{-1}}$	Predominant radical	Radical yield G
CH_3SCH_3	2.8×10^9	9.0×10^4	$\dot{C}H_2SCH_3$	0.3
$C_2H_5SC_2H_5$	3.3×10^9	1.4×10^6	$CH_3\dot{C}HSC_2H_5$	1.3
$CH_3SC_2H_5$	4.2×10^9	1.6×10^6	$CH_3S\dot{C}HCH_3$	0.9
$CH_3S{-}C_3H_7$-n	2.1×10^9	3.3×10^6	$CH_3S\dot{C}HC_2H_5$	0.8
$CH_3S{-}C_4H_9$-n	2.2×10^9	2.2×10^6	$CH_3S\dot{C}HC_3H_7$	1.2
$CH_3SCH(CH_3)_2$	3.2×10^9	1.5×10^6	$CH_3S\dot{C}(CH_3)_2$	1.3

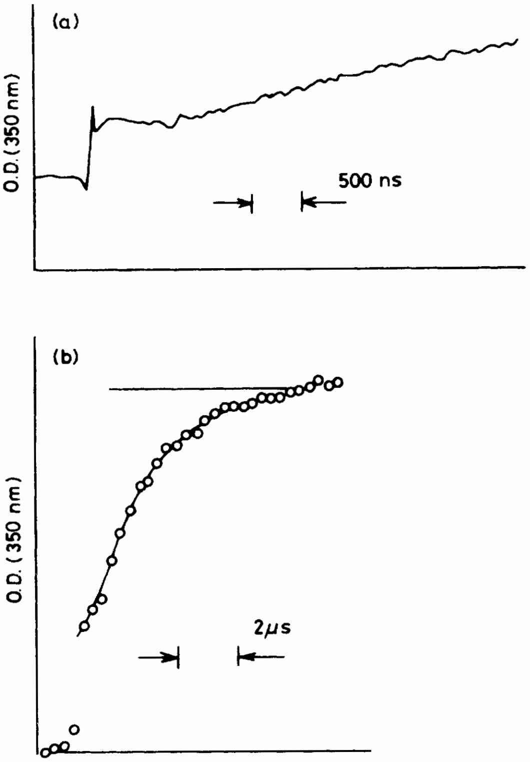


Figure 4. Optical absorptions *vs.* time curves at 350 nm for pulse-irradiated, N_2O-saturated solutions containing (a) $CH_3SCH_2CH_2CH_3$ (5×10^{-4} mol dm^{-3}) and TNM (1×10^{-4} mol dm^{-3}); (b) $CH_3SCH(CH_3)_2$ (5×10^{-4} mol dm^{-3}) and TNM (2.6×10^{-4} mol dm^{-3}). (Initial fast steps are due to direct reduction of TNM by $e_{aq.}^-$)

(Figure 4a), and $CH_3SCH(CH_3)_2$ (5×10^{-4} mol dm^{-3}) and TNM (2.6×10^{-4} mol dm^{-3}) (Figure 4b).

In order to minimize error limits the k_2 and k_1 values listed in Table 1 for various sulphides were evaluated from both the k' *vs.* [TNM] plots and computer analysis of individual absorption–time curves according to equations (11) and (12). The averaged data thus derived are considered to be accurate to within ±20%.

The second-order rate constants k_2 are seen to be similar for all compounds. The same does not apply, however, for the first-order rate constant k_1 which is more than one order of magnitude lower for the CH_3SCH_3 system than for all the other systems. This latter result finds reasonable interpretations in both our mechanisms.

