One-electron Reduction of Sulphonium Salts in Aqueous Solution: a Pulse Radiolysis Study

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Absolute rate constants have been measured for the reduction of 1-alkylthiolanium (**1a–c**), 1-alkylthianium (**2a–e**), 1-(n-carboxyalkyl)thiolanium (**3a,b**) and 1-(n-carboxyalkyl)thianium (**4a,b**) salts, and ω-dimethylsulphonioalkanoic acids (**5a,b**), including biologically active *S*-methylmethionine (**6**) and dimethyl-β-propiothetin (**5b**), by hydrated electrons in aqueous solutions using the pulse radiolysis method. This reaction was found to occur very rapidly (*k* in the range 10^9–10^{10} dm^3 mol^{-1} s^{-1}), the individual rate constants being dependent on the electron inductive power of the substituents on the positive sulphur centre. The sulphuranyl radical $R_3S^•$, a possible reaction intermediate, could not be detected within the 0.1 μs time resolution of the applied technique. No reaction was observed between *S*-methylmethionine and $CO_2^{•-}$ or $Me_2\dot{C}OH$ under experimental conditions. The one-electron reduction potential of this sulphonium salt has been estimated to be < -1.8 V. *C*-centred radicals produced upon the reduction of the cyclic sulphonium salts 1-methyl- and 1-ethylthiolanium and 1-methylthianium salts by e^-_{aq} were characterized by using *p*-benzoquinone as a radical scavenger. It was found that ring opening is the predominant process rather than the cleavage of methyl or ethyl radicals.

One-electron reduction of sulphonium salts has been extensively studied, primarily by use of electrochemical methods[1,2] or chemicals[3,4] as reducing agents. This process was generally found to be irreversible, leading to carbon–sulphur σ-bond cleavage and the formation of a sulphide and a carbon-centred radical. However, the first step, the addition of an electron to the sulphonium salt, formally gives rise to a sulphuranyl radical followed by homolytic C–S bond cleavage [eqn. (1)].[5,6] Also, the formation of triorganosulphuranyl radicals as

$$R_3S^+ + e^- \longrightarrow [R_3S^•] \longrightarrow R_2S + R^• \qquad (1)$$

intermediates has been considered in the homolytic displacement of alkyl or aryl radicals on sulphides[7–11] and in reactions of sulphonium salts with alkoxide nucleophiles.[12,13] Sulphuranyl radicals have been observed in a number of systems[14–17] for the compounds having at least one electronegative heteroatom attached to the central sulphur. There is, however, no experimental evidence for trialkyl- or triaryl-sulphuranyl radicals, for which low stability has been proposed.[11,18] As for the reduction of alkyl- and aryl-sulphonium salts, the controversy is still unresolved as to whether sulphuranyl radicals are formed as intermediates or whether the electron addition and C–S bond cleavage are simultaneous processes.

From the yield of sulphides formed upon chemical reduction of phenylalkylsulphonium salts, Beak and Sullivan[3] determined the leaving group propensity of benzyl > secondary > primary > methyl in a ratio of 28:6:1:0.5. Similar results have been obtained in many other works[1,4] (electrochemical or chemical reduction). As this series follows the decrease of the radical stability, it was generally accepted that the most stable carbon-centred radical would be cleaved preferentially.[1] On the other hand, Saeva and Morgan[2] have suggested a concerted or nearly concerted electron addition and bond-breaking reaction rather than a two-step process [eqn. (1)]. This conclusion was based on cyclic voltametric measurements of the reduction potentials of arylalkylsulphonium salts, which were highly sensitive to the electronegativity of the ligand rather than to the stability of the leaving radical. They proposed electron acceptance to the σ* antibonding orbital of the C–S bond to be cleaved, the energy of which decreases with the increasing electron-withdrawing power of the ligand.[2]

The Arrhenius parameters for the intramolecular displacement reaction of primary alkyl radicals at sulphur in 4-(alkylthio)butyl radicals have been determined and discussed in terms of possible sulphuranyl radical formation as the rate-determining step.[11] The obtained selectivity and activation barriers were, in contrast, consistent with a transition state involving radical product structure formation as the rate-determining process.[11]

