solutions were thermostated at 25 °C.

Conclusion

The importance of the observation of the oscillatory and oligo-oscillatory change of hydrogen ion concentration is at least twofold. First, the electrochemically determined hydrogen ion concentration is quite reliable, while the calculation of the concentration of any species from redox or ion-selective electrode measurements in most cases is far from being unambiguous. Second, the measurement of hydrogen ion concentration changes will make necessary and possible the refinement of the mechanisms of these intriguing reactions. Furthermore, these findings may give an impetus to seek novel types of chemical oscillators, including biochemically relevant ones exhibiting periodic changes of the hydrogen ion concentration.

Acknowledgment. The kind help of Dr. V. Gáspár and Mr. I. Lengyel in the CSTR experiments is gratefully acknowledged.

Registry No. H_2M, 141-82-2; SO_3^{2-}, 14265-45-3; IO_3^-, 15454-31-6; $S_2O_3^{2-}$, 14383-50-7; ClO_2^-, 14998-27-7; hydroxylamine, 7803-49-8; thiourea, 62-56-6.

Oxidation of Thiols by Radical Cations of Organic Sulfides

M. Bonifačić, J. Weiss, Shamim A. Chaudhri, and K.-D. Asmus*

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany *(Received: January 31, 1985)*

Sulfur-centered radical cations from organic sulfides have been found to oxidize thiols and thiolates to yield thiyl radicals. Absolute rate constants have been measured for the reaction of $(t\text{-But})_2S^{+}\cdot$ with EtSH (1.6×10^9 M^{-1} s^{-1}), C_6H_5SH (6.0×10^9 M^{-1} s^{-1}), and cysteine, CySH (1.9×10^9 M^{-1} s^{-1}). The reactions of $Me_2S^{+}\cdot$ with EtSH, *t*-ButSH, C_6H_5SH, and cysteine occur with $k = 1.8 \times 10^9$, 2.5×10^9, 7.2×10^9, and 9.4×10^8 M^{-1} s^{-1}, respectively. The three-electron bonded $(Me_2S\therefore SMe_2)^+$ radical cation oxidizes the cysteine anion (CyS^-) with $k = 8.1 \times 10^9$ M^{-1} s^{-1} and C_6H_5SH with $k = 5 \times 10^8$ M^{-1} s^{-1}, while its reactions with EtSH, *t*-ButSH, and CySH are slower by several orders of magnitude. The results of kinetics and product analysis are discussed in view of the pronounced tendency of the thiyl radical to undergo electrophilic addition reactions. The optical absorption spectrum of $C_6H_5S\cdot$ is also reported and shown to exhibit maxima at 460 and 295 nm with extinction coefficients of 2500 and 10000 M^{-1} cm^{-1}, respectively.

Introduction

Considering the results from numerous recent publications it appears that chemical reactions of sulfur-centered radicals are of quite variable nature and often constitute redox processes.[1] The thiyl radical RS·, for example, has been found to be an oxidant which is able to oxidize compounds like phenothiazines, vitamin C,[2] and flavins.[3] Other oxidants, and in fact much stronger then RS·, are the radical cations from organic sulfides[4,5] and disulfides,[6-8] $R_2S^{+}\cdot$ and $RSSR^{+}\cdot$, respectively. The disulfide radical anion, $(RS\therefore SR)^-$, on the other hand, is a good reductant.[9]

The $(RS\therefore SR)^-$ is formed upon electron addition to a disulfide molecule but also results from association of a thiyl radical to a thiolate anion in the forward reaction of the equilibrium[10,11]

$$RS\cdot + RS^- \rightleftharpoons (RS\therefore SR)^- \qquad (1)$$

A pronounced electrophilicity, which is another important characteristic of all sulfur-centered radicals containing an unpaired p electron, is the basis for the establishment of the sulfur-sulfur 3-electron bond. A species of similar electronic structure is, for example, formed in the forward reaction of the equilibrium[4,12]

$$R_2S^{+}\cdot + R_2S \rightleftharpoons (R_2S\therefore SR_2)^+ \qquad (2)$$

The three-electron bond in these and many corresponding species results from the interaction of the unpaired p electron with a free p-electron pair with two electrons establishing a σ-bond and the third electron being promoted into an antibonding σ^* orbital.[13]

