198. Pulse Radiolytic Studies of 1-Halo-2-(methylthio)ethanes in Hexane and 1,2-Dichloroethane: Formation of an Intermolecular Species with a Three-Electron Bond between Sulfur and Iodine

by **Elke Anklam***, **Hari Mohan**[1]), and **Klaus-Dieter Asmus**

Hahn-Meitner-Institut Berlin GmbH, Glienicker Strasse 100, D-1000 Berlin 39

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1-Iodo-2-(methylthio)ethane was synthesized *via* a ring-opening reaction of thiirane with MeI in MeCN. The S-centered radical cation of this compound undergoes an intermolecular stabilization with the I substituent of a second unattacked substrate molecule to yield an $(>S\therefore I-)^{+}$ bonded radical cation. The oxidation was initiated by solvent radical cations in irradiated 1,2-dichloroethane and hexane solutions. The $2\sigma/\sigma^{*}$ three-electron-bonded species exhibits an optical absorption band at 410 nm, detectable by pulse radiolysis. During its decay, a new, longer-lived absorption band is formed at 380 nm which is assigned to $I_2^{\cdot -}$. The latter is suggested to result from anchimeric assistance in the generation of a cyclic sulfonium salt. The radical cations of 1-bromo- and 1-chloro-2-(methylthio)ethane are assumed to undergo rapid cyclization to the sulfonium salt without stabilization in any intermolecular S-Br or S-Cl interaction.

Introduction. – Recently, we reported on the formation of the $2\sigma/\sigma^{*}$ three-electron-bonded radical cation **1** by ·OH radical oxidation of 1-iodo-3-(methylthio)propane (**2**), wherein the oxidized S-atom is stabilized by an intramolecular association with the I-atom [1] *(Scheme 1)*. In aqueous solutions, **1** shows a transient absorption spectrum in the VIS (λ_{max} = 440 nm) which decays exponentially with $\tau_{1/2}$ = 110 µs. Similar results were obtained with other 1,*n*-iodo(alkylthio)alkanes (n ⩾ 3) [2].

Scheme 1

2 **1**

The bromo analogue of **2** is also oxidized to yield an intramolecular three-electron-bonded radical cation $(^{\frown}\underline{S\therefore Br})^{+}$, but only in very dilute solutions (< 10^{-4} M). At high solute concentrations, intermolecular interactions result in the formation of a S–S bonded radical cation [2].

To obtain further insight into the competition between these intra- and intermolecular processes, we undertook pulse radiolytic studies of 1-iodo-, (**3**), 1-bromo-, (**4**), and 1-chloro-2-(methylthio)ethane (**5**) in 1,2-dichloroethane (DCE) and hexane solutions.

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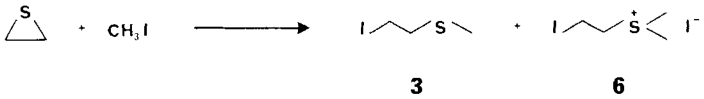
[1]) Present address: Chemistry Division, Bhabha Atomic Research Centre, Bombay 400085, Republic of India.

3 X = I
4 X = Br
5 X = Cl

Compounds **3**–**5** can be looked at as mustard derivatives. Compound **5** was commercially available, and **4** has been synthesized by the reaction of 2-(methylthio)ethanol with PBr_3 [3] or by a ring opening of thiirane with MeBr [4]. The synthesis of **3** has not been reported in the literature. Generally 1,*n*-halo(alkylthio)alkanes can be obtained *via* reaction of 1,*n*-dihalogenated alkanes with thiolates [5]. It is, however, not possible to isolate **3** in this manner, because of its instability during the workup procedure. Thus, another method had to be applied, and it will be described here for the first time.

