asymmetry of the radical which is likely to yield different energy levels of the overlapping SOMO and HOMO of the R_2S and RS constituents.

A better match of the energy levels and therefore higher stability of the three-electron bond can be achieved by introducing unequal substituents. Thus $R_2S\therefore SCF_3$ and $R_2S\therefore SCOR'$ could be stabilized in solution and their structure evaluated from ESR experiments.[18] It would now appear that the stability of these $R_2S\therefore SR$ type radicals is enhanced by the CF_3 or COR′ substituents, both of which are good electron-withdrawing substituents,[31] i.e., would reduce the electron density in the antibonding orbital.

Another interesting result reported in the literature is a λ_{max} of 430 nm for $(R'R''S\therefore SR'R'')^+$ with $R' = C_2H_5$ and $R'' = CH(CH_3)SC_2H_5$.[5] This λ_{max} is considerably blue-shifted compared to those radical cations obtained from the simple aliphatic sulfides (see Table I). Since steric effects would rather lead to a red shift, this experimental result would strongly indicate a net electron withdrawal from the antibonding orbital of the three-electron bond. Going into the $(R_2S\therefore SR_2)^+$ curve in Figure 2, the combined substituent effect would correspond to +0.15 of Taft's σ^* scale. At least qualitatively, this is quite plausible owing to the electronegativity of the sulfur atom and the fact that mesomery between the $S\therefore S$ bond and the β-sulfur atom in R″ is not possible across the $CH(CH_3)$ group in between.

The present investigation also allows us to separate electron induction from steric effects. The latter may act through widening of the C–S–C bond angle in the sulfide constituents of $(R_2S\therefore SR_2)^+$ and $R_2S\therefore Br$. This, in turn, would affect the direction and at least in $(R_2S\therefore SR_2)^+$ the possible extent of the p-orbital overlap. In addition, steric hindrance could also occur through space across the three-electron-bonded sulfur bridge in $(R_2S\therefore SR_2)^+$ with the result of a sulfur–sulfur bond lenghtening. Similar observations of steric hindrance across an odd-electron-bonded bridge have also been made for oxidized hydrazines ($R_2N\dot{-}NR_2^+$ with 2σ, 2π, and 1π* electrons between the two nitrogen atoms).[37]

Acknowledgment. The support given for this work by the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie, and the Int. Büro of the KFA Jülich within the terms of an agreement on Cooperation in Scientific Research and Technical Development between the Federal Republic of Germany and the Socialist Federal Republic of Yugoslavia is gratefully acknowledged.

Registry No. $H_2SSH_2^{+\cdot}$, 77386-59-5; $Me_2SSMe_2^{+\cdot}$, 63228-83-1; $Et_2SSEt_2^{+\cdot}$, 51137-16-7; $Pr_2SSPr^{+\cdot}$, 91523-20-5; $Bu_2SSBu_2^{+\cdot}$, 91523-21-6; *i*-Bu_2SS-*i*-$Bu_2^{+\cdot}$, 91523-22-7; *i*-Pr_2SS-*i*-$Pr_2^{+\cdot}$, 72517-96-5; *sec*-Bu_2SS-*sec*-$Bu_2^{+\cdot}$, 91523-23-8; $HSSH^{-\cdot}$, 91523-24-9; $MeSSMe^{-\cdot}$, 34527-95-2; $EtSSEt^{-\cdot}$, 91603-20-2; *i*-PrSS-*i*-$Pr^{-\cdot}$, 34525-29-6; *t*-BuSS-*t*-$Bu^{-\cdot}$, 34525-33-2; $BrH_2S\cdot$, 91523-25-0; $Me_2BrS\cdot$, 71149-19-4; $Et_2BrS\cdot$, 66851-58-9; *i*-$Pr_2BrS\cdot$, 91523-26-1; *t*-$Bu_2BrS\cdot$, 91523-27-2.

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A Method To Generate and Study $(CH_3)_2S^{+\cdot}$ Radical Cations. Reduction of Me_2SO by H· Atoms in Aqueous $HClO_4$ Solutions

