Mechanism of the Oxidation of *o*-Nitro- and *o*-Benzoylbenzeneselenenic Acids by Peracids, Hydroperoxides, and Hydrogen Peroxide[1]

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The oxidations of *o*-nitro- (**1a**) and *o*-benzoylbenzeneselenenic (**1b**) acids by peroxybenzoic acids (eq 4), hydroperoxides (eq 2, R = *t*-Bu or PhCMe$_2$), and hydrogen peroxide (R = H) have been studied kinetically over a range of pH in 60% dioxane. With the peroxybenzoic acids oxidation of **1a** and **1b** occurs at comparable rates, is not acid catalyzed, and is believed to take place by a mechanism (eq 7) involving nucleophilic attack by the selenium of the selenenic acid on peroxide oxygen that is analogous to the mechanism for oxidation of alkyl sulfides by peracids. With the hydroperoxides and H$_2$O$_2$ the oxidations are subject to acid catalysis, and the *o*-benzoyl compound (**1b**) is oxidized ~10^4 times faster than **1a**. The much faster rate of oxidation of **1b** is due to the fact that it reacts by a mechanism (eq 13) where there is reversible formation of a peroxyhemiketal (**4**), followed by *intramolecular* attack of selenium of one of the peroxide oxygens in protonated **4**. Such a mechanism is not available to **1a**, which therefore must react by much slower bimolecular pathways (eq 10 and 11) that are equivalent to the mechanisms for the acid-catalyzed and uncatalyzed oxidations of alkyl sulfides by hydroperoxides and hydrogen peroxide. At pH ≥2 the oxidation of **1a** by hydrogen peroxide exhibits marked autocatalysis. This is due to equilibrium formation from H$_2$O$_2$ and the oxidation product, *o*-O$_2$NC$_6$H$_4$SeO$_2$H, of some *o*-nitroperoxybenzeneseleninic acid, *o*-O$_2$NC$_6$H$_4$Se(O)OOH, which, like a peroxybenzoic acid, is a much more reactive oxidizing agent for **1a** than is hydrogen peroxide itself. Comparison of the previously determined (ref 5) rates of reaction of **1a** and **1b** with thiols with their rates of oxidation by hydroperoxides suggests that the selenenic acid functionality thought (ref 3) to be an intermediate in the reaction cycle for the enzyme glutathione peroxidase should be consumed under physiological conditions almost exclusively by reaction with glutathione rather than be oxidized further by hydroperoxides to a seleninic acid.

Selenenic acids are frequently encountered as reactive intermediates in organoselenium chemistry,[2] and a selenenic acid functionality has also been postulated[3] to play a key role in the reaction cycle for the essential mammalian enzyme, glutathione peroxidase. Despite their importance in both the organic and the physiological chemistry associated with selenium, little detailed information is available regarding the mechanisms of reactions of selenenic acids and about factors influencing their reactivity. This doubtless has its origin in the fact that most selenenic acids are too unstable to be able to be isolated, with the result that study of the mechanisms of their reactions in the usual fashion is not possible.

There are, however, two monosubstituted benzeneselenenic acids, *o*-nitrobenzeneselenenic acid, *o*-O$_2$NC$_6$H$_4$SeOH (**1a**), and *o*-benzoylbenzeneselenenic acid, *o*-PhC(O)C$_6$H$_4$SeOH (**1b**), where relatively stable solutions of the selenenic acid can be generated easily by acid-catalyzed hydrolysis of the corresponding selenenic anhydride in aqueous organic solvents.[4]

In previous research[5] the mechanism of the reaction of a thiol with these selenenic acids (eq 1) has been elucidated. In the present study we have examined the oxidation of these same two substrates to the corresponding seleninic acids (eq 2) by peroxyacids (R = Ar'C(O)), hydroperoxides (R = *t*-Bu or PhCMe$_2$), and hydrogen peroxide (R = H).

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$$\text{ArSeOH} + \text{RSH} \xrightarrow{k_{RSH}} \text{ArSeSR} + \text{H}_2\text{O} \qquad (1)$$

$$\text{1a, Ar} = o\text{-O}_2\text{NC}_6\text{H}_4$$

$$\text{1b, Ar} = o\text{-PhC(O)C}_6\text{H}_4$$

$$\text{ArSeOH} + \text{ROOH} \rightarrow \text{ArSeO}_2\text{H} + \text{ROH} \qquad (2)$$

1a, Ar = *o*-O$_2$NC$_6$H$_4$	**2a**, Ar = *o*-O$_2$NC$_6$H$_4$
1b, Ar = *o*-PhC(O)C$_6$H$_4$	**2b**, Ar = *o*-PhC(O)C$_6$H$_4$

The mechanisms of these oxidations are of interest for several reasons. First, in the synthetically important olefin-forming elimination of alkyl aryl selenoxides (eq 3, step a) oxidation of the areneselenenic acid liberated in step a to the areneseleninic acid by a peroxyacid or hydrogen peroxide (step b) is frequently necessary in order to prevent subsequent addition of ArSeOH across the alkene double bond (ArSeOH + C=C → ArSe-C-COH).[2a] Second, data on the relative reactivity toward selenenic acids of hydroperoxides vs. thiols are needed in order to assess the probable validity of the principal reaction pathway that has been proposed[3] for the selenenic acid functionality in the reaction cycle for glutathione peroxidase.

$$\underset{\underset{O}{\overset{\|}{\underset{ArSe}{|}}}}{-\overset{|}{C}}-\overset{|}{\underset{H}{C}}- \xrightarrow{(a)} \diagup C=C \diagdown + [\text{ArSeOH}] \xrightarrow[\substack{\text{or} \\ \text{H}_2\text{O}_2 \\ (b)}]{\text{Ar'CO}_3\text{H}} \text{ArSeO}_2\text{H} \qquad (3)$$

Results

Oxidation of 1a and 1b by Peroxyacids. Oxidation of selenenic acids **1a** and **1b** to the corresponding seleninic acids **2a** and **2b** by peroxyacids (eq 4) in 60% dioxane (v/v) is extremely rapid but can be followed conveniently by a stopped-flow spectrophotometry. The kinetics were

$$\underset{\text{1a or 1b}}{\text{ArSeOH}} + \text{YC}_6\text{H}_4\text{CO}_3\text{H} \xrightarrow{k_{PA}} \underset{\text{2a or 2b}}{\text{ArSeO}_2\text{H}} + \text{YC}_6\text{H}_4\text{CO}_2\text{H}$$

$$(4)$$

Table I. Kinetics of the Oxidation of o-Nitro- and o-Benzoylbenzeneselenenic Acids by Peroxybenzoic Acids in 60% Dioxane at 25 °C

selenenic acid, concn, M	Y in $YC_6H_4CO_3H$	$10^3[HClO_4]$, M	$10^3[ArCO_3H]$, M	k_1, s^{-1}	$k_{PA} = k_1/[ArCO_3H]$, M^{-1} s^{-1}
1a, 1×10^{-4}	p-CH$_3$	3.75	1.04	0.049	47
			2.07	0.101	49
	p-H	3.75	1.20	0.073	61
			2.40	0.149	62
	m-Cl	1.87	1.02	0.097	95
			2.04	0.21	103
		3.75	1.02	0.103	101
			2.04	0.21	103
		7.50	1.02	0.099	97
			2.04	0.21	103
	p-NO$_2$	3.75	1.01	0.17	168
			2.03	0.36	177
1b, 5×10^{-5}	p-CH$_3$	3.75	1.02	0.23	225
			2.03	0.44	216
	p-H	3.75	1.14	0.31	272
			2.27	0.65	286
	m-Cl	3.75	1.00	0.46	460
			2.01	0.95	472
	p-NO$_2$	3.75	1.01	0.81	801
			2.01	1.61	801

studied with the peroxyacid present in large stoichiometric excess over the selenenic acid. Under such conditions the disappearance of the selenenic acid follows good first-order kinetics. The experimental first-order rate constants, k_1, for the various runs (Table I) reveal the following: (a) The oxidation is, as expected, first order in peracid. (b) The oxidation is *not* subject to catalysis by added strong acid (HClO$_4$). (c) With a given peracid the rate of oxidation of 1b is about 4.5 times faster than the rate of oxidation of 1a. (d) For both selenenic acids a Hammett plot of log k_{PA} vs. σ for Y is linear with a slope (ρ) of +0.6.

