The plateau between pH 1 and 2.5 can involve a spontaneous ring closure of the carboxylic acid. But this reaction is made difficult both by the low electrophilicity of the carboxylic group and by the poor nucleophilicity of the amidic nitrogen. However, if the base-catalyzed reaction involves the enolate anion, it may exist as a small quantity in the enolic form of the ureido group, more nucleophilic than the amide which can cyclize by a rate-determining uncatalyzed reaction.

The acid-catalyzed reaction at pHs less than 1 can involve the spontaneous ring closure of the enolic form of the acid protonated on the carboxylic group.

In the hydrochloric acid solution where the solvent deuterium isotope effect has been measured, $\alpha = 1$ and $k_{IS} = k_{EH}K_{a3}/K'_a$. The lack of significant kinetic solvent isotope effects ($k_{EH}/k_{ED} \simeq 1$) suggests that no proton transfer occurs in the cyclization of the enol. Then, the experimental kinetic isotope effect of 1.0 can be assigned to a cancelling of the equilibrium isotope effects on K_{a3} and K'_a.

The mechanism proposed here for the specific base-catalyzed reaction implies that the breaking of T^- to the products with departure of OH^- is faster than its return to the reactants with leaving of an ureido anion. This suggestion is consistent with the relative basicities of OH^- ($pK_a = 15.97$) and of the *N*-isopropylureido group ($pK_a \simeq 18$ for the *N*-methylurea).[20]

The relative basicities of the leaving groups were opposite in the formation of iprodione: the ureido anion bearing an aromatic substituent was less basic than the hydroxide anion and the rate-determining step was then the acid-catalyzed leaving of OH^-.

The nucleophilic attack of an ureido anion on a carboxylate group by a specific base-catalyzed reaction has been proposed by Hegarty and Bruice[19] for the cyclization of the 2-ureido benzoate while Kirby et al. have suggested a specific base–general acid catalyzed reaction leading to an intermediate similar to T^- for the cyclization of 2,2,3,5-tetramethylhydantoic acid.[16]

In conclusion, it appears that very different kinetic results for the formation of iprodione and that of its isomer lead to very similar mechanisms. Both involve the reaction of the enolate anion and are different only by the rate-determining step.

Acknowledgment. We thank Dr. A. J. Kirby for helpful discussions and Miss C. Vidal for technical assistance. This paper formed part of a thesis by O. Belafdal.

Supplementary Material Available: Rate data for the cyclization of *N*-[(3,5-dichloroanilino)carbonyl]-*N*-[(isopropylamino)carbonyl]glycine and for the formation of iprodione and its isomer in HCl solutions and buffers (Tables S1 and S2) and example of determination of k_{IP} and k_{IS} in acetate buffer (Tables S3 and S4) (9 pages). Ordering information is given on any current masthead page.

(19) Hegarty, A. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1970**, *92*, 6575–6588.

(20) Molday, R. S.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6739–6745.

Equilibrium and Kinetic Studies of Some Reactions of 1-Anthraquinonesulfenic Acid and Its Methyl Ester[1]

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1-Anthraquinonesulfenic acid (**2**) is a stable arenesulfenic acid. Its pK_a, and the products and kinetics of its reactions, and those of its methyl ester (**3**), with both a thiol (*n*-BuSH) and *m*-chloroperoxybenzoic acid (MCPBA), have been determined. The results are compared with those for the corresponding reactions of two stable areneselenenic acids (**1a** and **1b**). The pK_a of **2** (7.51) shows it to be ~3 p*K* units *stronger* acid than *o*-$O_2NC_6H_4SeOH$ (**1a**). Reaction of **2** and **3** with *n*-BuSH occurs at comparable rates and gives *n*-butyl 1-anthraquinonyl disulfide (**5**) via a reaction that is acid catalyzed. The rate of reaction of **2** with the thiol is ~10^4 *slower* than the rate of reaction of the structurally analogous areneselenenic acid, *o*-$PhC(O)C_6H_4SeOH$ (**1b**). The probable reason for this large difference in rates is outlined. The difference in the rates of oxidation of **2** and **1b** by MCPBA is much smaller, the selenenic acid being oxidized only 6 times faster than **2**. Just as was found with selenenic acid **1a** and its methyl ester, the rate of oxidation of sulfenic acid **2** by MCPBA is much faster than the rate of oxidation of its methyl ester.