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Abstract: Radical cations $(CH_3)_2S^{+\cdot}$ were found to be formed as intermediates in the reaction of dimethyl sulfoxide with hydrogen atoms in aqueous solutions containing high concentrations of $HClO_4$. This method allows one to study the properties of this cation, e.g., by pulse radiolysis, under conditions which are not disturbed by the usually rapid complexation with excess sulfide. Absolute rate constants were measured for the reactions of $(CH_3)_2S^{+\cdot}$ with $(CH_3)_2S$ ($k = (3.0 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$), CH_3SSCH_3 ($k = (4.0 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$), and $(t\text{-}Bu)_2S$ ($k = 2.1 \times 10^9\ M^{-1}\ s^{-1}$). The latter reaction leads to the formation of $\{(CH_3)_2S\therefore S(t\text{-}Bu)_2\}^+$ three-electron-bonded radical cations which exhibit an optical absorption at 545 nm and equilibrate with the molecular radical cation $(t\text{-}Bu)_2S^{+\cdot}$ (λ_{max} 310 nm). In the presence of chloride ions $(CH_3)_2S\therefore Cl$ (or its protonated form) with λ_{max} 380 nm is formed. The $(CH_3)_2S^{+\cdot}$ itself absorbs at 285 nm and is, in fact, assumed to exist as $\{(CH_3)_2S\therefore O(H)ClO_3\}^+$, possibly in equilibrium with $\{(CH_3)_2S\therefore OH_2\}^+$, i.e., in stoichiometrically defined three-electron-bonded complexes with $HClO_4$ or H_2O. In pure $H_2O/HClO_4$ matrix an optically absorbing transient with λ_{max} 335 nm is observed which is attributed to $(HClO_4)_2^{+\cdot}$.

Molecular radical cations $R_2S^{+\cdot}$ from one-electron oxidation of aliphatic sulfides are generally difficult to observe directly. This is mainly due to the usually rapid reaction of these species with excess sulfide in the forward reaction of the equilibrium

$$R_2S^{+\cdot} + R_2S \rightleftharpoons (R_2S\therefore SR_2)^+ \qquad (1)$$

and stabilization in a three-electron-bonded radical cation.[1-10] An exception in the aliphatic series is only the $(t\text{-}Bu)_2S^{+\cdot}$ radical cation which, mainly for steric reasons, is not able to associate with an unattacked *tert*-butyl sulfide molecule.[3,10] In aqueous solutions the $(t\text{-}Bu)_2S^{+\cdot}$ has been found to exhibit an optical absorption

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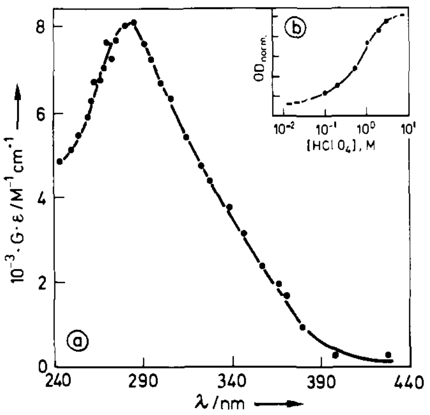

Figure 1. (a) Optical absorption spectrum obtained immediately after a ca. 1-μs pulse in deoxygenated aqueous solution of 10^{-1} M Me_2SO and 3 M $HClO_4$. (b) Normalized yield of the optical absorption at 285 nm as a function of $HClO_4$ concentration in pulse-irradiated aqueous 10^{-1} M Me_2SO solutions.

peaking around 310 nm. The $(R_2S\therefore SR_2)^+$ species are also characterized by strong optical absorptions with maxima at, however, considerably higher wavelengths in the visible.[2,3,5,6,8-10] The latter have been attributed to a $\sigma \rightarrow \sigma^*$ transition (in first approximation) in the three-electron bonds which contain two bonding σ electrons and one antibonding σ^* electron.[5,6]

The particular interest in the molecular $R_2S^{+}\cdot$ species arises from the fact that they are generally more reactive than $(R_2S\therefore SR_2)^+$.[2] The kinetics of $R_2S^{+}\cdot$ reactions are consequently always affected by equilibrium 1, and in time-resolved optical pulse radiolysis experiments one has, in fact, mostly to rely on the observation of the $(R_2S\therefore SR_2)^+$ absorption rather than the $R_2S^{+}\cdot$ itself. These complications could, in principle, be avoided if the $R_2S^{+}\cdot$ radical cations could be produced in a system which does not contain any sulfide. In the present work we wish to report on such a system, namely the generation of $(CH_3)_2S^{+}\cdot$ radical cations in the reduction of dimethyl sulfoxide (Me_2SO) by hydrogen atoms in solutions containing high concentrations of $HClO_4$ and other acids.

Experimental Section

The chemicals used were generally of ≥99% purity. If necessary, purification was achieved by fractional distillation and checked by GC/MS. $HClO_4$ solutions were prepared from 70% perchloric acid (Merck), H_2SO_4 solutions from 95–97% sulfuric acid (Merck), and HBF_4 solutions from 50% perfluoroboric acid (Fluka). The solvent was deionized, Millipore-filtered water. Deoxygenation of the solutions was achieved by bubbling with N_2 for ca. 1 h/dm^3 solution.

Pulse radiolysis studies were carried out by applying short pulses of high-energy electrons from a 1.5 or 3.8 MeV Van de Graaff accelerator to the solutions. Pulse durations were typically 1–5 μs and 50 ns for the two machines, respectively. The formation of transient species was recorded via time-resolved optical measurements. Details on this technique and on the evaluation of data from pulse radiolysis experiments have already been published.[11]

Dosimetry was based on the reduction of tetranitromethane to nitroform.[11c,12-14] Typical doses per pulse were in the order of 3–10 J kg^{-1} (3–10 Gy, 300–1000 rd), yielding a total of primary radicals in the irradiated system of about 6×10^{-7} M per J kg^{-1} absorbed dose. In the very acidic solutions used in the present experiments, $\cdot OH$ radicals and $H\cdot$ atoms account for about 50% each.