The bond-weakening character of the third electron satisfactorily explains the relative ease to break the newly formed sulfur-sulfur bond, i.e., it can thus be taken as the rationale for the establishment of the equilibria. On the other hand, the formation of the three-electron bond constitutes a significant stabilization of the system relative to the $R_2S^{+}\cdot$ and RS·. Generally, the three-electron bonded species are not as good an oxidant as their one-p-electron counter radicals (RS· or $R_2S^{+}\cdot$). An example for this is the oxidation of disulfides by the sulfide-derived radical cations to yield disulfide radical cations, $RSSR^{+}\cdot$.[5] The rate of this process decreases significantly with increasing R_2S concentration as a consequence of equilibrium 2. Considering this reaction and a more recent finding that $RSSR^{+}\cdot$ readily oxidizes

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thiolate, RS^-,[8] it can be expected that radical cations from organic sulfides also oxidize thiolate and possibly the neutral thiols, RSH, as well (the latter are not oxidized by $RSSR^{+}\cdot$). After reporting a preliminary result[1] indicating that such reactions do indeed occur we now present a detailed account on the general reaction scheme:

$$R_2S^{+}\cdot,\ (R_2S\therefore SR_2)^+ + R'SH,\ R'S^- \rightarrow R'S\cdot + (2)R_2S + (H^+) \qquad (3)$$

Pulse radiolysis experiments will provide rate constants for these processes and in particular their dependence on the sulfide concentration. Supporting evidence for reaction 3 is given by quantitative analysis of the products arizing from the thiyl radicals, $R'S\cdot$, in solutions containing both sulfides and thiols. The sulfur compounds investigated were mainly of simple aliphatic and aromatic nature but also included the amino acid cysteine.

Experimental Section

Materials and Solutions. The sulfur organic compounds were of commercially available grades. The purity of the liquid compounds was checked by gas chromatography. If less than 99% the purity was accordingly improved by fractional distillation. All non-sulfur compounds were of analytical grade and used as received.

Solutions were generally prepared from Millipore filtered deionized water, the quality of which corresponded to triply distilled water. The pH of the solutions was generally adjusted with NaOH or $HClO_4$ solutions. Deoxygenation was achieved by bubbling with N_2, ca. 1 h/dm^3 of solution. In order to convert hydrated electrons into ·OH radicals (at pH $\geq$ 3) the deoxygenated solutions were subsequently saturated with N_2O to induce the reaction $N_2O + e_{aq}^- \rightarrow N_2 + OH^- + \cdot OH$. At pH $\leq$ 3 the hydrated electrons were converted into hydrogen atoms via $H^+ + e_{aq}^- \rightarrow H\cdot$.

The samples were kept in the dark as long as possible to avoid photochemical degradation of the thiols. All experiments were carried out at room temperature.

Irradiations. The pulse radiolysis experiments were performed by exposing the solutions to short pulses of high-energy electrons from 1.6- or 3.8-MeV van de Graaff accelerators. Typical pulse durations were 0.5–5 μs and 15–50 ns for the two machines, respectively. Dosimetry was based on the ·OH radical induced oxidation of thiocyanate, i.e., the formation of $(SCN)_2^{-}\cdot$ radical anions.[14] Absorbed doses per pulse generally were in the range of 1–10 Gy (J kg^{-1}). This corresponds to an ·OH radical concentration of ca. (0.6–6) × 10^{-6} M generated per pulse in an N_2O-saturated solution, and approximately half these concentrations of both ·OH and H· in strongly acidic solutions. Further details on the pulse radiolysis equipment and the evaluation of data from time-resolved optical absorption measurements have already been described.[15]

γ-Radiolysis experiments were carried out by irradiating the samples (usually 0.4 dm^3) in the field of a ca. 7000-Ci ^{60}Co γ-source at absorbed dose rates of ca. 1500 or 440 J kg^{-1} h^{-1}. The actual dose rates were determined by Fricke dosimetry taking $G(Fe^{3+}) = 15.6$ in air-saturated solutions. Radiolysis yields were calculated from initial slopes of concentration–dose plots of at least three individual points. Total doses were limited to keep solute conversion to less than 10%.

Product Analysis. Radiation chemically formed products were generally extracted from the aqueous phase by CCl_4 and thus concentrated by a factor of 16. The CCl_4 phase was then analyzed with a Varian 3700 gas chromatograph equipped with a 6 ft × $^1/_8$ in. column of 10% OV-17 on Chromosorb WHP 80–100 mesh and FID detector.[16] Identification of the various products was achieved by conventional GC-MS methods. Quantitative analysis was based on either comparison with original reference compounds or internal standards.[17]

