spectrum with the assignments is shown in Figure 1 (supplementary material).

Sulfonation Reactivities. The relative substrate reactivities have been determined from the initial slopes of graphs of log |ArH| vs. the reaction time, using $\ln \{|ArH|/|ArH|_0\} = -_{ps}k_1 t$, thus presuming pseudo first order kinetics. For 3 and 4 the plots of log $\{|ArH|/|ArH|_0\}$ vs. time were linear up to ca. 50% substrate conversion. The reactivity of 1 is so high that only the tail of the plot, >89% substrate conversion, could be measured. For the calculation of the $_{ps}k_1$ of 1 it was assumed that the relative curvature is the same for 1 and 3. The reaction mixtures were made up by adding a solution of 0.25 mmol of the [10]annulene in 0.40 mL dioxane-$^2H_8$ at 35 °C to a homogeneous solution of 0.50 mmol SO_3 in 1.00 mL of dioxane-$^2H_8$ and subsequent homogenization at 35 °C.

Preparation of Monocations. The method of preparation of the 1,6-methano[10]annulenium ions and the recording of their ^1H NMR spectra was similar as described for the monocations of the methylphenanthrenes.[36] The assignment of ^1H NMR signals of the cations of 3 and 4 were made by comparison with the fully assigned ^1H NMR spectrum of protonated 1.[13] The doublets at lowest and highest field in the vinylic part of the spectrum were taken to be the hydrogens para and peri to the protonated center, respectively. The triplet at 7.82 ppm in the spectrum of protonated 3 is ascribed to H(9) of 8 [and not to H(4) of 7], as its chemical shift is very similar to that of H(4) of 6. More important the difference between the chemical shifts of the low field parts of the AB absorptions of the protonated centers of the two annulenium ions is much greater (0.33 ppm) than that between the two corresponding high field parts (0.05 ppm, cf. Table IV). The highest shielded hydrogen, viz., that at 4.15 ppm, is therefore ascribed to the hydrogen in closest vicinity to the electronegative fluorine. Thus the 4.15 + 4.9[5] AB system is ascribed to $C(2)H_2$ of 7 and the 4.48 + 4.90 AB to $C(7)H_2$ of 8, and the 4.15 and 4.48 absorptions are ascribed to the *endo*-hydrogens and the 4.9 ppm absorptions to the *exo*-hydrogens.

Acknowledgment. The authors thank Prof. Dr. E. Vogel for stimulating this study and for generously supplying samples of the various [10]annulenes.

Registry No. 1, 2443-46-1; 2-MeO-5-HO_3S-1, 90913-12-5; 3, 71671-89-1; 3-SO_3H (isomer 1), 90913-13-6; 3-SO_3H (isomer 2), 91048-23-6; 4, 19026-91-6; 5, 58853-55-7; 8, 90900-68-8.

Supplementary Material Available: ^1H NMR spectral data of 1, 3-5 (in $[^2H_8]$dioxane) their sulfo products (in $[^2H_6]$acetonitrile) the cations 6-9 in HSO_3F/SO_2ClF, and the 250-MHz ^1H shift correlated 2D NMR spectrum of the mixture of the potassium salts of the 2- and 7-sulfonic acids of 3 (in $[^2H_6]$acetonitrile) (5 pages). Ordering information is given on any current masthead page.

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Mechanism of the Hydrolysis of *o*-Nitro- and *o*-Benzoylbenzeneselenenic Anhydrides[1]

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The hydrolyses (eq 1) of *o*-nitro- (**2a**) and *o*-benzoylbenzeneselenenic (**2b**) anhydrides to the corresponding selenenic acids (**1a** and **1b**) have been studied kinetically over a range of pH in a series of buffers in 60% dioxane. Both hydrolyses require acid catalysis. The hydrolysis of **2a** exhibits general-acid catalysis, with a *nonlinear* Brønsted plot where $\alpha = 0$ for catalyzing acids with a $pK_a \leq pK_a$ of trichloroacetic acid and $\alpha = 0.7$ for acids with $pK_a \geq pK_a$ of dichloroacetic acid. This behavior seems best accounted for by a preassociation mechanism (eq 8) in which addition of water to a selenium in the encounter complex **2a**·HA gives a highly unstable intermediate ($I^{\pm}$·HA) that then collapses to products (step k_p) via a proton transfer to the departing *o*-$O_2NC_6H_4SeO$- group that is coincident with the cleavage of the Se–OSe bond. With the stronger acid catalysts formation of $I^{\pm}$·HA from **2a**·HA plus water is rate determining and $\alpha = 0$. With weaker acids as catalysts the transfer of the proton within $I^{\pm}$·HA becomes rate determining, and $\alpha = 0.7$. The hydrolysis of the *o*-benzoyl compound (**2b**) is much faster than that of **2a** and exhibits specific-H^+ catalysis under most reaction conditions. The pH–rate profile for the H_3O^+-catalyzed hydrolysis of **2b** shows an inflection between pH 2.5 and 4. This pH–rate profile, and the other aspects of the behavior of the hydrolysis, can be best explained by a mechanism (eq 10) in which the reactive intermediate (**3**) is the carbonyl hydrate of **2b**. In buffers at higher pH's buffer-catalyzed establishment of the **2b** + $H_2O \rightleftarrows$ **3** equilibrium is rapid, and H_3O^+-catalyzed conversion of **3** to products is rate determining; but in dilute HCl or $HClO_4$ H_3O^+-catalyzed formation of **3** from **2b** becomes rate determining. The stabilization of **2a** (and **2b**) by direct interaction of the *o*-NO_2 (or PhC(O)) group with selenium is thought to prevent facile, one-step displacement of ArSeO by a nucleophile and to be the reason that the two hydrolyses are forced to adopt the more complex mechanisms outlined above.

Selenenic acids are generated as reactive intermediates in a considerable number of reactions in organoselenium chemistry. For example, the widely used, olefin-forming oxidative elimination of an arylseleno group gives an alkene plus an areneselenenic acid (ArSeOH), and the subsequent fate of the selenenic acid (determined by the specific reaction conditions employed) can have a significant effect on the yield of alkene that is obtained.[2] Areneselenenic acids are also thought to be formed as reactive intermediates during the reduction of areneseleninic acids (Ar-SeO_2H) by a wide variety of reagents.[3] In physiological

(1) This research supported by the National Science Foundation, Grant CHE-79-18877.

(2) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1967. (b) Hori, T.; Sharpless, K. B. *Ibid.* **1978**, *43*, 1689.

