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Fast Oxygen Atom Transfer from in Situ Generated Peroxynitrous Acid to Thiolato Sulfur Coordinated to Cobalt(III)

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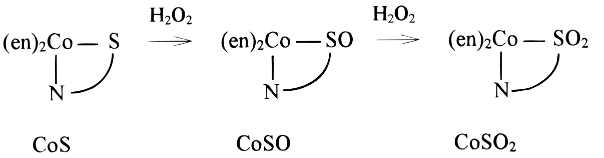
Introduction

It has been shown by Deutsch and co-workers that, according to reaction 1, the oxidation of the chelated thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (= CoS) with H_2O_2 leads to the corresponding S-bonded sulfenato complex, $[(en)_2Co(S\{O\}CH_2CH_2NH_2)]^{2+}$ (= CoSO), which is finally converted to the S-bonded sulfinato complex, $[(en)_2Co(S\{O_2\}CH_2CH_2NH_2)]^{2+}$ (= $CoSO_2$).[1] The chemistry of the cationic cobalt(III) species CoSO and $CoSO_2$ has been thoroughly established.[1a,b] The kinetics of the step CoS → CoSO have been found to follow the rate law in eq 2.[1c,2]



(1)

$$\text{rate} = k_2[\text{CoS}][H_2O_2] \tag{2}$$

$$k_2 = a + b[H^+] \tag{3}$$

According to eq 3, there are two pathways which have been ascribed to the nucleophilic attack of the sulfur atom of CoS on H_2O_2 (rate constant a) and $H_3O_2^+$ (rate constant b).[1c]

It is well-known that protons[3] and transition metals[4] can raise the reactivity of the oxidant H_2O_2 considerably. As shown by Thompson and co-workers, the oxidation of CoS to CoSO and $CoSO_2$ according to eq 1 is much faster in the presence of oxoperoxo complexes of Mo(VI), W(VI), and V(V), acting as catalysts for the oxygen atom transfer reaction from H_2O_2 to CoS and CoSO.[5]

In addition to the activation of H_2O_2 by protons and transition metals, it is also possible to activate H_2O_2 by nitrous acid. In acidic medium, H_2O_2 oxidizes HNO_2 rapidly to peroxynitrous acid, ON-OOH, an unstable isomer of nitric acid. Peroxynitrous acid is a much more powerful oxidant than H_2O_2.[6] The role of peroxynitrite in biological systems is of rapidly growing interest.[7] Depending on the substrate, oxidation reactions of peroxynitrous acid can follow one-electron and/or two-electron pathways.[7a,8] In the case of nucleophilic substrates such as thioethers, the two-electron process results in oxygen atom transfer, i.e. formation of sulfoxides. We have shown recently that ON-OOH, when generated in situ from nitrite and H_2O_2 in acidic medium, rapidly transfers oxygen to organic sulfides, which is of interest for the fast preparation of sulfoxides.[9] The use of ON-OOH for the oxidation of a substrate is limited by the fact, however, that this oxidant, as generated according to eq 4, isomerizes at ambient temperature with a half-life of ca. 0.5 s to form nitric acid according to eq 5.

$$HNO_2 + HOOH \xrightarrow{k_f} \text{ON-OOH} + H_2O \tag{4}$$

$$\text{ON-OOH} \xrightarrow{k_d} HNO_3 \tag{5}$$

$$A + \text{ON-OOH} \xrightarrow{k_A} A{=}O + HNO_2 \tag{6}$$

The oxidation of a substrate A according to eq 6 competes, therefore, with the decay of ON-OOH according to eq 5. As a consequence, this approach is applicable only when the rate of eq 6 is higher than that of eq 5, i.e., when $k_A[A] \gg k_d$. One should note that reactions 4 and 6 form a catalytic cycle in which the catalyst HNO_2 converts H_2O_2 into the more powerful oxidant ON-OOH. The number of cycles is controlled by the competition between reactions 5 (decay of ON-OOH) and 6 (oxidation of the substrate by ON-OOH).