γ-Radiolysis experiments were carried out by irradiating the samples (usually 1/2 dm^3) within the field of a 7000 Ci ^{60}Co source at an absorbed dose rate of 414 J kg^{-1} h^{-1}. The latter was determined by Fricke dosimetry.[15]

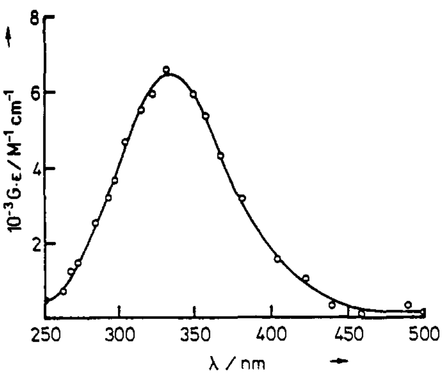

Figure 2. Optical absorption spectrum obtained immediately after a ca. 1-μs pulse in deoxygenated aqueous solution of 3 M $HClO_4$.

Quantitative analysis of radiation chemically formed stable sulfides was done with reverse-phase-bonded-phase HPLC using the equipment and analytical techniques described and developed by Möckel et al.[16] All experiments have been carried out at room temperature.

Results

(1) Formation of Optically Absorbing Transients. Pulse radiolysis of very acidic solutions of dimethyl sulfoxide reveals the formation of a transient, optically absorbing species. Its spectrum, recorded immediately after application of a 1-μs electron pulse (1.5 MeV) to a deoxygenated aqueous solution containing 10^{-1} M Me_2SO and 3 M $HClO_4$, is shown in Figure 1a. A pronounced maximum is observed at 285 nm. The first half-life of the absorption is about 50–60 μs under the experimental conditions.

The formation of this absorption requires high concentrations of the perchloric acid. This transient is not observable in solutions containing less than 10^{-2} M $HClO_4$. A quantitative plot of the absorption yield (at 285 nm) as a function of the $HClO_4$ concentration in irradiated 10^{-1} M Me_2SO solutions is shown in Figure 1b. The curve appears to be S-shaped; a maximum plateau value could, however, not be achieved experimentally, although the curve starts to level off above 2–3 M $HClO_4$.

The yield of this absorption also depends on the Me_2SO concentration. Below 10^{-2} M it is more and more replaced by another absorption band which, in completely Me_2SO-free solutions, peaks at 335 nm, as can be seen in Figure 2. The yield of the latter shows a similar dependence on the $HClO_4$ concentration as the 285-nm species. For quantitative comparison, the absorption at 335 nm in pure 3 M $HClO_4$ solutions amounts to ca. 80% of the absorption at 285 nm in the Me_2SO-containing system (3 M $HClO_4$ and 10^{-1} M Me_2SO).[17]

When one looks at the two spectra in Figures 1a and 2, it is obvious that the 335-nm absorption band cannot fully be part of the 285-nm band as, for example, the total absorptivity at 335 nm in the $Me_2SO/HClO_4$ system is already lower than in the Me_2SO-free system. In other words, the 335-nm species observable in the pure $HClO_4$ solutions seems to be formed at a much lower yield, if at all, in the presence of Me_2SO, the reason possibly being a competitive process.

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(17) The exact yield of the primary species, $\cdot OH$ and particularly $H\cdot$, is difficult to assess at the high acid concentrations. Compared with low solute concentration solutions, the yields are increased due to spur reactions. On the other hand, an increasing amount of radiation energy is directly absorbed by the solute. In our systems the latter would probably result in a lower $\cdot OH$ yield while its effect on the $H\cdot$ atom yield is not known. The *G* values used are therefore likely to include relatively large error limits (possibly 10–20%). For this reason we have not evaluated any numerical numbers, like extinction coefficients etc., which in principle could easily be derived from the experimental data.

Very similar results are obtained if the Me_2SO solutions contained H_2SO_4 instead of $HClO_4$. Upon pulse radiolysis of solutions containing 3 M H_2SO_4, 10^{-1} M Me_2SO, for example, a transient optical absorption is observed which peaks at 290 ± 10 nm and otherwise matches the corresponding absorption band of the $HClO_4$ solutions in shape and height within experimental limits of error. In solutions containing only H_2SO_4 the well-known $(HSO_4)\cdot$ absorption with λ_{max} around 450 nm is observed.[18,19]

When 3 M HBF_4 is used as acid, a pronounced UV absorption band is also observed with λ_{max} 275 ± 10 nm and a yield which amounts to ca. 80% of the maximum absorption yield in the $HClO_4$ and H_2SO_4 systems. The HBF_4 results are, however, more ambiguous. Thus an additional and as yet unidentifiable absorption band showed up between 400 and 500 nm which kinetically could not be correlated with the UV band. A possible source for this latter species could be a particular radiation-induced process in HBF_4 but also an impurity which is either contained in the HBF_4 or is generated under the extreme conditions of the 3 M HBF_4 solution.