Sulfenic (RSOH) and selenenic (RSeOH) acids play important roles as reactive intermediates in organosulfur and organoselenium chemistry, respectively. Because the vast majority are too unstable to be isolated, study of their chemistry and the mechanisms of their reactions in the normal fashion is not possible, and, as Davis et al.[3] have pointed out, much of our knowledge of their reactions has been derived indirectly, via rationalization of end products.

In recent years Davis and his co-workers[3,4] have used flash vacuum pyrolysis (FVP) to generate a variety of unstable sulfenic acids. These were deposited on a cold finger at −196 °C, and their chemistry was then explored

(1) This research supported by the National Science Foundation.
(2) (a) University of Denver. (b) Texas Tech University.
(3) Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3647.

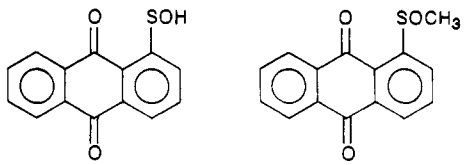
(4) (a) Davis, F. A.; Jenkins, R. H., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7967. (b) Davis, F. A.; Billmers, R. L. *Ibid.* **1981**, *103*, 7016. (c) Davis, F. A.; Awad, S. B.; Jenkins, R. H., Jr.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* **1983**, *48*, 3071. (d) Davis, F. A.; Billmers, R. L. *Ibid.* **1985**, *50*, 2593. (e) Davis, F. A.; Jenkins, L. A.; Billmers, R. L. *Ibid.* **1986**, *51*, 1033.

0022-3263/89/1954-4198$01.50/0

by allowing the condensate of sulfenic acid (and other reagents desired) to warm gradually to higher temperatures. These studies have significantly enhanced our understanding of sulfenic acid chemistry.

In our laboratory a different approach has been used to explore selenenic acid chemistry. This has involved the use of two relatively stable areneselenenic acids, *o*-$O_2NC_6H_4SeOH$ (**1a**) and *o*-$PhC(O)C_6H_4SeOH$ (**1b**),[5a] as substrates to study the mechanisms of some of the important reactions of selenenic acids (reaction with thiols,[5b] oxidation by peroxides,[6] selenenate ester formation,[7a] anhydride formation[7b]) as well as to determine their pK_a.[7c] The success of using the few examples of relatively stable areneselenenic acids to probe selenenic acid chemistry and mechanisms suggested that a similar approach to the study of sulfenic acids might be equally rewarding and yield information of a different type than the FVP studies noted earlier.

1-Anthraquinonesulfenic acid (**2**) is a stable arenesulfenic acid that has been known for a long time.[8] In the present study we have measured the pK_a of **2**, and we have determined the products and kinetics of the reactions of **2**, and its methyl ester (**3**), with both thiols and peracids.

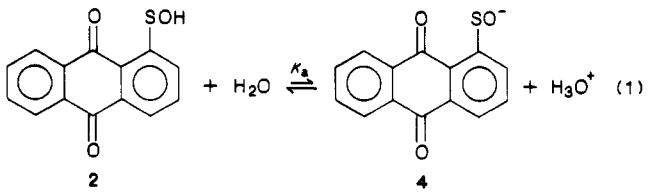


2 **3**

The results are then compared to those previously obtained for the corresponding reactions of stable areneselenenic acids **1a** and **1b** and their methyl esters.

Results

pK_a of 1-Anthraquinonesulfenic Acid (2). The marked difference in the visible absorption spectra of **2** and its anion (**4**)[8a] allows the pK_a of **2** to be determined easily. A solution of **2** in 15% acetonitrile–85% H_2O has a long wavelength λ_{max} at 462 nm (ϵ 3800). Upon addition of sufficient 1 N sodium hydroxide to give a solution with $[OH^-]$ = 0.02 M, this λ_{max} shifts to 676 nm (ϵ 3100) due to the conversion of **2** to its anion (**4**). Upon acidification of the solution, the spectrum reverts to that for **2**, demonstrating the anticipated instantaneous reversibility of the equilibrium in eq 1.



2 **4**

The fraction, *f*, of **2** converted to **4** was measured by determining the changes in the optical density of a 10^{-4} M solution of **2** at both the λ_{max} for **2** and for **4** that accompanied the addition of a series[9] of tris buffers covering a pH range from 7.5 to 8.7. Values of $[4]/[2] = f/(1-f)$ for each buffer are shown in Table I. From $[4]/[2]$ the pK_a for **2** was calculated by using the relationship

$$pK_a \text{ of } 2 = pH - \log [4]/[2]$$

The results for the various buffers give the pK_a for **2** as 7.51 ± 0.06.