The succcessful application of the very reactive but unstable reagent ON-OOH for the oxidation of thioethers[9] led us to try the fast oxidation of metal-bound thiolato sulfur with peroxynitrous acid. As an example, the present paper summarizes the results obtained for the thiolato cobalt(III) complex CoS. The unstable oxidant ON-OOH was generated by acidification of alkaline solutions of the anion ON-OO^- according to eq 7 (procedure A)[10] or, in some experiments, prepared in situ in acid solution according to eq 4 (procedure B).

$$\text{ON-OO}^- + H^+ \rightleftharpoons \text{ON-OOH} \tag{7}$$

Experimental Section

Chemicals. All commercial chemicals were reagent grade. Complexes $[\text{CoS}](ClO_4)_2$ = (2-aminoethanethiolato-*N*,*S*)bis(1,2-diaminoethane)cobalt(III) perchlorate[11] and $[\text{CoSO}](ClO_4)_2$ = (2-sulfenatoethylamine-*N*,*S*)bis(1,2-diaminoethane)cobalt(III) perchlorate[1b] were

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[†] This contribution presents main results of the Dr.-Ing. Dissertation submitted to Technische Universität Darmstadt, D17, by Stéphane Vayssié in 1999.

(1) (a) Lange, B. A.; Libson, K.; Deutsch, E.; Elder, R. C. *Inorg. Chem.* **1976**, *15*, 2985. (b) Adzamli, I. K.; Libson, K.; Lydon, J. E.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303. (c) Adzamli, I. K.; Deutsch, E. *Inorg. Chem.* **1980**, *18*, 1366.

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(4) Conte, V.; di Furia, F.; Modena, G. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; pp 559−598.

(5) (a) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1988**, *27*, 4766. (b) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1989**, *28*, 3647. (c) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1990**, *29*, 4457.

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(7) (a) See review "The chemistry of peroxynitrite: A product from the reaction of nitric oxide with superoxide" (Pryor, W. A.; Squadrito, G. L. *Am. J. Physiol.* **1995**, *268*, L699) and references therein. (b) In contrast to the present study the effect of ON-OOH on biological systems is mainly studied in the pH range 6.5−8 with solutions of peroxynitrite as the source.

(8) Jensen, J. L.; Miller, B. L.; Zhang, X.; Hug, G. L.; Schöneich, C. *J. Am. Chem. Soc.* **1997**, *119*, 4749.

(9) Vayssié, S.; Elias, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2088.

(10) In contrast to the acid ON-OOH, the anion ON-OO^- is much more stable and can be stored in alkaline solution.

(11) Nosco, D. L.; Deutsch, E. *Inorg. Synth.* **1982**, *21*, 19.

10.1021/ic981423t CCC: $18.00

Table 1. Summary of Rate Data Obtained for the Sulfoxidation of the Complex Cation CoS with ON-OOH at 298 K under Variable Conditions

$[HClO_4]$ (M)	I (M)	[CoS] (μM)	$[HNO_2]^a$ (μM)	$[HOONO]^b$ (mM)	$k_{exp}{}^c$ (s^{-1})	$k_{exp1}{}^d$ (s^{-1})	$10^2k_{exp2}{}^d$ (s^{-1})
0.1	0.5	19		0.18	12.9 ± 0.2		
				0.22	16.6 ± 0.9		
				0.27	17.1 ± 1.7		
				0.36	24.6 ± 2.1		
				0.45	28.1 ± 1.5		
0.01	0.5	19		0.18	11.7 ± 0.7		
				0.22	18.6 ± 1.6		
				0.27	18.3 ± 1.1		
0.1	0.1	84	0^e		0.024 ± 0.03^f		
			2^e			0.68 ± 0.07	2.0 ± 0.2
			8^e			0.84 ± 0.09	3.5 ± 0.4
			15^e			1.1 ± 0.1	2.7 ± 0.3

[a] Procedure B. [b] Procedure A. [c] Obtained by fitting of the absorbance/time data with eq 8. [d] Obtained by fitting of the absorbance/time data with eq 9. [e] $[H_2O_2] = 15$ mM. [f] Obtained by fitting of the absorbance/time data with eq 10.