All the following experiments have been carried out with $HClO_4$ as acid component.

(2) Assignment of the Absorbing Species. The primary reactive radicals in an acidic aqueous solution are only H· atoms and ·OH radicals formed with about equal yields. Addition of *tert*-butyl alcohol, which is a relatively good ·OH ($k = 6.3 \times 10^8$ M^{-1} s^{-1} at pH 2) and a moderate H· atom scavenger ($k = 1.0 \times 10^5$ M^{-1} s^{-1}),[20] leads to a decrease of both absorptions, with the effect being much more pronounced for the 335-nm absorption in the $HClO_4$ system than for the 285-nm absorption in the $Me_2SO/HClO_4$ system.

Addition of 10^{-3} M O_2 (oxygen-saturated solutions) or 10^{-2} M $Fe(CN)_6^{3-}$, both of which are good H· atom scavengers ($k = 2 \times 10^{10}$ M^{-1} s^{-1} and $\geq 7.5 \times 10^9$ M^{-1} s^{-1} at low pH, respectively[20]), to the $Me_2SO/HClO_4$ system results in a complete disappearance of the 285-nm absorption. Considering also that, at least at pH >2, Me_2SO is known to be a very good ·OH radical scavenger leading to nonabsorbing species in the reaction[21-23]

$$(CH_3)_2SO + \cdot OH \rightarrow (CH_3)_2SO(OH)\cdot \rightarrow \dot{C}H_3 + CH_3SO_2H \qquad (2)$$

the experimental results so far clearly identify the H· atom as the precursor of the 285-nm species.

From earlier studies it is known that Me_2SO can be reduced by hydrated electrons ($k = 1.7 \times 10^6$ M^{-1} s^{-1}) to yield a $(CH_3)_2SO^-\cdot$ radical anion which is relatively stable in basic solutions (pH >9) and exhibits an optical absorption at 350 nm.[22] Its neutralized form $(CH_3)_2S(OH)\cdot$ has so far not been detected in the reduction of Me_2SO but is clearly evidenced as a comparatively much shorter lived transient in the ·OH radical induced oxidation of sulfides.[2] On the basis of these considerations and the experimental data we assign the 285-nm absorption to the $(CH_3)_2S^{+}\cdot$ radical cation formed via H· atom addition to the oxygen atom

$$(CH_3)_2SO + H\cdot \rightarrow (CH_3)_2S(OH)\cdot \qquad (3)$$

followed by the acid-assisted ionization

$$(CH_3)_2S(OH)\cdot + H^+ \rightarrow (CH_3)_2S^{+}\cdot + H_2O \qquad (4)$$

and stabilization of the radical cation. The latter requires some structural considerations and will be discussed in the last section.

Table I. Yield of $(CH_3)_2S$ from γ-Irradiated, Deoxygenated Solutions Containing 1 M HClO and Various Me_2SO and $Fe(CN)_6^{3-}$ Concentrations (Yields Expressed as G = Species Per 100-eV Absorbed Energy)

$[Me_2SO]$	$[Fe(CN)_6^{3-}]$	$G\{(CH_3)_2S\}$
$\leq 10^{-3}$		
10^{-2}		0.40 ± 0.05
10^{-1}		0.95 ± 0.1
1		1.25 ± 0.1
1	10^{-5}	1.20 ± 0.1
1	10^{-4}	0.90 ± 0.1
1	10^{-3}	0.45 ± 0.05
1	$\geq 10^{-2}$	

(Protonation of the sulfoxide prior to H· atom addition can probably be excluded at least at the lower $HClO_4$ concentrations, owing to a $pK_b = -1.54$ of the Me_2SO.)[24]

The 335-nm absorption in Me_2SO-free solutions is mainly attributed to a reaction of the ·OH radical, namely the oxidation of perchlorate ions ($HClO_4$ is still dissociated even at the highest applied concentrations).

$$\cdot OH + ClO_4^- \rightarrow (ClO_4)\cdot + OH^- \qquad (5)$$

The hydrogen atom is also known to exhibit oxidizing properties in very acidic solutions, acting probably as an $H_2^{+}\cdot$ radical cation. A reaction

$$H\cdot + H^+ + ClO_4^- \rightarrow (ClO_4)\cdot + H_2 \qquad (6)$$

is therefore also possible. Its yield must, however, be very small since addition of $Fe(CN)_6^{3-}$ (10^{-4} M) has practically no effect on the absorption at 335 nm.