One-electron reduction potentials of trialkylsulphonium salts lie at relatively negative potentials and close to the limiting values where the decomposition of the solvent and supporting electrolyte occurs.[1] Also, trialkylsulphonium salts could not be reduced by potassium in graphite.[3] Attachment of electronegative substituents to the sulphur centre causes a significant shift to the less negative potentials.[12]

The purpose of the present study was to investigate the reduction of selected cyclic and open-chain alkylsulphonium salts by some powerful reducing radicals, namely the hydrated electron (e^-_{aq}), $CO_2^{•-}$ and $Me_2\dot{C}OH$. Particular emphasis was placed on the reactions of *S*-methylmethionine and dimethyl-β-propiothetin owing to their biological activity.[19] Using the pulse radiolysis technique, the kinetics of the process were followed in real time. As far as we are aware, this is the first time that the absolute rate constants have been measured for any one-electron reduction of a sulphonium salt. Formation of sulphuranyl radicals as possible intermediates was examined spectrophotometrically with a time resolution of 0.1 μs. Identification of the respective alkyl radicals obtained by the reduction of selected sulphonium compounds was performed using the *p*-benzoquinone method.[20]

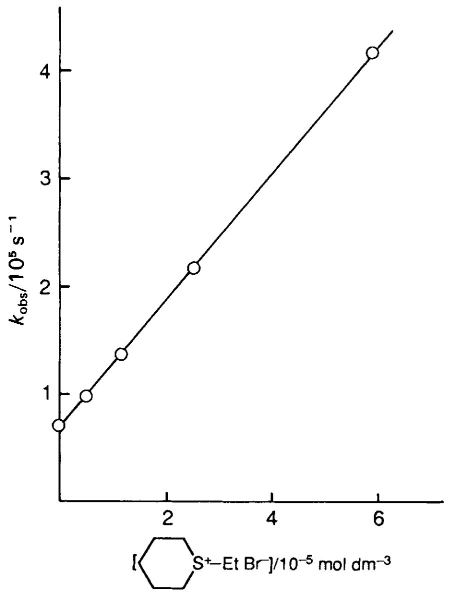
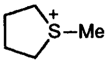
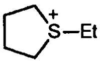
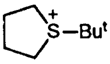
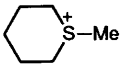
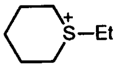
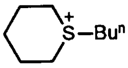
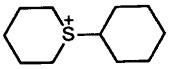
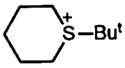
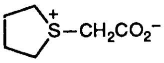
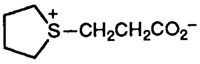
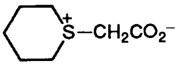
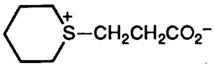


Fig. 1 Plot of first-order rate constant for e^-_{aq} decay at 650 nm observed on pulse radiolysis of deaerated, neutral aqueous solution containing 0.1 mol dm^{-3} 2-methylpropan-2-ol as a function of 1-ethylthianium bromide (**2b**) concentration

Table 1 Second-order rate constants for the reduction of sulphonium salts by e^-_{aq} in neutral aqueous solutions. Estimated error ± 10%.

R_3S^+		Rate constant/dm^3 mol^{-1} s^{-1}
	**1a**	1.6×10^{10}
	**1b**	1.6×10^{10}
	**1c**	9.0×10^{9}
	**2a**	7.1×10^{9}
	**2b**	5.9×10^{9}
	**2c**	4.3×10^{9}
	**2d**	2.0×10^{9}
	**2e**	8.0×10^{8}
	**3a**	7.6×10^{9}
	**3b**	6.9×10^{9}
	**4a**	3.8×10^{9}
	**4b**	2.6×10^{9}
$Me_2\overset{+}{S}CH_2CO_2^-$	**5a**	5.1×10^{9}
$Me_2\overset{+}{S}CH_2CH_2CO_2^-$ (dimethyl-β-propiothetin)	**5b**	4.0×10^{9}
$Me_2\overset{+}{S}CH_2CH(\overset{+}{N}H_3)CO_2^-$ (*S*-methylmethionine)	**6**	1.25×10^{10}

