rate constant for OH^- is 5 times larger than that for Cl^-, while the value of the deintercalation rate constant for OH^- is 3 times smaller than that for Cl^-. This indicates that OH^- may interact strongly with the solid host lattice in the layers of the Ni–HT(Cl).

Similar kinetic investigations in aqueous suspensions of layered intercalation compounds are in progress and the results will be reported in the near future.

Acknowledgment. We thank Kyowa Chemical Co. for the supply of the synthetic hydrotalcite-like compound and thank Mr. Shigeo Miyata for his useful suggestions.

Mechanism of Reduction of Bis(2-hydroxyethyl) Trisulfide by e_{aq}^- and $\cdot CO_2^-$. Spectrum and Scavenging of RSS· Radicals

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Each of the reducing radicals e_{aq}^-, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$ cleaves bis(2-hydroxyethyl) trisulfide in aqueous solution to produce (2-hydroxyethyl)perthiyl (RSS·) radicals and 2-hydroxyethanethiol. The RSS· radical had λ_{max} = 374 nm, $\epsilon_{max} = 1630 \pm 50\ M^{-1}\ cm^{-1}$, and a second-order rate constant for dimerization $2k_{12} = (1.4 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$ ($2RSS\cdot \rightarrow RS_4R$ (12)). It is able to abstract H atoms from dihydroflavin adenine dinucleotide (FH_2), but not from formate. Thus, in aqueous solution D_{RSS-H} must be greater than 60 but less than 90 kcal mol^{-1}. Although tetrasulfide and thiol are the major initial products of reduction, secondary thermal reactions occur and produce sulfanes (RS_nH) and polysulfides (RS_nR). In the early stages of reduction products of $n = 2$ dominate. However, on prolonged reaction with $\cdot CO_2^-$ elemental sulfur is precipitated, and this is probably formed by elimination from sulfanes with n much larger and in the region of 8.

Introduction

Thermal and free-radical-initiated decompositions of polysulfides (RS_nR) and sulfanes (HS_nH) have been subjects of interest for many years.[2-5] However, although the products and rates of decomposition of higher polysulfides ($n \geq 3$) have been studied, fast reaction techniques do not appear to have been utilized to characterize short-lived intermediates and their reactions. Surprisingly, this situation exists despite relatively intense activity in the application of pulse radiolysis and other methods to the study of neutral (e.g., RS·),[6,7] cationic (e.g., RS^+R, $RS\cdot SR^+$),[8-10] and anionic ($RS\cdot SR^-$)[11] radical species in solutions of thiols, sulfides, and disulfides. The major reasons are probably the relatively low solubility of higher polysulfides in water, which is the best solvent for the application of radiation chemical techniques, and secondly the fact that these molecules are rapidly interconverted, e.g.

$$2RS_3R \rightleftharpoons RS_2R + RS_4R \tag{1}$$

in the presence of base.[5] The latter feature seriously limits the conditions of pH under which polysulfides can be investigated. However, with the proper choice of polysulfide, studies can be made in the pH region 4–7.

In this investigation the standard techniques of radiation chemistry[12] have been utilized to produce the radicals e_{aq}^-, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$ via reactions 2–5 and to study

$$4.2H_2O \rightsquigarrow 2.7e_{aq}^- + 0.6H\cdot + 2.8\cdot OH + 2.7H_{aq}^+ + 0.4H_2 + 0.7H_2O_2 \tag{2}$$

$$(CH_3)_2CHOH + \cdot OH\ (\text{or } H\cdot) \rightarrow (CH_3)_2\dot{C}OH + H_2O\ (\text{or } H_2) \tag{3}$$

$$e_{aq}^- + N_2O\ (+\ H_2O) \rightarrow \cdot OH + N_2 + OH^- \tag{4}$$

$$HCO_2^- + \cdot OH\ (\text{or } H\cdot) \rightarrow H_2O\ (\text{or } H_2) + \cdot CO_2^- \tag{5}$$

short-lived products of their reactions with bis(2-hydroxyethyl trisulfide by pulse radiolysis. This trisulfide was chosen for its low vapor pressure, water solubility, and stability in aqueous solution. The perthiyl RSS· radical, which has previously been postulated in thermal decompositions[2,3] and reported in flash photolysis[13] and one-electron oxidations[10] of certain disulfides, emerged as the major intermediate.

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The earlier interest[2-5] in the decomposition of polysulfides prompted us to examine the long-lived products of the $\cdot CO_2^-$-initiated decomposition as well. As in other work[6-12] reaction 6 was used to remove $\cdot OH$, when e_{aq}^- was

$$(CH_3)_3COH + \cdot OH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O \quad (6)$$

required to be the dominant reactive species. It should be noted that e_{aq}^-, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$ are all reducing in character.[14] The pH was held in the range 5–7 and, since the p*K*s of $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ are 1.4 and 12.2, respectively,[14] the forms shown are the dominant ones.