prepared as described. (**WARNING!** *Perchlorate salts are potentially explosive. They should be handled in small quantities and with caution.*) Stock solutions of the peroxynitrite anion $ON\text{-}OO^-$, prepared according to the procedure reported by Al-Ajlouni and Gould,[12] were stored at −28 °C. The concentration of peroxynitrite was determined spectrophotometrically ($\epsilon_{302} = 1670$ M^{-1} cm^{-1}).[13]

Instrumentation. UV/vis spectra were recorded with a diode array spectrophotometer (Zeiss, Specord S10). The kinetics of oxidation were monitored with a multiwavelength stopped-flow spectrophotometer described earlier.[14]

Kinetic Measurements. The oxidation of CoS by peroxynitrous acid according to eq 6 was studied by multiwavelength stopped-flow spectrophotometry at 298 K under pseudo-first-order conditions (procedure A, [ON-OOH] $\gg$ [CoS]; procedure B, $[H_2O_2] \gg$ [CoS], $[HNO_2]$). For procedure A, the two syringes of the stopped-flow apparatus were filled with the solution of CoS and $HClO_4$ and with the alkaline solution of NaOO-NO, respectively. For procedure B, the two syringes were filled with the solution of CoS and $NaNO_2$ and with the solution of H_2O_2 and $HClO_4$, respectively. In all of these solutions the ionic strength was adjusted with $NaClO_4$ to be $I = 0.5$ M (procedure A) and $I = 0.1$ M (procedure B), respectively. Monitoring was done in the range 260−420 nm to cover the disappearance of the species CoS ($\epsilon_{282} = 13\,800$ M^{-1} cm^{-1})[1b] and the appearance of the species CoSO ($\epsilon_{282} = 3700$ M^{-1} cm^{-1}, $\epsilon_{367} = 6700$ M^{-1} cm^{-1}).[1b] The absorbance/time data, as recorded for the formation of CoSO according to procedure A, were computer-fitted to eq 8 to obtain the experimental rate constant k_{exp}. Equation 8 takes into account that, parallel to the reaction of ON-OOH with CoS, ON-OOH decays with first-order rate constant k_d. The absorbance/time data, as obtained for some experiments carried out according to procedure B, were computer-fitted to eq 9 to obtain the experimental rate constants k_{exp1} and k_{exp2} (a_1, a_2 = amplitudes; mt = correction term for the photolytic decomposition of CoSO; see below).

$$\ln [(A - A_8)/(A_o - A_\infty)] = (k_{exp}/k_d)[\exp(-k_d t) - 1] \qquad (8)$$

$$A = a_1 \exp(-k_{exp1}t) + a_2 \exp(-k_{exp2}t) + mt + A_\infty \qquad (9)$$

The absorbance/time data obtained for the oxidation of CoS by H_2O_2 in the absence of HNO_2 were computer-fitted to eq 10.

$$A = (A_o - A_\infty)\exp(-k_{exp}t) + A_\infty \qquad (10)$$

Results and Discussion

Oxidation of CoS by H_2O_2. Deutsch and co-workers[1c] studied the sulfoxidation of CoS by H_2O_2 at an ionic strength of $I = 1.0$ M. The present data were collected at $I = 0.5$ M. To consider possible ionic strength effects, we measured the sulfoxidation of CoS by H_2O_2 at $I = 0.5$ M ($[HClO_4] = 0.5$ M). The absorbance/time data were fitted with eq 10. The experimental rate constant, k_{exp}, obtained at variable concentration of H_2O_2 increases linearly with $[H_2O_2]$ (see Table S1) with a slope of $k_2 = 2.5 \pm 0.1$ M^{-1} s^{-1}. According to eq 3, the data reported for a and b at $I = 1.0$ M ($a = 1.18$ M^{-1} s^{-1} and $b = 1.8$ M^{-2} s^{-1} at 298 K)[1c] lead to $k_2 = 2.1$ $M^{-1}s^{-1}$ at $[HClO_4] = 0.5$ M. This minor difference in k_2 means that there are no substantial ionic strength effects at the given concentration level.