Table I. Measurement of the pK_a of 1-Anthraquinonesulfenic Acid[a]

buffer composition				
[tris], M	[HCl], M	pH[b]	*f*[c]	pK_a
0.050	0.0403	7.5	0.57 ± 0.01	7.39 ± 0.01
	0.0345	7.8	0.62 ± 0.03	7.59 ± 0.05
	0.0292	8.0	0.73 ± 0.01	7.57 ± 0.01
	0.0262	8.1	0.78	7.55
	0.0229	8.2	0.84	7.49
	0.0103	8.7	0.95	7.48
				Av: 7.51 ± 0.06

[a] Measured in 15% MeCN–85% H_2O at 25 °C. [b] Reference 9. [c] $f = [ArSO^-]/([ArSOH] + [ArSO^-])$.

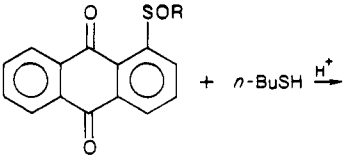
Table II. Kinetics of the Reaction of 1-Butanethiol with 2 and 3 at 25 °C

substrate	solvent	$[H^+]$,[a] M	[*n*-BuSH], M	$k_1 \times 10^4$, s^{-1}	k_{RSH}, $M^{-1}\ s^{-1}$[b]
3	MeOH	0.051	0.042	2.7	0.0065
			0.063	4.1	
		0.103	0.021	2.7	0.0131
			0.043	5.8	
			0.062	8.2	
2	50% aqueous MeCN	0.102	0.020	1.5	0.0057
			0.040	2.6	
			0.060	3.7	
		0.153	0.021	2.5	0.0094
			0.040	4.4	
			0.051	5.4	
			0.062	6.8	
			0.081	8.2	
		0.200	0.020	3.8	0.0133
			0.040	6.6	
			0.064	9.8	

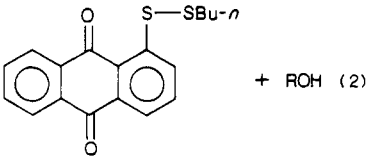
[a] Strong acid used was CF_3SO_3H; initial concentration of **2** or **3**, 1.0×10^{-4} M. [b] Slope of a plot of k_1 vs [*n*-BuSH].

The results for the various buffers give the pK_a for **2** as 7.51 ± 0.06.

Reaction of 1-Butanethiol with 2 and 3. Both 1-anthraquinonesulfenic acid (**2**) and its methyl ester (**3**) react with 1-butanethiol in acid solution to form *n*-butyl 1-anthraquinonyl disulfide (**5**) in >90% yield (eq 2).



2, R = H
3, R = CH_3



5
(>90%)

The kinetics of the reaction of the thiol with **2** or **3** were studied with the thiol present in large stoichiometric excess, so that the disappearance of **2** or **3** (followed by monitoring the decrease in the absorbance of the solution at either 462 nm (**2**) or 450 nm (**3**)) followed first-order kinetics. To avoid possible complication from hydrolysis

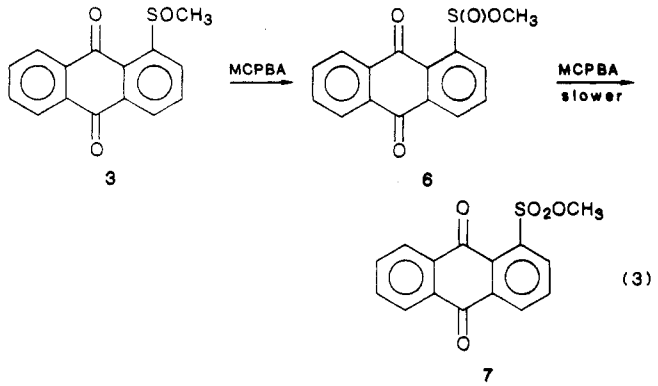
(5) (a) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* **1984**, *49*, 3100. (b) *Ibid.* **1984**, *49*, 3106.
(6) Kice, J. L.; Chiou, S.; Weclas, L. *J. Org. Chem.* **1985**, *50*, 2508.
(7) (a) Kang, S.-I.; Kice, J. L. *J. Org. Chem.* **1986**, *51*, 295. (b) *Ibid.* **1985**, *50*, 2968. (c) *Ibid.* **1986**, *51*, 287.
(8) (a) Fries, K. *Chem. Ber.* **1912**, *45*, 2965. (b) Bruice, T. C.; Sayigh, A. B. *J. Am. Chem. Soc.* **1959**, *81*, 3416.
(9) Bates, R. G.; Bower, V. E. *Anal. Chem.* **1956**, *28*, 1322.