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chemistry a selenenic acid functionality has been postulated[4] to occupy a central position in the reaction cycle for the action of the key enzyme, glutathione peroxidase. All of this suggests that information about the mechanisms of the reactions of selenenic acids themselves, and about factors influencing their reactivity, should be of considerable value.

Unfortunately, despite the frequency with which they appear as reactive intermediates, little of a detailed nature is known about the mechanisms of the various important reactions of selenenic acids (such as disproportionation, or reactions with oxidizing or reducing agents). This lack of information is doubtless due to the fact that most selenenic acids are too unstable to be isolable, thus making straightforward study of the mechanisms of their reactions in the usual fashion impossible.

Some years ago Rheinboldt and Giesbrecht[5] reported what they believed was the successful isolation of two monosubstituted benzeneselenenic acids, *o*-nitrobenzeneselenenic acid (**1a**) and *o*-benzoylbenzeneselenenic acid (**1b**). These two compounds, the only reported examples of isolable areneselenenic acids of simple structure, appeared ideal substrates to use for studies of the mechanisms of some of the principal reactions of areneselenenic acids.

Upon repeating the preparation of these compounds we found that they are not the selenenic acids, as thought by Rheinboldt and Giesbrecht,[5] but are instead the corresponding selenenic anhydrides, **2a** and **2b**.[6,7] Solutions of selenenic acids **1a** and **1b** can, however, be easily generated from the anhydrides by acid-catalyzed hydrolysis of **2a** and **2b** (eq 1).[6]

$$\underset{\mathbf{2}}{\mathrm{ArSeOSeAr}} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} 2\underset{\mathbf{1}}{\mathrm{ArSeOH}} \qquad (1)$$

a, Ar = *o*-$O_2NC_6H_4$
b, Ar = *o*-$PhC(O)C_6H_4$

The present paper reports the results of a kinetic study of the hydrolyses of **2a** and **2b** over a range of pH in 60% dioxane as solvent. The two hydrolyses exhibit unexpected, and mechanistically significant, differences in behavior. These are described and discussed.

An accompanying paper[8] deals with a study of the kinetics of the reactions of both the two anhydrides (**2a** and **2b**) and the two selenenic acids (**1a** and **1b**) with a simple alkanethiol in the same medium. Reaction of a selenenic acid function with the thiol group of glutathione has been suggested[4] to be one of the important steps in the reaction cycle for the enzyme glutathione peroxidase.

Results

The hydrolyses of selenenic anhydrides **2a** and **2b** to the corresponding selenenic acids (eq 1) in 60% dioxane (v/v) as solvent are conveniently followed by monitoring the decrease in the absorbance of the solution at longer wavelengths that accompanies the hydrolysis (430–460 nm for **2a**, 410–440 nm for **2b**).[6] Once the hydrolysis is complete there is no further change in the absorbance of the solution over an extended period of time,[9] indicating that dilute (10^{-4} M) solutions of selenenic acids **1a** and **1b** are quite stable. Therefore, although the compounds actually isolated by Rheinboldt and Giesbrecht[5] were the anhydrides (**2a** and **2b**) rather than the acids (**1a** and **1b**), their claim that **1a** and **1b** are stable areneselenenic acids is indeed correct.

The kinetics of the hydrolyses of **2a** and **2b** were studied at 25 °C. The disappearance of both anhydrides followed good first-order kinetics as evidenced by the excellent linearity of plots of log ($A - A_\infty$) vs. time, and experimental first-order rate constants for hydrolysis, k_{hyd}, were obtained from the slope of these plots.

Kinetics of Hydrolysis of 2a. Rates of hydrolysis of **2a** were determined at constant ionic strength (0.02) in a series of buffers, and in dilute perchloric acid solutions,

Table I. Kinetics of the Hydrolysis of *o*-Nitrobenzeneselenenic Anhydride (2a) in 60% Dioxane at 25 °C[a]

reactn conditions	pH[b]	[HA], M	[A⁻], M	[$LiClO_4$], M	$k_{hyd} \times 10^3$, s^{-1}
0.02 N $HClO_4$	1.7	0.020		0.00	8.1
0.01 N $HClO_4$	2.0	0.010		0.010	3.7
1:1 CF_3CO_2H–$CF_3CO_2^-$ buffer	2.8	0.020	0.020	0.00	8.3
		0.015	0.015	0.005	6.8
		0.010	0.010	0.010	4.3
		0.005	0.005	0.015	2.5
1:1 $PhSO_3H$–$PhSO_3^-$ buffer	3.3[c]	0.020	0.020	0.00	6.3
		0.015	0.015	0.005	4.6
		0.010	0.010	0.010	3.2
		0.005	0.005	0.015	1.7
1:1 Cl_3CCO_2H–$Cl_3CCO_2^-$ buffer	3.3[c]	0.020	0.020	0.00	7.0
		0.015	0.015	0.005	5.4
		0.010	0.010	0.010	3.5
		0.005	0.005	0.015	1.7
1:1 Cl_2CHCO_2H–$Cl_2CHCO_2^-$ buffer	4.03	0.020	0.020	0.00	1.4
		0.015	0.015	0.005	1.0
		0.010	0.010	0.010	0.71
		0.005	0.005	0.015	0.36
1:1 $NCCH_2CO_2H$–$NCCH_2CO_2^-$ buffer	5.1[c]	0.020	0.020	0.00	0.32
		0.015	0.015	0.005	0.22
		0.010	0.010	0.010	0.14
		0.005	0.005	0.015	0.072
1:1 $ClCH_2CO_2H$–$ClCH_2CO_2^-$ buffer	5.48	0.020	0.020	0.00	0.24
		0.015	0.015	0.005	0.16
		0.010	0.010	0.010	0.093
		0.005	0.005	0.015	0.050
2:1 HCO_2H–HCO_2^- buffer	5.80	0.040	0.020	0.00	0.71
		0.030	0.015	0.005	0.43
		0.020	0.010	0.010	0.21
		0.010	0.005	0.015	0.075
1:2 HCO_2H–HCO_2^- buffer	6.40	0.010	0.020	0.00	0.17
		0.0075	0.015	0.005	0.114
		0.005	0.010	0.010	0.054
		0.0025	0.005	0.015	0.019

[a] Initial concentration of **2a** in all runs, 5×10^{-5} M. [b] pH's of trifluoroacetate, dichloroacetate, monochloroacetate, and formate buffers calculated from known (ref 10) pK_a's for these acids in 60% dioxane; pH's of other buffers estimated (see footnote c). [c] pH estimated from pK_a of acid in water and assumption that ΔpK_a for transfer from water to 60% dioxane is 2.7 pK units (the average value for ΔpK_a for the transfer of weak acids HA from water to 60% dioxane[10]).