Oxidation of CoS by ON-OOH (Procedure A). When the oxidant H_2O_2 is replaced by an excess of the oxidant ON−OOH, generated according to procedure A, the absorbance/time data recorded within 0.6 s can be satisfyingly fitted with eq 8 to obtain rate constant k_{exp} (see Table 1) with $k_d = 1.8$ s^{-1} at pH 1 and $k_d = 1.2$ s^{-1} at pH 2.[15] This means that (i) the oxidation of CoS according to reaction 11 is first-order in CoS and (ii) the subsequent oxidation of CoSO to the sulfone $CoSO_2$ is too slow to occur at this time scale.[16]

$$\text{CoS} + \text{ON}{-}\text{OOH} \xrightarrow{k_{CoS}} \text{CoSO} + \text{HNO}_2 \qquad (11)$$

The oxidation of CoS according to eq 10 occurs in less than 0.3 s under the given conditions.[17] Within the limits of error, the total change in absorbance observed within 0.6 s at 367 nm (formation of CoSO) is found to be the same for the lowest (0.18 mM) and highest concentration of ON-OOH (0.45 mM).[18] The data obtained for k_{exp} at pH 1 and at variable concentration of ON-OOH in the range 0.18−0.45 mM (see Table 1) increase linearly with [ON-OOH] and the slope of this linear dependence

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(12) Al-Ajlouni, A.; Gould, E. S. *Inorg. Chem.* **1996**, *35*, 7892.

(13) Hughes, M. N.; Nicklin, H. G. *J. Chem. Soc. (A)* **1968**, 450.

(14) Drexler, C.; Elias, H.; Fecher, B.; Wannowius, K. J. *Fresenius J. Anal. Chem.* **1991**, *340*, 605.

(15) According to the literature (Benton, D. J.; Moore, P. J. *J. Chem. Soc. A* **1970**, 3179), the rate constant k_d for the decay of ON−OOH at 298 K is 1.8 s^{-1} at pH 1 and 1.2 s^{-1} at pH 2.

(16) We have shown recently that the oxidation of dimethyl sulfoxide to dimethyl sulfone by ON-OOH is by 3 orders of magnitude slower than the sulfoxidation of dimethyl sulfide.[6] The oxidation of CoSO to $CoSO_2$ by H_2O_2 was found to be by almost 4 orders of magnitude slower than the sulfoxidation of CoS.[1b]

(17) This finding is in agreement with the data obtained for k_{exp} (see Table 1). It follows from these data that the half-life $t_{1/2}$ for the oxidation process is 54 and 25 ms, respectively, at the lowest and highest concentrations of the excess partner ON-OOH. This means that the oxidation of CoS by ON-OOH has practically come to an end after 0.27 and 0.13 s, respectively, which corresponds to $5t_{1/2}$.

(18) The experimentally observed total change in absorbance at 367 nm, $\Delta A = A_o - A_\infty$, corresponds to 70−75% of the expected total change in absorbance, as calculated on the basis of the given concentration of CoS and absorptivity of CoSO. This finding points to the occurrence of unidentified side reactions.

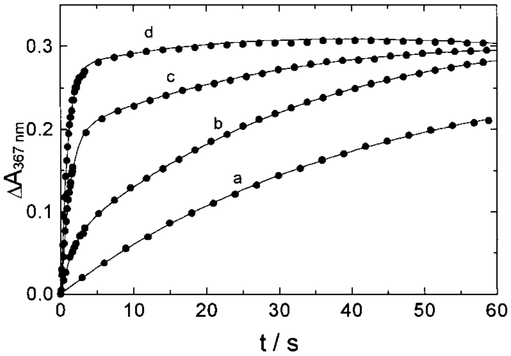

Figure 1. Time dependence of the change in absorbance at 367 nm for the oxidation of the complex cation CoS by H_2O_2 at pH 1 and 298 K in the absence of HNO_2 (a) and at $[HNO_2] = 2\ \mu M$ (b), 8 μM (c), and 15 μM (d) ($[CoS] = 84\ \mu M$, $[H_2O_2] = 15$ mM). The solid lines were obtained by fitting of the data with eq 10 (curve a) and eq 9 (curves b−d).

