were made at from 5 to 11 different pH's separated by 0.1 pH unit. Because of the marked difference in the absorption spectra of $ArSeO^-$ and ArSeOH, particularly the lack of significant absorbance by the selenenic acid at the wavelength where the anion has its maximum, the fraction, *f*, of the selenic acid present as the selenenate, $f = [ArSeO^-]/([ArSeO^-] + [ArSeOH])$, can be calculated easily from the optical density of the buffer solution at λ_{max} for $ArSeO^-$ plus the previously determined relationship between the ϵ's for ArSeOH and $ArSeO^-$ at their respective absorption maxima.

Registry No. **1a**, 56790-60-4; **1b**, 99809-29-7; **1c**, 65848-43-3; **1d**, 99809-30-0; **3a**, 99809-31-1; **3b**, 99809-32-2; **3c**, 65275-57-2; **3d**, 99809-33-3; *o*-nitrophenyl selenocyanate, 51694-22-5; *p*-chloro-*o*-nitrophenyl selenocyanate, 99809-34-4; *p*-methyl-*o*-nitrophenyl selenocyanate, 65275-29-8; *p*-methoxy-*o*-nitrophenyl selenocyanate, 63816-14-8; *o*-nitrophenyl ethyl selenoxide, 94650-41-6; *p*-chloro-*o*-nitrophenyl ethyl selenoxide, 99809-35-5; *p*-methyl-*o*-nitrophenyl ethyl selenoxide, 65275-44-7; *p*-methoxy-*o*-nitrophenyl ethyl selenoxide, 99809-36-6; benzeneselenenic acid, 5818-99-5; ethanol, 64-17-5.

Supplementary Material Available: Tabulation of the ratio of selenenate to selenenic acid and calculated pK_a's for selenenic acids in different buffers (Table I) (2 pages). Ordering information is given on any current masthead page.

Rates of Oxidation of *o*-Nitrobenzeneselenenyl Compounds by *m*-Chloroperoxybenzoic Acid and the Rate of Reaction of *o*-Nitrobenzeneselenol with *o*-Nitrobenzeneselenenic Acid[1a]

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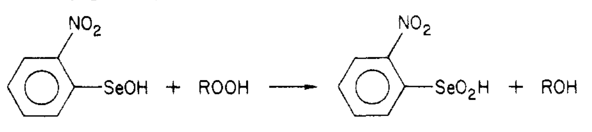
Received August 1, 1985

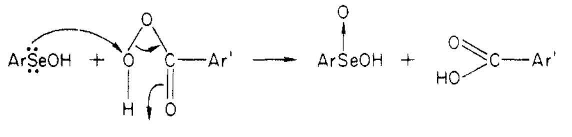
Rate constants for the oxidation of a series of *o*-nitrobenzeneselenenyl derivatives ($Ar = o\text{-}O_2NC_6H_4$) by *m*-chloroperoxybenzoic acid (MCPBA) have been measured at 25 °C in ethanol (compound, k_{PA} ($M^{-1}\ s^{-1}$)): ArSeH, 1.1×10^4; ArSeOH, 80; ArSeOSeAr, 12; ArSeOEt, 4; ArSeSeAr, 0.15. The rate constant ($k_{ArSeH} = 1.0 \times 10^2\ M^{-1}\ s^{-1}$) for the reaction of ArSeH with ArSeOH to give ArSeSeAr (eq 3), which is pH independent in acid solution, has also been determined. Significant practical consequences of these and related results include the following: (a) the rate of oxidation of selenol (ArSeH) to selenenic acid (ArSeOH) is enough faster than either the oxidation of ArSeOH to seleninic acid ($ArSeO_2H$) or eq 3 so that oxidation of the selenol with 1 molar equiv of MCPBA gives ArSeOH in high yield; (b) with a weaker oxidant, hydrogen peroxide, the rate of oxidation of the selenol is enough slower than the rate of eq 3 that the diselenide (ArSeSeAr) becomes the almost exclusive product; (c) the rate of oxidation of the diselenide is so much smaller than that of any of the other compounds that its initial oxidation to ArSeOSeAr is far and away the slowest step in its overall oxidation to seleninic acid by excess peracid.