Oxidation of 1a by Cumene and *tert*-Butyl Hydroperoxides. Oxidation of 1a by either cumene hydroperoxide or *tert*-butyl hydroperoxide (eq 2, R = Me$_2$CPh or Me$_3$C) also gives o-nitrobenzeneseleninic acid (2a), but the rate of the reaction is *much* slower than the oxidation of 1a by peroxybenzoic acids, and hydroperoxide concentrations in the range 0.1–0.4 M are necessary in order to have conveniently measurable rates. Table II lists the experimental first-order rate constants, k_1, for the disappearance of 1a under the various reaction conditions examined. At a given pH k_1 depends linearly on [ROOH], indicating that the reactions are first-order in hydroperoxide. Values of $k_{ROOH} = k_1/[ROOH]$, the second-order rate constants for the oxidation of 1a by the two hydroperoxides, are given in the right most column of Table II. These show that, unlike the oxidation of 1a by peracids, the oxidation of 1a by hydroperoxides is subject to marked catalysis by added strong acid. Plots of log k_{ROOH} vs. pH indicate the following pH–rate profiles for the hydroperoxide oxidations of 1a.

For cumene hydroperoxide:

$$k_{ROOH} \ (M^{-1} \ s^{-1}) = 1.3 \times 10^{-2}a_{H^+} + 5 \times 10^{-5} \quad (5a)$$

For *tert*-butyl hydroperoxide:

$$k_{ROOH} \ (M^{-1} \ s^{-1}) = 3.1 \times 10^{-2}a_{H^+} + 8 \times 10^{-5} \quad (5b)$$

Note also that initial addition of a large amount of o-nitrobenzeneseleninic acid (2a) to the reaction solutions has no significant effect on k_1. This observation is both important and significant, since in the oxidation of 1a with hydrogen peroxide (vide infra) initial addition of o-O$_2$NC$_6$H$_4$SeO$_2$H leads to a large acceleration in rate.

Oxidation of 1a with Hydrogen Peroxide. As with the hydroperoxides, oxidation of 1a with hydrogen per-

oxide (eq 2, R = H) in 60% dioxane also results in the formation of 2a and occurs at about the same rate as the oxidations with *t*-BuOOH or cumene hydroperoxide. At pH $\simeq$1.0, with hydrogen peroxide (0.1–0.2 M) present in large stoichiometric excess over 1a (1×10^{-4} M), the kinetic behavior of the reaction is the same as that seen in the oxidations of 1a by the two hydroperoxides, i.e., a plot of log [1a] vs. time shows no apparent deviation from linearity out to at least 90% reaction, k_1 is proportional to [H$_2$O$_2$], and the reaction is acid catalyzed. However, in less acidic solutions (pH $\geq$2) under otherwise similar conditions plots of log [1a] vs. time begin to show pronounced downward curvature (increase in the apparent first-order rate constant) after only about 40% reaction.

The origin of this acceleration in k_1 with increasing percent reaction was established by a separate series of experiments in which varying amounts of the product of eq 2, i.e., 2a, were added intially to reaction solutions of 1a and hydrogen peroxide. These experiments (section A, Table III) reveal that at pH 2 the oxidation of 1a by hydrogen peroxide is accelerated 5-fold by the presence of as little as 5×10^{-4} M 2a, and that the disappearance of 1a under such conditions now once again follows excellent first-order kinetics. The experimental first-order rate constant, k_{cat}, for the disappearance of 1a in this "2a-catalyzed" oxidation by H$_2$O$_2$ exhibits a first-order dependence on the concentrations of both 2a and H$_2$O$_2$. Experiments over a pH range from 1.0 to 2.5 show that k_{cat} is independent of a_{H^+}.

In the kinetic runs in Table III where no 2a was added initially (section B) the concentration of 2a will increase during the course of each run from zero at the start to 1 $\times 10^{-4}$ M at the end. At a given time, t, during any particular run the value of k_1 will be:

$$k_1 = (k'_{H_2O_2}a_{H^+} + k''_{H_2O_2})[H_2O_2] + k_{cat}[H_2O_2][2a]_t$$

At pH 1, $k'_{H_2O_2}a_{H^+}$ is enough larger than $k_{cat}[2a]_t$ throughout the reaction so that k_1 does not show a detectable increase with increasing extent of reaction. Higher pH's, however, lead to a large enough decrease in $k'_{H_2O_2}a_{H^+}$ so that $k_{cat}[2a]_t$ becomes significant compared to ($k'_{H_2O_2}a_{H^+}$ + $k''_{H_2O_2}$) once sufficient 1a has been converted to 2a, and from that point on k_1 increases as the percent reaction increases.

The k_1 values in Table III for the kinetic runs for the oxidation of 1a by hydrogen peroxide in the absence of

Table II. Kinetics of the Oxidation of *o*-Nitrobenzeneselenenic Acid by Cumene and *tert*-Butyl Hydroperoxides in 60% Dioxane at 25 °C[a]

hydroperoxide	[HClO$_4$], M	pH	[ROOH], M	$10^4 k_1$, s^{-1}	$10^4 k_{ROOH} = 10^4 k_1/[ROOH]$, M^{-1} s^{-1}
Me$_2$C(Ph)OOH	0.087	1.06	0.184	2.1	11.2
			0.092	1.15	12.5
	0.075	1.13	0.110	1.21	11.0
	0.063	1.20	0.187	1.52	8.1
	0.044	1.35	0.223	1.35	6.1
			0.149	0.92	6.2
	0.043	1.37	0.186	1.13	6.1
				1.09[b]	5.9
			0.206	1.19[c]	5.8
	0.033	1.48	0.224	1.03	4.6
			0.149	0.68	4.6
			0.074	0.36	4.8
	0.022	1.65	0.074	0.28	3.8
	0.015	1.82	0.374	0.93	2.5
			0.280	0.64	2.3
			0.187	0.46	2.5
	0.0094	2.03	0.369	0.68	1.9
	0.0075	2.12	0.187	0.30	1.6
	0.0049	2.31	0.367	0.44	1.2
	0.0028	2.55	0.368	0.33	0.89
t-BuOOH	0.102	0.99	0.202	6.2	31
			0.0974	3.0	31
	0.057	1.25	0.202	3.6	18
			0.0974	1.8	19
	0.047	1.33	0.0934	1.45	15.5
	0.044	1.36	0.194	2.7	14
	0.038	1.42	0.202	2.5	13
	0.036	1.45	0.226	2.6	12
			0.0949	1.1	12
	0.029	1.54	0.194	1.9	9.5
	0.0254	1.59	0.195	1.8	9.0
			0.096	0.83	8.6
	0.0150	1.82	0.236	1.4	6.0
	0.0112	1.95	0.200	0.86	4.3
			0.0964	0.44	4.5

[a] Initial concentration **1a** in all runs, 0.0001 M. [b] *o*-Nitrobenzeneseleninic acid, 0.027 M, added. [c] *o*-Nitrobenzeneseleninic acid, 0.084 M, added.

added **2a** are therefore all rate constants obtained from the slope of the initial portion of the plot of log [**1a**] vs. time before curvature begins to be apparent. Other kinetic runs (not shown in Table III) at pH 2–3 in which the ionic strength was kept constant at 0.02 by the addition of lithium perchlorate gave rates similar to those for the runs at the same pH without added lithium perchlorate.