Results and Discussion

(*1*) *Pulse Radiolysis Measurements.* (*1.1*) *Reaction of $R_2S^{+}\cdot$ and $(R_2S\therefore SR_2)^+$ with Thiolate Anions.* The reaction of radical cations from the oxidation of dimethyl sulfide (existing in equilibrium 2) with cysteine thiolate, CyS^-, was studied in pulse-irradiated, N_2O-saturated solutions of 1 × 10^{-2} M Me_2S and different cysteine concentrations at pH 10. The Me_2S concentration was always at least 50 times higher than the cysteine concentration ($\leq$2 × 10^{-4} M). Under these conditions all ·OH radicals react primarily with the dimethyl sulfide to yield $Me_2S^{+}\cdot$ and further on to $(Me_2S\therefore SMe_2)^+$ within less than 1 μs.[4] Thus the characteristic 465-nm absorption band of the three-electron bonded radical cation is present practically instantaneously after application of the pulse. In the presence of cysteine this $(Me_2S\therefore SMe_2)^+$ absorption then decays exponentially with the half-life being inversely proportional to the actual CyS^- concentration (the latter has been calculated by a formula given by Benesch and Benesch[18]). From these experimental data a second-order rate constant of 8.1 × 10^9 M^{-1} s^{-1} is calculated for the oxidation of the thiolate. Changing the Me_2S concentration to 3 × 10^{-3} M did not affect the decay rates of the $(Me_2S\therefore SMe_2)^+$ absorption. In principle, this could be interpreted in terms of an equally fast reaction of both $(Me_2S\therefore SMe_2)^+$ and $Me_2S^{+}\cdot$. Considering, however, that the measured half-lives for the decay of the $(Me_2S\therefore SMe_2)^+$ absorption at, e.g., 10^{-4} M CyS^-, and for the first-order dissociation of $(Me_2S\therefore SMe_2)^+$ into $Me_2S^{+}\cdot$ according equilibrium 2 amount to ca. 1 and 45 μs (at 20 °C),[19] respectively, it has to be concluded that oxidation of CyS^- in this case occurs only directly via

$$(Me_2S\therefore SMe_2)^+ + CyS^- \rightarrow CyS\cdot + 2Me_2S \qquad (4)$$

The result therefore identifies the three-electron-bonded radical cation also as a good oxidant. It further shows that although $Me_2S^{+}\cdot$ (and in general $R_2S^{+}\cdot$) is the more reactive species[5] equilibration via the back-reaction of eq 2 is not always required for the chemical action of these radical cations.

Supporting pulse radiolysis evidence for reaction 4 was provided by the association of the CyS· radical with thiolate to yield the cysteine radical anion:

$$CyS\cdot + CyS^- \rightleftharpoons (CyS\therefore SCy)^- \qquad (5)$$

The $(CyS\therefore SCy)^-$ has been identified by its optical absorption with λ_{max} = 420 nm.[20]

Considering the redox properties of $(Me_2S\therefore SMe_2)^+$ and $(CyS\therefore SCy)^-$ the sequence of reactions 4 and 5 constitutes the conversion of strongly oxidizing into reducing species. $(CyS\therefore SCy)^-$ like other disulfide radical anions readily transfer an electron to molecular oxygen, for example.[9a]

(*1.2*) *Reaction of $R_2S^{+}\cdot$ with Neutral Thiols.* Reactions of $R_2S^{+}\cdot$ radical cations can be investigated undisturbed by equilibrium 2 for R = methyl and *t*-butyl. For *t*-butyl sulfide, electron induction and steric hindrance prevent stabilization of the $(t\text{-}But)_2S^{+}\cdot$ in its corresponding $(R_2S\therefore SR_2)^+$ type radical cation after the initial oxidation of the *t*-butyl sulfide molecule.[21,22] Thus,

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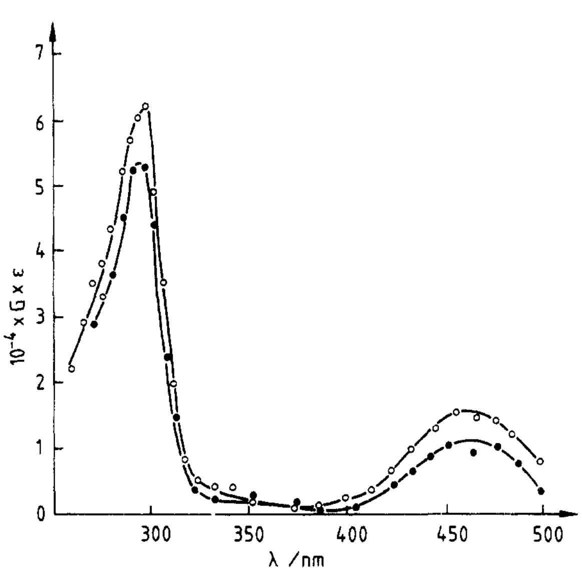