In contrast to the vast majority of areneselenenic acids, solutions of *o*-nitrobenzeneselenenic acid, **1** (ArSeOH, $Ar = o\text{-}O_2NC_6H_4$), are quite stable, and the mechanisms of reactions of **1** are therefore subject to investigation in a straightforward fashion, something that is not possible with most selenenic acids. In earlier work,[2] the oxidation (eq 1) of **1** by peroxyacids (R = ArC(O)), hydroperoxides (R = *t*-Bu or $PhCMe_2$), and hydrogen peroxide (R = H) in 60% dioxane was examined. The mechanism for the oxidation of **1** by peroxyacids was found to be that shown in eq 2. This mechanism, which is analogous to that[3] for oxidation of alkyl sulfides by peracids, involves nucleophilic attack by the selenenic acid on one of the peroxide oxygens of the peracid.



(1)

1 2



(2)

It is of interest to determine how the rates of peroxyacid oxidation of other related *o*-nitrobenzeneselenenyl compounds (ArSeH, ArSeSeAr, ArSeOSeAr, ArSeOEt) compare with that of **1**. Also of interest is how the rate of reaction of *o*-nitrobenzeneselenol (**3**) with **1** (eq 3) compares with the rate of oxidation of **3** (eq 4). Since the oxidation of the diselenide **4** is much slower than any of the other oxidations, the relative rates of eq 3 and 4 are critical in determining whether oxidation of selenol **3** by excess oxidant under a given set of conditions will lead primarily to seleninic acid **2** or to diselenide **4**. This paper reports the results of experiments providing information on these points.

$$\underset{\mathbf{3}}{\mathrm{ArSeH}} + \underset{\mathbf{1}}{\mathrm{ArSeOH}} \xrightarrow{k_{\mathrm{ArSeH}}} \underset{\mathbf{4}}{\mathrm{ArSeSeAr}} + \mathrm{H_2O} \tag{3}$$

$$\underset{\mathbf{3}}{\mathrm{ArSeH}} + \mathrm{Ar'CO_3H} \xrightarrow{k_{\mathrm{PA}}} \underset{\mathbf{1}}{\mathrm{ArSeOH}} + \mathrm{Ar'CO_2H} \tag{4}$$

$$\mathrm{Ar} = o\text{-}\mathrm{O_2NC_6H_4};\ \mathrm{Ar'} = m\text{-}\mathrm{ClC_6H_4}$$

Results

Oxidation of *o*-Nitrobenzeneselenol (3) by *m*-Chloroperoxybenzoic Acid (MCPBA). Solutions of $o\text{-}O_2NC_6H_4Se^-$ in ethanol were prepared by reduction of *o*-nitrophenyl selenocyanate ($o\text{-}O_2NC_6H_4SeCN$) with an equimolar amount of sodium borohydride.[4] Because of

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[1] (a) This research supported by the National Science Foundation, Grant CHE-82-15140. (b) Present address: Department of Chemistry, University of Denver, Denver, CO 80208.

[2] Kice, J. L.; Chiou, S.; Weclas, L. *J. Org. Chem.* **1985**, *50*, 2508.

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Table I. Kinetics of Oxidation of *o*-Nitrobenzeneselenenyl Compounds by *m*-Chloroperoxybenzoic Acid[a]

10^4[compound], M	$10^3[HClO_4]$, M	10^3[MCPBA], M	k_1,[b] s^{-1}	k_2,[c] $M^{-1}\ s^{-1}$	k_{PA},[d] $M^{-1}\ s^{-1}$
		A. *o*-Nitrobenzeneselenol			
1.0	2.6	1.0	10.3		1.0×10^4
		2.0	23		1.1×10^4
		4.0	46		1.1×10^4
		B. *o*-Nitrobenzeneselenenic Acid			
1.4	0.0	0.36		79	79
		0.29		82	82
		0.22		81	81
		C. *o*-Nitrobenzeneselenenic Anhydride			
1.0	0.0	0.26		12	12
		0.63		12	12
0.55	0.00	0.32		12	12
		0.63		12	12
		D. *o*-Nitrophenyl Diselenide			
0.98	0.0	1.47	0.00022		0.15
		1.95	0.00030		0.15
		2.91	0.00044		0.15
		E. Ethyl *o*-Nitrobenzeneselenenate			
1.0	1.3	1.23	0.0047		3.8
		0.93	0.0037		3.9
		0.63	0.0024		3.8

[a] All experiments at 25 °C in ethanol as solvent. [b] Experimental first-order rate constant for runs where MCPBA in sufficient excess over substrate that good first-order kinetics observed. [c] Experimental second-order rate constant. [d] Second-order rate constant for oxidation of substrate by MCPBA.

the sensitivity of the selenol to air oxidation this procedure and subsequent operations with the selenol were carried out under nitrogen with strict exclusion of air. Quantitative formation of $o\text{-}O_2NC_6H_4Se^-$ from the selenocyanate was established by the isolation of *o*-nitrophenyl benzyl selenide in 98% yield after reaction of the final solution with benzyl bromide. Solutions of **3** for use in kinetic experiments were prepared by adding aliquots of the $ArSe^-$ solution to ethanol containing perchloric acid.