Experimental

Sulphonium salts (iodide, bromide or tetrafluoroborate) were prepared according to the literature[21–25] with the exception of *S*-methylmethionine bromide, which was purchased from Aldrich. *p*-Benzoquinone (Merck) was vacuum sublimed prior to use. All other chemicals were commercially available and were used as obtained.

Solutions were prepared using deionized water (Millipore filtered). The pH of the solutions was adjusted, where necessary, with NaOH and $HClO_4$. Deaeration was achieved by bubbling with N_2 for *ca.* 1 h/dm^3 sample. Subsequent saturation with N_2O was applied if hydrated electrons were to be converted into HO$^•$ radicals ($N_2O + e^-_{aq} \longrightarrow HO^• + HO^- + N_2$). The reactions of e^-_{aq} were studied in solutions containing 2-methylpropan-2-ol (0.1 mol dm^{-3}) in order to scavenge HO$^•$ radicals.

The experiments were conducted using the radiation chemical technique of pulse radiolysis.[26,27] Radicals were generated by exposing the solutions to short (0.1–1 μs) pulses of high energy electrons from 1.55 or 3.8 MeV Van de Graaff accelerators at the Hahn-Meitner-Institut, Berlin. Dosimetry was based on the HO$^•$ radical-induced oxidation of thiocyanate in N_2O-saturated solutions using $\varepsilon_{(SCN)_2^{•-}} = 7200$ dm^3 mol^{-1} cm^{-1} at 500 nm, $G = 5.5$ ($G = 1$ corresponds to *ca.* 0.1 μmol of changed species per joule of absorbed energy and generally denotes the number of chemically changed species per 100 eV absorbed energy). Absorbed doses per pulse were in the range of 1–10 Gy. Experiments were performed at room temperature.

Results

Reduction with Hydrated Electrons.—Neutral solutions. The rate constants (k_2) for the reaction [eqn. (2)] of sulphonium

$$R_3S^+ + e^-_{aq} \xrightarrow{k_2} \text{products} \qquad (2)$$

salts with e^-_{aq} were measured in the pulse-irradiated, deaerated aqueous solutions containing 0.1 mol dm^{-3} 2-methylpropan-2-ol and various R_3S^+ concentrations. The decay kinetics of e^-_{aq} were followed spectrophotometrically at 650 nm. The obtained pseudo-first-order rate constants were plotted as a function of [R_3S^+] as shown, for example, in Fig. 1 for 1-ethylthianium bromide (**2b**). From the slope of the straight line, the second-order rate constant $k_2 = 5.9 \times 10^9$ dm^3 mol^{-1} s^{-1} was calculated. (The intercept reflects the natural decay rate of e^-_{aq} in the absence of R_3S^+.) Table 1 summarizes the rate constants obtained for all investigated sulphonium salts **1**–**6**.

pH Dependence. The rate constants for the reaction of e^-_{aq} with sulphonium salts at different pH were determined for *S*-methylmethionine (**6**) and dimethyl-β-propiothetin (**5b**). The results are shown in Fig. 2. Whereas no change was observed for the latter compound in the pH range 5–13, the values for **6** decrease with increasing pH, forming a characteristic p*K* curve with the inflection point at pH 8.7. At pH >10, the rate constants were equal for both compounds.

Optical absorption measurements. For all sulphonium salts investigated, no optical absorption was observed in the solutions in the range of 250–700 nm after the disappearance of the e^-_{aq} spike (λ_{max} 720 nm) and the correction for the weak absorption of the $Me_2C(OH)\dot{C}H_2$ radical in the UV, *i.e.* of the radical formed by the reaction of 2-methylpropan-2-ol with HO$^•$. Measurements were performed with the time resolution of 0.1 μs. The change in the optical absorption of the solutions was followed from the actual time of pulse to *ca.* 1 ms after the pulse.