of the ester the reaction of 3 with the thiol was conducted in methanol; the reaction involving 2 was carried out in 50% aqueous acetonitrile. To proceed at a reasonable rate both reactions require a strong acid be present as catalyst. The experimental first-order rate constants, k_1, for the reactions of 2 and 3 with the thiol under various conditions are shown in Table II.

With the sulfenic acid (2) plots of k_1 vs [*n*-BuSH] at each [H^+] are linear, but with a small intercept, k_i, whose magnitude increases linearly with [H^+]. Since other studies showed that 2 disappears slowly in acid solution in 50% acetonitrile in the absence of thiol at a rate similar to k_i, acid-catalyzed decomposition of 2 is thought to be responsible for these small intercepts in plots of k_1 vs [*n*-BuSH] for the reaction of 2 with the thiol. With the methyl ester (3) there was no evidence of a similar intercept, k_1/[*n*-BuSH] being a constant independent of thiol concentration for each [H^+]. The linearity of plots of k_1 vs [*n*-BuSH] indicates that the reaction of the thiol with each substrate is, as anticipated, first-order in thiol.

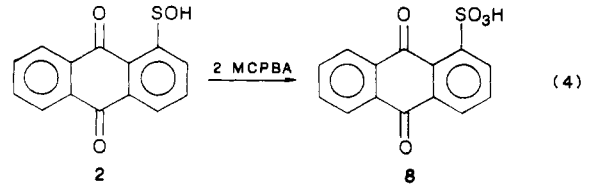
The slope of each plot of k_1 vs [*n*-BuSH] gives k_{RSH}, the second-order rate constant for the reaction. Values of k_{RSH} for the two substrates and the different strong acid concentrations are tabulated in the rightmost column of Table II. From them it is evident that k_{RSH} is proportional to [H^+], with k_{RSH} (M^{-1} s^{-1}) = 0.064[H^+] for 2 in 50% MeCN and k_{RSH} (M^{-1} s^{-1}) = 0.130[H^+] for 3 in methanol.

Oxidation of 2 and 3 by *m*-Chloroperoxybenzoic Acid. Treatment of methyl 1-anthraquinonesulfenate (3) in chloroform with 1 molar equiv of *m*-chloroperoxybenzoic acid (MCPBA) led to the formation in 84% yield of a compound identified as methyl 1-anthraquinonesulfinate (6). When 3 was reacted with 2 molar equiv of MCPBA, a significantly longer time was required for consumption of the second mole of peracid. The major final product (80% yield) under such conditions was a substance whose spectral properties and elemental analysis indicated it to be methyl 1-anthraquinonesulfonate (7).



3 6 7 (3)

Oxidation of sulfenic acid 2 with 2 molar equiv of MCPBA at room temperature in aqueous acetone gave a single major product (eq 4) which was identified as 1-anthraquinonesulfonic acid (8) by conversion to its sodium salt and comparison with a known sample of the same compound. When only 1 mol of MCPBA was used to



2 8 (4)

oxidize 2, an impure product, believed to be a *mixture* of 8 and 1-anthraquinonesulfinic acid (9), was obtained. This suggests that the rate of oxidation of 9 to 8 by MCPBA in aqueous acetone is comparable to the rate at which 2 is oxidized to 9. This contrasts with the behavior of the oxidation of the methyl ester (3) in chloroform (eq 3) where oxidation of 6 by the peracid proceeded at a considerably slower rate than the oxidation of 3.