Treatment of an ethanol solution of **3** (1×10^{-4} M) with an equimolar amount of MCPBA resulted in the immediate appearance of the λ_{max} at 430 nm characteristic[5] of selenenic acid **1**. If a two- or threefold excess of MCPBA was used, the peak for **1** formed first and then disappeared, due to oxidation of **1** to **2** by MCPBA.

The kinetics of the oxidation of **3** by MCPBA were studied by stopped-flow spectrophotometry with the peracid present in sizeable stoichiometric excess over **3**. Oxidation of **3** to **1** was enough faster than oxidation of **1** to **2** so that the absorbance (A_∞^i) at 430 nm corresponding to completion of the oxidation of **3** to **1** was easily determined. Experimental first-order rate constants (k_1), obtained from the slope of plots of log ($A_\infty^i - A$) vs. time are presented in section A of Table I; as would be expected, k_1 is proportional to [MCPBA].

Oxidation of *o*-Nitrobenzeneselenenic Acid (1) and *o*-Nitrobenzeneselenenic Anhydride by MCPBA. The rate of oxidation of **1** (generated by fragmentation of *o*-nitrophenyl ethyl selenoxide[6]) by MCPBA in ethanol was measured by following the decrease in absorbance (A) at the absorption maximum of **1**. Since the runs were carried out with MCPBA present in only modest stoichiometric excess over **1**, the kinetics of the absorbance change followed those expected[7] for a second-order reaction with one component (MCPBA) present in slight excess. The second-order rate constants, k_2, for each run are shown in section B of Table I; k_2 is, of course, equal to k_{PA}, the rate constant for the oxidation of **1** to **2** by MCPBA in ethanol. The value for k_{PA} (80 $M^{-1}\ s^{-1}$) is about 20% smaller than that (100 $M^{-1}\ s^{-1}$)[2] for the oxidation of **1** by MCPBA in 60% dioxane, showing that the change in solvent has only a modest effect on the oxidation rate.

Reaction of ethanol with *o*-nitrobenzeneselenenic anhydride (**5**, ArSeOSeAr, Ar = $o\text{-}O_2NC_6H_4$) is slow enough in the absence of an acid catalyst so that the rate of oxidation of **5** by MCPBA can be measured easily. The runs, followed by observing the decrease in absorbance at the long wavelength λ_{max} of **5**, are shown in section C of Table I; k_{PA} is about 6 times smaller than k_{PA} for oxidation of **1**.

Oxidation of *o*-Nitrophenyl Diselenide (4) by MCPBA. Treatment of **4** (1×10^{-4} M) in ethanol with excess MCPBA (0.0015–0.0030 M) resulted in the slow disappearance of the λ_{max} for **4** at 370 nm. Scans of the spectrum of the solution during the course of the reaction showed no build-up of any intermediate such as **1**, or ArSeOSeAr, during the oxidation. This is undoubtedly because the oxidation of **4** is much slower than the oxidation of these other species.

With peracid present in large stoichiometric excess over **4** plots of log ($A - A_\infty$) at 370 nm vs. time were linear, and the experimental first-order rate constants, k_1, for such runs are given in section D of Table I; k_1/[MCPBA] is a constant, 0.15 $M^{-1}\ s^{-1}$.

Oxidation of Ethyl *o*-Nitrobenzeneselenenate (6) by MCPBA. As described in detail in an accompanying paper,[8] in ethanol in the presence of an acid catalyst *o*-nitrobenzeneselenenic acid (**1**) is rapidly converted to ethyl *o*-nitrobenzeneselenenate (**6**) (eq 5). Dilute solutions of

$$\underset{\mathbf{1}}{\mathrm{ArSeOH}} + \mathrm{EtOH} \rightarrow \underset{\mathbf{6}}{\mathrm{ArSeOEt}} + \mathrm{H_2O} \qquad (5)$$

$$\mathrm{Ar} = o\text{-}\mathrm{O_2NC_6H_4}$$

6 in ethanol are therefore easily prepared, and their oxidation by MCPBA can be studied kinetically by moni-