Experimental Section

Materials. The bis(2-hydoxyethyl) trisulfide was prepared by the general method described by Harpp et al.[15] 2-Hydroxyethanethiol (0.91 g, 11.65 mmol) was added to a solution of 1,1′-thiobis(benzimidazole) (1.72 g, 6.47 mmol) in 40 mL of dichloromethane. After 15 min, the solution was concentrated in vacuo and chromatographed over 30 g of silica gel. Elution with ethyl acetate afforded 1.01 g (94%) of the trisulfide as a clear, viscous oil: ^1H NMR ($CDCl_3$) δ 3.93 (t, J = 6 Hz, 4 H), 3.03 (t, J = 6 Hz, 4 H), 2.65 (bs s, 2 H); mass spectrum, m/e 186 (M^+). Bis(2-hydroxyethyl) disulfide was prepared by the method given in ref 16, and its purity was checked with IR, NMR, and MS. Deuterated formic acid (HCOOD) was produced by heating a mixture of P_2O_5, $NaHCO_2$, and purified D_2O. Deuterium oxide (99.75 mol % D_2O, Bio-Rad Laboratories) was refluxed with NaOH and $KMnO_4$ for a few hours and distilled before use.

The following chemicals were used as supplied: 2-hydroxyethanethiol (Fluka), "ridox" reagent (Fisher), *tert*-butyl alcohol (Baker Analyzed Reagent), sublimed sulfur (The McArther Chemical Co., Ltd.), and flavin adenine dinucleotide (F) (Sigma). All other chemicals were ACS certified grade.

Methods and Apparatus. All solutions were prepared from triply distilled water and saturated with N_2O (Matheson) or other high-purity gases as indicated. These were first passed through a column of ridox to remove traces of oxygen. Solutions were buffered with formate or phosphate buffers.

The pulse radiolysis experiments were performed by utilizing 2-μs pulses of electrons from the 1.5-MeV Van de Graaff generator described earlier.[17] A 1.0-cm path length optical cell was used with a fresh solution for each pulse. Dosimetry was based on absorbance changes in a N_2O-saturated 7×10^{-3} M potassium ferricyanide solution with $G\epsilon_{420}$ taken as 6.4×10^3 molecules ($(100\ eV)^{-1}\ M^{-1}\ cm^{-1}$). Here G is the yield of the product (ferricyanide) in molecules per 100 eV of radiation energy absorbed and ϵ_{420} the molar absorbance coefficient at 420 nm.

Steady-state radiolyses were performed at either 23 ± 2 or 1 ± 1 °C in an AECL ^{60}Co γ cell with a steady dose rate of about 14 Gy min^{-1}. The dose rate was determined by ferrous sulfate dosimetry, assuming $G(Fe^{3+})$ = 15.6 molecules per 100 eV,[12] and checked periodically.

Analyses. Sulfhydryl analyses were carried out by the method of Ellman,[18,19] using 5,5′-dithiobis(2-nitrobenzoic acid) (DTNB) from the Aldrich Chemical Co. Sulfhydryl concentrations were determined from standard curves of absorption vs. RSH concentration in the presence of RS_3R at concentrations similar to those for radiolysis experiments.

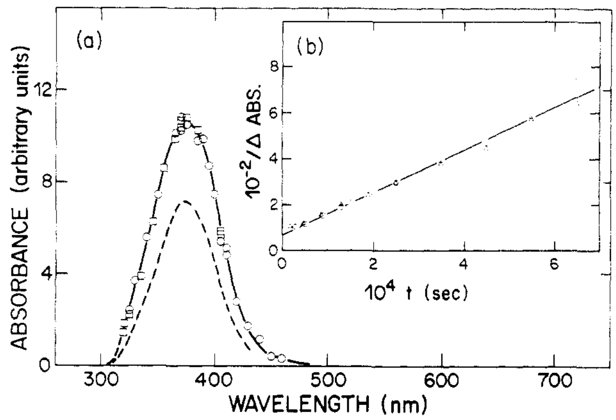

Figure 1. (a) Transient spectra 30 μs after pulse irradiation of aqueous bis(2-hydroxyethyl) trisulfide (RS_3R). Reacting radical: $\cdot CO_2^-$ at pH ~6.0 with 5.8×10^{-4} M RS_3R (O), and 2×10^{-4} M RS_3R (□) in N_2O-purged formate solutions; e_{aq}^- at pH 7.0 with 2×10^{-4} M RS_3R in 0.1 M *tert*-butyl alcohol, Ar purged (– – –). (b) Second-order plots of the decay of the transient at λ = 390 nm formed by the reaction of $\cdot CO_2^-$ with RS_3R (5.8×10^{-4} M) in N_2O-saturated 0.02 M HCOONa solution at pH 5.7, 10-Gy pulses.