In mechanism I the ($CH_2SCH_3 \cdots$ TNM)$^\cdot$ adduct would decay much more slowly than ($CH_3CHSC_2H_5 \cdots$ TNM)$^\cdot$ and all the adducts from the asymmetric sulphides. These are expected to be predominantly of the types ($RCHSCH_3 \cdots$ TNM)$^\cdot$ and ($R_2CSCH_3 \cdots$ TNM)$^\cdot$ since secondary and tertiary hydrogen atoms are more labile than primary ones. The observed acceleration of the decay of the adduct radical could be explained by the effect of the electron-donating properties of the substituents R and thus would agree with similar findings with the corresponding (TNM $\cdots$ α-alkoxyalkyl)$^\cdot$ radical adducts.[6] One might, of course, expect k_1 to be particularly high for the $(CH_3)_2CHSCH_3$-derived species. However, unambiguous experimental verification would require such high TNM concentrations that the competing direct reduction of TNM by $e_{aq.}^-$ would become the dominating process. It is further suspected that for this isopropyl substituted compound the observed kinetics may only partially, if at all, be associable with reaction (9b).

In the alternative mechanism II the k_1 values listed in Table 1 would not yet represent the true first-order rate constants for the deprotonation of the molecular radical cations. Since this reaction (7) competes with the formation of the 3-electron-bonded radical cation [forward reaction of equation (6)] the true values of k for reaction (7) are obtained by multiplication of the respective k_1 values by the relative yields for the deprotonation. The latter are obtained from the optical absorptions at 350 nm (corrected for the $R_2S\overset{+}{\because}SR_2$ absorption at this wavelength) and amount to $G(NF^-)/G(\cdot OH) = G(NF^-)/6$ with the absolute nitroform yields, $G(NF^-)$, listed in Table 1. The value $k = 4.2 \times 10^3$ s^{-1} thus evaluated for reaction (7) in the case of the dimethyl sulphide system is in very good agreement with values of 2.5×10^3 and 4.2×10^3 s^{-1} for the deprotonation of $(CH_3SCH_3)^{+\cdot}$ determined in separate studies.[8,12] The other comparable value of 2.9×10^5 s^{-1} for the diethyl sulphide differs, however, by almost one order of magnitude from those of the independent determinations (3.3×10^4 and 4.6×10^4 s^{-1}). Nevertheless it does not seem justified so far to explain the data obtained by either of our two mechanisms with certainty.

Variation of TNM Concentration.—An immediate consequence of mechanism II would be the requirement that the yield of reaction (7) and thus of $C(NO_2)_3^-$ would increase with decreasing sulphide concentration, *i.e.* decreasing yield of the competing forward reaction of equation (6). This is indeed the case as could be shown for the dimethyl sulphide system. (Corresponding investigations for the other sulphides were experimentally not feasible because too high TNM concentrations would be required.) The relative yields $G(NF^-)/G(\cdot OH) = G(NF^-)/G\{(CH_3SCH_3)^{+\cdot}\}$ increased from 0.027 to 0.076, 0.22, and 0.27 for 5×10^{-3}, 5×10^{-4}, 1×10^{-4}, and 5×10^{-5} mol dm^{-3} of CH_3SCH_3, respectively (*ca.* 5×10^{-5} mol dm^{-3} of TNM; pH 3.5). However, the associated requirement, *i.e.* a corresponding apparent decrease in the rate of NF^- formation with decrease in sulphide concentration, was not observed. Rather, the respective $t_{\frac{1}{2}}$ values are found to be

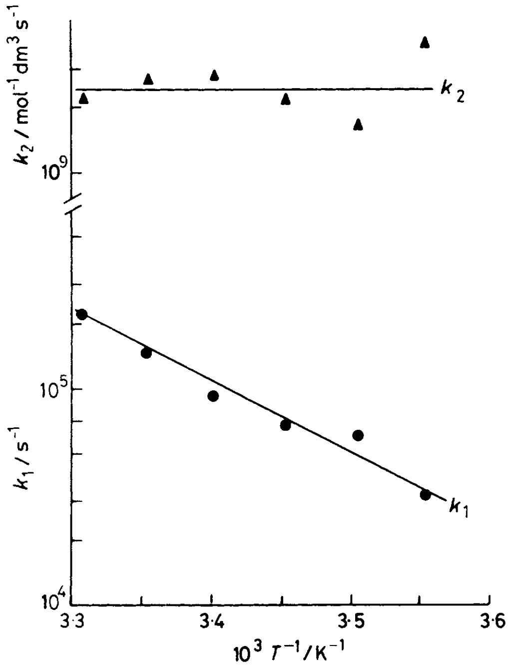


Figure 5. Arrhenius plot of k_2 and k_1 for the formation and decay of the $^{\cdot}CH_2SCH_3$–TNM adduct [N_2O-saturated solution of $(CH_3)_2S$ (5×10^{-4} mol dm^{-3}); various TNM concentrations; pH 3.5]

practically constant with random variation between 6.4 and 9.6 μs.