The variation of $k_{H_2O_2}$ with pH in section B of Table III can be fitted by the following equation.

$$k_{H_2O_2} \ (M^{-1} \ s^{-1}) = 6.0 \times 10^{-2} a_{H^+} + 2.2 \times 10^{-4} \quad (5c)$$

Oxidation of 1b by Hydroperoxides and Hydrogen Peroxide. Oxidation of *o*-benzoylbenzeneselenenic acid (**1b**) by either hydroperoxides or hydrogen peroxide (eq 2) occurs approximately 10^4 more rapidly than the oxidation of the *o*-nitro selenenic acid (**1a**) under the same conditions. This is in marked contrast to the oxidation of the two selenenic acids by peracids, where, as noted earlier, **1b** and **1a** are oxidized at comparable rates.

The most extensive study of the kinetics of the oxidation of **1b** by a hydroperoxide or hydrogen peroxide was carried out with cumene hydroperoxide. The results are presented in Table IV. The hydroperoxide was present in large stoichiometric excess over **1b** in all runs. Under such conditions the disappearance of **1b** follows good first-order kinetics, and the experimental first-order rate constant, k_1, at a given pH shows a linear dependence on [ROOH]. The rightmost column of Table IV gives the second-order rate constant, $k_{ROOH} = k_1/[ROOH]$, under the various
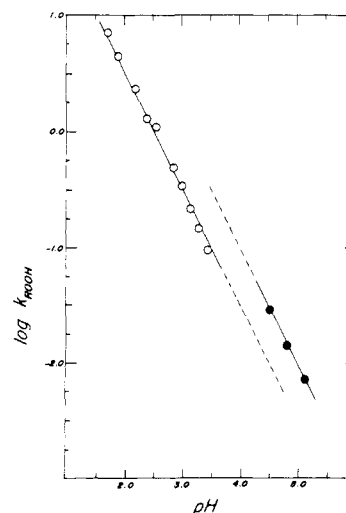
Figure 1. pH–rate profile for the reaction of **1b** with cumene hydroperoxide in 60% dioxane: ○, runs in the presence of perchloric acid; ●, runs in H$_3$PO$_4$–H$_2$PO$_4^-$ buffers. All data at 25 °C at ionic strength = 0.02.

reaction conditions. It is evident that k_{ROOH} is markedly dependent on pH. A plot of log k_{ROOH} vs. pH is shown in Figure 1. The particularly interesting and significant feature of this pH–rate profile is that the data for the runs in perchloric acid (0.00036 to 0.019 M) solutions fall on one line of unit slope, fitted by the relation: k_{ROOH} (M^{-1} s^{-1}) = 3.5 × 10$^2 a_{H^+}$; while the data for the runs in a series of

Table III. Kinetics of the Oxidation of *o*-Nitrobenzeneselenenic Acid by Hydrogen Peroxide in 60% Dioxane at 25 °C[a]

[HClO$_4$], M	pH	[H$_2$O$_2$], M	$10^3 k_1°$, s^{-1} [b]	10^3[ArSeO$_2$H], M	$10^3 k_1$, s^{-1}	$k_{cat} = (k_1 - k_1°)/$ [H$_2$O$_2$][2a], M^{-2} s^{-1}
		Section A. Runs in the Presence of Added o-O$_2$NC$_6$H$_4$SeO$_2$H (2a)				
0.11	0.96	0.0513	0.26	4.87	2.47	8.8
		0.102	0.52	4.84	5.0	9.1
0.050	1.30	0.0513	0.14	4.90	2.17	8.1
		0.102	0.27	4.87	4.26	8.0
0.0114	1.94	0.0513	0.04	4.92	2.01	7.8
		0.102	0.08	4.89	4.12	8.1
0.010	2.0	0.101	0.08	14.9	13.2	8.7
				7.43	6.3	8.3
		0.205	0.16	5.23	9.1	8.3
		0.101	0.08	2.48	1.99	7.6
				1.49	1.30	8.1
				0.50	0.49	8.1
0.0055	2.25	0.102	0.05	4.87	3.94	7.8
		0.205	0.10	4.81	7.53	7.5
0.0034	2.47	0.102	0.04	4.88	3.94	7.8
		0.205	0.08	4.82	7.53	7.5

[HClO$_4$], M	pH	[H$_2$O$_2$], M		$10^3 k_1$, s^{-1} [c]	$k_{H_2O_2} = k_1/$[H$_2$O$_2$], M^{-1} s^{-1}
		Section B. Runs in the Absence of Added o-O$_2$NC$_6$H$_4$SeO$_2$H			
0.091	1.04	0.102		0.51	0.0050
0.068	1.17	0.128		0.44	0.0034
0.045	1.34	0.159		0.41	0.0026
0.034	1.47	0.174		0.33	0.0019
0.023	1.65	0.190		0.275	0.00145
0.0112	1.95	0.206		0.17	0.00082
0.00393	2.41	0.205		0.089	0.00043
		0.304		0.151	0.00049
0.00193	2.71	0.205		0.065	0.00032
0.00098	3.01	0.205		0.057	0.00028

[a] Initial concentration of **1a** in all runs, 0.0001 M. [b] $k_1°$ is the experimental first-order rate constant for the oxidation in the absence of added seleninic acid at the same pH and [H$_2$O$_2$]. [c] All k_1 values are obtained from the slope of the initial portion of a plot of log [**1a**] vs. time before any curvature begins to be apparent (see text).

Table IV. Kinetics of the Oxidation of *o*-Benzoylbenzeneselenenic Acid by Cumene Hydroperoxide in 60% Dioxane at 25 °C[a]

reaction conditions	pH	[HA], M	[A$^-$], M	10^2[ROOH], M	$10^2 k_1$, s^{-1}	$k_{ROOH} = k_1/$[ROOH], M^{-1} s^{-1}
0.019 N HClO$_4$	1.72	0.019		0.19	1.32	7.1
0.0126 N HClO$_4$	1.89	0.0126		0.29	1.30	4.5
0.0063 N HClO$_4$	2.20	0.0063		0.37	0.78	2.1
				0.47	1.05	2.2
				0.94	2.7	2.8
0.0043 N HClO$_4$	2.37	0.0043		0.37	0.49	1.3
0.00285 N HClO$_4$	2.54	0.00285		1.87	2.0	1.1
				2.87	3.05	1.1
0.00142 N HClO$_4$	2.84	0.00142		1.87	0.92	0.49
0.00107 N HClO$_4$	2.97	0.00107		2.80	0.96	0.34
0.00071 N HClO$_4$	3.14	0.00071		3.73	0.80	0.215
0.00054 N HClO$_4$	3.27	0.00054		4.21	0.61	0.145
0.00036 N HClO$_4$	3.44	0.00036		3.74	0.35	0.094
				4.67	0.44	0.095
2:1 H$_3$PO$_4$–H$_2$PO$_4^-$	4.5[b]	0.020	0.010	3.74	0.11	0.030
				5.60	0.153	0.027
buffer		0.010	0.005	1.12	0.032	0.028
				5.60	0.165	0.030
				11.2	0.33	0.030
1:1 H$_3$PO$_4$–H$_2$PO$_4^-$	4.8[b]	0.020	0.020	4.69	0.061	0.013
				10.3	0.14	0.014
buffer		0.010	0.010	10.3	0.14	0.014
				18.8	0.27	0.014
1:2 H$_3$PO$_4$–H$_2$PO$_4^-$	5.1[b]	0.005	0.010	5.60	0.039	0.0071
				11.2	0.083	0.0074
buffer						

[a] Initial concentration of **1b** in all runs, 0.0001 M; all data at ionic strength = 0.02. [b] pH's of phosphate buffers in 60% dioxane previously determined (see ref 5).