Sulfur analyses were performed by centrifuging the irradiated solutions. The sulfur precipitate was dissolved in NaCN–acetone–water solution to produce SCN^-, and the absorbance of the ferric thiocyanide complex was measured at 466 nm (see ref 20 for details).

NMR spectra were run on an XL-200 NMR spectrometer (Varian) at 1 ± 1 and 23 ± 2 °C. The solutions were prepared in purified D_2O. The pDs of the solutions were adjusted to the desired point in the range 5.5–6.2 by adding HCOOD and $NaHCO_2$. The proton peak due to $NaHCO_2$ served as an internal standard.

As found in earlier work,[5] the positions of the two sets of triplets due to the α and β protons changed with the number of S atoms present. The differences were greatest for the α protons, for which the chemical shifts of the center lines in ppm relative to Me_4Si were 2.68_3, 2.93_7, 3.10_1, and 3.17_8 for RSH, RS_2R/RS_2H, RS_3R, and RS_4R, respectively, in D_2O.

Since there was no evidence of C–S cleavage, it was assumed that the total integrated intensity of the α-proton peaks correspond to the molarity of α-CH_2 groups in the initial RS_3R solution. From the fraction of total intensity due to peaks for RSH, RS_3R, and RS_4R in irradiated solutions, their concentrations could be calculated. For RS_2H and RS_2R only the sum of R-group concentrations could be determined, since their peaks were not resolved.

Results and Discussion

Pulse Radiolysis. The transient spectrum produced on reaction of $\cdot CO_2^-$ with trisulfide in nitrous oxide-saturated sodium formate solutions at pH 5.7–6.2 is shown by the solid line and data points in Figure 1a. The spectrum shape was independent of trisulfide concentration over the range 2×10^{-4}–6×10^{-4} M and was the same when $(CH_3)_2\dot{C}OH$ from 0.02 M 2-propanol was the reducing radical. At pH 7 a similar spectrum (dashed line in Figure 1a) was obtained on reduction of RS_3R with e_{aq}^- in ar-

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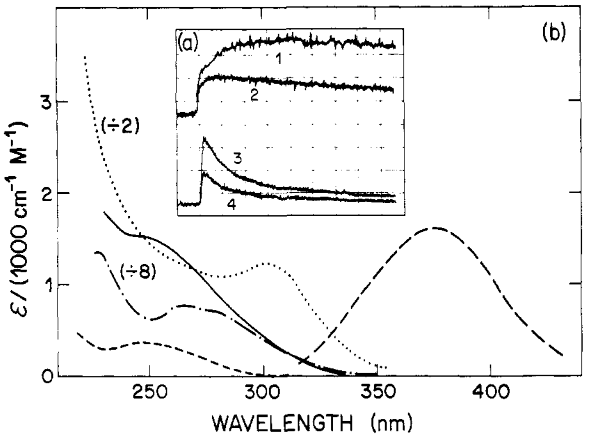

Figure 2. (a) Oscillograph traces of transients at (1) 330, (2) 340, (3) 390, and (4) 410 nm produced under the conditions of Figure 1b. Time scale: 20 μs per division for 1 and 2 and 100 μs for 3 and 4. (b) Absorption spectra of RSS· (– – –), RS_2R (- - -), RS_3R (—) from this study and S_8 (– · –) and RS_4R (· · ·) from ref 21.

gon-purged 0.1 M *tert*-butyl alcohol solutions.

The growth of the 370-nm absorbance in formate solutions at pH 5.7 was pseudo first order. From the dependence of that rate constant on RS_3R concentration in the range 1×10^{-4}–7×10^{-4} M a second-order rate constant of $(5 \pm 1) \times 10^8$ M^{-1} s^{-1} was estimated for the reaction between $\cdot CO_2^-$ and RS_3R. The electron rate constant at pH 7 was much faster.

Examples of traces showing the decay of the transient have been presented in Figure 2a. At and above 370 nm pure second-order decay was observed. This is illustrated by the plot of reciprocal absorbance vs. time in Figure 1b. The second-order rate constant ($=(1.4 \pm 0.3) \times 10^9$ M^{-1} s^{-1}) was independent of ionic strength, which was varied over the range 0–0.84 M by addition of $NaClO_4$ at pH 6.2. (The zero value was taken with 2-propanol radicals as reductant.) This feature indicates that the transient species is uncharged and cannot be $R\dot{S}_3R^-$, formed via

$$\cdot CO_2^- \text{ (or } e_{aq}^-) + RS_3R \rightarrow R\dot{S}_3R^- + CO_2 \quad (7)$$