Furthermore, the deprotonation mechanism II would result in a true bimolecular rate constant for the radical cation complexation [reaction (6)] of $k_1 \times [R_2S]^{-1} \times \{G(R_2S^{+\cdot}) - G(NF^-)\}/G(R_2S^{+\cdot})$, *i.e. ca.* 1.7×10^7 mol^{-1} dm^3 s^{-1} for 5×10^{-3} mol dm^{-3} of CH_3SCH_3. This would result in a $t_{\frac{1}{2}}$ value for the formation of $(CH_3)_2S\overset{+}{\therefore}S(CH_3)_2$ of *ca.* 8 μs which is in clear disagreement with the experimentally observed $t_{\frac{1}{2}}$ value of <1 μs at this sulphide concentration.

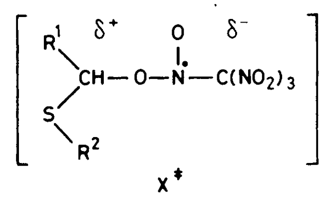
Since the dependence of the NF^- yield on the sulphide concentration could also be associated with a deprotonation of $(CH_3SCH_3)^{+\cdot}$ resulting from fast equilibration of the primarily formed $(CH_3)_2S\overset{+}{\therefore}S(CH_3)_2$, particularly at low sulphide concentration, we feel that our data *in toto* provide stronger evidence for mechanism I than for mechanism II. We shall therefore interpret all the following experimental results in terms of the TNM-radical adduct mechanism.

Temperature Dependence.—The overall formation of nitroform from reactions (9a) and (9b) depends strongly on temperature. Extensive measurements have been carried out with solutions of $(CH_3)_2S$ and $(C_2H_5)_2S$ at temperatures ranging from 8 to 29 °C. This relatively small temperature range is due to experimental limitations [increasing turbidity at the lower end and evaporation of the sulphide at the higher end; the boiling point of $(CH_3)_2S$, for example, is only 37.3 °C]. The rate constants k_2 and k_1 obtained for $(CH_3)_2S$ solutions from the respective $t_{\frac{1}{2}}$ *vs.* $[TNM]^{-1}$ plots are shown, as an example, in Figure 5. It is noted that k_2 is practically unaffected by the change in temperature. A clear, linear dependence is obtained in the Arrhenius plot (*i.e.* log k *vs.* T^{-1}), however, for the rate constant k_1. A similar picture is also obtained for the $(C_2H_5)_2S$ system.

The thermodynamic data which can be derived from the Arrhenius diagram for the unimolecular decay of the radical adduct are summarized in Table 2. The values obtained are of the same magnitude as for the corresponding α-alkoxyalkyl–TNM adducts [6] and thus substantiate the conclusions derived from those systems. Most important seems the significant positive change in activation entropy $\Delta S^{\ddagger}$, which suggests that in the sulphur-containing radical adduct also the final products are already preformed in the transition state $X^{\ddagger}$ by bond lengthening and charge separation. This process can certainly be expected to be facilitated by the high polarity of the solvent water. The rather low activation energy of only 57—58 kJ mol^{-1} (typical gas-phase values for monomolecular reactions are [13] 150—300 kJ mol^{-1}) probably indicates that there is some polarization even in the radical adduct itself.

Table 2. Activation energy, E, activation entropy, $\Delta S^{\ddagger}$, and activation enthalpy, $\Delta H^{\ddagger}$ (at 20 °C), for the decay of the $^{\cdot}CH_2SCH_3$–TNM and $CH_3\dot{C}HSC_2H_5$–TNM adducts

Sulphide	E/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}
CH_3SCH_3	58.0	+40.1	55.5
$C_2H_5SC_2H_5$	56.9	+62.4	54.4



The formation of the adduct from the radicals and TNM involves practically no activation energy and enthalpy. The activation entropy, $\Delta S^{\ddagger}$, for this process is calculated to be -30 and -40 J mol^{-1} K^{-1} for the $(CH_3)_2S$ and $(C_2H_5)_2S$ derived systems, respectively. These negative values are of course to be associated with the loss of the translational degree of freedom upon adduct formation.