Table III. Kinetics of the Oxidation of 2 and 3 with MCPBA at 25 °C[a]

substrate	solvent	10^3[H^+], M[b]	10^3-[MCPBA], M[c]	$k_1 \times 10^3$, s^{-1}	k_{MCPBA}, M^{-1} s^{-1}[d]
2	15% MeCN–85% H_2O	0.00	0.41	35.4	86
			0.68	59	
			0.82	71	
		1.00	0.38	32.6	85
			0.62	52	
			0.81	70	
3	MeOH	0.00	1.02	0.87	0.86
			2.03	1.7	
			3.03	2.6	
			4.06	3.5	
		1.00	2.00	1.6	0.82
			3.20	2.6	

[a] Initial concentration of 2 or 3, 1×10^{-4} M. [b] Strong acid used was CF_3SO_3H. [c] MCPBA = *m*-chloroperoxybenzoic acid. [d] Slope of plot of k_1 vs [MCPBA].

The kinetics of the oxidation with MCPBA were studied for 3 in methanol as solvent and for 2 in 15% aqueous acetonitrile. Both oxidations were studied under conditions where the peracid was present in large stoichiometric excess, so that the disappearance of 2 (or 3) followed first-order kinetics. The reactions were followed by monitoring the decrease with time of the absorbance of a 10^{-4} M solution of the substrate at either 450 nm (3) or 462 nm (2). The experimental first-order rate constants, k_1, for the different reaction conditions are shown in Table III.

The results indicate that the oxidations are first-order in peracid, k_1/[MCPBA] being a constant (k_{MCPBA}) independent of [MCPBA]. The fact that k_{MCPBA} is the same in the presence or absence of added strong acid shows that acid catalysis is not important for either oxidation; k_{MCPBA} for 2 (85 M^{-1} s^{-1}) is 100 times larger than k_{MCPBA} for the oxidation of 3 (0.85 M^{-1} s^{-1}) by the same reagent.

Discussion

pK_a of 1-Anthraquinonesulfenic Acid (2). The pK_a of 2 (15% MeCN–85% H_2O, 25 °C) is 7.51 ± 0.06. This makes it approximately 3 pK units *stronger* acid than selenenic acid **1a**, whose pK_a is 10.45.[7c] With oxyacids X–OH, the more electronegative and the smaller is X, the more the electrons associated with the oxygen are pulled toward X and the larger the dissociation constant for loss of the proton. Since sulfur (2.5) is slightly more electronegative than selenium (2.4) and has a smaller covalent radius,[10] a sulfenic acid would be predicted to be a stronger acid than a selenenic acid. The observed difference in pK_a between 2 and **1a** is, however, surprisingly large. It is pertinent to note that a similarly large difference in pK_a (3.5 pK units) exists between arenesulfinic acids ($PhSO_2H$, pK_a = 1.2)[11a] and areneseleninic acids ($PhSeO_2H$, pK_a = 4.79).[11b]

(10) Data on electronegativity and covalent radius for S and Se are tabulated by Klayman, D. H. *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. H., Gunther, W. H. H., Eds.; John Wiley & Sons: New York, 1973; p 729.

(11) (a) Ritchie, C. D.; Saltiel, J. D.; Lewis, E. S. *J. Am. Chem. Soc.* **1961**, *83*, 4601. (b) McCullogh, J. D.; Gould, E. S. *Ibid.* **1949**, *71*, 674.

The pK_a of a 1-naphthalenesulfenic acid intermediate is part of the rate expression for the complex kinetics of the reaction of sulfite ion with naphtho[1,8-*cd*]-1,2-dithiole 1-oxides.[12] To fit the kinetic behavior observed for this reaction it was necessary to assume that the pK_a of this sulfenic acid intermediate was ≤ 8.3.[12] The two electron-withdrawing carbonyl groups ortho and meta to the sulfenic acid functionality in **2** should make **2** a somewhat stronger acid than an unsubstituted arenesulfenic acid. The measured pK_a for **2** concurs satisfactorily with the earlier estimate of arenesulfenic acid pK_a from the kinetic study by Boduszek and Kice.[12]

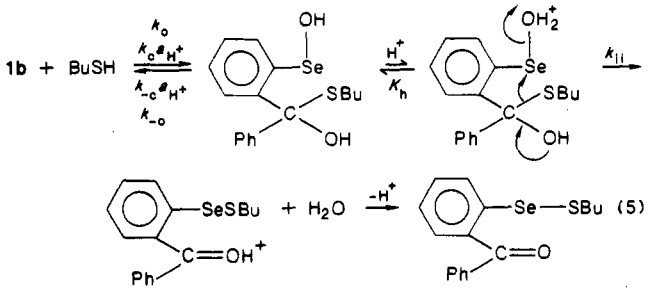
Reaction of 2 and 3 with a Thiol. Reaction of a thiol (*n*-BuSH) with either the sulfenic acid (**2**) or its methyl ester (**3**) leads to the formation of *n*-butyl 1-anthraquinonyl disulfide (**5**), eq 2. The reactions require acid catalysis and show a first-order dependence on both the concentration of thiol and strong acid catalyst, i.e., the experimental first-order rate constant (k_1) under conditions where the thiol is present in large stoichiometric excess over **2** (or **3**) is given by

