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.

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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

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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:

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

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

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

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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