Reduction by $CO_2^{•-}$ *and* $Me_2\dot{C}OH$.—*Formate radical.* Formate radical anions were produced by the pulse irradiation

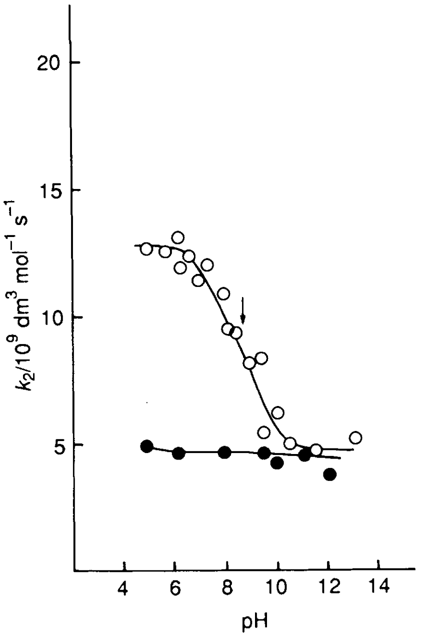


Fig. 2 Plot of second-order rate constant for the reduction of *S*-methylmethionine (**6**) (○) and dimethyl-β-propiothetin (**5b**) (●) by e^-_{aq} as a function of pH

of deaerated, N_2O-saturated aqueous solutions containing 0.1 mol dm^{-3} formate. Under these conditions, hydrated electrons were converted into $HO^•$ radicals in the reaction with N_2O, and $CO_2^{•-}$ was already formed *via* reaction (3) during the pulse.

$$HO^•/H^• + HCO_2^- \longrightarrow CO_2^{•-} + H_2O/H_2 \qquad (3)$$

The eventual reduction of sulphonium salts by $CO_2^{•-}$ radicals was investigated for *S*-methylmethionine (**6**) (neutral solutions) using tetranitromethane (TNM, 1×10^{-5} mol dm^{-3} solution) as a competitor [eqns. (4) and (5)]. The yield of nitroform

$$CO_2^{•-} + R_3S^+ \longrightarrow \text{products} \qquad (4)$$

$$CO_2^{•-} + C(NO_2)_4 \xrightarrow{k_5} C(NO_2)_3^- + NO_2 + CO_2 \qquad (5)$$

anions measured at 350 nm (ε = 15 000 dm^3 mol^{-1} cm^{-1}) in the absence of sulphonium salt corresponded to *G* 6.2, *i.e.* to the complete conversion of $CO_2^{•-}$ into this anion. It was not changed by the addition of 1×10^{-2} mol dm^{-3} *S*-methylmethionine. Based on $k_5 = 4 \times 10^9$ dm^3 mol^{-1} s^{-1},[28] the rate constant for reaction (4) can, consequently, be estimated as $< 10^6$ dm^3 mol^{-1} s^{-1}.

2-Hydroxypropan-2-yl radical. Deaerated, N_2O-saturated, neutral aqueous solutions containing 1 mol dm^{-3} propan-2-ol and 1×10^{-5} mol dm^{-3} *p*-nitroacetophenone (PNAP) were irradiated in the absence and presence of *S*-methylmethionine (**6**). As in the situation with the formate-containing solutions, all the primarily formed water radicals were converted into $Me_2\dot{C}OH$ [eqn. (6)]. This radical then quantitatively reduced PNAP to PNAP$^{•-}$ radical anion [eqn. (7)], which could

$$HO^•/H^• + Me_2CHOH \longrightarrow Me_2\dot{C}OH + H_2O/H_2 \qquad (6)$$

$$Me_2\dot{C}OH + PNAP \xrightarrow{k_7} PNAP^{•-} + Me_2CO + H^+ \qquad (7)$$

be measured spectrophotometrically (λ_{max} = 360 nm, ε = 17 600 dm^3 mol^{-1} cm^{-1}).[29] No decrease in the PNAP$^{•-}$ yield was observed upon the addition of 2×10^{-3} mol dm^{-3} **6**. When the value $k_7 = 3.0 \times 10^9$ dm^3 mol^{-1} s^{-1} (as reported for the water–10% v/v propan-2-ol mixture[30]) is used, reaction (8), *i.e.* reduction of **6** by $Me_2\dot{C}OH$, would have to occur with a