The decrease in the 335-nm absorption upon addition of Me_2SO is then explained by an increasing competition of reactions 2 and 3 with reactions 5 and possibly 6, respectively. Since the perchloric acid is, however, also required for the $(CH_3)_2S^{+}\cdot$ formation in reaction 4, it is not feasible to extract any relative rate constants from experiments with varying $HClO_4/Me_2SO$ concentration ratios.

The absorbing species could be the $(ClO_4)\cdot$ radical or a species derived from it; this structure-related consideration will also be discussed in the last section.

(3) Chemical Evidence for the Formation of $(CH_3)_2S^{+}\cdot$. The formation of a $(CH_3)_2S^{+}\cdot$ as an intermediate in the H· atom induced reduction of Me_2SO should lead to $(CH_3)_2S$ as one of the stable reaction products. This compound can be formed via a disproportionation of either the radical cation or its deprotonated form, $\dot{C}H_2SCH_3$.[2] Both processes are indicated from pulse radiolysis and steady-state experiments in the radiation chemically induced oxidation of sulfides. HPLC product analysis of γ-irradiated, deoxygenated solutions of 1 M $HClO_4$ and various concentrations of Me_2SO do indeed prove this assumption. The radiation chemical yields of $(CH_3)_2S$, as listed in Table I, are $G = 1.25 \pm 0.1$, 0.95 ± 0.1, and 0.40 ± 0.05 at Me_2SO concentrations of 1, 10^{-1}, and 10^{-2} M, respectively. (G defines the number of species formed per 100 eV absorbed energy, and multiplied by 10^{-7} gives the number of moles formed per J absorbed energy.) At $\leq 10^{-3}$ M Me_2SO no $(CH_3)_2S$ is formed anymore. Since the dimethyl sulfide results from a disproportionation process, these numbers have to be compared with half the hydrogen atom yield, i.e., $^1/_2G(H\cdot) \approx 1.7$.[17] Qualitatively the results are in agreement with the expectation that the yield of $(CH_3)_2S^{+}\cdot$ formation is both a function of the Me_2SO and the $HClO_4$ concentration. The highest yield of $(CH_3)_2S$ ($G = 1.25$) obtained from 1 M Me_2SO/1 M $HClO_4$ solutions amounts to about two-thirds of the above $^1/_2G(H\cdot)$. By comparison with the yields of the 285-nm absorption shown in Figure 1b, this would suggest that the yield of $(CH_3)_2S^{+}\cdot$ radical cations at 3 M $HClO_4$ is already close to the limiting value.

Addition of the H· atom scavenger $Fe(CN)_6^{3-}$ reduces the $(CH_3)_2S$ product yield, and at 10^{-2} M and above $(CH_3)_2S$ is no longer formed (see Table I).

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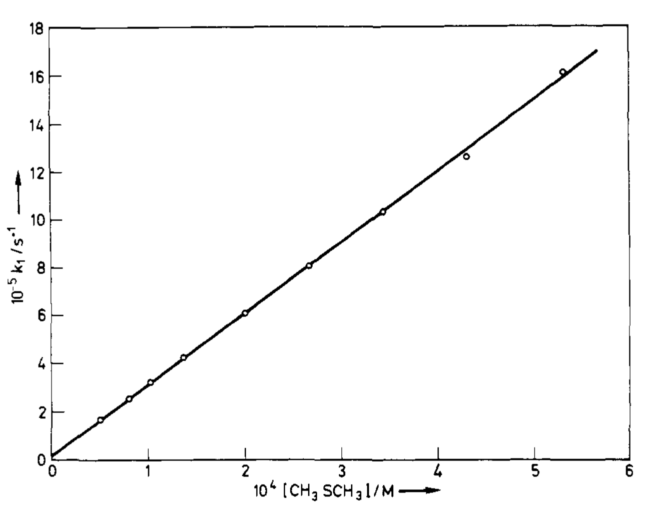

Figure 3. Plot of $k_1 = (\ln 2)/t_{1/2}$ vs. $[(CH_3)_2S]$ for the formation of $\{(CH_3)_2S\therefore S(CH_3)_2\}^+$ in pulse-irradiated, deoxygenated aqueous solutions of 0.5 M DMSO, 3 M $HClO_4$, and various $(CH_3)_2S$ concentrations.