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(9) After the hydrolysis was complete solutions were observed for periods of time up to 10 times the half-life for the hydrolysis. During this time there was no detectable change in the absorption spectrum of the solutions.

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Table II. Catalytic Constants for Catalysis of the Hydrolysis of 2a by Various Acids in 60% Dioxane at 25 °C

acid	pK_a in 60% dioxane	k_{HA}, M^{-1} s^{-1}	k_2 (eq 2b),[c] M^{-2} s^{-1}
H_3O^+	−1.30	0.40	
CF_3CO_2H	2.8	0.39	*a*
$PhSO_3H$	3.3[b]	0.31	*a*
Cl_3CCO_2H	3.3[b]	0.34	*a*
Cl_2CHCO_2H	4.03	0.068	*a*
$NCCH_2CO_2H$	5.1[b]	0.013	0.105
$ClCH_2CO_2H$	5.48	0.0086	0.148
HCO_2H	6.10	0.0038	0.695

[a] Too small to measure. [b] pK_a estimated (see footnote *c* of Table I). [c] For definition of k_2 see eq 2b.

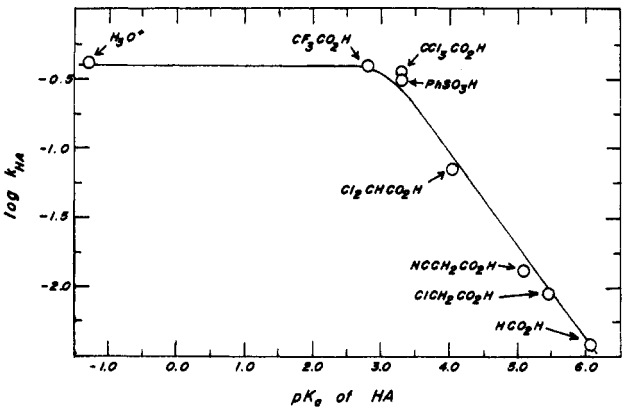


Figure 1. Brønsted plot of log k_{HA} vs. pK_a of HA for the general-acid catalyzed hydrolysis of *o*-nitrobenzeneselenenic anhydride (**2a**) in 60% dioxane.

covering a pH range from 6.4 (1:2 formic acid–formate buffer) to 1.7 (0.02 N $HClO_4$). The results are tabulated in Table I.

The data in Table I show that the hydrolysis of **2a** is general acid catalyzed, catalysis by both H_3O^+ and the various buffer acids being evident. For buffer acids more acidic than cyanoacetic acid k_{hyd} is given by an equation of the following form.

$$k_{hyd} = k_{H_3O^+}[H_3O^+] + k_{HA}[HA] \qquad (2a)$$

$k_{H_3O^+}$, both as evaluated (a) from the variation of k_{hyd} with $[H_3O^+]$ for the runs in 0.01 and 0.02 N $HClO_4$ and (b) from the intercept of plots of k_{hyd} vs. [HA] for the different buffers (and the pH of the buffers), is equal to 0.4 M^{-1} s^{-1}. Values of k_{HA}, the catalytic constants for the buffer acids, obtained from plots of k_{hyd} vs. [HA], are given in Table II. For the cyanoacetate, chloroacetate, or formate buffers the variation of k_{hyd} with buffer concentration (eq 2b) is slightly more complex.

$$k_{hyd} = k_{H_3O^+}[H_3O^+] + k_{HA}[HA] + k_2[HA][A^-] \qquad (2b)$$

The term $k_2[HA][A^-]$ representing catalysis by both buffer acid and its conjugate base makes a modest contribution to k_{hyd} in cyanoacetate and chloroacetate buffers and a sizeable one for the runs in formate buffers. For these three acids plots of $(k_{hyd} - k_{H_3O^+}[H_3O^+])/[HA]$ vs. $[A^-]$ were constructed; their intercept at $[A^-] = 0.00$ is equal to k_{HA}, their slope to k_2. The values of k_{HA} for these three acids are also given in Table II.

Figure 1 is a plot of log k_{HA} vs. pK_a. This Brønsted plot is *nonlinear*, with $\alpha = 0$ for acids having a $pK_a \leq pK_a$ of benzenesulfonic acid, and $\alpha = 0.7$ for acids having a $pK_a \geq pK_a$ of dichloroacetic acid.

Kinetics of Hydrolysis of 2b. Rates of hydrolysis of **2b** were also determined at constant ionic strength (0.02) in a series of buffers and in dilute perchloric and hydrochloric acid solutions. The results are collected in Table III.

Table III. Kinetics of the Hydrolysis of *o*-Benzoylbenzeneselenenic Anhydride (2b) in 60% Dioxane at 25 °C[a]

reactn conditions	pH[b]	[HA], M	[A^-], M	[$LiClO_4$], M	$k_{hyd} \times 10^3$ s^{-1}
0.021 N HCl	1.67	0.021		0.00	15.8 × 10^3
0.020 N $HClO_4$	1.70	0.020		0.00	13.1 × 10^3
0.011 N HCl	1.96	0.011		0.009	8.4 × 10^3
0.010 N $HClO_4$	2.00	0.010		0.010	6.0 × 10^3
1:2 CF_3CO_2H–$CF_3CO_2^-$ buffer	3.1	0.010	0.020	0.00	2.5 × 10^3
		0.005	0.010	0.010	1.8 × 10^3
1:1 Cl_2CHCO_2H–$Cl_2CHCO_2^-$ buffer	4.03	0.020	0.020	0.00	2.3 × 10^2
		0.010	0.010	0.010	2.4 × 10^2
1:2 Cl_2CHCO_2H–$Cl_2CHCO_2^-$ buffer	4.33	0.010	0.020	0.00	1.4 × 10^2
1:1 H_3PO_4–$H_2PO_4^-$ buffer	4.8	0.020	0.020	0.00	36
1:1 $ClCH_2CO_2H$–$ClCH_2CO_2^-$ buffer	5.48	0.020	0.020	0.00	7.2
		0.015	0.015	0.005	7.2
		0.010	0.010	0.010	7.3
		0.005	0.005	0.015	7.7
1:1 HCO_2H–HCO_2^- buffer	6.10	0.020	0.020	0.00	1.4
		0.015	0.015	0.005	1.4
		0.010	0.010	0.010	1.5
		0.005	0.005	0.015	1.4
1:1 AcOH–AcO^- buffer	7.44	0.020	0.020	0.00	0.083
		0.010	0.010	0.010	0.083

[a] Initial concentration of **2b**, 3.5-5.0 × 10^{-5} M. [b] pH's calculated from known (ref 10) pK_a's in 60% dioxane of acids used for buffers.