Figure 1. Optical absorption spectra of $C_6H_5S\cdot$ radicals in pulse-irradiated, N_2O-saturated solution (pH 4) containing: (●) 1×10^{-3} M $(t\text{-But})_2S$ and 1×10^{-4} M C_6H_5SH or (○) 1 M propan-2-ol and 5×10^{-4} M C_6H_5SH.

in N_2O-saturated solutions of, e.g., 10^{-3} M $(t\text{-But})_2S$ (pH 4), only the 310-nm absorption band of $(t\text{-But})_2S^{+}\cdot$ can be observed as the result of an $\cdot OH$ radical induced oxidation of the *tert*-butyl sulfide. Addition of increasing amounts of thiols leads to an increasingly faster and exponential decay of this absorption according to

$$(t\text{-But})_2S^{+}\cdot + RSH \rightarrow RS\cdot + H^+ + (t\text{-But})_2S \qquad (6)$$

(In principle this reaction is quite likely to proceed via an adduct intermediate $\{(t\text{-but})_2S{\therefore}SRH\}^+$. However, no experimental evidence is apparent for such a species. If formed, it is expected to be relatively unstable and thus very short-lived owing to electronic and possibly also steric reasons.) From this dependence second-order rate constants of 1.6×10^9 and 1.9×10^9 M^{-1} s^{-1} for RSH = ethyl mercaptane (EtSH) and cysteine (CySH), respectively, were derived. Consecutive stabilization of the $RS\cdot$ radical to the corresponding $(RS{\therefore}SR)^-$ radical anion does not occur in these systems since the required high RS^- concentration is not available at the experimental pH. However, production of $RS\cdot$ radicals via reaction 6 is clearly evidenced when C_6H_5SH is used as the thiol. In contrast to the nonaromatic $RS\cdot$ radicals the $C_6H_5S\cdot$ radical exhibits a strong optical absorption with maxima at 460 and 295 nm.

Figure 1 shows the $C_6H_5S\cdot$ spectrum obtained via reaction 6 in pulse-irradiated, N_2O-saturated (pH 4) solutions of 1×10^{-3} M $(t\text{-But})_2S$ and 1×10^{-4} M C_6H_5SH (filled circles) (under these conditions ca. 90% of the $\cdot OH$ radicals react with the di-*tert*-butyl sulfide; the remainder also produces $C_6H_5S\cdot$ by direct hydrogen abstraction from C_6H_5SH or leads to an $\cdot OH$ adduct at the aromatic ring). For comparison $C_6H_5S\cdot$ radicals were generated via

$$(CH_3)_2\dot{C}OH + C_6H_5SH \rightarrow C_6H_5S\cdot + (CH_3)_2CHOH \qquad (7)$$

in N_2O-saturated (pH 4) solutions of 1 M propan-2-ol and 5×10^{-4} M C_6H_5SH. The obtained spectrum (open circles) indicates that $C_6H_5S\cdot$ production by $(t\text{-But})_2S^{+}\cdot$ and $(CH_3)_2\dot{C}OH$ is almost equally efficient.

The extinction coefficients of the $C_6H_5S\cdot$ radical are estimated to 2500 ± 250 and 10 000 ± 1 000 M^{-1} cm^{-1} at 460 and 295 nm, respectively.

The second-order rate constant for the reaction of $(t\text{-But})_2S^{+}\cdot$ with C_6H_5SH was found to be 6.0×10^9 M^{-1} s^{-1}.

$Me_2S^{+}\cdot$ radical cations formed in the Me_2S containing solution will immediately associate with a second sulfide to $(Me_2S{\therefore}SMe_2)^+$ and thus prevent direct observation of $Me_2S^{+}\cdot$ reactions. In a recent investigation[23] we could show, however, that it is also possible to generate $Me_2S^{+}\cdot$ in a Me_2S free solution, namely via reduction of dimethyl sulfoxide (DMSO) by $H\cdot$ atoms in very acid (e.g., $>10^{-2}$ M $HClO_4$) solution. The $Me_2S^{+}\cdot$ thus formed (and likely to be associated to one H_2O or $HClO_4$ molecule) also exhibits an optical absorption (λ_{max} = 285 nm) through which it is possible to monitor reactions of this radical cation. The rate constant for the reaction