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Table II. Kinetics of the Reaction of *o*-Nitrobenzeneselenol (3) with *o*-Nitrobenzeneselenenic Acid (1) in 60% Dioxane[a]

acid or buffer	pH	$10^4[\mathbf{1}]_o$, M	$10^4[\mathbf{3}]$, M	10^2k_1, s^{-1}	k_{ArSeH},[b] M^{-1} s^{-1}
0.02 N $HClO_4$	1.70	0.96	9.5	8.4	96
			7.0	5.8	
			4.4	3.6	
0.005 N $HClO_4$	2.30	0.96	9.5	8.8	1.0×10^2
			7.0	5.9	
			4.4	3.8	
0.002 N $HClO_4$	2.70	0.96	9.3	9.1	1.0×10^2
			8.0	8.1	
			6.7	6.4	
			5.4	5.1	
1:1 $Cl_2CHCO_2HCl_2CHCO_2^-$ buffer, 0.02 M $Cl_2CHCO_2^-$	4.03	0.96	9.5	12.2	1.3×10^2
			7.0	8.9	
			4.4	5.7	
			3.1	4.0	
1:1 $Cl_2CHCO_2HCl_2CHCO_2^-$ buffer, 0.10 M $Cl_2CHCO_2^-$	4.03	0.96	6.0	6.3	1.3×10^2
			4.9	4.2	
			3.9	3.4	
			2.8	2.1	

[a] All runs at 25 °C. In the runs using perchloric acid the ionic strength was maintained at 0.02 by the addition of the appropriate amount of lithium perchlorate. [b] Rate constant k_{ArSeH} for eq 3 obtained from slope of plot of k_1 vs. [**3**] for runs at each pH.

toring the disappearance of the λ_{max} for **6**. The kinetic results for a series of runs where MCPBA was present in sufficient stoichiometric excess over **6** so that the disappearance of the ester followed pseudo first-order kinetics are presented in section E of Table I. Interestingly, k_{PA} for the oxidation of **6** is 20 times smaller than k_{PA} for the oxidation of **1**.

Reaction of *o*-Nitrobenzeneselenol (3) with *o*-Nitrobenzeneselenenic Acid (1). The ease of conversion of **1** to **6** in ethanol in acid solution dictated that the reaction of **3** with **1** (eq 3) be investigated in 60% dioxane, rather than ethanol. The kinetics of eq 3 were studied at 25 °C at constant ionic strength (0.02) in solutions containing 0.002–0.02 M perchloric acid and in a 1:1 dichloroacetic acid–dichloroacetate buffer (pH 4.03 in 60% dioxane[9]). The selenol was present in sufficient excess over **1** that the disappearance of **1** (monitored by observing the decrease in absorbance at 450 nm) followed pseudo-first-order kinetics. The experimental first-order rate constants, k_1, for the various runs are listed in Table II. Values of k_{ArSeH}, the rate constant for eq 3, were obtained for the runs at each pH from the slope of a plot of k_1 vs. [ArSeH] and are listed in the table.

It is evident that k_{ArSeH} is effectively independent of a_{H^+} for the runs at different perchloric acid concentrations. In a 1:1 Cl_2CHCO_2H–$Cl_2CHCO_2^-$ buffer k_{ArSeH} is apparently slightly larger, but the effect is not large, and the fact that an increase in buffer concentration does not lead to an increase in k_{ArSeH} shows that buffer catalysis is not important for eq 3.

Discussion

The present study provides data on the relative rates of oxidation of a series of *o*-nitrobenzeneselenenyl compounds by *m*-chloroperoxybenzoic acid (MCPBA). Within the series their reactivity differs by a factor of $\sim 10^5$; the second-order rate constants (M^{-1} s^{-1}) for oxidation of the different substrates by MCPBA at 25 °C in ethanol are as follows: ArSeH, 1.1×10^4; ArSeOH,80; ArSeOSeAr 12; ArSeOEt, 4; and ArSeSeAr, 0.15.

Since the selenol (ArSeH, **3**) is oxidized to the selenenic acid (ArSeOH, **1**) $\sim$150 times faster than the latter is oxidized to the seleninic acid ($ArSeO_2H$, **2**), oxidation of the selenol with 1 molar equiv of MCPBA does not result in the formation of a significant amount of seleninic acid. When more than 1 molar equiv of MCPBA is used, oxidation of **3** to **1** (eq 4) is complete before oxidation of **1** to **2** (eq 1) begins to be observed. This contrasts with the relative ease of oxidation of an alkanethiol, *t*-BuSH, vs. the corresponding alkanesulfenic acid, *t*-BuSOH. Davis and Billmers[10] have found that oxidation of 2 equiv of the thiol with 1 equiv of 2-(benzenesulfonyl)-3-phenyloxaziridine gives an 80% yield of 2-methyl-2-propanesulfinic acid, *t*-$BuSO_2H$, showing that the rate of oxidation of the sulfenic acid by the oxidant must be considerably faster than the rate of oxidation of the thiol. The different behavior of the **3** → **1** → **2** oxidation sequence is not necessarily indicative of any fundamental difference between selenenic acids and sulfenic acids in their ease of oxidation relative to selenols and thiols, respectively. More likely it results from the markedly enhanced stability, and presumably decreased reactivity, of **1** as compared to other aromatic selenenic acids. The special stability of **1** is thought[11] to be due to coordination of an oxygen of the *o*-NO_2 group to selenium.