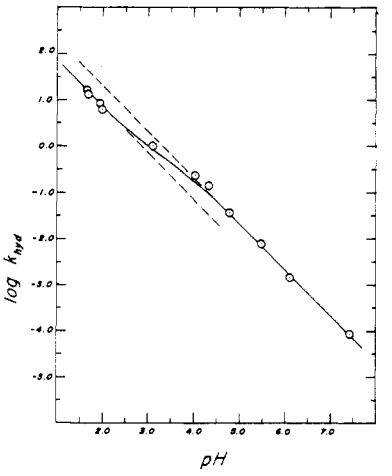


Figure 2. pH–rate profile for the H_3O^+-catalyzed hydrolysis of *o*-benzoylbenzeneselenenic anhydride (**2b**) in 60% dioxane: calculated from eq 3 (—); experimental data (⊙).

Comparison of the results for **2b** with those for **2a** (Table I) reveals several major differences. Except in trifluoroacetate buffers, catalysis of the hydrolysis of **2b** by buffer is not detectable, and even with trifluoroacetate it is of only modest importance compared to catalysis by H_3O^+. In contrast to the behavior of **2a**, catalysis of the hydrolysis of **2b** is due under all conditions, either exclusively, or almost entirely, to H_3O^+. Also $k_{H_3O^+}$ for **2b** is over three orders of magnitude larger than $k_{H_3O^+}$ for **2a**, so that the hydrolysis of **2b**, particularly in the more acid solutions, is very much faster than that of **2a**.

Figure 2 shows the pH–rate profile for the H_3O^+-catalyzed hydrolysis of **2b**. Between pH 2.5 and 4 there is a definite inflection in the plot of log k_{hyd} vs. pH. The data for buffers of pH ≥ 4.0 fall on a line given by the relation: $k_{hyd} = 2.2 \times 10^3\, a_{H^+}$. On the other hand, the data for dilute

perchloric and hydrochloric acid solutions fit the expression: $k_{hyd} = 0.72 \times 10^3\ a_{H^+}$. The solid line in the figure is that calculated for the following expression.

$$k_{hyd}\ (\text{for } \mathbf{2b}),\ s^{-1} = \frac{2.2 \times 10^3\ a_{H^+} + 3.5 \times 10^6\ a_{H^+}{}^2}{1 + 4.8 \times 10^3\ a_{H^+}} \quad (3)$$

Discussion

Acid catalysis is required for the hydrolysis of either **2a** or **2b** to occur at a reasonable rate; a spontaneous hydrolysis reaction is not kinetically significant for either anhydride. The character of the acid catalysis of the two hydrolyses is, however, quite different.

The hydrolysis of **2a** exhibits general-acid catalysis, and, what is most interesting, a plot of log k_{HA} vs. the pK_a of HA (Figure 1) gives a *nonlinear* Brønsted plot where α = 0 for acids with p$K_a \le$ pK_a of trichloroacetic acid and α = 0.7 for acids with p$K_a \ge$ pK_a of dichloroacetic acid. Nonlinear Brønsted plots where one of the legs has α (or β) = 0 have been encountered in a number of general-acid (or base) catalyzed reactions, and, thanks to the extensive and incisive work of Jencks and his collaborators,[11] their detailed mechanistic interpretation is now well understood. The particular behavior exhibited by the hydrolysis of **2a** (one leg with α = 0, and the other with $\alpha < 1$) is consistent with that expected for a preassociation mechanism of the type in eq 4. In this mechanism, as in other

$$\mathbf{2a} + HA \underset{}{\overset{K_{assoc}}{\rightleftharpoons}} \mathbf{2a}\cdot HA \quad (4a)$$

$$H_2O + \mathbf{2a}\cdot HA \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} I\cdot HA \xrightarrow{k_p} X^+ + \mathbf{1a} + A^- \quad (4b)$$

$$I\cdot HA \xrightarrow{\text{fast}} \mathbf{1a} + H^+$$

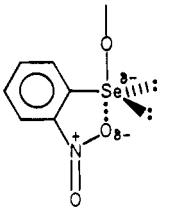
"preassociation"[11] mechanisms, K_{assoc} is assumed to be independent of the pK_a of HA. Step k_p involes a proton transfer from HA to I that is synchronous with other covalent changes in I; the stronger the acid HA, the faster the rate of step k_p. Step k_{-a} is very rapid. For the weaker catalyzing acids (those with p$K_a \ge$ pK_a of Cl_2CHCO_2H) $k_p < k_{-a}$, step k_p is rate determining, and $k_{HA} = k_p(k_a/k_{-a})K_{assoc}$. Since the proton is only partially transferred from HA to I in the transition state for step k_p, the Brønsted α for k_p (and therefore for k_{HA}) is <1.0. As the strength of the catalyzing acid increases sufficiently k_p becomes larger than k_{-a}. At that point (apparently reached when the p$K_a \le$ pK_a of Cl_3CCO_2H) step k_a (rather than k_p) will become rate determining. Since neither K_{assoc} nor k_a are dependent on the pK_a of HA, k_{HA} (now equal to k_aK_{assoc}) is no longer dependent on the pK_a of HA, and α = 0.

Acid catalysis of the hydrolysis of **2b** is due almost entirely to catalysis by H_3O^+. Figure 2 reveals that the pH–rate profile for the H_3O^+-catalyzed hydrolysis of **2b** has an inflection between pH 2.5 and 4. The pH–rate profile in Figure 2, which resembles that for semicarbazone formation from ketones,[12] can be easily explained if the H_3O^+-catalyzed hydrolysis of **2b** involves a mechanism of the general type shown in eq 5 where the reactive intermediate (**3**) is a carbonyl hydrate (>C(OH)$_2$)of **2b**. At

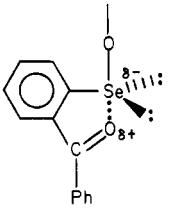
$$\mathbf{2b} + H_2O \underset{k_{-c}a_{H^+}\ \ k_{-bf}[buffer]\ \ k_{-0}}{\overset{k_0\ \ k_{bf}[buffer]\ \ k_ca_{H^+}}{\rightleftharpoons}} \mathbf{3} \xrightarrow{k_{II}a_{H^+}} \text{products} \quad (5)$$

higher pH's H_3O^+-catalyzed conversion of **3** to products ($k_{II}a_{H^+}$) is rate determining, and H_3O^+-catalyzed formation of **3** ($k_ca_{H^+}$) is kinetically unimportant compared to its formation via steps k_0 and k_{bf}[buffer]. As the pH decreases, $k_{II}a_{H^+}$, $k_{-c}a_{H^+}$, and $k_ca_{H^+}$ all increase linearly with a_{H^+}. Whenever reaction conditions are employed where $k_ca_{H^+} > (k_0 + k_{bf}[buffer])$, such as dilute solutions of $HClO_4$ or HCl, then, provided $k_{II} > k_{-c}$, the observed rate will be less than predicted from extrapolation of the data for lower pH's by the factor $[1/1 + (k_{II}/k_{-c})]$.