TABLE I: Rate Constants for the Reaction of Thiols and Thiolates with Sulfur-Centered Radical Cations from Organic Sulfides[a]

oxidizing radical	thiol/ thiolate	k, M^{-1} s^{-1}
$(t\text{-But})_2S^{+}\cdot$	EtSH	1.6×10^9
	C_6H_5SH	6.0×10^9
	CySH	1.9×10^9
$Me_2S^{+}\cdot$	EtSH	1.8×10^9
	t-ButSH	2.5×10^9
	C_6H_5SH	7.2×10^9
	CySH	9.4×10^8,[b] 2.4×10^8 [c]
$(Me_2S{\therefore}SMe_2)^+$	C_6H_5SH	5×10^8 [d]
	CyS^-	8.1×10^9 [e]
$Me_2S^{+}\cdot/(Me_2S{\therefore}SMe_2)^+$	t-ButSH	10.3×10^6 at 1×10^{-3} M Me_2S[f]
	t-ButSH	7.6×10^6 at 3×10^{-3} M Me_2S[f]
	t-ButSH	2.6×10^6 at 1×10^{-2} M Me_2S[f]

[a] Error limit ±10% unless marked otherwise. [b] Ionic strength of solution, 2 M $HClO_4$. [c] Corrected to zero ionic strength (the $HClO_4$ concentration was $>10^{-2}$ M, and CySH is positively charged at the amino group under these conditions). [d] Error limit ±50%. [e] At pH 10. [f] Rate constant depends on Me_2S concentration (see text).

$$Me_2S^{+}\cdot + EtSH \rightarrow EtS\cdot + H^+ + Me_2S \qquad (8)$$

has now been measured in pulse-irradiated solutions containing 2 M $HClO_4$, 0.5 M DMSO, and (2–6) $\times 10^{-5}$ M EtSH, and found to be 1.8×10^9 M^{-1} s^{-1}. Rate constants of 9.4×10^8, 7.2×10^9, and 2.5×10^9 M^{-1} s^{-1} were found for the corresponding reactions of $(CH_3)_2S^{+}\cdot$ with cysteine, thiophenol, and t-ButSH, respectively.

All these results (listed also in Table I) show that oxidation of the undissociated thiols by $R_2S^{+}\cdot$ occurs fast and with rate constants which are at least close to being controlled only by diffusion.

(1.3) Reaction of $(Me_2S{\therefore}SMe_2)^+$ with Neutral Thiols. The reaction

$$(Me_2S{\therefore}SMe_2)^+ + C_6H_5SH \rightarrow C_6H_5S\cdot + H^+ + 2Me_2S \qquad (9)$$

was investigated upon pulse radiolysis of N_2O-saturated, pH ≈4 solutions of (1–10) $\times 10^{-3}$ M Me_2S and (3–30) $\times 10^{-5}$ M thiophenol by monitoring either the decay of $(Me_2S{\therefore}SMe_2)^+$, e.g., at 465 nm, or the formation of the $C_6H_5S\cdot$ absorption, e.g., at 295 nm. An important observation is that the rate of this process depends only on the thiophenol concentration but not on the dimethyl sulfide concentration. Since the oxidation of the thiophenol occurs faster than the back-dissociation of the three-electron bonded species (back-reaction of equilibrium 2) the bimolecular rate constant of $k = (5 \pm 2) \times 10^8$ M^{-1} s^{-1} derived from these experiments is to be attributed exclusively to reaction 9.

A kinetically quite different picture is obtained in the oxidation of simple and substituted aliphatic thiols where the first-order decay rates of the $(Me_2S{\therefore}SMe_2)^+$ absorption depend on both the thiol and the sulfide concentration. This is illustrated in Figure 2 for t-ButSH as thiol, and dimethyl sulfide concentrations of 10^{-2}, 3×10^{-3}, and 10^{-3} M, respectively. (At the high thiol concentration some of the $\cdot OH$ radicals are already directly scavenged by the thiol. This results in a lower initial yield of $(Me_2S{\therefore}SMe_2)^+$ but does not affect the decay kinetics of the three-electron-bonded species.) Good straight lines with varying slopes and intercepts are obtained which is indicative for the involvement of equilibrium 2. Corresponding results were obtained also for other thiols, e.g., EtSH and CySH, and another sulfide, namely, Et_2S.