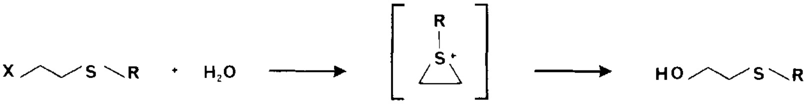
Results. – *Synthesis of* **3**. Recently, a simple method for the synthesis of **2** was described in [6]. The analogous ring opening of thiirane with MeI in MeCN leads to **3** and to the sulfonium salt **6** *(Scheme 2)*. Compounds **3** and **6** were characterized by ^{1}H-NMR, MS, and elemental analysis.

Scheme 2



Choice of Solvent. Most of our previous investigations were conducted in aqueous solution which, upon irradiation, provided ·OH radicals as oxidants. This is, however, not possible with compounds **3**–**5**, since 1-halogen-2-(alkylthio)ethanes undergo very fast hydrolysis [7] [8] *(Scheme 3)*.

Scheme 3



It has been demonstrated that oxidations can also conveniently be initiated in irradiated hydrocarbon or DCE solutions [9–14]. The oxidizing species in such systems is the primary radical cation formed in the general ionization process *(Eqn. 1)*.

$$\text{Solvent} \rightarrow (\text{Solvent})^{+\cdot} + e^- \qquad (1)$$

Pulse Radiolysis. Pulse radiolysis of 10^{-4}–10^{-2} M solutions of **3** in hexane, saturated with N_2O, leads to a transient absorption band at λ_{max} = 410 nm. The yield is dependent on the solute concentration. This is shown in *Fig. 1*, the yield is given in terms *Gε*. (The *G* value is the radiation chemical yield of generated species per 100 eV absorbed energy.) The decay of the transient absorption was analyzed at its maximum and found to be exponential. The first half-life of this species, **7**, is around 10 μs, and independent of dose and solute concentration, suggesting a purely monomolecular decay. The decay of **7** is

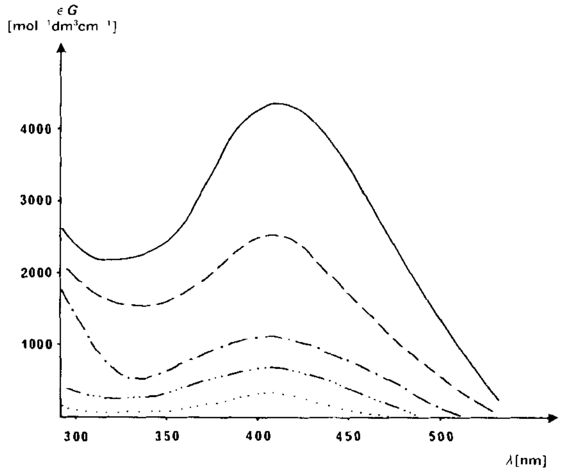


Fig. 1. *Optical absorption spectra of* **7** *obtained by pulse radiolysis of N_2O-saturated solutions of* **3** *in hexane, recorded 1.5 μs after a 5-μs pulse* (——: $c = 10^{-2}$ M; – – –: $c = 5 \times 10^{-3}$ M; –·–·–·: $c = 10^{-3}$ M; –···–···: $c = 5 \times 10^{-4}$ M; ····: $c = 10^{-4}$ M)

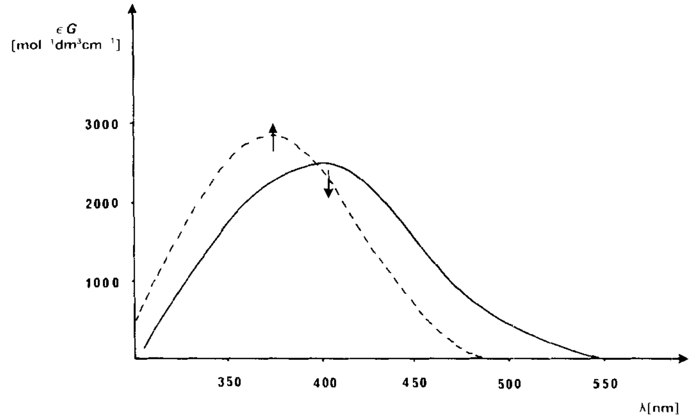


Fig. 2. *Optical absorption spectra of* **7** *and* **8** *obtained by pulse radiolysis of a N_2O-saturated 5×10^{-3}* M *solution of* **3** *in hexane, recorded at different times after a 5-μs pulse* (——: 1.5 μs after the pulse, – – – –: 20 μs after the pulse)