The latter must have a lifetime of ≤1 μs under our conditions. Likewise it cannot be identified as RS·, because λ_{max} and ϵ_{max} (~350 nm and 100–300 M^{-1} cm^{-1})[6,11,22] for that species do not correspond to those observed in Figure 1a (λ_{max} = 374 nm; and ϵ_{max} = 1630 M^{-1} cm^{-1} calculated from the yield of $\cdot CO_2^-$ per pulse). The absorption was therefore assigned to the perthiyl (RSS·) radical, produced in the following overall reactions

$$e_{aq}^- + RS_3R \rightarrow RSS\cdot + RS^- \quad (8)$$

$$\cdot CO_2^- + RS_3R \rightarrow RSS\cdot + RS^- + CO_2 \quad (9)$$

$$(CH_3)_2\dot{C}OH + RS_3R \rightarrow RSS\cdot + RSH + (CH_3)_2CO \quad (10)$$

in *tert*-butyl alcohol, formate, and 2-propanol solutions, respectively.

At the pHs used RS^- is protonated (pK ~ 8[23]). It is possible therefore that reactions of $R\dot{S}_3R^-$ with H^+ or H_2O contribute to its short lifetime, as is the case for disulfide ($RS\dot{S}R^-$) anions at pH 7 and below:[11]

$$R\dot{S}_3R^- + H^+ \text{ (or } H_2O) \rightarrow RSS\cdot + RSH \text{ (or } +OH^-) \quad (11)$$

Attempts will be made to observe $R\dot{S}_3R^-$ under other conditions. For the moment it remains a possible intermediate in reactions 8 and 9.

The oscilloscope traces at 390 and 410 nm in Figure 2a approached base line on the millisecond time scale, while at 330 nm there was growth and only slight decay at 340 nm. The product (or products) of decay of RSS· must therefore possess relatively strong absorbance at 340 nm and negligible absorbance at and above 390 nm. Also the isobestic point with RSS· must lie between 330 and 340 nm. As shown in Figure 2b, the spectrum of RS_4R (×$^1/_2$) yields an isobestic point with our RSS· spectrum at ~330 nm. This observation suggests that reaction 12 is probably

$$2RSS\cdot \rightarrow RS_4R \quad (12)$$

the major mode of decay of perthiyl radicals in the present system. For reasons given later reactions 13a and 13b are not considered important.

$$2RSS\cdot \rightarrow 2RS\cdot + S_2 \quad (13a)$$

$$2RSS\cdot \rightarrow RSH + HOCH_2CH{=}S + S_2 \quad (13b)$$

Sulfhydryl Yields and the Scavenging of RSS·. Yields of total sulfhydryl were determined in 10^{-3} M RS_3R solutions at 0 °C and in 1.4×10^{-4} M solutions at room temperature. The values of G(SH) were respectively 6.0 ± 0.5 and $7._2$ ± 0.7 molecules for 100 eV. The agreement with the expected yield of $\cdot CO_2^-$ radicals in 0.01–0.1 M formate solutions (~6.5 molecules per 100 eV)[12] is in accord with the stoichiometry of reaction 9 and the secondary processes discussed below.

As a test for hydrogen sulfide, several irradiated solutions were thoroughly purged with purified N_2O or N_2 before analysis for sulfhydryl groups. However, these gave the same yields as solutions analyzed directly, showing that there was no loss of sulfhydryl due to removal of H_2S.[24,25]

The perthiyl radical is considered to be relatively unreactive.[2,3] For this reason it was of interest to determine whether it could be made to react with hydrogen-donating molecules and other species. From the experiment described above, it clearly does not undergo reaction 14,

$$RSS\cdot + HCO_2^- \rightarrow RS_2H + \cdot CO_2^- \quad (14)$$

otherwise a chain reaction for the reduction of RS_3R would have occurred and much larger values of G(SH) would have been observed. This is the case, for example, with RS· radicals formed from disulfides at pH 5.5–6.5.[25,26]

The only reagent which scavenged RSS· in our experiments was dihydroflavin adenine dinucleotide. This compound (FH_2) was prepared in situ in a 0.18 M formate solution at pH 5.5 by the reduction of the flavin with $\cdot CO_2^-$.[27] Trisulfide was then added under anaerobic conditions to produce an RS_3R concentration of 5.7×10^{-3} M. Since the entire operation was carried out in an optical cuvette, changes in the concentration of dihydroflavin could be determined from the absorption at 350–500 nm.

There was a slow thermal oxidation of dihydroflavin, and corrections were made for this. On further irradiation FH_2 was oxidized with a net yield of 3.2 molecules per 100 eV of radiation energy absorbed, which corresponds to one-half the yield of $\cdot CO_2^-$ radicals ($g(\cdot CO_2^-)$ = 6.5 per 100 eV). This feature and the fact that G(SH) was doubled are

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[22] Work in this laboratory confirmed λ_{max} = 350 nm for $HOCH_2CH_2S\cdot$ and ϵ = 140 as found in ref 6.