H$_3$PO$_4$–H$_2$PO$_4^-$ buffers fall on a second line of unit slope that is displaced upward from the first by approximately 0.4 log unit, and that is fitted by the relation: k_{ROOH} (M^{-1} s^{-1}) = 10.0 × 10$^2 a_{H^+}$. A similar situation has been encountered[5] in the kinetics of the reaction of **1b** with an alkanethiol.

The kinetics of the oxidation of **1b** by either excess *tert*-butyl hydroperoxide or hydrogen peroxide were studied only in dilute perchoric acid solutions and over a less extensive pH range than for cumene hydroperoxide. The disappearance of **1b** followed excellent first-order kinetics under all conditions. In the oxidations using

**Table V. Kinetics of the Oxidation of
o-Benzoylbenzeneselenenic Acid by *tert*-Butyl Hydroperoxide
and Hydrogen Peroxide in 60% Dioxane at 25 °C[a]**

hydro-peroxide	10^2[HClO$_4$], M	pH	10^2[ROOH], M	$10^2 k_1$, s^{-1}	k_{ROOH} = k_1/ [ROOH], M^{-1} s^{-1}
t-BuOOH[b]	0.90	2.04	0.29	0.78	2.7
			0.57	1.72	3.0
	0.45	2.35	0.57	0.84	1.5
			0.95	1.41	1.5
	0.266	2.58	0.76	0.64	0.85
			0.95	0.83	0.87
	0.177	2.75	0.95	0.51	0.54
			1.94	1.05	0.54
	0.089	3.05	0.95	0.23	0.24
			1.75	0.41	0.24
H$_2$O$_2$[c]	0.43	2.36	0.28	1.67	6.0
			0.56	3.4	6.0
	0.35	2.45	0.27	1.19	4.3
	0.29	2.54	0.28	0.98	3.5
	0.215	2.66	0.56	1.57	2.8
	0.144	2.84	0.56	1.18	2.1
			1.13	2.44	2.2
			1.69	3.3	2.0
	0.108	2.96	0.56	0.71	1.3
	0.072	3.14	0.28	0.26	0.93
			0.57	0.50	0.89
	0.054	3.26	0.56	0.31	0.56
	0.036	3.44	0.57	0.22	0.39

[a] Initial concentration of **1b** in all runs, 0.0001 M. [b] All runs with ionic strength maintained at 0.01 by addition of lithium perchlorate. [c] No lithium perchlorate added to maintain constant ionic strength.

hydrogen peroxide there was no tendency for plots of log [**1b**] vs. time to show the type of downward curvature with increasing percent reaction observed in the oxidations of **1a** by this same reagent.

At a given pH the experimental first-order rate constants for the oxidations of **1b** by *t*-BuOOH or H$_2$O$_2$ show a first-order dependence on [*t*-BuOOH] and [H$_2$O$_2$], respectively. The oxidations are acid catalyzed. In dilute perchloric acid solutions in 60% dioxane k_{ROOH} for the oxidation of **1b** by hydrogen peroxide is given by: $k_{H_2O_2}$ (M^{-1} s^{-1}) = 1.1 × 10$^3 a_{H^+}$. The rate constant for the oxidation of **1b** by *t*-BuOOH is somewhat smaller ($k_{t\text{-BuOOH}}$ (M^{-1} s^{-1}) = 3 × 10$^2 a_{H^+}$) and is almost exactly the same as that for the oxidation of **1b** by cumene hydroperoxide under the same conditions.

Discussion

Mechanism of the Oxidation of 1a and 1b by Peracids.
Both **1a** and **1b** are very rapidly oxidized in 60% dioxane by peroxyacids to the corresponding seleninic acids (eq 4). The kinetic behavior of these oxidations (Table I) shows that they are first order in both selenenic acid and peroxyacid and that they are *not* subject to acid catalysis. The second-order rate constant (k_{PA}) for oxidation of **1b** by a given peracid is about 4.5 times greater than the corresponding rate constant for oxidation of **1a**.

For both **1a** and **1b** a Hammett plot of log k_{PA} vs. σ for Y in YC$_6$H$_4$CO$_3$H is linear with a slope (ρ) of +0.6. This value is quite similar to the ρ (+0.75) for the oxidation of methyl *p*-tolyl sulfoxide by peroxybenzoic acids in acidic aqueous dioxane (eq 6a),[6a] and somewhat smaller than ρ (+1.05) for the oxidation of *p*-chlorobenzyl sulfide by the same peracids in isopropyl alcohol (eq 6b).[6b] Both eq 6a

and 6b are known[6c,d] to take place by nucleophilic attack of the sulfur on the peroxyacid.
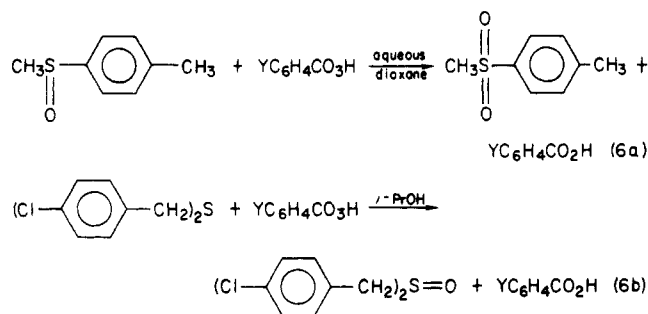
A simple mechanism (eq 7), which is the same for both **1a** and **1b** and which involves nucleophilic attack by the selenium of the selenenic acid on peroxide oxygen, is therefore proposed for the oxidation of the two stable selenenic acids by peroxyacids. This mechanism is analogous to those for eq 6a and 6b.
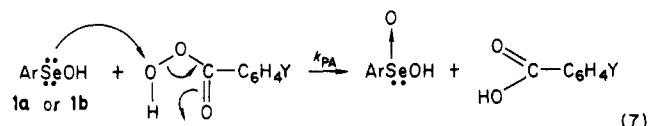

Mechanism of Oxidation of 1a by Hydroperoxides.
Oxidation of **1a** by hydroperoxides (*t*-BuOOH or cumene hydroperoxide) also gives the seleninic acid (eq 2), but the rate of the reaction, which is kinetically first order in both **1a** and hydroperoxide, is orders of magnitude slower than the rate of oxidation of **1a** by a peroxyacid. Unlike the peroxyacid oxidation the reaction is subject to marked catalysis by added strong acid (HClO$_4$).

Equations 5a and 5b which give k_{ROOH}, the experimental second-order rate constant for the oxidation of **1a** by cumene and *tert*-butyl hydroperoxides, respectively, show that k_{ROOH} is composed in each case of a pH-dependent (acid-catalyzed) and a pH-independent term. The latter, the rate constant for the uncatalyzed reaction of **1a** with the hydroperoxide, is over 10^6 smaller than the rate constant for the reaction of **1a** with *m*-chloroperbenzoic acid.