In the light of our previous discussion it should be pointed out that these thermodynamic data could well also be attributable to radical cation deprotonation. Thus, the positive activation entropy may result from a decreasing extent of solvation of the transition state as is often observed for ion reactions in polar solutions.

Radical Yields.—The yields of α-(alkylthio)alkyl radicals derived from their reaction with TNM determined *via* the 350 nm absorption and listed in the last column of Table 1 are considered to be accurate to within ±30% owing to the various processes and species contributing to the overall absorption changes at this wavelength. Nevertheless, the results substantiate the expectation that direct abstraction of primary hydrogen atoms, as in $(CH_3)_2S$, is much less probable than abstraction of secondary and tertiary hydrogen atoms. At a maximum, however, the yield of α-(alkylthio)alkyl radicals formed directly *via* reaction (2) accounts only for about 20% of the total $^{\cdot}OH$ radicals available. A similar percentage has incidentally also been found for the $^{\cdot}OH$ radical-induced oxidation of the sulphur-containing amino acid methionine.[9] It may further be argued that the extent of internal radical stabilization is reflected in these yields considering, for example, the high yield of $CH_2S\dot{C}(CH_3)_2$ radicals from methyl isopropyl sulphide. Any quantitative correlation is, however, hampered by the fact that for most of the ' high-yield ' compounds the respective sulphur-centred radical cation suffers a comparatively faster deprotonation process [8,14] according to equation (6), and thus some indirectly formed α-(alkylthio)alkyl radicals may also contribute to the TNM reduction on the time-scale of the investigation.

Oxidation of 2-(*Ethylthio*)*ethanol*.—The reduction of TNM will finally be used for the interpretation of an as yet unknown reaction mechanism, namely the ·OH radical-induced oxidation of 2-(ethylthio)ethanol, $C_2H_5SCH_2CH_2OH$. The data, incidentally, also support the TNM–radical adduct mechanism I since they cannot satisfactorily be explained by the deprotonation mechanism II.

In very acidic solutions at pH < 3 the situation is similar to that described for the other sulphides in the previous sections. In the presence of TNM, nitroform is produced from reaction of reducing radicals *via* the same mechanism as discussed in detail in connection with Figure 1a. Analysis of the data obtained from solutions (pH 1.5) of 2-(ethylthio)ethanol (5×10^{-4} mol dm^{-3}) and various TNM concentrations yields rate constants of $k_2 = 1.1 \times 10^9$ mol^{-1} dm^3 s^{-1} and $k_1 = 3.2 \times 10^6$ s^{-1} for the formation and consecutive decay of the radical adduct, respectively. The reducing radicals result in this case from abstraction reactions of ·OH radicals and H· atoms, both of which are present at the low pH in about equal quantities [reactions (13a—c)].

$$CH_3CH_2SCH_2CH_2OH + {}^{\cdot}OH/H^{\cdot} \longrightarrow$$

$$H_2O/H_2 + \begin{cases} CH_3\dot{C}HSCH_2CH_2OH & (13a) \\ CH_3CH_2S\dot{C}HCH_2OH & (13b) \\ CH_3CH_2SCH_2\dot{C}HOH & (13c) \end{cases}$$

These radicals, particularly $CH_3\dot{C}HSCH_2CH_2OH$, are expected to undergo the addition reaction with TNM. The $CH_3CH_2S\dot{C}HCH_2OH$ radical is known to rearrange in acid solution to $CH_3CH_2\overline{S^+CH_2CH}{}^{\cdot}$, the identity of which has been determined by e.s.r. measurements.[15] Since the redox properties of this sulphonium-type radical are not known, it is not possible to assess the $CH_3CH_2S\dot{C}HCH_2OH$-based contribution to the TNM reduction. The α-hydroxy radical $CH_3CH_2SCH_2\dot{C}HOH$ finally is likely to reduce TNM in a one-step electron-transfer mechanism (or *via* an adduct which is too short lived to be detectable) as seems to be the case with α-hydroxyalkyl radicals in aqueous solution in general.