Both **2a** and **2b** are significantly more stable than most areneselenenic anhydrides. X-ray crystallographic studies of other stabilized ortho-substituted benzeneselenenyl derivatives[13] indicate that direct interaction of the ortho functional group with selenium, as in **4a** and **4b**, is the



4a



4b

source of this stabilization and that the preferred conformation for **4a** and **4b** will be those shown—a trigonal bipyramid with the most electronegative ligands, the anhydride oxygen and the coordinating oxygen of the ortho group, occupying the two apical positions. Austad[14] has shown that such coordination of an *o*-nitro group to selenium results in a >10^6-fold decrease in the rate at which an areneselenenyl halide undergoes nucleophilic substitution. It does so because the oxygen atom of the nitro group, by occupying one apical position, prohibits facile, one-step displacement (eq 6a) of the halide from the other

$$Nu^- + ArSeX \rightarrow \left[Nu^{\delta-}\cdots Se(Ar)\cdots X^{\delta-}\right] \rightarrow ArSeNu + X^- \quad (6a)$$

$$Nu^- + ArSe{-}OSeAr \longrightarrow ArSeNu + ArSeO^- \quad (6b)$$

apical position. We would therefore expect that direct, one-step displacement of ArSeO by a nucleophile (eq 6b) should not be possible for either **2a** or **2b** and that their reactions with nucleophiles will proceed via more complex mechanisms.

For the hydrolysis of **2a** and **2b** the path followed depends upon whether the ortho functional group can itself react readily and reversibly with water. If, as with **2b**, it can, then the mechanism employed is one in which there is reversible formation of a carbonyl hydrate intermediate that then undergoes an intramolecular reaction at selenium that leads on to products. If it can't, then the mechanism that is followed is the one that will now be outlined for **2a**. (The detailed mechanism for **2b** will be presented subsequently.)

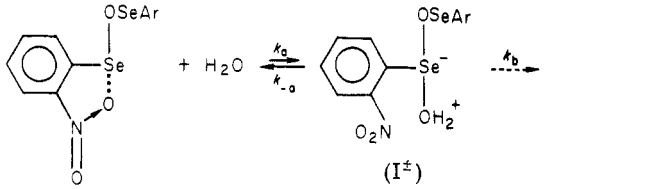
(11) (a) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425. (b) Barnett, R. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 6758. (c) Jencks, W. P.; Salvesen, K. *Ibid.* **1971**, *93*, 1419. (d) Sayer, J. M.; Jencks, W. P. *Ibid.* **1973**, *95*, 5637. (e) Fox, J. P.; Jencks, W. P. *Ibid.* **1974**, *96*, 1436. (f) Rosenberg, S.; Silver, S. M.; Sayer, J. M.; Jencks, W. P. *Ibid.* **1974**, *96*, 7986. (g) Gilbert, H. F.; Jencks, W. P. *Ibid.* **1977**, *99*, 7931. (h) Cox, M. M.; Jencks, W. P. *Ibid.* **1978**, *100*, 5956. (i) *Ibid.* **1981**, *103*, 572.

(12) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 4319.

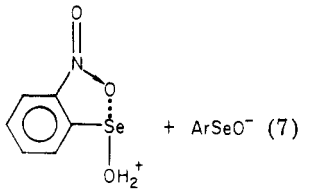
(13) Eriksen, R.; Hauge, S. *Acta Chem. Scand.* **1972**, *26*, 3153.

(14) (a) Austad, T. *Acta Chem. Scand., Ser. A* **1975**, *29A*, 895. (b) Austad, T. *Ibid.* **1977**, *31A*, 93.

If **2a**, rather than **2a**·HA, were to react with water, the first step would be the replacement of the *o*-NO_2 group as a ligand by H_2O (step k_a, eq 7). The resulting intermediate

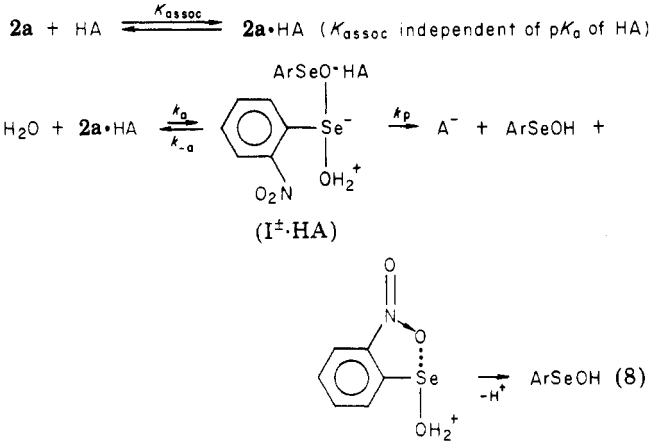


($I^{\pm}$)



(k_b <<< k_{-a})

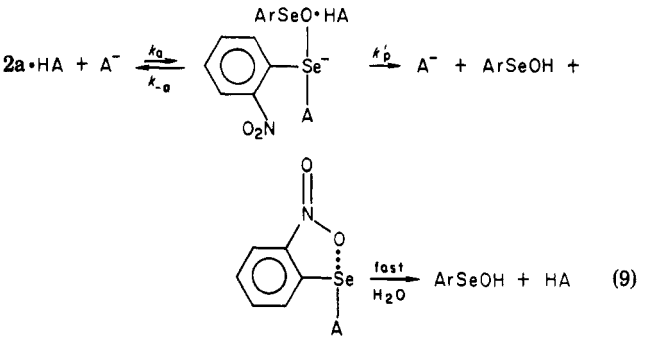
$I^{\pm}$ could then expel either H_2O (step k_{-a}), regenerating reactants, or $ArSeO^-$ (step k_b), leading to products. We believe step k_{-a} is extremely rapid, and is, in fact, so much faster than step k_b that the mechanism in eq 7 is unable to provide a kinetically significant route for hydrolysis.[15] Acid catalysis of the departure of the ArSeO group is therefore needed in order for its loss to be adequately competitive in rate with k_{-a}. However, the lifetime of $I^{\pm}$ is so short that general-acid catalysis of the departure of ArSeO must employ the preassociation mechanism shown in eq 8, i.e., the catalyzing acid HA must already be present