Of particular interest is how the rate of oxidation of **3** *to* **1** by MCPBA (eq 4) compares with the rate of reaction of **3** *with* **1** to give diselenide (eq 3). The second-order rate constants for the two reactions at 25 °C are

$$k_{ArSeH}\text{ (eq 3)} = 1.0 \times 10^2\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{PA}\text{ (eq 4)} = 1.1 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$$

Since k_{PA} for MCPBA is $\sim 10^2$ larger than k_{ArSeH}, even when only an equimolar amount of MCPBA is used as oxidant for **3**, k_{PA}[MCPBA]/k_{ArSeH}[ArSeOH] will be enough greater than unity throughout the course of the reaction that a negligible amount of diselenide will be formed.

Study of the oxidation of **1**,[2] or alkyl sulfides,[3,12] by hydroperoxides and hydrogen peroxide has shown that these reagents are as much as 10^6 less reactive than MCPBA as oxidants for such substrates. If, as seems likely, a similar difference in reactivity as oxidizing agents between MCPBA and ROOH also exists for oxidation of

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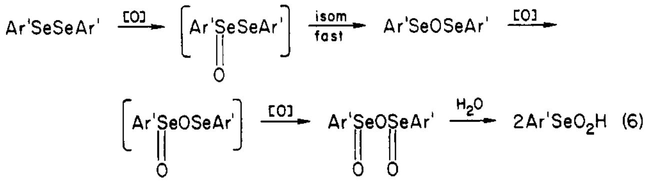
selenol **3**, then k_{ROOH} will be so much smaller than k_{ArSeH} that the principal product of the oxidation of **3** with these weaker oxidizing agents will be the diselenide; and this will be true even when the oxidant is used in considerable molar excess over **3**. The spectral changes that occurred when **3** was treated with excess H_2O_2 indicated that this was indeed the case. Since it is oxidized much more slowly than any of the other *o*-nitrobenzeneselenenyl compounds, the diselenide, once formed from **3** and **1** via eq 3, disappears only very slowly even when considerable excess oxidant is present.

The final product of the oxidation of aryl diselenides (Ar′SeSeAr′) by either peracids or hydrogen peroxide is normally the seleninic acid (Ar′SeO$_2$H), and oxidation of aryl diselenides by hydrogen peroxide is one of the standard synthetic routes for the formation of areneseleninic acids.[13] Oxidation of an aryl diselenide to areneseleninic acid in all probability involves the sequence of steps, mostly oxidations, outlined in eq 6 (presumed



$$\text{Ar'SeSeAr'} \xrightarrow{[\text{O}]} \left[\text{Ar'}\underset{\underset{\text{O}}{\|}}{\text{Se}}\text{SeAr'}\right] \xrightarrow[\text{fast}]{\text{isom}} \text{Ar'SeOSeAr'} \xrightarrow{[\text{O}]} \left[\text{Ar'}\underset{\underset{\text{O}}{\|}}{\text{Se}}\text{OSeAr'}\right] \xrightarrow{[\text{O}]} \text{Ar'}\underset{\underset{\text{O}}{\|}}{\text{Se}}\text{O}\underset{\underset{\text{O}}{\|}}{\text{Se}}\text{Ar'} \xrightarrow{H_2O} 2\text{Ar'SeO}_2\text{H} \quad (6)$$

highly unstable intermediates are shown in brackets). The present results show that in the *o*-nitrobenzeneselenenyl system oxidation of ArSeSeAr (**4**) is ~100 times slower than oxidation of ArSeOSeAr (**5**) and ~500 times slower than the oxidation of the selenenic acid **1**. The initial oxidation of the diselenide is therefore far and away the slowest step in the overall oxidation of **4** to seleninic acid **2**. A similar relationship between ease of oxidation of diselenide and selenenic anhydride seems likely for aryl diselenides generally. This behavior of the selenium compounds contrasts with the behavior of the analogous sulfur compounds. In the sulfur series disulfides are oxidized at almost the same rate as their monooxidation products—ArS(O)SAr, thiosulfinates (sulfenic anhydrides).[14]

Why the diselenide is oxidized so much less rapidly than the selenenic anhydride or selenenic acid is not known with certainty. One possibility is back-donation of unshared electron pairs on Se to vacant d orbitals on the adjacent selenium, which is, of course, not possible in the selenenic anhydride or acid.