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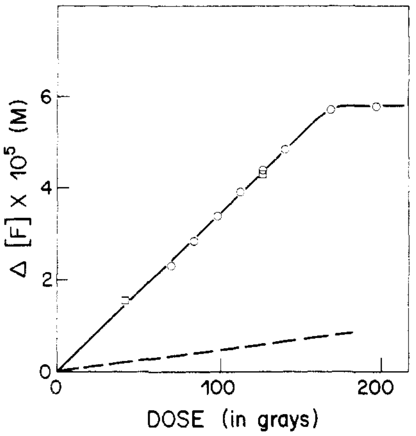

Figure 3. Changes in flavin adenine dinucleotide (F) concentration in the N_2O-saturated aqueous solutins containing 0.82 × 10^{-4} M dihydroflavin adenine dinucleotide (FH_2), 5.7 × 10^{-3} M RS_3R, and 0.18 M $NaHCO_2$ at pH 5.5 and at 23 ± 2 °C: (O, □) after irradiation with ^{60}Co γ-rays; (- - -) after thermal reaction between FH_2 and RS_3R for equivalent time.

TABLE I: Dependence of Product Concentrations[a] on (e^-), the Equivalents of $\cdot CO_2^-$ Reacted at 1 ± 1 °C

initial RS_3R	(e^-)	RSH	RS_4R	RS_2R, RS_2H	
12	3.5	$1._3$ ($1._6$)	$1._0$ ($1._0$)		$2._3$[b]
12	5.2	$2._2$ ($2._5$)	$1._1$ ($1._2$)		$3._1$[b]
12	6.9	$2._5$ ($3._1$)	$1._4$ ($1._6$)		$4._1$[b]
120	6.9	$6._7$	$10._1$	$6._0$	$0._2$[c]
120	10.4	$7._1$	$9._2$	$7._5$	$3._3$[c]
120	10.4 + 22-h thermal reaction	$4._1$	$12._3$	34	$6._3$[c]

[a] In mol L^{-1} × 10^4. Based on NMR results, except for those in parentheses, which are from UV absorbance. [b] Concentrations are equal to 2[RS_2R] + [RSSH], since there is no basis for separating the two species. [c] [RS_2H] assumed equal to [$\cdot CO_2^-$] − [RSH]; [RS_2R] calculated from NMR integrated intensity minus RS_2H contribution.

consistent with the occurrence of reaction 9 followed by reactions 15 and 16. A plot of the changes in flavin (F)

$$RSS\cdot + FH_2 \rightarrow RS_2H + FH\cdot \quad (15)$$

$$RSS\cdot + FH\cdot \rightarrow RS_2H + F \quad (16)$$

concentration vs. dose is shown in Figure 3. Also shown is the correction applied to take account of the thermal reaction, which takes place during irradiation and while the solutions are being transported and analyzed by spectrophotometry.

Long-Lived Products and Secondary Reactions at pH 5.5–5.7. Polysulfides and other products were determined from NMR spectra, chemical analysis, and changes in ultraviolet absorbance of solutions of RS_3R in 0.1 M sodium formate irradiated by ^{60}Co γ rays. Since sulfur was formed primarily in secondary thermal reactions (see below), several experiments were performed at 1 ± 1 °C to delay sulfur formation and simplify the reactions occurring. Unirradiated solutions were found to be stable for at least 24 h at either 23 ± 2 or 1 ± 1 °C.

NMR Spectra. The dependence of product concentrations computed from integrated intensities (see Experimental Section) on the equivalents of $\cdot CO_2^-$ reacted have been presented in Table I. It is evident that the simple stoichiometry

$$RS_3R + (e^-) + H^+ \rightarrow RSH + {}^1/_2RS_4R \quad (17)$$

where (e^-) represents 1 equiv of reducing radicals, is not obeyed. This can be explained by the lability of RS_3R in the presence of RSH. In particular it was found that in the absence of radiation addition of 0.1 mM RSH to 1 mM RS_3R at pD 5.5 in D_2O always resulted in strong peaks due to RS_2R and RS_2H, and only a small intensity of RSH. Reaction 18 must therefore have a half-life of a few minutes.