accompanied by the generation of a new species, **8**, which absorbs around 380 nm. This is shown in *Fig. 2* which exhibits absorption curves obtained upon pulse radiolysis of a 5×10^{-3} M solution of **3** in hexane at 1.5 μs and 20 μs after the pulse, respectively. Pulse irradiation of N_2-saturated solutions of **3** in hexane yields only the band at 380 nm. Its identity is not yet known, but it is noted that $I_2^{\cdot-}$ absorbs at this wavelength. This radical anion can be formed as a result of dissociative electron capture by **3** [15] [16]. Similar results are obtained by pulse radiolysis using DCE as the solvent.

Pulse radiolysis of the Br analogue **4** and Cl analogue **5** shows a single absorption band at 365 nm (species **9**) and 350 nm (species **10**), respectively. The *Gε* values depend on the solute concentrations, and a mixed-order decay is found for these relatively long-lived species.

Discussion. – The results of this study establish the formation of various transient radical and molecular species in the oxidation of 1-halogen-2-(methylthio)ethanes. The first problem which has to be addressed is the identity of the radical cation **7** derived from the iodo compound **3**.

It is most reasonable to assume the S-atom to be the primary site of oxidation. This has recently been demonstrated for the oxidation of the homologue 1-iodo-3-(methylthio)propane (**2**) [1]. All solely S-centered molecular radical cations are known to be very unstable, and furthermore to absorb in the UV around 300 nm (in aqueous solution) [17]. This precludes assignment of the present optical absorption at 410 nm to such a species. The generally high tendency of an unpaired p electron on a S-atom to associate with a free p-electron pair of a second unoxidized heteroatom [17] is, therefore, likely to be a high enough driving force for a consecutive stabilization reaction.

Several possibilities must, however, be considered for such a stabilization process. The first would be an intramolecular association of the oxidized S- with the I-atom and generation of a four-membered ring structure analogous to **1** *(Scheme 1)*. A major argument can, however, be advanced against such an assignment in case of **7**. In previous studies [17], it has been established that the optical absorption of a $2\sigma/\sigma^*$ three-electron bond is a direct measure of the degree of p-orbital overlap and, thus, of the bond strength between the two interacting heteroatoms. Generally, an overlap and higher bond strength is associated with a blue-shift in absorption, and *vice versa*. A four-membered ring system, as would be established upon intramolecular S-I interaction, is sterically much less favorable with respect to p-orbital overlap than a five-membered ring as in **1**. Consequently, and in analogy to corresponding oxidized dithiaalkanes [17] [18], its absorption should be red-shifted relative to $\lambda_{max} = 440$ nm of **1**. The observed $\lambda_{max} = 410$ nm of our species **7** is, thus, not compatible with an intramolecular $\diagdown\underbracket{S\therefore I}$ interaction.

Optical considerations also eliminate the second possibility, namely, intermolecular stabilization to $(>S\therefore S<)^+$ with formation of a $2\sigma/\sigma^*$ three-electron bond between two S-atoms. Such species are known to absorb at even higher wavelengths, 450–550 nm [2] [17].

It is noted, however, that the absorption of **7** is very similar to that of $R_2S\therefore I$ radicals which arise from interaction of $R_2S^{\cdot+}$ with I^- [19]. We, therefore, assign the 410-nm absorption to a species which results from intermolecular association of the oxidized S function in **11** with the I-atom of a second molecule **3** to yield the bimolecular radical cation **7**.