The same kind of kinetic behavior has been found[6d,7,8] for the oxidation of alkyl or aryl sulfides by hydroperoxides in protic solvents (eq 8). In the case of eq 8 the pH-de-

$$RSR' + R''OOH \rightarrow RS(O)R' + R''OH \qquad (8)$$
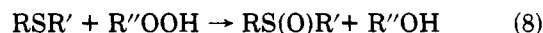
pendent term represents a specific H$^+$ catalyzed reaction in which the rate-determining step is nucleophilic attack of the sulfide on the protonated hydroperoxide.[6d] The pH-independent term, whose magnitude is strongly dependent on the hydrogen bond donating ability of the solvent, represents a reaction of the sulfide with the hydroperoxide in which a molecule of the protic solvent (SOH) plays an essential role in the transition state in effecting a proton shift that obviates the alkoxy group being displaced as RO$^-$ (eq 9).[6d,7a]

It therefore seems reasonable to propose that for the oxidation of **1a** by hydroperoxides the acid-catalyzed reaction takes place in the manner shown in eq 10, while the
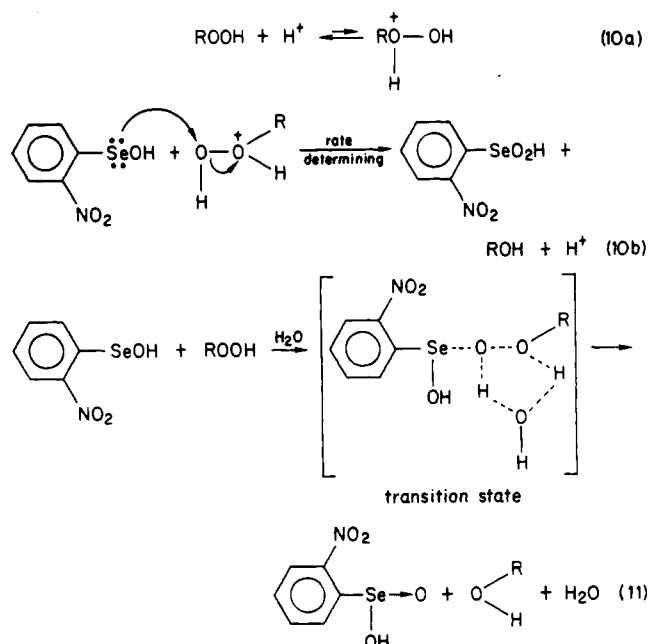
(6) (a) Curci, R.; Giovine, A.; Modena, G. *Tetrahedron* 1966, *22*, 1235. (b) Overberger, C. G.; Cummins, R. W. *J. Am. Chem. Soc.* 1953, *75*, 4250. (c) Curci, R.; Modena, G. *Tetrahedron Lett.* 1963, 1749. (d) Behrman, E. J.; Edwards, J. O. *Prog. Phys. Org. Chem.* 1967, *4*, 93.

(7) (a) Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H.-Y. *J. Am. Chem. Soc.* 1968, *90*, 3209. (b) Edwards, J. O.; Fortnum, D. H. *J. Org. Chem.* 1962, *27*, 407. (c) Bateman, L.; Hargrave, K. R. *Proc. R. Soc., Sect. A* 1954, *224*, 389, 399.

(8) Edwards, J. O. "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Interscience: New York, 1960; p 67.

$$\text{(9)}$$
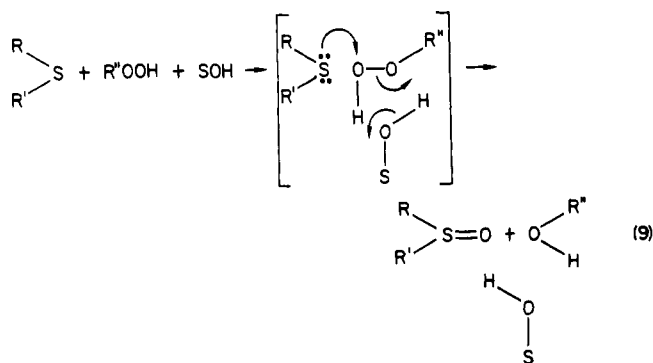
mechanism for the reaction whose rate is independent of pH is that shown in eq 11.

$$\text{ROOH} + \text{H}^+ \rightleftharpoons \text{R}\overset{+}{\text{O}}\text{—OH} \qquad \text{(10a)}$$

$$\text{ROH} + \text{H}^+ \qquad \text{(10b)}$$

transition state

$$\text{(11)}$$

Mechanism of Oxidation of 1b by Hydroperoxides. As noted earlier, the *o*-benzoyl selenenic acid (**1b**) is oxidized by peroxyacids only about 5 times more rapidly than the *o*-nitro selenenic acid (**1a**). In marked contrast, however, when the oxidant is a *hydroperoxide* **1b** is oxidized ~10^4 faster than **1a**. This dramatic difference in rates, which would certainly not be expected based on the behavior of the two selenenic acids with peroxyacids, would clearly seem to require that there be available to **1b** a pathway for reaction with a hydroperoxide that is not available to **1a** and that allows **1b** to be oxidized by a hydroperoxide much faster than would be possible if **1b** had to react via the type of mechanisms shown in eq 10 and 11.

Analogous markedly enhanced reactivity of **1b** relative to **1a** has been observed[5] previously in the acid-catalyzed reaction of **1b** with a thiol, a reaction that also exhibits the same type of unusual pH–rate profile seen in Figure 1 for the reaction of **1b** with cumene hydroperoxide. The mechanism of the acid-catalyzed reaction of **1b** with a thiol has been established[5] to be that shown in eq 12. The particular pH–rate profile observed arises because in buffers of pH ≥4 establishment of the equilibrium between **1b** and hemithioketal **3** is rapid compared to the acid-catalyzed conversion of **3** to products and $k_{exp} = k_{II}K_{eq}a_{H^+}[\text{RSH}]$; on the other hand, in dilute perchloric acid solution (low pH, no buffer) $k_{bf}[\text{buffer}] = 0$, $k_c a_{H^+} > k_0$, and since $k_{II} > k_{-c}$, $k_{exp} = k_{II}K_{eq}a_{H^+}[\text{RSH}]/(1 + k_{II}/k_{-c})$. Although the equilibrium constant for the formation of **3**

$$\text{(12)}$$

$$K_{eq} = (k_0/k_{-0}) = (k_{bf}/k_{-bf}) = (k_c/k_{-c})$$
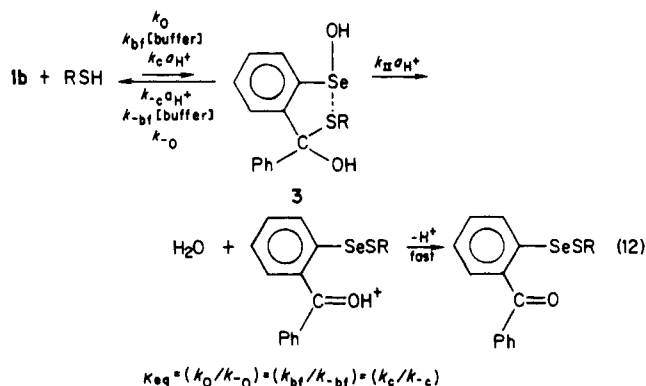
from **1b** and the thiol is small, reversible addition of RSH to **1b** to form **3**, followed by *intramolecular* reaction of the RS group from the thiol with selenium, provides a much faster route from reactants to products than does direct reaction of RSH with selenium.[5] Since reversible addition of a thiol to a nitro group is unknown in organic chemistry, **1a** is unable to react with RSH via an analogous mechanism.
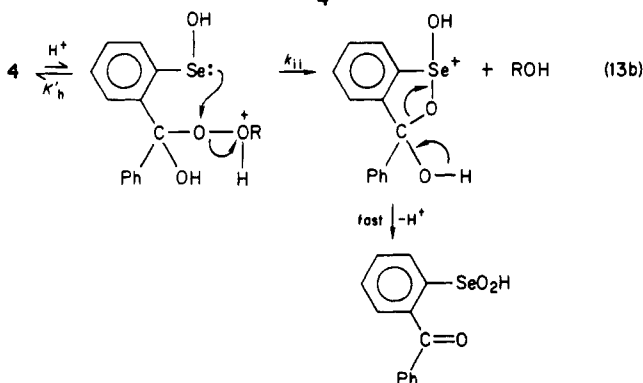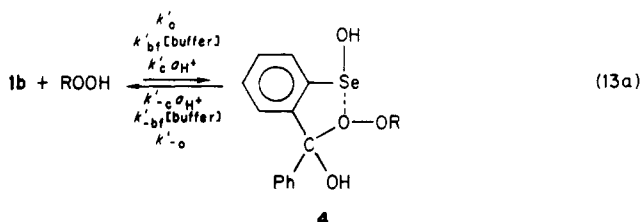
Reversible addition of hydroperoxides and hydrogen peroxide to the carbonyl groups of aldehydes and ketones is well-known[9] and is subject to both buffer and acid catalysis.[9a] The equilibrium constant for addition of H_2O_2 ($K_{H_2O_2}$) is typically about 2000 times larger than the equilibrium constant for hydration (K_{H_2O}) of the same carbonyl compound.[9a,b] For acetone $K_{H_2O_2}$[9b] is also about 10 times larger than the equilibrium constant for hemithioketal formation[10] (K_{RSH}) from 3-mercaptopropionic acid and this ketone.