(see Figure S1) yields $k_{CoS} = (6.6 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$. It follows from these results that the oxidation of CoS by ON-OOH can be described as a second-order reaction according to eq 12.

$$d[CoSO]/dt = k_{CoS}[CoS][ON\text{-}OOH] \qquad (12)$$

One should note that the data obtained for k_{exp} at pH 2 are very close to those obtained at pH 1 (see Table 1 and Figure S1), which means that there is no substantial pH effect at this level of acid concentration.

Oxidation of CoS by in situ Generated ON-OOH (Procedure B). It is to be expected that, from the kinetic point of view, the situation is much more complex when ON-OOH is generated in situ according to eq 4 (procedure B) by mixing HNO_2 and H_2O_2 in a stopped-flow apparatus. The fast formation of ON-OOH will overlap with its decay and the oxidation of CoS by ON-OOH will overlap with the slower oxidation by H_2O_2. Furthermore, oxygen atom transfer from ON-OOH to CoS releases the catalyst HNO_2, which is oxidized by H_2O_2 to form again ON-OOH. Figure 1 shows examples for the time dependence of the absorbance at 367 nm at variable concentration of HNO_2 (0−15 μM) and in the presence of an excess of H_2O_2 (15 mM) and CoS (84 μM). The observed increase in absorbance describes the formation of CoSO. Curve a, as obtained in the absence of HNO_2, describes the oxidation of CoS by H_2O_2 and follows the rate law in eq 10. Curves b−d in Figure 1 clearly show that there is an additional faster oxidation process when HNO_2 (in the form of $NaNO_2$) is admixed to the system. The contribution of this faster process increases with $[HNO_2]$. At $[HNO_2] = 15\ \mu M$ (curve d), ca. 90% of the observed overall oxidation reaction appear to be due to this fast process, occurring within 1−2 s. It is important to note that, in the case of curve d, the ratio $[CoS]/[HNO_2]$ is 5.6:1 which means that the number of catalytic cycles according to eqs 4 and 6 ($HNO_2 \rightarrow ON\text{-}OOH \xrightarrow{CoS \rightarrow CoSO} HNO_2$) has to be of the order of 5 to explain the observed fast sulfoxidation of the thiolato complex CoS. In other words, one molecule of the catalyst HNO_2 oxidizes approximately five molecules of CoS via the rapidly formed but unstable intermediate oxidant ON-OOH. As in the case of thioethers,[9] this fast and experimentally convenient method of HNO_2-catalyzed sulfoxidation with H_2O_2 should be of preparative interest.

The absorbance/time data for curves b−d in Figure 1 can be satisfyingly fitted with eq 9. The fitting procedure leads to rate constants k_{exp1} and k_{exp2} (see Table 1) and to the correction factor m (photolytic decomposition of CoSO[19]). Rate constant k_{exp2} ranges from 0.02 to 0.035 s^{-1} and does not vary systematically with $[HNO_2]$. It follows from the comparison with $k_{exp} = 0.024\ s^{-1}$, as obtained under identical conditions at $[H_2O_2] = 15$ mM in the absence of HNO_2 (see Table 1), that k_{exp2} obviously describes the oxidation of CoS by H_2O_2. Rate constant k_{exp1}, ranging from 0.68 to 1.1 s^{-1} and increasing slightly with $[HNO_2]$, is a measure for the oxidation of CoS by ON-OOH. Any attempt however to assign and interpret k_{exp1} more specifically would be rather speculative because (i) due to the decay of ON-OOH with rate constant $k_d = 1.8\ s^{-1}$ at pH 1, the condition $[HNO_2]_o = [ON\text{-}OOH]_o$ is not fulfilled[20] and the exact concentration of ON−OOH, when generated according to procedure B, is not known therefore, (ii) the catalyst HNO_2 cycles according to eqs 4 and 6 and, parallel to that, its concentration decreases due to the isomerization $ON\text{-}OOH \xrightarrow{k_d} HNO_3$, which complicates the situation from the point of formal kinetics, and (iii) the decay of ON-OOH forms highly oxidizing intermediates that can react with CoS and CoSO, thus affecting the expected yield of CoSO. As a matter of fact, the increase in absorbance at 367 nm ($\Delta A \approx 0.3$) observed for curve d in Figure 1 corresponds only to ca.. 70% of the expected yield of CoSO, which indicates the occurrence of unidentified side reactions in agreement with the last argument. In addition, there is the photolytic decomposition of the species CoSO, as mentioned above.[19]