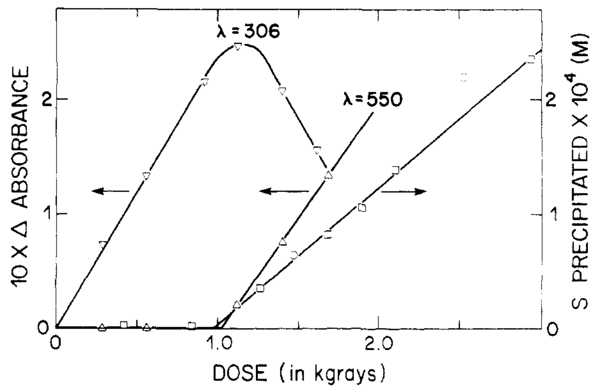

Figure 4. Changes in absorption and yields of sulfur precipitated from N_2O-saturated aqueous 1 × 10^{-3} M RS_3R solution in 0.1 M $NaHCO_2$ irradiated with ^{60}Co γ-rays at pH 5.7 and 1 ± 1 °C: (□ and O) sulfur from duplicate experiments; absorbance changes at λ = 306 (▽) and 550 (△) nm.

$$RS_3R + RSH \rightleftharpoons RS_2R + RS_2H \quad (18)$$

Reaction 18 can account for the fact that RSH yields in 1.2 mM RS_3R solutions are lower than the equivalents of $\cdot CO_2^-$ in Table I. The smaller than expected RS_4R concentrations (i.e., <0.5(e^-)) may be attributed to similar reactions:

$$RS_4R + RSH \rightleftharpoons RS_3R + RS_2H \quad (19)$$

$$RS_4R + RSH \rightleftharpoons RS_3H + RS_2R \quad (20)$$

However, *the RS_3R concentration must have an important* influence on secondary product concentrations, for in 12 mM solutions the RS_4R concentrations were *larger* than (e^-). Actually this can be explained by the increased [RS_3R], if one writes the equilibrium constant expression for reaction 19 in the form [RS_4R]/[RS_2H] = [RS_3R]/(K_{19}[RSH]).

The free-radical reactions 21 and 22 could in principle

$$RS_2\cdot + RS_3R = RS_4R + RS\cdot \quad (21)$$

$$RS\cdot + RS_3R = RS_2R + RS_2\cdot \quad (22)$$

provide a pathway for the conversion of RS_3R to RS_4R. However, from our conclusions above and earlier studies[2,3] RSS· is a more stable radical than RS·, and reaction 21 is expected to be ≥10 kcal mol^{-1} endothermic. Reaction 21 cannot therefore be of great importance. In our view the major pathways for the conversion of RS_3R to RS_2R and RS_4R, seen particularly in the 12 mM solutions (Table I), are the thermal reactions 18 and 18a. That these and

$$RS_3R + RS_2H \rightleftharpoons RS_4R + RSH \quad (18a)$$

other thermal processes occur is proven by comparison of the last two lines in Table I, which demonstrate the effect of standing after $\cdot CO_2^-$ production ceased.

It may be noted that in the latter instance 2.7 mM of elemental sulfur was also formed on standing. It appears that this could arise through a slow buildup of higher polythiols via sequences of reactions such as reactions 18a and 20, which have an overall effect equivalent to reaction 23, viz

$$RS_xH + RS_3R \rightarrow RS_{x+1}H + RS_2R \quad (23)$$

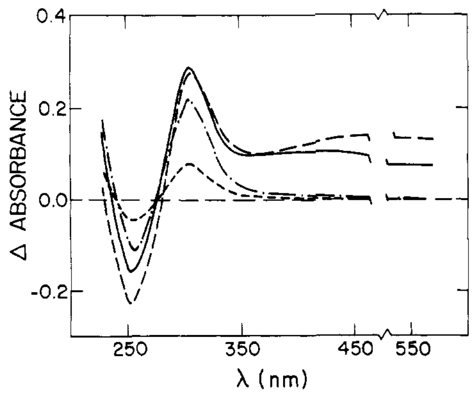

Figure 5. Difference spectra of N_2O-saturated 1 × 10^{-3} M RS_3R in 0.1 M $NaHCO_2$ irradiated with ^{60}Co γ-rays at 1 ± 1 °C and pH 5.7: after 280 (- - -), 840 (–••–), 1400 (—), and (– – –) 1680 Gy.

followed by elimination of S_8 (or smaller rings) when x becomes sufficiently large:

$$RS_xH \rightarrow RS_{x-8}H + S_8 \qquad (24)$$

This mechanism is somewhat similar to that proposed for sulfur elimination from sulfanes.[4]

Before we leave this section, it should be recognized that radical yields in D_2O are about 7% larger than in H_2O.[12] However, this difference is not significant for present purposes, and H_2O was used for the remaining γ radiolysis experiments described below.