$$Me_2\dot{C}OH + R_3S^+ \longrightarrow \text{products} \qquad (8)$$

rate constant $<2 \times 10^6$ dm^3 mol^{-1} s^{-1} (if occurring at all).

Competition studies can sometimes be misinterpreted if the products of the reaction under investigation [in our systems eqn. (4) or (8)] react with the competitor leading to the same product as the primary species. This possibility could be excluded here. The eventual reduction of *S*-methylmethionine by $CO_2^{•-}$ or $Me_2\dot{C}OH$ would result in the formation of methyl and/or $\dot{C}H_2CH_2CH(NH_3^+)CO_2^-$ radicals as reactive products. (The $R_3S^•$ radical most probably does not appear as an intermediate—see the Discussion.) These radicals are not good one-electron donors and are not expected to react with TNM or PNAP on the microsecond time-scale applied.[31]

Experiments with p-*Benzoquinone.*—*p*-Benzoquinone (Q) was used as a scavenger for alkyl radicals which were expected to be produced in the reaction of sulphonium salts with e^-_{aq} [eqn. (2)]. Deaerated aqueous solutions containing 2-methylpropan-2-ol (1 mol dm^{-3}), 1-methylthiolanium tetrafluoroborate (**1a**) (5×10^{-2} mol dm^{-3}) and Q (1×10^{-3} mol dm^{-3}) were pulse irradiated at pH 6 and 2.3. Optical absorption spectra taken *ca.* 15 μs after the pulse corresponded to the known spectra of the unsubstituted semiquinone radicals in the deprotonated ($Q^{•-}$, pH 6) and protonated ($HQ^•$, pH 2.3) forms.[20,32] (Semiquinone is known to be a transient product generated in the reaction of alkyl radicals with quinone in a two-step process.[20]) The absorptions were built up exponentially with $t_{\frac{1}{2}}$ = 2.5 μs with a yield of *G* = 2.7. This was calculated using ε(310) = 19 000 dm^3 mol^{-1} cm^{-1} and ε(290) = 13 400 dm^3 mol^{-1} cm^{-1} as reported for $Q^{•-}$ and $HQ^•$, respectively.[20] [Much slower development of some additional absorption was observed through the whole spectrum. This was attributed to the reaction of the $Me_2C(OH)\dot{C}H_2$ radical with Q as also observed in the N_2O-saturated system with no sulphonium salt added, which was not further investigated.]

Additional support for the assignment of the above absorption to the semiquinone radicals is achieved by measurements of the absorbance at 310 nm as a function of pH [Fig. 3(*a*)]. The obtained p*K* value of 3.9 is in good agreement with 3.9–4.1 for the $Q^{•-}/HQ^•$ couple reported in the literature.[20,32,33]

The second-order rate constants for semiquinone radical formation were obtained from the pseudo-first-order formation kinetics of its optical absorption bands at different *p*-benzoquinone concentrations [Fig. 3(*b*)]. This was performed in deaerated aqueous solutions containing 2-methylpropan-2-ol (1 mol dm^{-3}) and R_3S^+ (1×10^{-2} mol dm^{-3}) at pH 6. For R_3S^+ = **1a**, **2a** and **1b**, the respective values of 2.6×10^8, 4.8×10^8 and 4.1×10^8 dm^3 mol^{-1} s^{-1} were obtained.