Concluding Remarks. In extension of earlier work on the sulfoxidation of thioethers by oxygen atom transfer from peroxynitrite[7a,8] and peroxynitrous acid[6,9] the present contribution provides kinetic data for the sulfoxidation of metal-bound anionic sulfur by peroxynitrous acid in aqueous solution at pH 1−2. It follows from the experiments with ON-OOH, as generated from peroxynitrite by acidification, that the sulfoxidation of the thiolato sulfur in the coordination sphere of the cobalt(III) complex CoS is a second-order process, according to rate $= k_{CoS}[CoS][ON\text{-}OOH]$. Second-order rate constant $k_{CoS} = (6.6 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$ at 298 K is by more than 4 orders of magnitude larger than the corresponding rate constant for the sulfoxidation of CoS by H_2O_2 (see Table S2). In addition, k_{CoS} is more than 20-fold larger than the second-order rate constant found for the sulfoxidation of dimethyl sulfide by ON-OOH at 293 K,[6] which reflects the higher nucleophilicity of the anionic sulfur in CoS compared to the neutral sulfur in dimethyl sulfide. The present data show that sulfoxidation of CoS, leading to the corresponding sulfenato complex, can also be achieved with peroxynitrous acid, generated in situ from HNO_2 and H_2O_2 in acidic medium. In this procedure, HNO_2 acts as a catalyst, activating H_2O_2 by fast oxygen atom transfer from H_2O_2 to the sulfur via the rapidly formed, but unstable intermediate oxidant ON-OOH. Due to the reactivity of short-lived ON-OOH, the fast sulfoxidation is accompanied by side reactions which lower the yield.

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(19) Especially curve d in Figure 1 indicates that, from $t > 40$ s on, the absorbance decreases slowly. This decrease is obviously due to the photochemical decomposition of CoSO, which was observed by Deutsch and co-workers especially for solutions of CoSO at low pH.[1b] As a matter of fact, the multiwavelength stopped-flow apparatus applied in the present study sheds intense white light onto the sample under study. The correction factor m, taking into account the photolytic degradation of the species CoSO, was found to be approximately $-10^{-3}\ s^{-1}$ under the given conditions. As to be expected, in additional stopped-flow experiments with *monochromatic* light the photochemical decomposition of CoSO was much smaller.

(20) Saha, A.; Goldstein, S.; Cabelli, D.; Czapski, G. *Free Radical Biol. Med.* **1998**, *24*, 653.

As pointed out recently for the sulfoxidation of thioethers,[9] the most interesting aspect of oxidations with in situ generated unstable peroxynitrous acid is the short reaction time. Short reaction times may well be a crucial factor in the case of sulfur compounds of pharmaceutical and biological interest, which are not stable enough to stand longer reaction times with the oxidant H_2O_2.

Thompson and co-workers reported that thiolato sulfur atoms coordinated to cobalt(III) can be rapidly oxidized by H_2O_2 via oxoperoxo complexes of tungsten(VI) and molybdenum(VI), formed in solution by equilibration of H_2O_2 with tungstate and molybdate, respectively.[5a−c] The present data show (see Table S2 in the Supporting Information) that, from the kinetic point of view, ON-OOH (even when generated in situ) can well compete with the reactivity of the species $WO(O_2)_2$ and $MoO(O_2)_2$. The advantage of the catalytic activation of H_2O_2 by HNO_2 might be that HNO_2 is a nonexpensive, commercial chemical which, in the presence of an excess of H_2O_2, forms finally nitric acid. Nitric acid and nitrate, respectively, are simple byproducts which need not to be recovered.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, Verband der Chemischen Industrie e.V. and Otto-Röhm-Stiftung. The authors appreciate the assistance of Frank Maass in the computer-aided evaluation of the rate data.