It should be noted that the pronounced dependence of the transient yield on the solute concentration is not a conclusive argument in favor of an intermolecular process in hexane and DCE, since such a functional relationship may just reflect the competition between solute oxidation and geminate recombination in these low dielectric solvents.

The oxidation mechanism of the ethane derivative **3** (and the same, in principle, holds for **4** and **5**) is, therefore, significantly different from the propane derivative and higher homologues. It seems that the difference arises from the molecular properties of the 1-halogen-2-(alkylthio)ethanes.

The following mechanism accounts for the events in the pulse radiolysis of **3**. Irradiation of DCE first leads to the formation of radical cations and electrons [9–11]. The latter are removed by reaction with further DCE molecules (*Eqns. 2* and *3*).

$$\mathrm{DCE} \longrightarrow \mathrm{DCE}^{+\cdot} + e^- \quad (2)$$

$$e^- + \mathrm{DCE} \longrightarrow \mathrm{Cl{-}CH_2{-}\dot{C}H_2} + \mathrm{Cl}^- \quad (3)$$

Irradiation of alkanes, *e.g.* hexane, as the solvent correspondingly yields alkane radical cations [12–14]. The electrons are in this case scavenged by N_2O (*Eqns. 4* and *5*) which was added at saturation concentration.

$$C_6H_{14} \longrightarrow C_6H_{14}^{+\cdot} + e^- \quad (4)$$

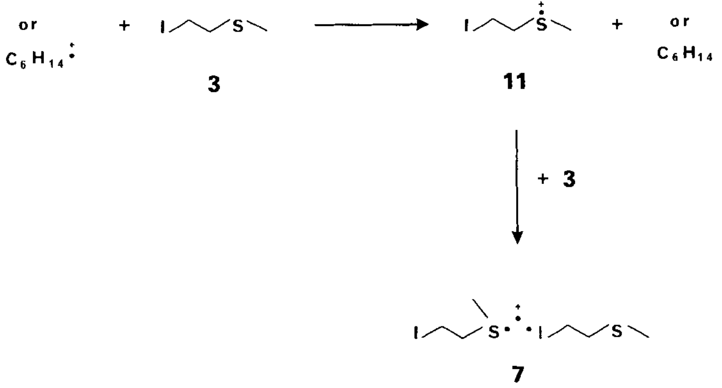
$$e^- + N_2O \longrightarrow N_2 + O^{-\cdot} \quad (5)$$

Another reactive species, which has to be considered, is a neutral alkyl radical, because of the easy deprotonation of the radical cation *(Eqn. 6)*.

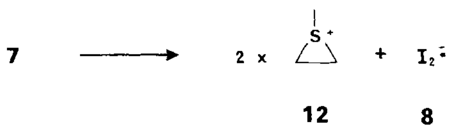
$$C_6H_{14}^{+\cdot} \longrightarrow H^+ + (C_6H_{13})\cdot \quad (6)$$

These primary events are followed by oxidation of **3** to the S-centered radical cation **11**, which finally stabilizes, by intermolecular interaction with the I-atom of an unattacked molecule **3**, to the three-electron-bonded $2\sigma/\sigma^*$ species **7** *(Scheme 4)*. The decay of **7** is suggested to result in the formation of the cyclic sulfonium salt **12** and $I_2^{-\cdot}$ by anchimeric assistance [20] [21] *(Scheme 5)*. The $I_2^{-\cdot}$ is positively identified by its known optical absorption and decay kinetics [15] [16] [22].