The bimolecular rate constants derived from the slopes of the $\ln 2/t_{1/2}$ vs. [thiol] plots from Figure 2 are listed in Table I for

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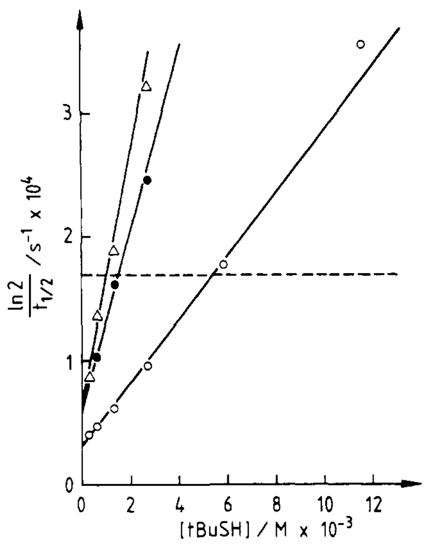
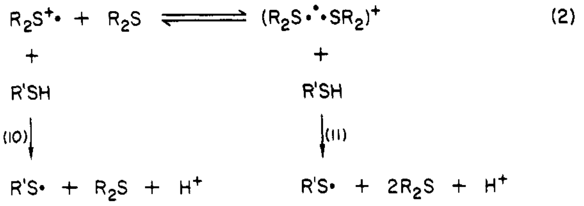


Figure 2. Plot of ln $2/t_{1/2}$ vs. [t-ButSH] for the decay of $(Me_2S\therefore SMe_2)^+$ radical cations in pulse-irradiated, N_2O-saturated aqueous solution (pH 4.5) of (△) 1 × 10^{-3}, (●) 3 × 10^{-3} and (○) 1 × 10^{-2} M Me_2S, respectively, and various t-ButSH concentrations.

comparison. They clearly indicate that the oxidation of the thiol becomes slower with increasing sulfide concentration. This means that the $(R_2S\therefore SR_2)^+$ radical cation is less reactive than the $R_2S^{+}\cdot$ radical cation, which is in agreement with earlier observations on the oxidation of disulfides in sulfide-containing systems.[5]

A significant result in the present experiments is the fact that $t_{1/2}$ for the $(Me_2S\therefore SMe_2)^+$ decay at high t-ButSH concentration becomes smaller than $t_{1/2}$ for the first-order dissociation of the three-electron bond, i.e., the back-reaction of equilibrium 2. The latter has been determined as 45 μs at 20 °C.[19] (The corresponding ln $2/t_{1/2}$ = 1.5 × 10^4 s^{-1} value is shown as dashed line in Figure 2.) This result therefore shows that the decay of the $(Me_2S\therefore SMe_2)^+$ absorption is not only controlled by equilibrium 2 and reaction 10 in the general scheme



$$\begin{array}{ccc} R_2S^{+}\cdot + R_2S & \rightleftharpoons & (R_2S{\cdot}^{\bullet}{\cdot}SR_2)^+ \\ + & & + \\ R'SH & & R'SH \\ (10)\downarrow & & \downarrow(11) \\ R'S\cdot + R_2S + H^+ & & R'S\cdot + 2R_2S + H^+ \end{array} \qquad (2)$$

but also by reaction 11, i.e., direct oxidation of the thiol by the three-electron-bonded species.

A similar result was obtained for the oxidation of EtSH by $(Me_2S\therefore SMe_2)^+$, while the corresponding CySH oxidation is so slow that the measured $t_{1/2}$ at any cysteine concentration stayed above the 45-μs mark. Any interpretation of the decay rate with respect to the underlying reactions must therefore remain ambiguous. This is also true for all results obtained with diethyl sulfide. The first-order dissociation rate of $(Et_2S\therefore SEt_2)^+$ has in fact not been determined yet but should be even faster (i.e., the critical $t_{1/2}$ should be below 45 μs) owing to the known lower thermodynamic stability of $(Et_2S\therefore SEt_2)^+$ as compared to $(Me_2S\therefore SMe_2)^+$.[4,22]

In any case, the rate constants for the oxidation of aliphatic thiols by the three-electron-bonded radical cations (reaction 11) appear to be several orders of magnitude below that for the oxidation of C_6H_5SH. A plausible explanation would be the high resonance stabilization of the $C_6H_5S\cdot$ radical.

No attempt has been made to evaluate exact rate constants from the kinetic analysis according to the above given scheme. The reason is that such a treatment involves not only a precise knowledge of k_{10} and the equilibrium constant for reaction 2 but also would have to include further thiol-independent decay modes

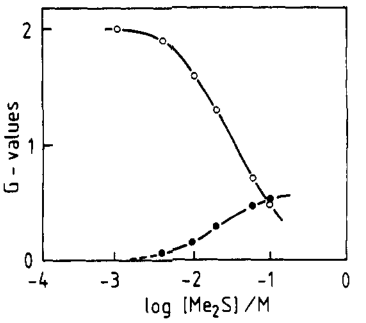


Figure 3. Yields of (○) n-ButSS-n-But and (●) n-ButSSEt vs. log [Me_2S] in γ-irradiated, N_2O-saturated aqueous solution (pH 4) of 2 × 10^{-4} M n-ButSH and various Me_2S concentrations.