Sulfur Yields. As illustrated by the plot of sulfur yield vs. dose in Figure 4, there was a threshold for sulfur production. At 1 ± 1 °C it was 1000 Gy in 1.2 mM and above 2500 Gy in 12 mM solutions of RS_3R. These radiation doses correspond to 0.5_1 and $>0.1_3$ equiv of $\cdot CO_2^-$ per mole of RS_3R present initially. At 23 °C the threshold doses were smaller: $0._0$ and 840 Gy, respectively, for the same concentrations. Also solutions irradiated to doses below the threshold at 1 ± 1 °C produced sulfur, if warmed to 23 °C and allowed to stand.

UV Absorption Spectra. Absorbance changes in an initially 1 mM RS_3R solution in 0.1 M sodium formate at pH 5.7 after four successive doses of γ radiation at 1 ± 1 °C are shown in Figure 5.

From a comparison of the spectra in Figure 2b, the increase in absorbance in the 280–350-nm region is in agreement with production of RS_4R. The spectrum of $S_2(^3\Sigma_g^-)$ is not shown in Figure 2b. However, it has a maximum at 280 nm and a threshold at about 320 nm.[28] The decrease in absorbance seen in Figure 4 between 240 and 280 nm implies that S_2 and S_8 never reach significant concentrations, which is not unexpected because of the trivially small solubility of elemental sulfur in water.[29]

The general rise in absorption at large doses for all wavelengths above 350 nm was accompanied by the appearance of cloudiness. It is attributed to light scattering by sulfur particles. Confirmation of this is seen from the fact that at 550 nm it is linear in dose and has the same threshold as the sulfur production (Figure 4).

Quantitative analysis of the absorbance changes in Figure 5 is complicated by the occurrence of reaction 18, and particularly also reactions 19 and 20. However, if one assumes that the absorptions of $RS_2H + RS_3R$ and $RS_2R + RS_3H$, the products of reactions 19 and 20, are similar, the following treatment can be used. Reaction 17 per se produces an absorbance change per equivalent of $\cdot CO_2^-$ given by $\Delta\epsilon_{17} = {}^1/_2\epsilon(RS_4R) + \epsilon(RSH) - \epsilon(RS_3R)$. Assuming reactions 18 and 19 consume equal amounts of RSH and coupling them with reaction 17, one obtains

$$RS_3R + (e^-) + H^+ = RS_2H + {}^1/_2RS_2R \qquad (25)$$

for which $\Delta\epsilon_{25} = \epsilon(RS_2H) + {}^1/_2\epsilon(RS_2R) - \epsilon(RS_3R)$. Using values of $\epsilon(RS_4R)$ from ref 21 and absorbance coefficients determined for other species here, we calculated $\Delta\epsilon_{17} = 800$ M^{-1} cm^{-1} and $\Delta\epsilon_{25} = 29$ M^{-1} cm^{-1} at 306 nm, where RS_4R was the main absorbing long-lived product. Allowing for the stoichiometry of both reactions 17 and 25, and recognizing that $[RSH] + [RS_2H] = (e^-)$, one then has for $\Delta A(306)$ before S precipitation

$$\Delta A(306) = 800[RSH] + 29\{(e^-) - [RSH]\} \qquad (26)$$

Concentrations of RSH and RS_4R calculated with eq 26 are given in parentheses in Table I. Agreement with the NMR results is satisfactory.

A comparison of the dose dependence of the RS_4R and sulfur yields is particularly intriguing. The difference between ΔA at 306 nm and ΔA at 550 nm, which is now employed as a base-line correction for light scattering at doses where sulfur precipitation occurred, may be used as a measure of $[RS_4R]$. It passes through a maximum at the threshold dose for sulfur formation and then falls abruptly (see Figure 4). Similar observations were made for a 10^{-2} M solution at room temperature. This effect and the dose dependence of the sulfur yields confirm that sulfur is a secondary product, formed at the expense of RS_4R and possibly other polysulfides (see above). The concentrations of those must, however, be low, for they do not give rise to significant peaks in the NMR spectra.

Summary and Conclusions

The values of $\lambda_{max} = 374$ nm and $\epsilon_{max} = 1630$ M^{-1} cm^{-1} for perthiyl are in excellent accord with the data of Morine and Kuntz,[13] who produced similar spectra by photolysis of a variety of disulfides. For penicillamine, which gave the largest perthiyl yield in acidic aqueous solution, they reported $\epsilon_{max} \sim 1700$ M^{-1} cm^{-1}, and $\lambda_{max} \simeq 375$ nm from their Figure 1. It is also in agreement with an assignment made earlier for an intermediate formed in the one-electron oxidation of disulfides containing β-amino groups.[10] Actually the radical appears to have been observed previously in a variety of different systems subjected to photolysis or radiolysis, but its true identity was not recognized.[10,13] This study confirms the assignments in ref 10 and 13.