In view of the similar character of the pH–rate profiles for the **1b**-cumene hydroperoxide and **1b**-thiol reactions, and the fact that the equilibrium constant for peroxyhemiketal (**4**) formation from **1b** and ROOH is probably more favorable than K_{eq} for formation of **3** from **1b** and the thiol, it seems entirely reasonable to attribute the fast reaction of **1b** with hydroperoxides to a mechanism (eq 13) in which the oxidant first adds reversibly (eq 13a) to the carbonyl group of **1b** to give **4**; this is then followed by *intramolecular* nucleophilic attack by selenium on one of the peroxide oxygens in protonated **4** (eq 13b). Because the equilibrium constant for addition of a peroxyacid (Ar′CO₃H) to the C=O group of **1b** should be much smaller than that for addition of ROOH, and because direct attack of the selenium in **1b** on a peroxyacid (eq 7) is much faster than direct attack of ArSeOH on a hydroperoxide (eq 11), a mechanism of the type shown in eq 13 is not competitive in rate with eq 7 when the oxidant is Ar′CO₃H. For this reason, oxidation of **1b** and **1a** by perbenzoic acids takes place at comparable rates, and via the mechanism in eq 7 in both cases, even though the oxidation of **1b** by a hydroperoxide occurs much faster than the oxidation of **1a** by the same reagent, and proceeds by a quite different mechanism, eq 13, instead of eq 10 and 11.

Mechanisms for the Oxidation of 1a and 1b by Hydrogen Peroxide. The rapid rate, and acid-catalyzed nature, of the oxidation of **1b** by hydrogen peroxide (eq 2, R = H, Ar = *o*-PhC(O)C₆H₄) suggest that the mechanism of this reaction is presumably exactly analogous, i.e., eq 13, R = H, to that for the oxidation of **1b** by hydroperoxides.

(9) (a) Sander, E. G.; Jencks, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 4377. (b) Hine, J.; Redding, R. W. *J. Org. Chem.* **1970**, *35*, 2769. (c) Antonovskii, V. L.; Terent'ev, V. A. *Zh. Fiz. Khim.* **1969**, *43*, 2727.
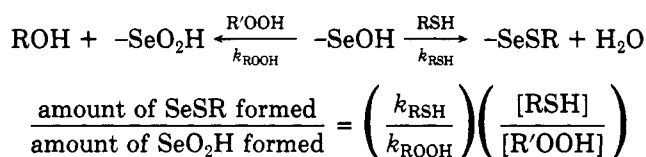
(10) Burkey, T. J.; Fahey, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 868.

$$\text{1b} + \text{ROOH} \underset{\substack{k'_{-c}{}^{a}\mathrm{H}^{+} \\ k'_{-b f}[\text{buffer}] \\ k'_{-o}}}{\overset{\substack{k'_{o} \\ k'_{bf}[\text{buffer}] \\ k'_{c}{}^{a}\mathrm{H}^{+}}}{\rightleftharpoons}} \quad \textbf{4}$$ (13a)

$$\textbf{4} \underset{K'_{h}}{\overset{\mathrm{H}^{+}}{\rightleftharpoons}} \qquad \xrightarrow{k_{ii}} \qquad + \text{ROH}$$ (13b)

fast $\big|$ $-\mathrm{H}^{+}$

In sufficiently acid solution (pH 1) the oxidation of **1a** by hydrogen peroxide (eq 2, R = H, Ar = o-O$_2$NC$_6$H$_4$), which is ~2 × 10^4 slower than the oxidation of **1b** by this reagent under the same conditions, behaves kinetically in an identical fashion to the oxidation of **1a** by hydroperoxides. The logical presumption is therefore that it takes place by an analogous mechanism. At low pH, where the acid-catalyzed term in eq 5c is dominant kinetically, this would mean that the mechanism for the oxidation of **1a** by H$_2$O$_2$ would be that shown in eq 10 with R = H. The non pH-dependent term in eq 5c, of increasing relative importance at higher pH's, presumably is associated with the mechanism in eq 11, again with R = H.

Autocatalysis by 2a of the Oxidation of 1a by Hydrogen Peroxide. Although the oxidations of **1a** by hydrogen peroxide and hydroperoxides behave kinetically in an identical fashion at pH 1, the same is not true in less acid solutions. In less acid solutions (pH ≥2) a marked autocatalysis (increase in experimental rate constant with increasing extent of reaction after ~40% reaction) is observed in the oxidation with H$_2$O$_2$ that is not seen in the oxidation of **1a** with hydroperoxides under the same reaction conditions. Experiments (Table III, section A) in which varying amounts of seleninic acid **2a** (the oxidation product of **1a**) were added initially to solutions of **1a** and hydrogen peroxide demonstrated unequivocally that the observed autocatalysis is due to a reaction process that is first-order in both **2a** and hydrogen peroxide, i.e., $k_{\mathrm{exp}} = k_{\mathrm{cat}}[\text{H}_2\text{O}_2][\textbf{2a}]$.

Grieco[11a,b] and Sharpless[2b] have both shown that in the presence of hydrogen peroxide areneseleninic acids can be converted to the corresponding peroxyseleninic acids (**5**), eq 14. The reaction is presumably reversible. Just as a

$$\text{ArSeO}_2\text{H} + \text{H}_2\text{O}_2 \underset{}{\overset{K_e}{\rightleftharpoons}} \text{ArSe(O)OOH} + \text{H}_2\text{O} \quad (14)$$
$$\textbf{2a} \qquad\qquad\qquad\qquad \textbf{5a}$$

$$\underset{\textbf{1a}}{\text{ArSeOH}} + \underset{\textbf{5a}}{\text{ArSe(O)OOH}} \xrightarrow{k_{\mathrm{PSA}}} \text{ArSeO}_2\text{H} + \text{ArSeO}_2\text{H}$$
(15)

peroxybenzoic acid (Ar'CO$_3$H) is much more reactive than hydrogen peroxide toward **1a** as an oxidizing agent, so too

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(11) (a) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 2034. (b) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Ohfune, Y. *Chem. Commun.* **1977**, 870.

Chart I. Proposed Mechanism for Glutathione Peroxidase

would **5a** be expected to oxidize **1a** (eq 15) at a more rapid rate than does H$_2$O$_2$, i.e., $k_{\mathrm{PSA}} \gg k_{\mathrm{H}_2\mathrm{O}_2}$. In addition, by analogy to the behavior of the oxidations with perbenzoic acids, oxidation of **1a** by perseleninic acid **5a** would not be expected to be catalyzed by H$^+$, and in agreement with this, there is no dependence of k_{cat} on pH (see Table III, section A).