$$k_1 = k_{RSH}a_{H^+}[RSH]$$

The fact that k_{RSH} for **2** (0.064 M^{-1} s^{-1}) and **3** (0.130 M^{-1} s^{-1}) differ by only a factor of 2 suggests that both substrates are reacting with the thiol by similar mechanisms. Were the sulfenic acid reacting by an entirely different mechanism than the ester, k_{RSH} for the two compounds might be expected to differ by much more than this.[13]

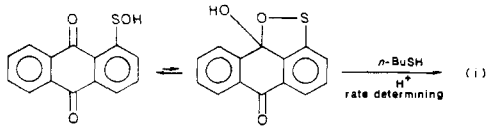
While the formal kinetics ($k_1 = k_{RSH}a_{H^+}[RSH]$) for the reaction of **2** or **3** with *n*-BuSH at pH ≤ 2 are the same as for the reaction of this thiol with selenenic acids **1a** and **1b**, or the methyl ester of **1a**, the rate constants (k_{RSH}) for the reactions involving **2** or **3** are much smaller. Thus, k_{RSH} for the reaction of ester **3** with *n*-BuSH is ~300 times smaller than k_{RSH} for the reaction of o-$O_2NC_6H_4SeOCH_3$ with *n*-BuSH;[7a] k_{RSH} for the reaction of sulfenic acid **2** with the thiol is ~150 times smaller than k_{RSH} for selenenic acid **1a** and ~10 000 times smaller than k_{RSH} for selenenic acid **1b**.[5b]

o-Benzoylbenzeneselenenic acid (**1b**) reacts much faster than *o*-nitrobenzeneselenenic acid (**1a**) because it uses a mechanism (eq 5) involving initial reversible addition of the thiol to form a hemithioketal, followed by intramolecular, acid-catalyzed transfer of the thioalkyl group to selenium that is not available to the *o*-nitro acid.[5b]

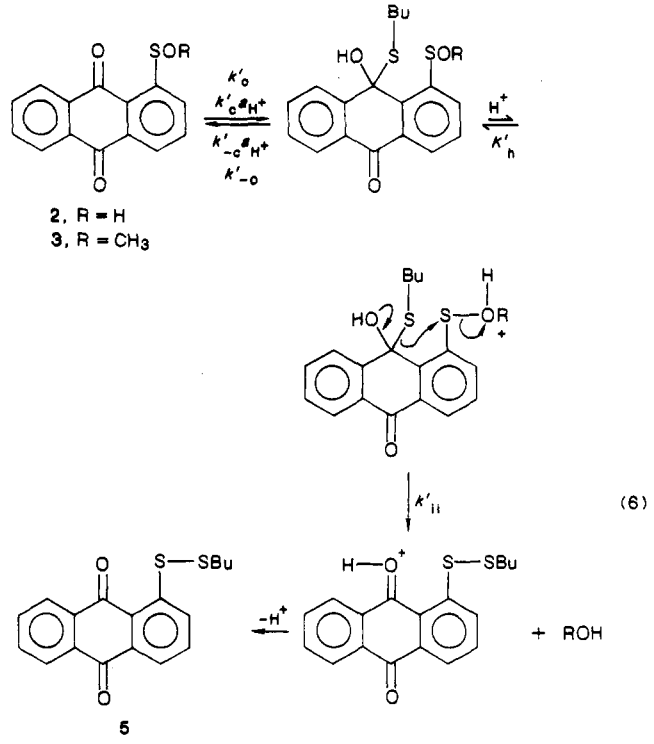


(12) Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 3199.

(13) In particular, a mechanism (eq i) for the reaction of **2** with the thiol involving initial addition of the SOH functionality across a C=O group appears to be ruled out, because a similar addition is not possible for the $-SOCH_3$ group in **3**.