Discussion

One-electron Reduction Rate Constants.—Sulphonium salts are found to be readily reduced by hydrated electrons. The process occurs with the diffusion- or near diffusion-limited rate constants as determined for the aliphatic compounds **1**–**4**, and also includes the biologically active sulphonium salts **5** and **6** (Table 1). Although all values are very high, some decrease is noticeable with an increasing number of the substituents R of the methylene groups within any class of compounds. This parallels the increasing electron inductive power of the substituents and, consequently, the decrease in the effective positive charge on the sulphur centre. The attempt to quantify this effect by plotting the rate constant data as a function of the

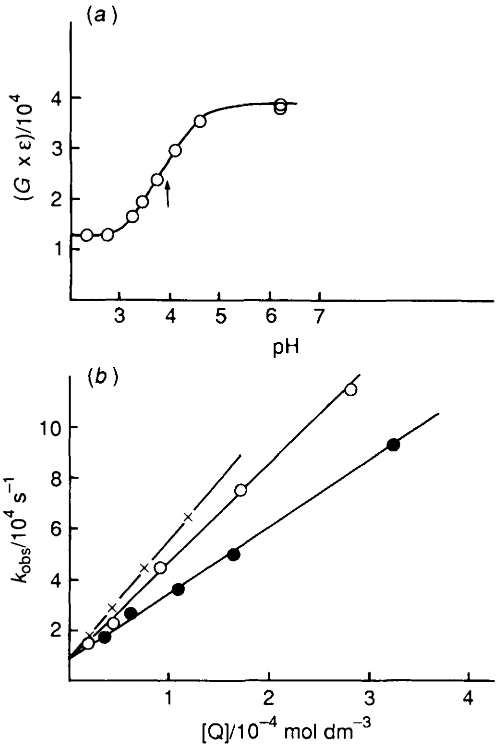


Fig. 3 (*a*) Absorbance expressed as $G \times \varepsilon$ at 310 nm *vs.* pH obtained in pulse-irradiated, deaerated aqueous solution of 1 mol dm^{-3} 2-methylpropan-2-ol, 5 × 10^{-2} mol dm^{-3} 1-methylthiolanium tetrafluoroborate (**1a**) and 1 × 10^{-3} mol dm^{-3} *p*-benzoquinone. (*b*) First-order rate constant for semiquinone radical anion formation at 310 nm observed on pulse radiolysis of deaereated aqueous solutions (pH 6) containing 1 mol dm^{-3} 2-methylpropan-2-ol and 1 × 10^{-2} mol dm^{-3} sulphonium salt *vs.* *p*-benzoquinone concentration: (×) **2a**, (○) **1b** and (●) **1a**.

Taft induction parameter σ^*[34] was not satisfactory. Most probably the rate constants are too close to the diffusion-controlled limit and the substituent induction effect could not show up completely. There is not even any difference observed in the rate constant upon the substitution of the methyl group by ethyl in the smallest, most easily reducible cations **1**.

The observed pH dependency of k_2 for *S*-methylmethionine (**6**), in contrast with dimethyl-β-propiothetin (**5b**) (Fig. 2), is also due to the change in the substituent electronegativity. The experimentally obtained inflection point at pH 8.7 is comparable to the pK 7.9 for the NH_2/NH_3^+ equilibrium of **6**.[35] No acid–base change occurs, of course, in the case of **5b** over the pH range 5–13.

The results are in accordance with the observations from the electrochemical reduction of sulphonium salts. One-electron reducing potentials were found to increase to less negative values by changing the substituents R on the sulphur atom by more electron-withdrawing groups.[1,2] Also, the polarographic half-wave potentials were found to be independent of pH over the range where the salts show no acid–base change.[1]