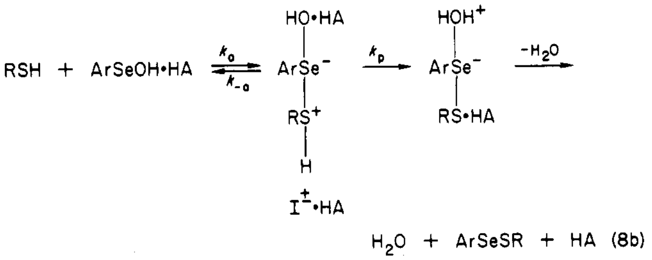
The relative rates of MCPBA oxidation of the different *o*-nitrobenzeneselenenic acid derivatives are as follows: ArSeOH, 20; ArSeOSeAr, 3; ArSeOEt, 1. Since *o*-$O_2NC_6H_4SeO$ should be electron-withdrawing compared to OH, the slower rate of oxidation for the selenenic anhydride relative to the acid is understandable. On the other hand, at present we have no satisfying explanation for the rate of oxidation of the selenenate ester being only 1/20th that of the acid.

The reaction of the selenol **3** with selenenic acid **1** (eq 3), is not significantly acid-catalyzed. This contrasts with the reaction of alkanethiols with **1** (eq 7) where acid catalysis is required in order for the reaction to proceed at

$$\underset{\mathbf{1}}{\text{ArSeOH}} + \text{RSH} \xrightarrow{\text{H}^+} \text{ArSeSR} + \text{H}_2\text{O} \qquad (7)$$

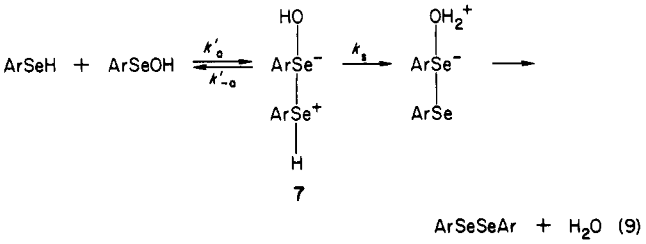
a reasonable rate.[11] The mechanism that has been proposed[8,11] for eq 7 is shown in eq 8, with acid catalysis of

$$\text{ArSeOH} + \text{HA} \overset{K_{\text{assoc}}}{\rightleftharpoons} \text{ArSeOH}\cdot\text{HA} \qquad (8a)$$



$$\text{RSH} + \text{ArSeOH}\cdot\text{HA} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{\mathbf{I}^{\pm}\cdot\text{HA}}{\text{ArSe}^-(\text{HO}\cdot\text{HA})(\text{RS}^+\text{H})} \xrightarrow{k_p} \text{ArSe}^-(\text{HOH}^+)(\text{RS}\cdot\text{HA}) \xrightarrow{-H_2O} \text{H}_2\text{O} + \text{ArSeSR} + \text{HA} \qquad (8b)$$

the departure of the OH group being necessary in order for its loss to be adequately competitive in rate with step k_{-a}. It is possible that in the reaction of the selenol with **1** the lifetime of the intermediate (**7**, eq 9) analogous to I$^{\pm}$ is enough longer than that of I$^{\pm}$, i.e., $k'_{-a} \ll k_{-a}$, so that a "proton-switch"[15] process (step k_s) can in this system afford a kinetically viable route for converting the OH function to the needed leaving group $-\text{OH}_2^+$.



$$\text{ArSeH} + \text{ArSeOH} \underset{k'_{-a}}{\overset{k'_a}{\rightleftharpoons}} \underset{\mathbf{7}}{\text{ArSe}^-(\text{HO})(\text{ArSe}^+\text{H})} \xrightarrow{k_s} \text{ArSe}^-(\text{OH}_2^+)(\text{ArSe}) \longrightarrow \text{ArSeSeAr} + \text{H}_2\text{O} \qquad (9)$$

Chart I. Rates of Oxidation (by MCPBA) and Other Reactions of *o*-Nitrobenzeneselenenyl (Ar = *o*-$O_2NC_6H_4$) Compounds