Further evidence for the formation of $(CH_3)_2S^{+\cdot}$ radical cations is provided by pulse radiolysis experiments. Thus addition of small amounts of $(CH_3)_2S$ ((5×10^{-5})–(5×10^{-4}) M) to deoxygenated 3 M $HClO_4$–0.5 M Me_2SO solutions leads to a replacement of the 285-nm $(CH_3)_2S^{+\cdot}$ absorption by the well-known 465-nm absorption of the complexed three-electron-bonded radical cation formed in the forward reaction of the equilibrium:[2,6,10]

$$(CH_3)_2S^{+\cdot} + (CH_3)_2S \rightleftharpoons \{(CH_3)_2S\therefore S(CH_3)_2\}^+ \quad (7)$$

Figure 3 shows a plot of the measured first-order rate constants $k_1 = (\ln 2)/t_{1/2}$ (obtained from the exponential formation of the 465-nm absorption) as a function of dimethyl sulfide concentration. From the slope of the straight line the bimolecular rate constant $k_7 = (3.0 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$ is derived. The back reaction of equilibrium 7 apparently is slow and does not contribute to the overall kinetics. This can be deduced from the fact that the k_1 vs. $[(CH_3)_2S]$ relationship almost passes through the origin.[25] (It should be noted that this rate constant and that of reaction 8 would have to be corrected if part of the oxidation occurred through $ClO_4\cdot$ or oxidants other than $(CH_3)_2S^{+\cdot}$; the experimental data provide, however, no measurable evidence for this.)

Addition of dimethyl disulfide to the aqueous $Me_2SO/HClO_4$ matrix reveals the occurrence of

$$(CH_3)_2S^{+\cdot} + CH_3SSCH_3 \rightarrow (CH_3SSCH_3)^{+\cdot} + (CH_3)_2S \quad (8)$$

The disulfide radical cation was identified through its known optical absorption at 440 nm. Reaction 8 has been shown already to occur in solutions where $(CH_3)_2S^{+\cdot}$ was generated from dimethyl sulfide.[26] Our present experiment allows us now to evaluate the reaction kinetics undisturbed by equilibrium 7. The bimolecular rate constant $k_8 = (4.0 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$ derived from the slope of a $k_1 = (\ln 2)/t_{1/2}$ vs. $[CH_3SSCH_3]$ plot substantiates the only other reliable rate constant for a corresponding disulfide ($C_2H_5SSC_2H_5$) oxidation by $(t\text{-}Bu)_2S^{+\cdot}$ radical cations ($k = 5 \times 10^9\ M^{-1}\ s^{-1}$).[26]

Another interesting result is obtained if $(t\text{-}Bu)_2S$ is added to the solutions. In this case an optically absorbing species with λ_{max} 545 nm is formed with $k_9 = 2.1 \times 10^9\ M^{-1}\ s^{-1}$. The rate constant is derived from the slope of a $k_1 = (\ln 2)/t_{1/2}$ vs. $[(t\text{-}Bu)_2S]$ plot and attributed to the formation of the three-electron-bonded species in the forward reaction of the equilibrium

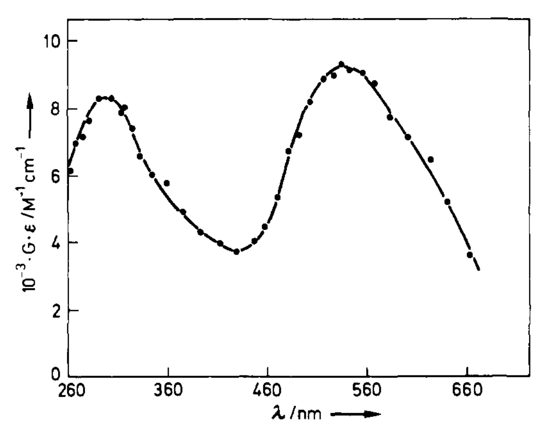

Figure 4. Optical absorption spectrum obtained immediately after a ca. 1-μs pulse in deoxygenated aqueous solutions of 2 M $HClO_4$, 0.5 M Me_2SO, and 10^{-3} M $(t\text{-}Bu)_2S$.

$$(CH_3)_2S^{+\cdot} + (t\text{-}Bu)_2S \rightleftharpoons \{(CH_3)_2S\therefore S(t\text{-}Bu)_2\}^+ \quad (9)$$

In addition to the 545-nm band, also, a 310-nm band attributable to the molecular $(t\text{-}Bu)_2S^{+\cdot}$ radical cation[27] is observed which may stem from some direct oxidation of the $(t\text{-}Bu)_2S$ (including by $ClO_4\cdot$) but also from equilibration of the three-electron-bonded species according to

$$\{(CH_3)_2S\therefore S(t\text{-}Bu)_2\}^+ \rightleftharpoons (CH_3)_2S + (t\text{-}Bu)_2S^{+\cdot} \quad (10)$$

The latter dissociation should in fact be favored over the back reaction of equilibrium 9 since the ionization potential of di-*tert*-butyl sulfide is lower than that of dimethyl sulfide (8.07 vs. 8.68 eV in the gas phase). The fact that equilibration does play a role is kinetically indicated by an appreciable intercept in the k_1 vs. $[(t\text{-}Bu)_2S]$ plot[28] and the same decay rate of both the absorption bands. (Further equilibration to a $\{(t\text{-}Bu)_2S\therefore S(t\text{-}Bu)_2\}^+$ does not occur since this species cannot be stabilized, as mentioned before.)[10]