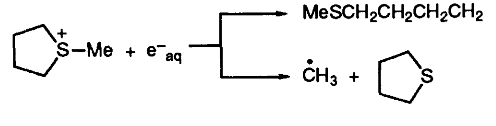
The radicals $CO_2^{\bullet -}$ and $Me_2\dot{C}OH$ are less powerful reducing agents compared with e^-_{aq} ($E°$ *vs.* NHE for e^-_{aq}, $CO_2^{\bullet -}$ and $Me_2\dot{C}OH$ are −2.9, −1.82 and −1.39 V, respectively).[36,37] These radicals seem not to be able to transfer the electron to the positive sulphur atom of the investigated sulphonium salts **1**–**6**. The polarographic half-wave potential of −1.85 and below −2 V *vs.* SCE in aqueous solutions has been reported for trimethyl- and triethylsulphonium salts, respectively.[5,38] This corresponds to −1.6 and < −1.75 V *vs.* NHE. The sulphonium salts studied in this work are expected to show similar or more negative values than Me_3S^+ owing to the higher electron inductive power of their substituents. Their one-electron reduction potential, according to the results above, could be estimated to be less than −1.8 V, *i.e.* more negative than the $CO_2^{\bullet -}$ redox potential. This is generally in agreement with electrochemical measurements.[1,5,38]

It is interesting to note that no reaction of the triphenylsulphonium cation with $Me_2\dot{C}OH$ (aqueous solutions, pulse radiolysis study)[39] and $Ph_2\dot{C}OH$ (flash photolysis in CH_2Cl_2 solution)[40] was detected despite the relatively low reduction potential of Ph_3S^+ (−1.2 V *vs.* SCE).

Because sulphonium salts **5b** and **6** are important naturally occurring compounds essential for a number of biological processes,[19] it is interesting to note that they only accept an electron from very powerful reductants ($E° < -1.8$ V) and do not react efficiently, if at all, with organic free radicals, not even with such a strongly reducing radical as $CO_2^{\bullet -}$.

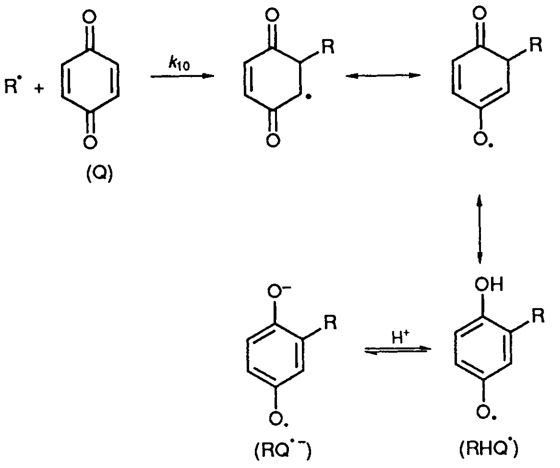
Reaction Mechanism.—Sulphuranyl radical as a reaction intermediate. UV-visible absorption spectra are known for several sulphuranyl radicals. Thus, λ_{max} at 370–430 nm and relatively high extinction coefficients ε of 5000–8000 dm^3 mol^{-1} cm^{-1} have been reported for $R_2\dot{S}X$ (X = Cl, Br or I).[41] Radicals of the type $-{}^{\bullet}\overline{S{-}O{-}C}{=}O$ derived from one-electron oxidation of methionine,[42] 4-(methylthio)propanoic acid,[43] 6-*endo*-methylthio-2-*endo*-carbonylnorbornane derivative[44] and butyl 2-(methylthio)peroxybenzoate[45] have been found to have λ_{max} at 390–410 nm. Sulphuranyl radicals R(R′)$\dot{S}$SR (R′ = H or alkyl) have also been found to absorb light within a similar region,[46] whereas $(RO)_3S^{\bullet}$ radicals show an absorption maximum at a somewhat lower wavelength (λ 330–340 nm).[45] All these sulphuranyl radicals possess at least one bond between sulphur and a second heteroatom. A prediction of the optical properties of the sulphyranyl radical having only carbon atoms attached to sulphur is not possible. The fact that we found no spectrophotometric evidence for the formation of such an intermediate could be due to several reasons: (*a*) the extinction coefficient of $R_3S^{\bullet}$ is too low (*i.e.* ε ≪ 500 dm^3 mol^{-1} cm^{-1}) to be detectable under the experimental conditions employed; (*b*) λ_{max} could lie beyond the experimentally accessible screening range of 250–700 nm; (*c*) the very short half-life of the species (<0.1 μs); and (*d*) no sulphuranyl radical is formed and the reduction mechanism is indeed a synchronous electron addition–bond rupture as suggested by Saeva and Morgan[2] (see above).