Scheme 4



Scheme 5

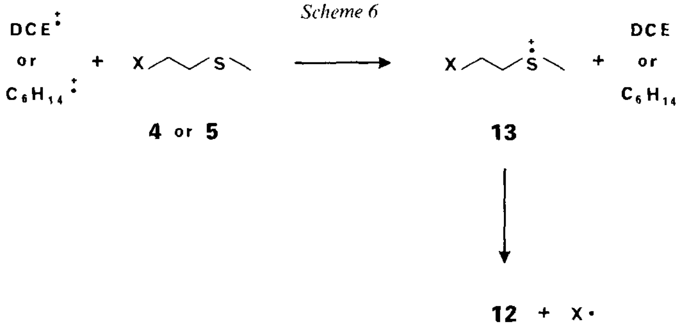


The presence of hexane radicals or of Cl^- ions does not exert a strong effect in the case of the iodine compound **3**. These species seem to play a more significant role, however, in the pulse radiolysis of the Br and Cl analogues **4** and **5**, as discussed below. The only absorbing transients generated from these substrates are the relatively long-lived species **9** and **10**. Their optical absorption maxima at 365 nm and 350 nm identify them as $Br_2^{-\cdot}$ and

$Cl_2^{\cdot-}$, respectively [23] [24]. No absorption band due to a S-Br or S-Cl interaction is observed. By analogy, any such species would be expected to absorb at slightly red-shifted wavelengths relative to $Br_2^{\cdot-}$ or $Cl_2^{\cdot-}$. The reduced stabilities of (S∴Br) and (S∴Cl) are understandable on the basis of the much greater difference in electronegativities between the respective heteroatoms, as compared to (S∴I) [19].

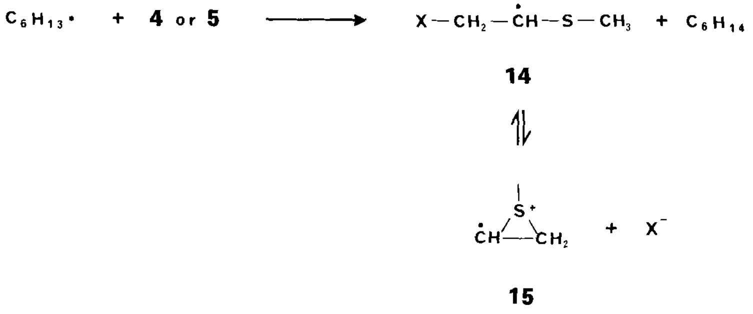
Oxidation of **4** and **5** leads primarily to the S-centered radical cations **13**. It is known that sulfur exerts a strong neighbouring group effect. As a consequence, **13** is considered to be stabilized by anchimeric assisted C–X cleavage and generation of a cyclic sulfonium salt **12** *(Scheme 6)*. This mechanism would, thus, be a source of free halogen atoms.

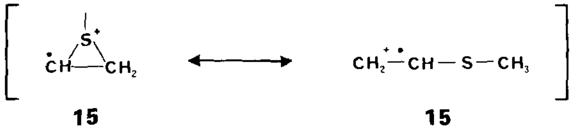
Scheme 6



Hexane radicals are expected to undergo H abstraction to form the α-thio radicals **14**. Such species have been shown to rearrange to the cyclic radical cation **15** by anchimerically assisted halide elimination [25]. The cyclic radical cation **15** is suggested to oxidize a

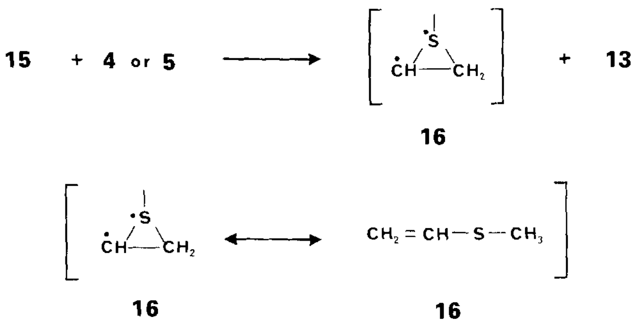
Scheme 7





further molecule **4** or **5**, thereby generating a cyclic or open-chain vinyl sulfide **16**, and the S-centred radical cation **13** which can be stabilized by cyclization as already described *(Scheme 8)*. Neither **14**, **15** nor **16** have so far been positively identified. The UV absorption below 300 nm would, however, be compatible at least with the absorptions expected for the radical species. Alternatively to *Scheme 8*, one can envisage a bimolecular radical-radical disproportionation reaction of **15** with one of the products of the latter process being the vinyl sulfide **16**.