Both $CH_3\dot{C}HSCH_2CH_2OH$ and $CH_3CH_2S\dot{C}HCH_2OH$ radicals are, of course, also formed by deprotonation of the sulphur-centred radical cation [reactions (3)—(7)]. Accordingly, some additional nitroform formation is detected on a relatively long time-scale (> *ca.* 100 μs), and the kinetics of this process can directly be correlated with the decay of the strong and characteristic optical absorption of the $>\overset{+}{S\therefore S}<$ radical cation from 2-(ethylthio)ethanol at 480 nm.

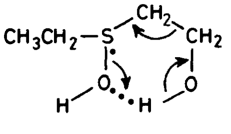
A different and very interesting picture is seen in less acidic solutions (pH > 3). First the complete lack of a transient absorption in the visible region indicates that $>\overset{+}{S\therefore S}<$ type radical cations are no longer stabilized. The yield of this species (relative to the yield of ·OH), plotted *vs.* pH, gives, in fact, a sigmoidal curve with 50% yield at pH 2.2. 2-(Ethylthio)-ethanol thus behaves like the sulphur-containing amino acid methionine for which a similar pH dependence of the $>\overset{+}{S\therefore S}<$ yield has been observed.[9,16] This is in contrast to the oxidation of unsubstituted aliphatic sulphides where these 3-electron-bonded species are stabilized over the entire pH range up to 10—11. For 2-(ethylthio)ethanol at pH > 3 the only transient absorption lies in the u.v. region with a distinct peak at 280 nm. The latter is associated with the α-thio radicals $CH_3\dot{C}HSCH_2CH_2OH$ and $CH_3CH_2S\dot{C}HCH_2OH$.

Addition of TNM to such solutions brings the second interesting aspect to light, namely that the nitroform formation, or, more precisely, the change in optical absorption at 350 nm, occurs *via* at least three distinguishable processes. An initial step-like increase in, for example, pulse-irradiated, N_2O-saturated solutions of 2-(ethylthio)ethanol (5×10^{-4} mol dm^{-3}) and TNM (3.1×10^{-4} mol dm^{-3}) results from a *ca.* 10% direct $e_{aq.}^-$ + TNM reaction and some tailing of the 280 nm band (see Figure 1a for comparison). This fast step is followed by a slower increase in absorption which, however, cannot be described by just a single process. Rather, fitting of the experimental curve is only possible by assuming two different processes which occur exponentially with half-lives of 1.4 and 7.1 μs, respectively, and a yield ratio of 3 : 1.

The total yield of nitroform formation from these two processes amounts to $G = 3.1 \pm 0.3$, *i.e.* to about 50% of the initially available ·OH radicals. This indicates that a considerable yield of species must also be formed which do not exhibit reducing properties and thus are not detectable *via* reaction with TNM.