The entire transient absorption spectrum as obtained from pulse radiolysis of 2 M $HClO_4$, 0.5 M Me_2SO, and 10^{-3} M $(t\text{-}Bu)_2S$ is shown in Figure 4. The considerable red shift in λ_{max} of $\{(CH_3)_2S\therefore S(t\text{-}Bu)_2\}^+$ compared to $\{(CH_3)_2S\therefore S(CH_3)_2\}^+$ (465 nm) is explained by electron induction through the *tert*-butyl groups into the antibonding σ^* orbital and possibly also some steric hindrance. Both effects lead to bond weakening, i.e., smaller σ/σ^* energy differences and consequently to a red shift in the $\sigma \rightarrow \sigma^*$ transitions.[10]

Finally, if the aqueous $Me_2SO/HClO_4$ matrix also contains chloride ions (2×10^{-3} M) an additional absorption band with λ_{max} 380 nm appears upon pulse irradiation. This is characteristic for a $(CH_3)_2S\therefore Cl$ radical[29] which in our system is suggested to be formed in the forward reaction of the equilibrium

$$(CH_3)_2S^{+\cdot} + Cl^- \rightleftharpoons (CH_3)_2S\therefore Cl \quad (11)$$

The absorption clearly differs from that of $Cl_2^{-\cdot}$ (λ_{max} 345 nm) which could, in principle, also be a possible transient oxidation product of chloride in acid solutions[30] but which does not seem to be formed. It is possible, however, that our 380-nm species is the $\{(CH_3)_2S\therefore ClH\}^+$ radical cation at the high acid concentration considering theoretical predictions that protonation would increase the stability[31] of such species.

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(25) The kinetics for the formation of a product being in equilibrium with the reactants is generally given by $k_l = k\rightarrow + k\leftarrow$, and k_1 being the observed first-order rate constant for the product formation ($=(\ln 2)/t_{1/2}$) and $k\rightarrow$ and $k\leftarrow$ being the true rate constants for the forward and back reactions, respectively. For equilibrium 7, $k\rightarrow$ is of pseudo first order, i.e., $k\rightarrow = k_7$ $[(CH_3)_2S]$. With $k\leftarrow = k_{-7}$, $k_1 = k_7\ [(CH_3)_2S] + k_{-7}$. Thus the slope of the k_l vs. $[(CH_3)_2S]$ plot yields the bimolecular rate constant for the forward reaction, and the first-order rate constant for the back reaction is given by the intercept.

(26) Bonifačić, M.; Asmus, K.-D. *J. Phys. Chem.* **1976**, *80*, 2426.

(27) (a) Asmus, K.-D. In "Fast Processes in Radiation Chemistry and Biology"; Adams, G. E., Fielden, E. M., Michael, B. D., Eds.; Wiley: New York, 1975; p 40. (b) Janata, E.; Veltwisch, D.; Asmus, K.-D. *Radiat. Phys. Chem.* **1980**, *16*, 43.

(28) See ref 25 with application to $(t\text{-}Bu)_2S$ instead of $(CH_3)_2S$.

(29) Bonifačić, M.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 758.

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All these chemical reactions also clearly support the conclusion that $(CH_3)_2S^{+}\cdot$ radical cations are formed in the reduction of Me_2SO by hydrogen atoms in $HClO_4$-containing solutions.

(4) Rate Constant for the H· + Me_2SO Reaction. An estimate for the rate constant of reaction 3 may be obtained from the effect of the H· atom scavenger $Fe(CN)_6^{3-}$ on the $(CH_3)_2S$ yields provided that the latter are indeed a direct measure for the H· atom induced reduction of Me_2SO. Taking the data listed in Table I and applying conventional competition kinetics between reactions 3 and

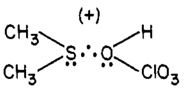
$$H\cdot + Fe(CN)_6^{3-} \rightarrow \text{products} \qquad (12)$$

a rate constant ratio $k_{12}/k_3 = 2.3 \times 10^3$ is obtained. With $k_{12} = 7.5 \times 10^9\ M^{-1}\ s^{-1}$,[20] a bimolecular rate constant $k_3 = 3.3 \times 10^6\ M^{-1}\ s^{-1}$ is derived. The error limit is probably high, but this value should be correct within the order of magnitude. It certainly is consistent with the observed facts that it needs only 10^{-3} M O_2 in 1 M Me_2SO solution or an about 100 times excess of *tert*-butyl alcohol over Me_2SO to prevent hydrogen atoms from direct reaction with Me_2SO.