Scheme 8



The proposed mechanism would explain the dependence of the $Br_2^{\cdot -}$ and $Cl_2^{\cdot -}$ (**9** and **10**, respectively) yields on the concentration of the solute molecules **4** and **5**, respectively. The presence of the Cl^-, formed, for example, in irradiated DCE *(Eqn. 3)*, allows direct reaction with the $Cl\cdot$ atoms generated *via Scheme 6*. In case of the bromine derivative, one has to envisage the formation of both $BrCl^{\cdot -}$ and $Br_2^{\cdot -}$. As the absorption of $BrCl^{\cdot -}$ is expected between that of $Cl_2^{\cdot -}$ and $Br_2^{\cdot -}$ (by extrapolation from mixed $BrSCN^{\cdot -}$ and $ClSCN^{\cdot -}$ [26] [27]), it will be difficult to make an unambiguous assignment.

We assume that the anchimeric assistance is due to the different behavior of the investigated 1-halo-2-(methylthio)ethanes relative to that of 1,*n*-halo(alkylthio)alkanes with $n \geqslant 3$. Stabilization of the oxidized compound **3** in an intermolecular three-electron-bonded $2\sigma/\sigma^*$ species with S-I interaction rather than S-S interaction is in accord with similar results obtained on the stability of $R_2S \therefore I$ *vs.* $(R_2S \therefore SR_2)^+$ [19]. Oxidation of **4** and **5**, on the other hand, only affords cyclization to sulfonium salts associated with C-halogen cleavage.

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Experimental Part

1. *General.* All solvents were of reagent grade (MeCN, DCE: *J.T. Baker Co.*; hexane: *Merck-Schuchardt*). MeI, MeBr, thiirane, and 1-chloro-2-(methylthio)ethane (**5**) were purchased from *Aldrich Co.* ^{1}H-NMR: *Varian EM 360* (δ in ppm; TMS as internal reference). MS: *Finnigan MAT 44*.

2. *Synthesis. 1-Iodo-2-(methylthio)ethane* (**3**): 15.6 g (0.11 mol) of MeI was slowly added to a soln. of 6 g (0.1 mol) of thiirane in 500 ml of MeCN. The mixture was stirred for 6 h at r.t. and the workup procedure was as described in [5]. The crude product was purified by bulb-to-bulb distillation (65°/2 Torr) to yield **3** in 30%. ^{1}H-NMR (90 MHz; $CDCl_3$): 3.40 (*t*, 2 H); 3.00 (*t*, 2 H); 2.20 (*s*, 3 H). MS: 202 (12, $M^{+\cdot}$), 127 (30), 75 (100). Anal. calc. for C_3H_7IS (202.06): C 17.83, H 3.49, I 62.81, S 45.87; found: C 17.75, H 3.38, I 62.75, S 45.00.

Compound **3** can be stored in hexane in the dark and at low temp. for several days without decomposition. It is very sensitive to light and hydrolysis.

The Br analogue **4** is more stable. It can be prepared together with the corresponding sulfonium salt in the same manner. The yield is much lower than for **3**. Higher yields could be obtained *via* bromination of the corresponding alcohol [3].

3. *Pulse Radiolysis.* The pulse radiolysis setup and procedure for optical detection are described in [28]. The compounds were dissolved in hexane or DCE (10^{-1} – -10^{-3} M). The solvents were deaerated by bubbling with N_2, hexane was further saturated by bubbling with N_2O. Due to the lack of a specific dosimeter system in hexane and DCE, the radiation chemical yields are given in terms *Gε* and calculated on the basis of an aq. thiocyanate dosimeter [29]. The actual concentration of the formed species is unknown, so *Gε* has to be viewed as an approximation.

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