

As pointed out recently for the sulfoxidation of thioethers,⁹ the most interesting aspect of oxidations with in situ generated unstable peroxyxynitrous 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 H₂O₂.

Thompson and co-workers reported that thiolato sulfur atoms coordinated to cobalt(III) can be rapidly oxidized by H₂O₂ via oxoperoxo complexes of tungsten(VI) and molybdenum(VI), formed in solution by equilibration of H₂O₂ 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(O₂)₂ and MoO(O₂)₂. The advantage of the catalytic activation of H₂O₂ by HNO₂ might be that HNO₂ is a nonexpensive, commercial

chemical which, in the presence of an excess of H₂O₂, forms finally nitric acid. Nitric acid and nitrate, respectively, are simple byproducts which need not to be recovered.

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Supporting Information Available: Rate constants for the sulfoxidation of CoS by H₂O₂ (Table S1), comparison of rate constants reported for the sulfoxidation of CoS (Table S2), and Figure S1 plot of rate constant k_{exp} vs [H₂O₂] for the sulfoxidation of CoS by H₂O₂ (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Additions and Corrections

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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:

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

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

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

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

Table 1. Photophysical Properties of [PS-CH₂CH₂NHCO(Ru^{II}_nMe_{m-n})](PF₆)_{2n} in CH₃CN at 25–28 °C

salt	$\langle\tau\rangle$ (ns)
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₂ Me ₉)](PF ₆) ₄	1213
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₇ Me ₄)](PF ₆) ₁₄	1025
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₁₁)](PF ₆) ₂₂	861
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₅ Me ₁₃)](PF ₆) ₁₀	1195
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₁₃ Me ₅)](PF ₆) ₂₆	975
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₁₈)](PF ₆) ₃₆	905
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₈ Me ₁₇)](PF ₆) ₁₆	1220
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₂₁ Me ₄)](PF ₆) ₄₂	523
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₂₅)](PF ₆) ₅₀	471

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 2. Irradiance Dependence (at 650 nm) of the Kinetic Decay Parameters for Eq 5 in CH₃CN at 25–28 °C

pulse energy ($\mu\text{J}/\text{mm}^2$)	$\langle\tau\rangle$ (ns)	pulse energy ($\mu\text{J}/\text{mm}^2$)	$\langle\tau\rangle$ (ns)
[PS-CH ₂ CH ₂ NHCO(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-CH ₂ CH ₂ NHCO(Ru ^{II} ₅ Me ₁₃)](PF ₆) ₁₀			
6.2	904	1.4	1043
3.6	990	0.9	1195
2.3	1024	0.3	1200
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₂ Me ₉)](PF ₆) ₄			
6.4	1131	0.9	1213

Table 3. Dependence of Emission Decay Kinetics (Eq 5) on Monitoring Wavelength in CH₃CN

λ_{monitor} (nm)	$\langle\tau\rangle$ (ns)	λ_{monitor} (nm)	$\langle\tau\rangle$ (ns)
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₁₈)](PF ₆) ₃₆			
600	793	700	964
625	949	725	982
650	959	750	945
675	994		
[PS-CH ₂ CH ₂ NHCO(Ru ^{II} ₅ Me ₁₃)](PF ₆) ₁₀			
600	1012	700	1150
625	1107	725	1157
650	1195	750	1120
675	1150	800	1157

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