($I^{\pm}$·HA)

in the encounter complex when $I^{\pm}$ is formed.[16] With acids whose $pK_a \leq pK_a$ of Cl_3CCO_2H, $k_p > k_{-a}$, and the reaction, while general-acid catalyzed, has a rate independent of the pK_a of the catalyzing acid. With weaker acids ($pK_a \geq pK_a$ of Cl_2CHCO_2H) $k_p < k_{-a}$, and step k_p is rate determining. The fact that $\alpha = 0.7$ (rather than 1.0) for such acids shows that the transfer of the proton from HA to $I^{\pm}$ is concerted with the cleavage of the Se–O bond, rather than there first being complete transfer of the proton (giving IH^+), followed by cleavage of IH^+. We presume that the conversion of $I^{\pm}$·HA to products is enforced to be concerted because of the extreme instability (lifetime less than a vibration period) of IH^+.

The $k_2[HA][A^-]$ term (eq 2b) that contributes to k_{hyd} in cyanoacetate, chloroacetate, and, especially, formate buffers is thought to be due to a variant of the mechanism in eq 8, with A^-, rather than water, acting as the nucleophile (eq 9). The variation in k_2 with buffer is consistent



with this picture. Variations in the basicity and steric requirements of A^- would be expected to have a larger effect on k_a'/k_{-a}' than variations in the acidity of HA have on k_p'. Since $k_2 = k_p'(k_a'/k_{-a}')K_{assoc}$, k_2 for formate (HCO_2^- is the smallest and most basic A^-) is considerably larger than k_2 for chloroacetate, and that, in turn, is somewhat larger than k_2 for cyanoacetate.

Several considerations demonstrate that the mechanism for the hydrolysis of **2b** cannot be the same as that (eq 8) for **2a**. While the requirement for acid catalysis suggests that protonation of the ArSeO group is also required in the hydrolysis of **2b** to assist the departure of that group, the fact that only catalysis by H_3O^+ is observed under almost all reaction conditions indicates that in the case of **2b** the system achieves equilibrium with respect to this proton transfer; yet, at the same time, the H_3O^+-catalyzed hydrolysis of **2b** is *over three orders of magnitude faster* than that of **2a**. Further, there is the inflection in the pH–rate profile for H_3O^+-catalyzed hydrolysis of **2b** between pH 2.5 and 4. There is no way to reconcile these observations with a mechanism for **2b** equivalent to that just outlined for **2a**. We can only conclude that there is available to **2b** a reaction path not available to **2a**, and that this pathway provides a much faster rate from **2b** to hydrolysis products than would be possible if **2b** were to undergo hydrolysis via the type of mechanism shown in eq 8. This reaction path must be one that will exhibit catalysis only by H_3O^+ under almost all of the reaction conditions employed and that will be able to account for the observed inflection in the pH–rate profile. It should also be one that is straightforward and reasonable from a chemical point of view.

We feel that the mechanism for **2b** shown in eq 10 meets these requirements. As in the hydration of other aldehydes and ketones,[17] the forward and reverse steps of the equilibrium between **2b** and **3** are presumed to be subject to buffer catalysis. In carboxylate buffers of pH ≥ 4 buffer-catalyzed establishment of the equilibrium between **2b** and **3** is rapid compared to the rate of H_3O^+-catalyzed conversion of **3** to products, and $k_{hyd} = k_{II}K_{eq}a_{H^+}C_{H_2O}$. While K_{eq} is probably quite small (given the usual magnitude of equilibrium constants for hydrate formation from ketones[17,18]), it should be orders of magnitude larger than (k_a/k_{-a}) in eq 8, and the mechanism in eq 10 can therefore

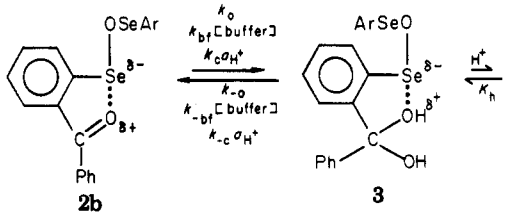
(15) In addition we believe that step k_{-a} is so rapid that a mechanism where there is proton transfer from $I^{\pm}$ to solvent (or another general base) is also unable to be involved.

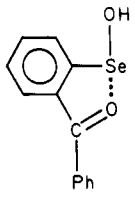
$$\mathbf{2a} + H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} I^{\pm} \underset{k_{-a}[BH^+]}{\overset{k_a[B]}{\rightleftharpoons}} HOSe(Ar)OSeAr \xrightarrow{k_b} ArSeOH + ArSeO^-$$

(16) Because of the low basicity of the anhydride oxygen in ArSeOSeAr, and the resulting extremely low equilibrium concentration of $ArSeO^+(H)SeAr$, the general-acid catalyzed, "preassociation" mechanism in eq 8 represents a kinetically more expeditious route for hydrolysis than the mechanism.

$$\mathbf{2a} + H^+ \rightleftharpoons \mathbf{2a}\text{–}H^+ \underset{f}{\overset{H_2O}{\rightleftharpoons}} IH^+ \rightarrow ArSeOH_2^+ + ArSeOH$$

(17) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1.
(18) Burkey, T. J.; Fahey, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 868.





(10)

$$k_{II} = k_{ii}K_h$$
$$K_{eq} = (k_0/k_{-0}) = (k_{bf}/k_{-bf}) = (k_c/k_{-c})$$

provide a much faster path to hydrolysis products for **2b** than would a mechanism of the type in eq 8.