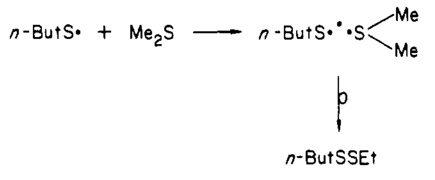
of $(R_2S\therefore SR_2)^+$ which are known to occur but for which no kinetic data are available as yet.[24]

(*2*) *Product Analysis from Steady-State Experiments.* The mechanism proposed for the pulse radiolysis experiments invokes the formation of thiyl radicals as an immediate product of the thiol oxidation by the sulfide radical cations. Dimerization of the thiyl radicals

$$2R'S\cdot \rightarrow R'SSR' \qquad (12)$$

yields the corresponding disulfide. This has been confirmed by product analysis. γ-Irradiation of N_2O-saturated solutions (pH 4) of 10^{-2} M Me_2S and 2 × 10^{-4} M in either n-C_3H_7SH, n-C_4H_9SH, or n-$C_5H_{11}SH$, for example, leads to the formation of n-C_3H_7SS-n-C_3H_7, n-C_4H_9SS-n-C_4H_9 and n-$C_5H_{11}SS$-n-C_5H_{11}, respectively. The corresponding yields account for 68%, 59%, and 80% of the oxidizing $Me_2S^{+}\cdot$ and $(Me_2S\therefore SMe_2)^+$ radicals demonstrating that the reactions 2, 10, and 11 given in the scheme, followed by reaction 12, represent indeed the main reaction pathways.

An interesting aspect is revealed, however, in Figure 3 which in curve ○ exhibits a plot of the n-ButSS-n-But yield in γ-irradiated N_2O, saturated solutions of 2 × 10^{-4} M n-ButSH as a function of the Me_2S concentration. It shows that the n-ButSS-n-But yield depends strongly on the sulfide concentration corresponding to about 75% efficiency at 10^{-3} M Me_2S and decreasing to as low as 20% at 10^{-1} M (solubility limit of Me_2S). This is due to competing processes, one of them being the n-ButS· radical reaction with Me_2S to yield a mixed disulfide EtSS-n-But as a product. The corresponding yield vs. [Me_2S] plot is given by curve ● in Figure 3. The underlying mechanism is an addition of the thiyl radical to the sulfide to form a three-electron-bonded radical followed by a rearrangement reaction in which a methyl group essentially migrates across the sulfur atom of the sulfide



$$\begin{array}{c} n\text{-ButS}\cdot + Me_2S \longrightarrow n\text{-ButS}{\cdot}^{\bullet}{\cdot}S(Me)_2 \\ \downarrow b \\ n\text{-ButSSEt} \end{array} \qquad (13)$$

This reaction pathway is of course favored by high sulfide concentrations and has also been observed in comparable systems with other thiols. Details on this novel rearrangement reaction have been published separately.[24] The results are very relevant to our present discussion in the sense that they explain the dependence of the disulfide yields on the sulfide concentration and illustrate the pronounced tendency of thiyl radicals to undergo addition reactions due to their electrophilic character.

Conclusion

Thiols and thiolate anions are readily oxidized by $R_2S^{+}\cdot$ radical cations with reaction rates which are essentially only controlled by the diffusion of the reactants. The same holds for the oxidation of thiolate anions by $(R_2S\therefore SR_2)^+$ radical cations. The latter are,

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[24] Goslich, R.; Weiss, J.; Möckel, H. J.; Mönig, J.; Asmus, K.-D. *Angew. Chem.* **1985**, *97*, 52. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 73.

however, generally much less reactive toward undissociated thiols owing to the internal stabilization of the three-electron-bonded species. The $R_2S^{+\cdot} + R_2S \rightleftarrows (R_2S\therefore SR_2)^+$ equilibrium therefore constitutes a system in which the sulfide concentration essentially controls the overall reactivity. A parameter which seems to affect the actual rate constant of the reaction of $(R_2S\therefore SR_2)^+$ with thiols is the stability of the resulting thiyl radical. This is apparent from the relatively fast oxidations of thiophenol compared to aliphatic thiols.