Discussion

The present experimental evidence for $(CH_3)_2S^{+}\cdot$ formation in irradiated aqueous $Me_2SO/HClO_4$ matrix suggests that molecular sulfide radical cations $R_2S^{+}\cdot$ may generally be accessible via H· atom induced reduction of sulfoxides under acid conditions. Some preliminary experiments with higher aliphatic sulfoxides and $C_6H_5SOCH_3$ do indeed indicate this. The observable radical cation yields seem to be much lower, however, and also other species are formed simultaneously in competitive processes. But this is understandable considering the relatively low rate constant for the H· atom reaction leading to the corresponding radical cations and the limited solubility of the higher sulfoxides in the aqueous solutions.

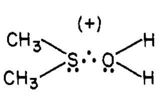
The formation of $(CH_3)_2S^{+}\cdot$ occurs only at high acid concentrations. The slight difference in absorption maxima (275–290 nm) found for the three acids $HClO_4$, H_2SO_4, and HBF_4 should not be overemphasized, but if they are real, they would suggest that the absorption characteristics of the radical cation also depend on the nature of the acid. Considering the well-documented strong tendency of an oxidized sulfur center to coordinate with a second sulfur or hetero atom which provides a free electron pair with p-character,[6] the establishment of a three-electron-bonded radical cation



I

as the absorbing species in the $HClO_4$ system could be envisaged. The corresponding species in H_2SO_4 would then exhibit the same structure with only the $-ClO_3$ group being replaced by an $-SO_3H$ group. In both cases also the deprotonated, neutral $(CH_3)_2S\therefore OClO_3$ and $(CH_3)_2S\therefore OSO_3H$ could be considered, but they would probably be less stable since they lack the possibility of charge delocalization. With HBF_4, in principle, an S∴F-bonded species could be considered, although it would probably not be very stable owing to the large difference in electronegativity of the two atoms. In fact, so far it has only been possible to find examples for S∴X-bonded radicals with X = Cl, Br, and I, but not for X = F.[29]

Another defined structure which, however, seriously has to be taken into consideration in a water containing system is



II

i.e., the association of $(CH_3)_2S^{+}\cdot$ with the elements of a water molecule. The S∴O bond energy in (II) is estimated to be rather low with about 5 kcal/mol (MNDO/2) but probably still sufficient for the establishment of this species.[32]

The radical cations I and II, if formed as such, would be likely to establish an equilibrium

$$\text{I} + H_2O \rightleftharpoons \text{II} + HClO_4 \qquad (13)$$

A similar consideration would apply to the H_2SO_4 (and possibly HBF_4) coordinated radical cation. Our data do not allow any quantification. We strongly feel, however, that in any case the radical cations generally denoted as $(CH_3)_2S^{+}\cdot$ should not considered to be simply a solvated species but rather a species with stoichiometrically defined structure.

The relative weakness of the S∴O bond is also evident from the rapid reaction of I/II with sulfides (e.g. eq 7 and 9); i.e., the S∴S bond is generally much stronger and the equilibrium

$$\text{I/II} + R_2S \rightleftharpoons \{(CH_3)_2S\therefore SR_2\}^{+} + HClO_4/H_2O \qquad (14)$$

usually lies on the right hand side. Yet, it is interesting to note that recently some more examples have been found, where S∴O bonds could be stabilized in the oxidation of sulfide function containing acids, particularly under sterically favorable conditions.[33]

Similar considerations may be applied on the structure of the species which absorbs at 335 nm in Me_2SO-free solutions and which has been denoted as $ClO_4\cdot$ radical in eq 5 and 6. Such a radical could associate with a ClO_4^- to yield a complex $(ClO_4)_2^{-}\cdot$ radical anion, similar to the $X_2^{-}\cdot$ formation from oxidized halides and pseudohalides (X = Cl, Br, I, SCN). In fact, such a species has already been detected by ESR in solid $KClO_4$[34] and acidic aqueous $HClO_4$ glasses[35] at low temperature and discussed by Symons[36] in terms of an oxygen–oxygen three-electron-bonded species, $(O_3ClO\therefore OClO_3)^-$. Since our species is only formed at high $HClO_4$ concentrations, we are, however, inclined to assign the absorption in our liquid $HClO_4/H_2O$ matrix to the doubly protonated form, $(HClO_4)_2^{+}\cdot$. So far, evidence for an oxygen–oxygen three-electron bond has been produced only for very few species[36] which is likely to be the result of the weakness of this bond. The fact that our species is formed only at very high $HClO_4$ concentrations is certainly in agreement with this consideration.

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Registry No. Me_2SO, 67-68-5; H, 12385-13-6; $(CH_3)_2S^{+}\cdot$, 34480-65-4; Me_2S, 75-18-3; MeSSMe, 624-92-0; t-Bu_2S, 107-47-1; $(CH_3)_2SCl\cdot$, 71149-16-1; HCl, 7647-01-0; $HClO_4$, 7601-90-3; H_2O, 7732-18-5; t-$Bu_2S^{+}\cdot$, 60991-58-4; $(HClO_4)_2^{+}\cdot$, 91712-48-0.

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