As shown in Figure 4 elemental sulfur is a secondary product and there is no evidence to support the occurrence of reactions 13a and 13b. Had the latter occurred to a significant extent, there would also have been unexplained NMR peaks arising from $HOCH_2CHS$ or its decay products. The conclusion that reaction 12 is the main mode of RSS· decay is in agreement with earlier work.[2] The apparent insignificance of reactions 13a and 13b is quite intriguing because the analogous processes are quite common in the decay of peroxy radicals.[30] Actually the comparative complexity[31] of the decay of peroxy radicals probably stems from the relatively weak bonding of the central oxygens in the tetroxide linkage. The activation energy for its dissociation is in the region of 10–15 kcal mol^{-1},[30] and much less than that reported for tetrasulfide—36 ± 2.6 kcal mol^{-1} for $CH_3S_4CH_3$.[2] Consequently tetrasulfide once formed and stabilized would be much less

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likely to undergo further reactions. The large value of the second-order decay constant $(1.4 \pm 0.3) \times 10^9$ M^{-1} s^{-1} reported above requires that reaction 12 occur on essentially every collision.

The fact that RSS· does not undergo reaction 14 implies that in water it forms an S–H bond weaker than RS–H, which has a dissociation energy of ~90 kcal mol^{-1}.[32] Perthiyl is, however, able to abstract H atoms from dihydroflavin (FH_2) and the flavin radical (FH·) in reactions 15 and 16. Since D_{FH-H} is ~59 kcal mol^{-1},[33] D_{S-H} of RSS· must be larger, and lie in the range 60–90 kcal mol^{-1}.

The total sulfhydryl yields and the observation of perthiyl radical are clearly consistent with the stoichiometry of reaction 9. However, the yields of tetrasulfide from reaction 12 and of RSH are obscured by the secondary thermal reactions 18–20. These are similar to reactions postulated earlier to explain exchanges in polysulfides.[5,34] As in those cases RS^- rather than RSH may be the active species,[34] but this point was not pursued here.

The net effect of the thermal reactions is to convert the trisulfide to lower *and* higher polysulfides, and *eventually* to produce elemental sulfur.

Acknowledgment. We acknowledge financial support from the University of Calgary and the Natural Sciences and Engineering Research Council of Canada.

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Photoexcited Inclusion Complexes of β-Naphthol with α-, β-, and γ-Cyclodextrins in Aqueous Solutions

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(Received: February 25, 1982; In Final Form: July 2, 1982)

Structural differences among inclusion complexes of α-, β-, and γ-cyclodextrins (CDx's) with β-naphthol (Naph) were studied by means of optical absorption, fluorescence, and circular dichroism (CD) spectrometry. The fluorescence study revealed that β-naphthol is very loosely packed in a γ-CDx cavity, whereas it is tightly packed in a β-CDx cavity. The rate of proton dissociation is markedly depressed by inclusion, particularly in the case of α-CDx inclusion. These facts, along with Corney–Pauling–Koltun (CPK) molecular model and CD studies, suggest that the hydroxyl group of β-naphthol is hidden in the α-CDx cavity, while the naphthyl group is largely exposed to a water phase. It is also found that the rate of fluorescence quenching of the inclusion complexes by iodide ion is dependent on the CDx cavity size. It is shown that not only the naphthyl group but also the hydroxyl group of β-naphthol plays an important role in the electron-transfer quenching.

Introduction

Cyclodextrin (CDx) consists of six or more linked glucopyranose rings and forms a doughnut-shaped compound.[1] The number of glucose units of CDx is designated α for six, β for seven, γ for eight, and so forth. The interior of the toruses of CDx's is relatively apolar compared to water and therefore is capable of including aromatic compounds, alkyl halides, gases, etc., as guest molecules in the cavity.[2]

In a previous study we found the marked effects of β-CDx inclusion on the absorption and fluorescence spectra of benzene derivatives.[3] The fluorescence enhancement observed in that system was interpreted in terms of the increase in the rate of the radiative process, the decrease in rotational freedom, and elimination of water molecules surrounding fluorescent molecules in the cavity. Obviously, these spectroscopic studies of CDx inclusion complexes provide information not only on interaction of CDx's with guest molecules but also on the changes of chemical properties of guest molecules by inclusion in the ground and photoexcited states.

The present study aims to reveal the difference in environmental changes around the guest molecule, β-naphthol, and its chemical property changes in the ground and photoexcited states by the inclusion of α-, β-, and γ-CDx's, such as molecular structure of the complex, rate of proton dissociation, and fluorescence quenching efficiency by I^- ion.

Experimental Section

β-Naphthol (Naph) was purified by sublimation under reduced pressure. Purified β-cyclodextrin (β-CDx) was obtained by recrystallizing it twice from aqueous solutions. α- and γ-CDx's were kindly provided by Dr. H. Horikoshi of The Institute of Physical and Chemical Research and used as received. Sodium iodide was used as supplied.

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