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Registry No. EtSH, 75-08-1; PhSH, 108-98-5; CySH, 52-90-4; *t*-BuSH, 75-66-1; CyS$^-$, 56-89-3; $(t\text{-Bu})_2S^{+\cdot}$, 60991-58-4; $Me_2S^{+\cdot}$, 34480-65-4; $(Me_2S\therefore SMe_2)^+$, 51137-15-6.

Kinetics of the Reactions of O(^{3}P) and O(^{1}D) with Cl$_2$

P. H. Wine,* J. M. Nicovich, and A. R. Ravishankara[†]

Molecular Sciences Branch, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332

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O(^{3}P) has been monitored by using time-resolved resonance fluorescence spectroscopy following 248-nm pulsed laser photolysis of $O_3/Cl_2/N_2$ and $O_3/Cl_2/He$ mixtures. Rate coefficients for the reaction $O(^3P) + Cl_2 \xrightarrow{k_1}$ products have been measured over the temperature range 245–371 K under conditions where the O(^{3}P) temporal behavior was unaffected by fast secondary reactions of O(^{3}P) with products. The data are well described by the following Arrhenius expression: $k_1(T) = (7.4 \pm 2.4) \times 10^{-12} \exp[(-1650 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1}. By monitoring the appearance of O(^{3}P), the rate coefficient for total removal of O(^{1}D) by Cl$_2$ has been determined to be $(2.81 \pm 0.42) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K. 25 ± 10% of the O(^{1}D) + Cl$_2$ quenching interactions result in formation of O(^{3}P).

Introduction

The reactions of ground-state and electronically excited oxygen atoms with molecular chlorine

$$O(^3P) + Cl_2 \rightarrow Cl + ClO + 6.5\ \text{kcal/mol} \tag{1a}$$

$$\xrightarrow{M} Cl_2O + 39\ \text{kcal/mol} \tag{1b}$$

$$O(^1D) + Cl_2 \rightarrow Cl + ClO + 52\ \text{kcal/mol} \tag{2a}$$

$$\xrightarrow{M} Cl_2O + 84\ \text{kcal/mol} \tag{2b}$$

$$\rightarrow O(^3P) + Cl_2 + 45\ \text{kcal/mol} \tag{2c}$$

are of interest to kineticists both for furthering our understanding of the rates and mechanisms of small molecule reactions and also as potential photolytic laboratory sources of the important stratospheric radical ClO. While kinetic data for both reaction 1[1–6] and reaction 2[7,8] are reported in the literature, neither k_1 nor k_2 is firmly established. Kinetics investigations of reaction 1 are subject to interferences from the fast secondary reactions

$$O(^3P) + ClO \rightarrow \text{products} \tag{3}$$

$$O(^3P) + Cl_2O \rightarrow \text{products} \tag{4}$$

None of the studies carried out to date employed sufficiently large Cl$_2$ to O(^{3}P) concentration ratios to avoid this complication. The only direct measurement of k_2 reported to date[7] employed an experimental approach which, based on comparison with results from several laboratories for a number of O(^{1}D) reactions, seems to systematically overestimate O(^{1}D) reaction rates by more than a factor of 2.

In this paper we report the results of a temperature-dependent kinetics study of reaction 1. Also, we report a 298 K study of reaction 2 where both the overall rate coefficient and the branching ratio for reactive vs. nonreactive quenching were determined. Both reactions were studied under experimental conditions where secondary removal or formation of O(^{3}P), the monitored species, was unimportant.

Experimental Section

The experimental approach is described elsewhere.[9–11] It involves time-resolved resonance fluorescence detection of O(^{3}P) following 248-nm pulsed laser photolysis of O$_3$. All experiments were carried out under slow flow conditions with the concentration of each component in the reaction mixture determined from measurements of the appropriate mass flow rates and the total pressure. In studies of reaction 1, where Cl$_2$ levels were relatively high, the Cl$_2$ concentration was measured directly by UV photometry at 326.1 nm; the Cl$_2$ absorption cross section at the monitoring wavelength was taken to be 2.58×10^{-19} cm^2.[12] The light source for the absorption measurement was a cadmium pen ray lamp and the absorption cell, plumbed in series with the reaction cell, was 60 cm in length. Experiments were carried out with the reaction mixture traversing the absorption cell both before and after flowing through the reactor. The observed kinetics were independent of the relative positions of the absorption cell and reactor.

The gases used in this study had the following stated minimum purities: He 99.999%, N$_2$ 99.995%, O$_2$ 99.99%, Cl$_2$ 99.96%. He,

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[†] Present address: Aeronomy Laboratory, NOAA/R/E/AL-2, 325 Broadway, Boulder, CO 80303.

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