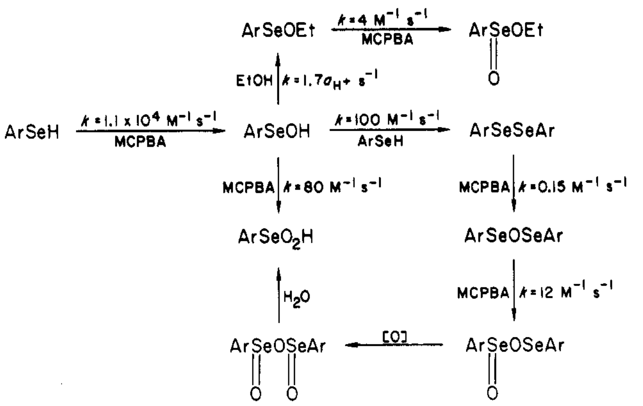


Chart I provides a pictorial summary of the interrelationship of the different reactions of the *o*-nitrobenzeneselenenyl derivatives examined in this and accompanying[8] work and, where measurable, their rate constants.

Experimental Section

Preparation and Purification of Materials. ***o*-Nitrobenzeneselenenic anhydride** (**5**) was synthesized and purified as previously described.[16]

***o*-Nitrophenyl Diselenide (4).** *o*-Nitrophenyl selenocyanate[4] (0.21 g) was dissolved in 3 mL of absolute ethanol, and 0.5 g of potassium hydroxide was added. The mixture was stirred vigorously for 3.5 h at room temperature, and the yellow precipitate that had formed was then filtered off, washed with absolute ethanol and water, and recrystallized from benzene, giving 0.12

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[13] (a) McCullogh, J. D.; Gould, E. S. *J. Am. Chem. Soc.* **1949**, *71*, 674; **1951**, *73*, 1109. (b) Fredga, A.; Evertsdotter, R. *Acta Chem. Scand.* **1959**, *13*, 1042. (c) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 666. (d) Defilippo, D.; Momicchioli, A. *Tetrahedron* **1969**, *25*, 5733.

[14] Marangelli, U.; Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1960**, *90*, 681.

[15] Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018.

[16] Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* **1984**, *49*, 3100.

g (65%) of **4**, mp 213–215 °C (lit.[17] 214 °C).

Solutions of *o*-nitrobenzeneselenenic acid (**1**) were prepared either by acid hydrolysis of a solution of selenenic anhydride **5** in aqueous dioxane in the manner described by Kice, McAfee, and Slebocka-Tilk[16] or by decomposition of *o*-nitrophenyl ethyl selenoxide at room temperature using the procedure outlined by Kang and Kice.[6,8]

***o*-Nitrobenzeneselenol (3).** All operations were conducted under nitrogen in an Aldrich Atmosbag. *o*-Nitrophenyl selenocyanate[4] (0.114 g, 0.5 mmol) was dissolved in 25 mL of anhydrous ethanol, 0.021 g (0.55 mmol) of sodium borohydride was added, and the solution was stirred at room temperature for 2–5 min until the reduction of the selenocyanate to the anion of the selenol ($o\text{-}O_2NC_6H_4Se^-$), which is accompanied by a change in the color of the solution from yellow to dark red, was complete. To verify that the reduction gave a quantitative yield of $o\text{-}O_2NC_6H_4Se^-$, an aliquot (8.0 mL) of the final reaction solution was treated with 33 μL (0.16 mL) of benzyl bromide, and the solution was allowed to stand at room temperature until the red color of the solution changed to a bright yellow. The ethanol was then removed under reduced pressure, and the residue was washed with water, followed by trituration with ether. The ether extract was dried. Upon removal of the ether there was obtained 0.044 g (98%) of benzyl o-nitrophenyl selenide, mp 99–101 °C (lit.[18] 100 °C).

Solutions of selenol **3** for use in kinetic experiments were prepared by the addition of measured aliquots of the final solution of $o\text{-}O_2NC_6H_4Se^-$ to either ethanol or 60% dioxane containing more than enough perchloric acid to neutralize the anion of the selenol.

The preparation of ethyl *o*-nitrobenzeneselenenate (**6**) from **1** is described in an accompanying paper.[8] Commerical dioxane was purified to remove water and peroxides by using the procedure of Fieser and Fieser.[19] After fractional distillation the purified solvent was frozen and stored at −20 °C to prevent the formation of peroxides prior to use. *m*-Chloroperoxybenzoic acid (Aldrich, 85%) and all other reagents used were of the highest purity commercially available and were used without further purification. All water used in kinetic runs was double distilled from glass.