Identification of the leaving radical. If the cyclic sulphonium cations are considered, two different radicals could be formed upon the addition of a hydrated electron. For example, in the case of **1a**, ring opening could occur besides cleavage of the methyl radical [eqns. (9a) and (9b)]. Using *p*-benzoquinone as a radical scavenger, we could distinguish between these two radicals on the pulse radiolysis time scale. According to Veltwisch and Asmus,[20] alkyl radical addition to *p*-benzoquinone is followed by a rapid electron transfer to a second *p*-benzoquinone molecule, forming a semiquinone radical [reactions (10) and (11)]. [Substituted and unsubstituted semiquinone radicals exist in several mesomeric, tautomeric and acid–base forms, as denoted in eqn. (10).] Therefore, an unsubstituted semiquinone radical ($HQ^{\bullet}$ or $Q^{\bullet -}$) is the reaction product which could be detected in the solution, the rate of its formation being determined by the initial alkyl radical addition to *p*-benzoquinone (k_{10}).



(9a)

(9b)



(10)

$$RHQ^{\bullet}/RQ^{\bullet -} + Q \longrightarrow RQ + HQ^{\bullet}/Q^{\bullet -} \qquad (11)$$

In the systems studied here, the formation of the unsubstituted semiquinone radicals were also detected *via* their characteristic optical spectra and p*K* values [Fig. 3(*a*)]. The yield of these radicals corresponded to *G* 2.7, *i.e.* to the quantitative conversion of e^-_{aq} into the alkyl radicals and further to the semiquinone radicals. The rate constants obtained for the semiquinone radical production $k_{10} = 2.6 \times 10^8$ and 4.8×10^8 dm^3 mol^{-1} s^{-1} for the radicals liberated from **1a** and **2a**, respectively, [Fig. 3(*b*)] differ significantly from the value 4.5×10^7 dm^3 mol^{-1} s^{-1} determined for the addition of the $\dot{C}H_3$ radical.[20] Therefore, it could be concluded that reaction (9a), *i.e.* ring opening upon electron addition, is an important, if not the predominant, process. A very similar value of $k_{10} = 4.1 \times 10^8$ dm^3 mol^{-1} s^{-1} was obtained for the radical from **1b**. For this compound ring opening is also proposed as the main process, assuming similar rate constants for the ethyl and methyl radicals.[47] The higher values obtained for $MeS(CH_2)_3\dot{C}H_2$ and $EtS(CH_2)_3\dot{C}H_2$ compared with the methyl radical for the addition reaction to the quinone electron-deficient C=C bond could be explained by the higher nucleophilic character of the sulphide radicals.[47] We are not able, however, to evaluate whether some (and in which ratio) $\dot{C}H_3$ or $\dot{C}H_2CH_3$ radicals are also formed because neither the absolute nor relative rate constants are known for the addition of similar radicals to quinones. An indication of partial methyl radical production from **1a** could be deduced from the lower rate constant compared with **1b**, although further kinetic and end-product measurements, which are beyond the scope of this work, are necessary to make more precise conclusions in this regard.

These results are generally in accordance with those of many analyses of end products after the electrochemical or chemical reduction of sulphonium salts.[1,3,4] Radicals formed upon ring opening could be considered to be more stable than the methyl or ethyl equivalents. On the other hand, in view of the simultaneous electron addition and S–C bond breaking mechanism[2] the σ* antibonding orbital between sulphur and carbon from methyl or ethyl groups could be considered as being higher in energy, thereby leaving ring opening to occur preferentially.

The radiolytical reduction of alkylsulphonium salts by hydrated electrons has been shown to be a convenient method for very rapid and quantitative production of alkyl radicals. In order to generate only one sort of alkyl radical at a time, application of trialkylsulphonium salts with identical ligands or with a known ratio of leaving radicals is recommended.

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