The TNM concentration dependence of the kinetics of both these two slower processes suggests again the existence of radical–TNM adducts as intermediates. The rate constants which can be evaluated for the formation and decay of two different adducts are $k_2 = 2 \times 10^9$ mol^{-1} dm^3 s^{-1} and $k_1 = 3.6 \times 10^6$ s^{-1}, and $k_2 = 3 \times 10^9$ mol^{-1} dm^3 s^{-1} and $k_1 = 1 \times 10^5$ s^{-1}, respectively. The most remarkable aspect of these data is that the slower of these two processes which may be associated with $k_1 = 1 \times 10^5$ s^{-1} can no longer be explained by a slow and indirect formation of $CH_3\dot{C}HSCH_2CH_2OH$ or $CH_3CH_2S\dot{C}HCH_2OH$ radicals *via* reactions (3)—(7), *i.e. via* deprotonation of a sulphur-centred radical cation as in the very acidic solutions. The results at pH > 3 instead suggest quite clearly that the slower part of the TNM reduction results now from at least two radicals of a different nature. The k_1 values in the 10^6 s^{-1} region are associated with $R\dot{C}HS^-$ type radicals ($R \neq H$) by comparison with the data in Table 1, *i.e.* $CH_3\dot{C}HSCH_2OH$ and possibly $CH_3CH_2S\dot{C}HCH_2OH$. By the same token, it is reasonable to assign the low $k_1 = 10^5$ s^{-1} rate constant to the decay of a radical–TNM adduct which has been formed by a $\dot{C}H_2S^-$ type radical. This conclusion is in fact substantiated by direct experimental data from an earlier e.s.r. study on the ·OH radical-induced oxidation of 2-(ethylthio)ethanol at pH 4.5.[17] In this study both $^{\cdot}CH_2SCH_2CH_3$ and $CH_3\dot{C}HSCH_2CH_2OH$ radicals could be detected, and furthermore in the same concentration ratio of 1 : 3 as deduced from our TNM experiments.

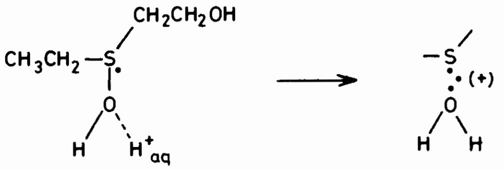
From the data at the various pH values it would appear that both the $^{\cdot}CH_2SCH_2CH_3$ radical and the $>\overset{+}{S\therefore S}<$ radical cation have a common precursor from which the respective species are formed *via* a competing, pH-dependent mechanism. This precursor is suggested to be the primary ·OH adduct to the sulphur function, *i.e.* $CH_3CH_2\dot{S}(OH)CH_2CH_2OH$. The formation of a $^{\cdot}CH_2SCH_2CH_3$ radical could then be explained by a 6-membered-ring mechanism [reaction (14)],



$$\longrightarrow {}^{\cdot}CH_2SCH_2CH_3 + CH_2O + H_2O \quad (14)$$

which occurs in the pH > 3 region with a yield of $G = ca.$ 0.8 (the remainder of the ·OH adduct is likely to yield $R\dot{C}HS^-$

type α-thio radicals in a non-cyclic process, and/or possibly undergo rearrangement or cleavage reactions). The key feature of the cyclic mechanism in reaction (14) is an intramolecular proton transfer from the alcoholic hydroxy group to the OH-function at the sulphur atom. The same picture also provides the explanation for the different findings in very acidic solutions. At low pH external protonation from the bulk of the solution will successfully compete with the intramolecular process of reaction (15), and yield a species which may be regarded as kind of a hydrated sulphur-centred radical cation (possibly with a $\overset{+}{\gt S\therefore O\lt}$ three-electron bond, or more simply $\gt S^{+\cdot}{}_{aq.}$). The latter would then be stabilized by reaction with a second sulphide molecule to form the $\overset{+}{\gt S\therefore S\lt}$ three-electron-bonded radical cation which in accordance with this picture is indeed only observable for solutions with high proton concentrations. In our system the rates for reactions (14) and (15) would be equal at pH 2.2.



(15)

Such a mechanism, which is based on the competition between intramolecular and external protonation of the OH function at the sulphur atom, could in fact also explain a large number of similar findings and results which have been obtained in the radical-induced oxidation of other substituted sulphides such as methionine, methionine derivatives, sulphur-containing amines *etc.*,[12,18] and furthermore would identify the primary ·OH radical adduct as the key intermediate.

Conclusion

The reactions of α-(alkylthio)alkyl radicals with TNM provide further evidence for a radical-induced reduction to proceed *via* an addition–dissociation process rather than by direct electron transfer. This emphasizes the possible general importance of such a mechanism in radical chemistry which seems to be becoming evident from an increasing number of similar findings in recent, particularly time-resolved, studies. The present investigation also serves, however, as a good example of the difficulties involved in the evaluation of a rather complex reaction mechanism which has to rely to a considerable extent on kinetic data.

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