Supporting Information Available: Rate constants for the sulfoxidation of CoS by H_2O_2 (Table S1), comparison of rate constants reported for the sulfoxidation of CoS (Table S2), and Figure S1 plot of rate constant k_{exp} vs $[H_2O_2]$ for the sulfoxidation of CoS by H_2O_2 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Additions and Corrections

1998, Volume 37

Duane A. Friesen, Toru Kajita, Earl Danielson, and Thomas J. Meyer*: Preparation and Photophysical Properties of Amide-Linked, Polypyridylruthenium-Derivatized Polystyrene.

Pages 2759−2761. The “average” lifetimes $\langle\tau\rangle$ from the fits to eq 5 were erroneously obtained by eq 19 in ref 44:

$$\langle\tau\rangle_{\mathrm{WW}} = \frac{1}{k\beta}\Gamma\left(\frac{1}{\beta}\right); \quad \Gamma\left(\frac{1}{\beta}\right) = \int_0^\infty x^{\left(\frac{1}{\beta}-1\right)} \mathrm{e}^{-x}\,\mathrm{d}x$$

This is the expression for average lifetimes obtained from fits to eq 4. The correct expression for the average lifetimes from fits to eq 5 is

$$\langle\tau\rangle_{\mathrm{DWW}} = \frac{1}{k^{\beta}\beta}\frac{1}{\Delta t^{\beta-1}}$$

This expression was obtained by integration of eq 5. For $\beta < 1$ at $t = 0$, eq 5 gives the physically unreasonable result that $I(t) = \infty$. The experimental data were refit from point $t = 0 + \Delta t$, where Δt is the experimental time resolution. The average lifetimes $\langle\tau\rangle$ in Tables 1−3 have been recalculated by using this procedure by Dr. Milan Sykora and Ms. Kimberly A. Maxwell. The average lifetimes calculated by correct expression show dramatic dependencies on Ru^{II} content (Table 1) and excitation power (Table 2). There is no apparent dependence of the $\langle\tau\rangle$ on the monitoring wavelength (Table 3) in agreement with the observation in the original report.

Table 1. Photophysical Properties of $[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_nMe_{m-n})](PF_6)_{2n}$ in CH_3CN at 25−28 °C

salt	$\langle\tau\rangle$ (ns)
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_2Me_9)](PF_6)_4$	1213
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_7Me_4)](PF_6)_{14}$	1025
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{11})](PF_6)_{22}$	861
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_5Me_{13})](PF_6)_{10}$	1195
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{13}Me_5)](PF_6)_{26}$	975
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$	905
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_8Me_{17})](PF_6)_{16}$	1220
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{21}Me_4)](PF_6)_{42}$	523
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{25})](PF_6)_{50}$	471

Table 2. Irradiance Dependence (at 650 nm) of the Kinetic Decay Parameters for Eq 5 in CH_3CN at 25−28 °C

pulse energy (μJ/mm^2)	$\langle\tau\rangle$ (ns)	pulse energy (μJ/mm^2)	$\langle\tau\rangle$ (ns)
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$			
8.1	635	1.6	848
5.4	703	0.8	959
4.1	724	0.3	1018
3.1	778		
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_5Me_{13})](PF_6)_{10}$			
6.2	904	1.4	1043
3.6	990	0.9	1195
2.3	1024	0.3	1200
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_2Me_9)](PF_6)_4$			
6.4	1131	0.9	1213

Table 3. Dependence of Emission Decay Kinetics (Eq 5) on Monitoring Wavelength in CH_3CN

$\lambda_{monitor}$ (nm)	$\langle\tau\rangle$ (ns)	$\lambda_{monitor}$ (nm)	$\langle\tau\rangle$ (ns)
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_{18})](PF_6)_{36}$			
600	793	700	964
625	949	725	982
650	959	750	945
675	994		
$[PS\text{-}CH_2CH_2NHCO(Ru^{II}{}_5Me_{13})](PF_6)_{10}$			
600	1012	700	1150
625	1107	725	1157
650	1195	750	1120
675	1150	800	1157

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