The kinetic behavior of the "2a-catalyzed" oxidation, i.e., $-\mathrm{d}[\textbf{1a}]/\mathrm{d}t = k_{\mathrm{cat}}[\textbf{2a}][\text{H}_2\text{O}_2][\textbf{1a}]$, indicates that the rate-determining step for the reaction is reaction of **1a** with **5a** (eq 15). This means that establishment of the equilibrium between **2a** and **5a** (eq 14) is apparently rapid enough under our reaction conditions compared to the rate of consumption of **5a** via reaction with **1a** so that the equilibrium concentration of **5a** is maintained throughout the course of the reaction.

As noted in the Introduction, excess hydrogen peroxide is often used to oxidize (eq 3, step b) the areneselenenic acid liberated (eq 3, step a) in the olefin-forming oxidative eliminations of arylseleno groups. This is done so that addition of the selenenic acid to the alkene (ArSeOH + >C=C< → ArSeC-COH) will not be a problem. The present results suggest that, except in the early stages, i.e., before much ArSeO$_2$H has been formed, the actual oxidizing agent is probably the peroxyseleninic acid ArSe(O)OOH, rather than hydrogen peroxide. They also suggest that in cases where addition of the selenenic acid to the alkene is especially facile deliberate addition of some seleninic acid to the initial reaction mixture, which should markedly accelerate the rate of oxidation of ArSeOH in the early stages, might be of significant value.

Comparison of the Rates of Reaction of Selenenic Acids with Hydroperoxides vs. Thiols. A selenenic acid functionality (E–SeOH) plays a central role in the reaction cycle for the essential mammalian enzyme glutathione peroxidase that has been proposed by Ganther[3] and that is shown in Chart I. In the proposed mechanism the SeOH intermediate can either be oxidized to a seleninic acid (E–SeO$_2$H) by a hydroperoxide (reaction d) or react with the thiol group of a glutathione molecule (reaction b). Ganther[3] has suggested that under normal circumstances E–SeOH is consumed almost exclusively by reaction with the thiol. If this is to be true, reaction b must be faster than reaction d. Whether or not this is reasonable to expect has not been known, however, because no data have been available on the relative reactivity of hydroperoxides vs. thiols toward selenenic acids.

With the present results and the earlier study[5] of the reaction of thiols with **1a** and **1b** such data are now available. For the o-nitro selenenic acid (**1a**) the rate constant for its H$_3$O$^+$-catalyzed reaction with 1-butanethiol (eq 1, R = n-Bu) is ~750 times larger than the rate constant for its H$_3$O$^+$-catalyzed oxidation by cumene hydroperoxide, and ~325 times larger than the rate constant for its acid-catalyzed reaction with *tert*-butyl hydroperoxide. For selenenic acid **1a**, therefore, it is certainly true that its rate constant for reaction with a thiol is much faster than the rate constant for its oxidation by a hy-

droperoxide. With the *o*-benzoyl selenenic acid (**1b**), where both the reaction with the thiol and that with a hydroperoxide involve mechanisms, eq 12 and 13, respectively, where there is an initial reversible addition of the reactant to the carbonyl group in **1b**, the difference in the magnitude of the rate constants is much smaller. At low pH in the absence of a buffer the rate constant for the H_3O^+-catalyzed reaction of **1b** with *n*-BuSH is only 1.8 times larger than the rate constant for the acid-catalyzed oxidation of **1b** by cumene hydroperoxide; at higher pH's in a H_3PO_4–$H_2PO_4^-$ buffer it is 4.3 times larger.

From these results it is apparent that the nature of the mechanisms involved in the reaction of a particular selenenic acid with a thiol or hydroperoxide can have a large effect on the relative reactivity of these two reagents toward the selenenic acid. However, as the arguments in the next paragraph will show, even if the SeOH group in glutathione peroxidase should be one that reacts with hydroperoxides and thiols by the same type of mechanism as employed by **1b**, and where the rate constants for its reaction with the two species are of comparable magnitude, E–SeOH should be consumed almost entirely via reaction with GSH, with little, if any, being oxidized to E–SeO$_2$H.

The partitioning of a selenenic acid intermediate between reaction with thiol and oxidation by hydroperoxide will be a function not only of the relative rate constants for the two reactions but also of the relative concentrations of thiol and hydroperoxide, i.e.,

$$ROH \; + \; -SeO_2H \; \xleftarrow[k_{ROOH}]{R'OOH} \; -SeOH \; \xrightarrow[k_{RSH}]{RSH} \; -SeSR + H_2O$$

$$\frac{\text{amount of SeSR formed}}{\text{amount of SeO}_2\text{H formed}} = \left(\frac{k_{RSH}}{k_{ROOH}}\right)\left(\frac{[RSH]}{[R'OOH]}\right)$$

Therefore, even when $(k_{RSH}/k_{ROOH}) \cong 1$, provided [thiol] is much larger than [hydroperoxide], almost all of the selenenic acid will be consumed by reaction with thiol. In physiological systems the concentration of glutathione (GSH) should normally be much larger than that of any hydroperoxides, and under ordinary circumstances the almost exclusive reaction pathway for E–SeOH in Chart I should be reaction with GSH (reaction b).

Experimental Section

Preparation and Purification of Materials. The preparation and purification of *o*-nitrobenzeneselenenic (**6a**) and *o*-benzoylbenzeneselenenic (**6b**) anhydrides has been described previously.[4] The generation of solutions of **1a** and **1b** from these anhydrides is described in the section Procedures for Kinetic Runs. *o*-Nitrobenzeneseleninic acid (**2a**), mp 181–183 °C, was prepared by the procedure of Behagel and Seibert.[12]

Peroxybenzoic acid was synthesized from benzoyl peroxide with a literature procedure[13] and was recrystallized from hexane, mp 37–41 °C. An iodometric titration method[14] indicated an active oxygen content of 92%. *p*-Methylperoxybenzoic acid was prepared following the procedure of McDonald and co-workers[15] and was purified by recrystallization from hexane–ether, mp 93–97 °C (90% active oxygen by titration). *p*-Nitroperoxybenzoic acid (Aldrich, 85%) and *m*-chloroperoxybenzoic acid (Aldrich, 85%) were used without further purification. The same was true for hydrogen peroxide (MCB, 30% aqueous solution), *tert*-butyl hydroperoxide (Aldrich, 90%), and cumene hydroperoxide (Sigma Chemical, 95%).

Dioxane was purified by the procedure described by Fieser and Fieser,[16] and after fractional distillation, the purified solvent was frozen and stored at –20 °C to prevent the formation of peroxides prior to use. All water used in the kinetic runs was double distilled from glass. All other reagents used were of the highest purity commercially available and were used without further purification.

Procedures for Kinetic Runs. Solutions of **1a** and **1b** in 60% dioxane were prepared by the acid-catalyzed hydrolysis[4] of selenenic anhydrides **6a** and **6b**, respectively. In the runs followed by conventional spectrophotometry the procedure was as follows. To a 60% dioxane solution (3.5 mL) containing the desired concentrations of perchloric acid (or H_3PO_4–$H_2PO_4^-$ buffer) and, where used, lithium perchlorate was added 35 μL of a stock solution of the selenenic anhydride (5×10^{-3} M) in dioxane. The absorbance of the solution (at 440 nm for the *o*-nitro compound, and at 425 nm for the *o*-benzoyl compound) was then monitored in order to determine when the hydrolysis of the selenenic anhydride to the selenenic acid was complete. Once the hydrolysis was complete the monitoring wavelength was changed, to 435 nm for **1a** and 385 nm for **1b**, and the oxidation reaction was then initiated by the addition via microsyringe of the appropriate amount of a stock solution of the hydroperoxide or hydrogen peroxide in 60% dioxane. The progress of the oxidation was followed by observing the decrease in the absorbance of the solution with time. In the runs investigating the oxidation of **1a** in the presence of initially added *o*-nitrobenzeneseleninic acid (**2a**) an aliquot of a stock solution of **2a** in 60% dioxane was added via microsyringe to the solution of **1a** immediately prior to the addition of the hydroperoxide or hydrogen peroxide.