The mechanism shown in eq 10 leads to the expression for k_{hyd} shown in eq 11a; this can be rearranged and rewritten in the form shown in eq 11b. In dilute hydrochloric

$$k_{hyd} = k_{II}a_{H^+}[(k_0 + k_c a_{H^+} + k_{bf}[\text{buffer}])/(k_{-0} + (k_{II} + k_{-c})a_{H^+} + k_{-bf}[\text{buffer}])]C_{H_2O} \quad (11a)$$

$$k_{hyd} = k_{II}K_{eq}a_{H^+}C_{H_2O}[(1 + (k_c/k_0)a_{H^+} + (k_{bf}/k_0) \times [\text{buffer}])/(1 + [(k_{II}/k_{-c}) + 1](k_c/k_0)a_{H^+} + (k_{bf}/k_0)[\text{buffer}])] \quad (11b)$$

and perchloric acid solutions (low pH and no buffer), $(k_c/k_0)a_{H^+} > 1$ and $(k_{bf}/k_0)[\text{buffer}] = 0$, so that k_{hyd} becomes eq 12. In such solutions k_{hyd}, while still proportional

$$k_{hyd}\ (\text{dilute } HClO_4 \text{ or HCl}) = (k_{II}K_{eq}a_{H^+}C_{H_2O})/(1 + (k_{II}/k_{-c})) \quad (12)$$

to a_{H^+}, will be smaller than predicted from extrapolation of the data for the higher pH buffers by the factor $1/[1 + (k_{II}/k_{-c})]$. Accordingly, the line of unit slope in Figure 2 for a plot of log k_{hyd} vs. pH for the high pH data lies above that for the low pH runs in dilute $HClO_4$ or HCl by an amount equal to log $[1 + (k_{II}/k_{-c})]$. From the results $(k_{II}/k_{-c}) = 2.0$ for **3**.

Rate constant k_c for the H_3O^+-catalyzed hydration of **2b** can be evaluated by rearranging eq 12 as shown below and substituting the known values of k_{hyd}/a_{H^+}, C_{H_2O}, and k_{II}/k_{-c}. The value of k_c for **2b**, 55 M^{-2} s^{-1} appears to be

$$k_c = \left[\frac{k_{hyd}(\text{dil } H^+)}{a_{H^+}}\right]\left[\frac{1 + (k_{-c}/k_{II})}{C_{H_2O}}\right] = 720\ M^{-1}\ s^{-1}\left[\frac{1 + 0.5}{20\ M}\right] = 55\ M^{-2}\ s^{-1}$$

several orders of magnitude larger than the rate constant for the H_3O^+-catalyzed hydration of acetone.[19] We suggest that this is because the substantial partial positive charge on the carbonyl oxygen in **4b** causes the rate of hydration of **2b** to be much larger than for an ordinary ketone.[21] To what extent this will also make K_{eq} for **2b** larger than for a simple ketone is not clear, since the partial positive charge on the Se-coordinated OH group in **3** may also cause k_{-c} for **3** to be considerably greater than for the hydrate of a typical ketone.

The mechanisms presented above for the acid-catalyzed hydrolyses of **2a** (eq 8) and **2b** (eq 10) are not only consistent with the kinetic features of the two hydrolyses, but, as will be seen in the accompanying paper,[8] they also fit easily into a single integrated picture with the mechanisms for the reaction of 1-butanethiol with both **2a** and **2b**, and **1a** and **1b**. An essential feature of both mechanisms is the fact that stabilization of the selenenic anhydrides by the ortho substituents in the fashion shown in **4a** and **4b** prevents a direct, one-step displacement of either ArSeO or $ArSeO^+H$ by the attacking nucleophile, thereby necessitating that an alternative mechanism be employed. Because of this the mechanisms in eq 8 and 10 should be representative only of what will be observed with other similarly "stabilized" selenenic anhydrides. The more commonly encountered, "reactive" areneselenenic anhydrides, such as PhSeOSePh, in all likelihood hydrolyze by a different and simpler mechanism. The need for acid catalysis of the departure of the ArSeO group, however, may well be a common feature of the hydrolyses of all areneselenenic anhydrides.

Experimental Section

Preparation and Purification of Materials. *o*-Nitrobenzeneselenenic anhydride (2a) was synthesized from *o*-nitrobenzeneseleninic acid in the manner described by Rheinboldt and Giesbrecht.[5a] Recrystallization of the crude product from benzene gave pure **2a**, mp 161–165 °C dec (lit.[5a] 165 °C dec).

***o*-Benzoylbenzeneselenenic anhydride (2b)** was prepared by the reduction of *o*-benzoylbenzeneseleninic acid[5b] with hydrazine following the procedure outlined by Rheinboldt and Giesbrecht.[5b] Final purification of **2b** was effected by treating the compound with carbon tetrachloride (~2 mL/g of **2b**) at room temperature, filtering to remove an insoluble impurity, and then precipitating pure **2b**, softening point 66–67 °C (lit.[5b] 65–70 °C), by the addition of 10 volumes of hexane.

After purification both **2a** and **2b** were stored in a dessicator at −20 °C when not being used. The evidence that the two compounds are the selenenic anhydrides (**2a** and **2b**), rather than the selenenic acids (**1a** and **1b**), as thought by Rheinboldt and Giesbrecht,[5] has been presented in earlier papers.[6,7]

Other Reagents. Dioxane was purified by the procedure described by Fieser and Fieser,[22] 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 kinetic runs was double distilled from glass. All other reagents used were of the highest degree of purity commercially available and were used without further purification.

Procedure for Kinetic Runs. All runs with **2a** and those with **2b** at pH ≥ 5.48 were followed by conventional spectrophotometry. The runs at pH ≤ 4.8 with **2b** were fast enough to require stopped-flow spectrophotometry.

A solution of the selenenic anhydride (**2a** or **2b**, 5×10^{-3} M) in anhydrous dioxane was prepared immediately prior to use. In the runs followed by conventional spectrophotometry 3.5 mL of a 60% dioxane solution containing the desired concentration of buffer (or dilute $HClO_4$) and lithium perchlorate was placed in a 1-cm spectrophotometer cell in the thermostatted cell compartment of a Cary Model 17 spectrophotometer. To this was then added by microsyringe with good mixing 35 μL of the solution

(19) The measurements of the H_3O^+-catalyzed rate of exchange of H_2O^{18} with $Me_2C{=}O$ in 90% acetone–10% water by Cohn and Urey[20] give $k_{H_3O^+}C_{H_2O}$ for hydration of acetone in that medium as 1.95 M^{-1} s^{-1}.

(20) Cohn, M.; Urey, H. C. *J. Am. Chem. Soc.* **1938**, *60*, 679.

(21) We also feel that this same factor could cause the Brønsted α associated with general-acid catalysis of the hydration of **2b** to be significantly smaller than the values found[17] for other carbonyl hydration reactions.