Procedure for Kinetic Runs. Oxidation of 3 by MCPBA. A degassed solution of *m*-chloroperoxybenzoic acid (0.002–0.008 M) and perchloric acid (0.0052 M) in absolute ethanol was placed in a vessel connected to one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped-flow spectrophotometer in such a fashion that the reservoir syringe could be filled from the vessel under nitrogen pressure and without any exposure of the solution to the atmosphere. An aliquot of the solution of the anion of **3**, prepared by reduction of *o*-nitrophenyl selenocyanate, was diluted with degassed absolute ethanol to give a solution containing 2×10^{-4} M $o\text{-}O_2NC_6H_4Se^-$, and this was placed in a second vessel connected to the other reservoir syringe of the stopped-flow spectrophotometer in a similar manner. After the reservoir syringes were loaded, the reaction of **3** with MCPBA was initiated by mixing the solutions in the two syringes using the stopped-flow device. The progress of the oxidation of **3** by MCPBA was monitored by observing the increase in the absorbance with time at 430 nm on the storage oscilloscope. The increase in absorbance at 430 nm due to the oxidation of **3** to **1** is then followed by a decrease in absorbance at this wavelength due to the oxidation of **1** to **2**. The rate of this latter oxidation is enough slower than the oxidation of **3** to **1** so that the absorbance (A_∞^{i}) corresponding to the completion of the oxidation of **3** to **1** can be determined accurately.

Oxidation of 1 by MCPBA. An aliquot (50 μL) of a freshly prepared 0.01 M solution of **1** in methylene chloride was added by microsyringe to 3.6 mL of anhydrous ethanol in a 1-cm cell in the thermostated cell compartment of a UV–visible spectrophotometer. The desired volume of a concentrated solution of MCPBA in ethanol was then added by microsyringe, and the oxidation of **1** by MCPBA was followed by observing the decrease in the absorbance of the solution at 427 nm.

Oxidation of 4 and 5 by MCPBA. The same general procedure as that just described for studying the oxidation of **1** was used. Aliquots of 0.01 M solutions of **4** or **5** in anhydrous dioxane, rather than methylene chloride, were employed. The oxidation of **5** was followed by monitoring the decrease in absorbance with time at 440 nm; that of **4** was followed by observing the decrease at 370 nm.

Oxidation of 6 by MCPBA. A 30-μL aliquot of a 0.01 M solution of **1** in dioxane was added to 3.0 mL of anhydrous ethanol containing 0.0013 M perchloric acid, and the solution was allowed to stand until repetitive scans of the absorbance in the range 415–500 nm established that conversion of **1** to **6** was complete.[8] The desired volume of a concentrated solution of MCPBA in ethanol was then added by microsyringe, and the oxidation of **6** was followed by measuring the decrease in optical density with time at 415 nm.

Reaction of 3 with 1. A 60% dioxane solution of **1** (10^{-4} M) and the appropriate amount of perchloric acid and lithium perchlorate (or dichloroacetate buffer) was carefully degassed, and 3.6 mL of this solution was transferred under nitrogen in an Aldrich Atmosbag into a 1-cm spectrophotometer cell that was then sealed with a stopper having a rubber septum. In the same Atmosbag an aliquot of a 0.02 M solution of $o\text{-}O_2NC_6H_4Se^-$, prepared as described above by the reduction of $o\text{-}O_2NC_6H_4SeCN$, was drawn into a microsyringe and the tip of the needle was sealed temporarily with a rubber cap. The spectrophotometer cell was placed in the thermostated cell compartment of a UV–visible spectrophotometer, and, once thermal equilibrium had been reached, the reaction was initiated by insertion of the needle of the microsyringe through the septum of the cell stopper and injection of the solution of the anion of **3**, followed by good mixing. The reaction of **3** with **1** was monitored by observing the decrease in absorbance with time at 450 nm.

Registry No. **1**, 56790-60-4; **2** (ethyl ester), 99655-78-4; **3**, 69612-65-3; **4**, 35350-43-7; **5**, 84250-76-0; **6**, 99642-70-3; MCPBA, 937-14-4; H_2O_2, 7722-84-1; ArSeCN, 51694-22-5; $ArSe^-$, 54019-83-9; $ArSeCH_2Ph$, 59079-21-9.

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[18] Behagel, O.; Hoffman, K. *Chem. Ber.* **1939**, *72*, 697.

[19] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1. p 333.