The procedure used for the runs followed by stopped-flow spectrophotometry was as follows. A solution of the selenenic anhydride (**6a** or **6b**) in 60% dioxane containing the desired amount of perchloric acid was prepared and the absorbance of an aliquot of this solution was observed at the appropriate wavelength (440 nm for **6a**, 425 nm for **6b**) in order to determine when the hydrolysis of the selenenic anhydride to the selenenic acid was complete. Once the hydrolysis was complete the remainder of the solution was placed in one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped-flow spectrophotometer and a solution containing the desired concentration of the peroxyacid in 60% dioxane was placed in the other reservoir syringe. The oxidation of the selenenic acid by the peroxyacid was initiated by mixing the two solutions with the stopped-flow device. The decrease in absorbance (at 435 nm for runs with **1a**, and at 385 nm for runs with **1b**) was recorded on a storage oscilloscope.

Product Studies. Oxidation of 1a. To confirm that *o*-nitrobenzeneseleninic acid (**2a**) is the oxidation product formed when **1a** is oxidized with either hydrogen peroxide, hydroperoxides, or peroxybenzoic acids the following experiments were carried out.

o-Nitrobenzeneselenenic anhydride (0.03 g, 0.07 mmol) was dissolved in a mixture of 3.5 mL of tetrahydrofuran and 35 μL of water, and 35 μL of 1 M aqueous perchloric acid was added to effect the hydrolysis of **6a** to **1a**. When the hydrolysis was complete, as judged by removal of a small aliquot of the solution, dilution, and measurement of the absorbance at 440 nm, 0.1 mL of aqueous 30% hydrogen peroxide was then added, and the solution was allowed to stand at room temperature for about 4 h. Most of the solvent was then removed at room temperature. The precipitate that separated was washed first with water, then with a small amount of ether, and dried under vacuum at room temperature. The material so obtained (0.025 g, 0.11 mmol, 76%) was identical with an authentic sample of **2a**.

In a second experiment 0.049 g (0.12 mmol) of **6a** dissolved in 1 mL of tetrahydrofuran containing 0.04 mL of water and 0.04 mL of 9.6 M HClO$_4$ was hydrolyzed to the selenenic acid, and 0.24 mmol of *m*-chloroperoxybenzoic acid dissolved in 0.5 mL of chloroform was then added. After 1 h the precipitate that had formed was filtered off and recrystallized from hot water, affording seleninic acid **2a**, mp 179–182 °C. The amount of **2a** obtained was 0.17 mmol (74%).

In a third experiment 0.1 mL of *tert*-butyl hydroperoxide (0.9 mmol) was added to a tetrahydrofuran–water solution of **1a** (0.18

(12) Behagel, O.; Seibert, H. *Chem. Ber.* **1933**, *66*, 708.

(13) Kergomard, A.; Philibert–Bigou, J. *Bull. Soc. Chim. Fr.* **1958**, 334.

(14) Swern, D. "Organic Peroxides"; Wiley: New York, 1970; Vol. 1, p 498.

(15) McDonald, R. N.; Steppel, R. N.; Dorsey, J. E. *Org. Synth. (N.Y.)* **1970**, *50*, 15.

(16) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 333.

mmol), prepared by acid-catalyzed hydrolysis of selenenic anhydride **6a**. After addition of the hydroperoxide the solution was allowed to stand at room temperature for several hours. Workup in the same manner as outlined for the **1a**–hydrogen peroxide reaction gave **2a** (0.09 mmol, 50%).

Oxidation of 1b. *o*-Benzoylbenzeneselenenic anhydride (**6b**), 0.0185 g (0.035 mmol), was dissolved in 0.1 mL of tetrahydrofuran and 0.03 mL of water, and 0.02 mL of 9.6 M aqueous perchloric acid was added. After hydrolysis of **6b** to **1b**, 0.05 mL of 30% aqueous hydrogen peroxide was added, and the solution was allowed to stand at room temperature for 15–20 min. At that point 2.5 mL of water was added, and the precipitate of *o*-benzoylbenzeneseleninic acid (**2b**), 0.013 g (65%), that separated was filtered off and recrystallized from hot water: mp 177–179 °C (lit.[17] mp 177–179 °C); IR spectrum identical with that of a known sample of **2b**.

(17) Kang, S.-I., unpublished results. In our laboratory we have never been able to obtain, even after repeated recrystallizations, the melting point (184–185 °C) for **2b** reported by Rheinboldt and Giesbrecht.[18] We believe their melting point for **2b** may be in error.

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Structures and Optical Absorption Spectra of Some Sulfuranyl Radicals in Solution[1]

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Optical absorption spectra due to the sulfuranyl radicals (*t*-BuO)₃Ṡ (**2**), *t*-BuO(S·)OC(Me)₂CH₂C(Me)₂O (**3**) and CH₃(·S)OC(O)(*o*-C₆H₆) (**4**) were detected by the use of laser flash photolysis. Both **2** and **3** have π structures and their optical spectra are significantly blue-shifted with respect to that of **4** which has a σ or σ* structure. The results suggest that optical absorption spectroscopy may be a useful guide in the assignment of the electronic structures of sulfuranyls.

Sulfuranyl radicals and their structures have been the subject of several investigations.[3-13] They have been classified into three basic types, σ, π, and σ*, Scheme I. However, assignments of their ground-state electronic structures have been both difficult and controversial.

In the σ structure, the sulfur atom and its three nearest neighbors adopt a T shape with the unpaired electron localized in an orbital which is in the plane of those atoms. On the basis of a single-crystal electron paramagnetic resonance (EPR) study, Morton et al. assigned this structure to F₃Ṡ[3a] and inferred that it was also adopted by the related sulfuranyl radicals (RO)₃Ṡ and (RO)₂ṠF (R = CF₃ or SF₅) which has been detected in solution.[3b] They

Scheme I

σ   π   σ*
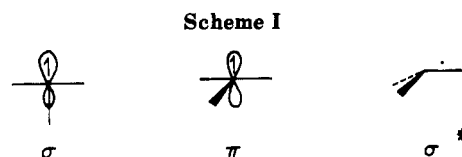
assumed that the ground-state structure would be unaffected by changes in the ligands and therefore contested the suggestion made by Roberts et al.[4,5,7] that the structures of the related radicals (RO)₃Ṡ and RṠ(OBu-*t*)₂ (where R = alkyl) were of the π type with the unpaired electron in an orbital which was perpendicular to the plane defined by the sulfur and its three nearest neighbors, Scheme I.

Although it is generally difficult to discriminate between the σ and π structures, there is good evidence that the π structure is adopted by the sulfuranyl PhṠ(OBu-*t*)₂.[5,9] Hydrogen hyperfine splittings in this radical have been detected from both the ortho and para hydrogens of the phenyl group, implying delocalization of the unpaired electron through the π system of the ligand. By contrast, the σ structure would only have been expected to give rise to hyperfine splittings by spin-polarization, which ought not to have extended to the para position (vide infra). It can, of course, be argued that this observation does not resolve the σ vs. π question in a broad sense, since the phenyl substituent would be bound to perturb the system so as to favor the π state. However, the hyperfine splittings involved were extremely small (0.8 G), indicating that the unpaired electron was effectively localized at sulfur and suggesting that perturbations induced by the phenyl group were negligible. Thus, while ṠF₃ may have the σ structure,[3a] it is possible that sulfuranyls with less electron withdrawing substituents may adopt the π configuration.

(1) National Research Council of Canada, issued as NRCC No. 24482.

(2) Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni.

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