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

of the selenenic anhydride in anhydrous dioxane, and the progress of the hydrolysis was monitored by following the decrease in the absorbance of the solution at the appropriate wavelength (440 nm for **2a**, 425 nm for **2b**).

For the runs followed by stopped-flow spectrophotometry an aliquot of the solution of **2b** in dioxane was diluted 70-fold with 60% dioxane to prepare a solution of **2b** (7×10^{-5} M) in 60% dioxane that was then placed in one of the reservoir syringes of a Durrum-Gibson stopped-flow spectrophotometer. A 60% dioxane solution containing the desired buffer (or dilute HCl or $HClO_4$), plus any lithium perchlorate needed to maintain constant ionic strength, was placed in the other reservoir syringe. The hydrolysis of **2b** was initiated by mixing the two solutions, and the decrease in absorbance with time at 425 nm was recorded on a storage oscilloscope.

Registry No. **1a**, 56790-60-4; **1b**, 84250-81-7; **2a**, 84250-76-0; **2b**, 84250-80-6; **3b**, 90990-68-4.

Mechanism of the Reaction of Thiols with *o*-Nitro- and *o*-Benzoylbenzeneselenenic Acids and Anhydrides[1]

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Received December 15, 1983

The kinetics of the reaction of an alkanethiol (*n*-BuSH) with *o*-nitro- (**1a**) and *o*-benzoylbenzeneselenenic (**1b**) acids (eq 3) and with the corresponding selenenic anhydrides (eq 4, **2a** and **2b**) have been investigated over a range of pH in a series of buffers in 60% dioxane. The pH–rate profiles show that acid catalysis is not important for the reaction of either anhydride with the thiol, and a mechanism (eq 12) is proposed in which replacement of the stabilizing ortho substituent as a ligand by either *n*-BuSH or *n*-BuS^- is followed by loss of $ArSeO^-$ from the resulting reactive intermediate ($I^{\pm}$). On the other hand, reaction of the *o*-nitro acid (**1a**) with the thiol requires acid catalysis, presumably because OH is enough poorer a leaving group than ArSeO that its departure must be assisted by a proton transfer. Acid catalysis is also important at pH < 6 for the reaction of the *o*-benzoyl acid (**1b**) with *n*-BuSH. In this case, however, the mechanism of the acid-catalyzed reaction involves reversible formation of hemithioketal **7** by acid- and buffer-catalyzed addition of the thiol to the carbonyl group of **1b**, followed by specific-H^+ catalyzed intramolecular decomposition of **7**. The *o*-benzoyl acid also reacts much more readily than expected with *n*-BuS^-; a mechanism involving reaction of the thiolate ion with an intermediate (**8**) formed by reversible intramolecular addition of the SeOH to the >C=O group in **1b** is suggested.

Ganther[2] has proposed that reaction of a selenenic acid functional group with the thiol group of glutathione (GSH) to afford a selenenyl sulfide (eq 1) is one of the important

$$\text{E–SeOH} + \text{GSH} \rightarrow \text{E–SeSG} + \text{H}_2\text{O} \qquad (1)$$

steps in the reaction cycle for the action of the essential mammalian enzyme, glutathione peroxidase. We therefore felt that a study, using a simple model system, of the mechanism of the reaction between a thiol and a selenenic acid should be valuable, in that information about the behavior (formal kinetics, pH–rate profile, etc.) of this reaction could be helpful in suggesting factors likely to be important for the occurrence of the process in the glutathione peroxidase reaction cycle.

Most selenenic acids are, of course, too unstable to be isolated and purified. However, Rheinboldt and Giesbrecht[3] reported some years ago what they believed was the successful isolation and purification of two selenenic acids, *o*-nitrobenzeneselenenic acid (**1a**) and *o*-benzoylbenzeneselenenic acid (**1b**). Since **1a** and **1b** represented the only reported examples of isolable selenenic acids of relatively uncomplicated structure, they were selected as substrates for the contemplated study.

When we repeated the preparation and isolation of the compounds described by Rheinboldt and Giesbrecht,[3] we discovered[4] that the compounds isolated are actually the selenenic anhydrides (**2a** and **2b**), rather than the selenenic acids.[5] *Stable* dilute *solutions* of **1a** and **1b** in aqueous organic solvents can, however, be easily prepared from **2a** and **2b** by hydrolysis (eq 2).[4,6]

$$\underset{\substack{\textbf{2a},\ \text{Ar} = o\text{-}O_2NC_6H_4 \\ \textbf{2b},\ \text{Ar} = o\text{-}PhC(O)C_6H_4}}{\text{ArSeOSeAr} + \text{H}_2\text{O}} \xrightarrow{\text{H}^+} \underset{\substack{\textbf{1b},\ \text{Ar} = o\text{-}PhC(O)C_6H_4 \\ \textbf{1a},\ \text{Ar} = o\text{-}O_2NC_6H_4}}{2\text{ArSeOH}} \qquad (2)$$

The present paper reports the results of a study of the kinetics of the reaction of a simple thiol (eq 3, R = *n*-Bu) with **1a** and **1b** over a range of pH in 60% dioxane as solvent.

$$\text{ArSeOH} + \text{RSH} \xrightarrow{k_{RSH}} \text{ArSeSR} + \text{H}_2\text{O} \qquad (3)$$

In addition, since hydrolysis of **2a** and **2b** (eq 2) is usually slower than their rate of reaction with *n*-BuSH (eq 4, R = *n*-Bu) we have also been able to study the kinetic behavior of eq 4 independently under most of the same

$$\text{ArSeOSeAr} + \text{RSH} \xrightarrow{k_{RSH}'} \text{ArSeSR} + \text{ArSeOH} \qquad (4)$$

reaction conditions for which kinetic data were obtained on eq 3. The two reactions, eq 3 and 4, exhibit marked differences in pH–rate profile and in the influence of the Ar group on rate. The reaction of the *o*-nitro acid (**1a**) also shows significantly different mechanistic behavior than is found for the *o*-benzoyl acid (**1b**).

(1) This research supported by the National Science Foundation, Grant CHE-79-18877.

(2) Ganther, H. E. *Chem. Scr.* **1975**, *8A*, 79.

(3) (a) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 666. (b) Rheinboldt, H.; Giesbrecht, E. *Ibid.* **1956**, *89*, 631.

(4) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *Tetrahedron Lett.* **1982**, *23*, 3323.

(5) Reich, H. J.; Willis, W. W., Jr.; Wollowitz, S. *Tetrahedron Lett.* **1982**, *23*, 3319.

(6) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.*, preceding paper in this issue.

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