In **2**, as in **1b**, there is a keto group attached to the aromatic ring at a position adjacent to the one bearing the acid functionality. This suggests that a mechanism (eq 6, R = H) for the reaction of the thiol with **2** that is analogous to eq 5 deserves serious consideration. Presumably the mechanism for the reaction of **3** would be similar (eq 6, R = CH_3).



If the mechanism for the reaction of *n*-BuSH with **2** or **3** is as shown in eq 6, it is necessary to explain why the rate of reaction of the thiol with sulfenic acid **2** is so much slower than the rate of reaction of the same thiol with selenenic acid **1b**. Two factors could be important. First, nucleophilic substitution at dicoordinate sulfur has been found to be much slower than the rate of the equivalent substitution (same nucleophile, same leaving group) at dicoordinate selenium.[14] This suggests that k'_{ii} in eq 6 is likely to be much smaller than k_{ii} in eq 5. Second, the equilibrium constant for formation of the hemithioketal from **2** could well be smaller than the equilibrium constant for the formation of the hemithioketal from **1b**.

In the case of selenenic acid **1b** the decisive experimental evidence for the mechanism in eq 5 was the presence of an inflection in the pH–rate profile at pH $\cong$ 3–4.[5b] This inflection is seen only because $k_{ii}K_h > k_{-c}$.[5] If, for the reason outlined above, k'_{ii} for **2** is much smaller than k_{ii} for **1b**, the situation where $k'_{ii}K'_h < k'_{-c}$ is likely to obtain for the reaction of **2** or **3** with *n*-BuSH, and no inflection will be observed in the pH–rate profile. This unfortunately means that the hemithioketal-intermediate mechanism (eq 6) for the reaction of **2** or **3** with the thiol cannot be confirmed experimentally in the manner that the analogous mechanism for **1b** (eq 5) was verified.

Oxidation of 2 and 3 by Peracid. Both **2** and **3** are oxidized by *m*-chloroperoxybenzoic acid (MCPBA) in a reaction that is first-order in peracid, and not subject to catalysis by added strong acid. The rate constant (k_{MCPBA}) is ~100 times larger for the sulfenic acid (**2**) than for its

(14) The rate of reaction of CN^- with $PhSSO_2Ph$ is 7×10^4 slower than with $PhSeSO_2Ar$ (Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899).

methyl ester (3). Similar behavior has been observed[15] in the oxidation of selenenic acid 1a and its methyl ester by MCPBA. In that case k_{MCPBA} for selenenic acid 1a was 20 times larger than k_{MCPBA} for its methyl ester. The reason that both the sulfenic and selenenic acid are oxidized so much faster than their methyl esters is not known. Conceivably there could be some hydrogen-bonding interaction of the OH group of the acid with the peracid in the transition state that facilitates the reaction. The OCH_3 group of the esters would not be capable of similar hydrogen bonding.

Sulfenic acid 2 is oxidized by MCPBA about 6 times slower than is o-benzoylbenzeneselenenic acid (1b). Reich[16] reports that the rate of oxidation of PhSMe by MCPBA is only slightly slower than the rate of oxidation of PhSeMe.[17] The difference in the rates of oxidation of 2 and 1b therefore seems consonant with what might be expected based on the relative rates of oxidation of other diccordinate sulfur and selenium substrates by this peracid.

With selenenic acid 1b oxidation by the peracid stops at the seleninic acid, o-$PhC(O)C_6H_4SeO_2H$;[6] there is no tendency for the seleninic acid to be oxidized further to a selenonic acid. With the sulfinic acid, however, further oxidation of the sulfinic acid (9) to a sulfonic acid (8) occurs readily, as does further oxidation of sulfinate ester 6 (the initial oxidation product from 3) to methyl 1-anthraquinonesulfonate (7). This difference in behavior between the analogous sulfur and selenium compounds results from the fact that in sulfur chemistry the S(VI) oxidation state is a more stable one than S(IV), while just the reverse is true for selenium, where Se(VI) compounds such as selenonic acids, are easily reduced to Se(IV) compounds.

In the oxidation of the sulfenate ester (3) with MCPBA, oxidation of 3 to 6 is faster than the further oxidation of 6 to 7. This is shown by the fact that oxidation of 3 with 1 mol of MCPBA gives 6 in good yield. On the other hand, in the case of the sulfenic acid (2) the rate of oxidation of the sulfinic acid (9) to 8 is competitive with that for oxidation of 2 to 9, and rather than a high yield of the sulfinic acid, oxidation of 2 with 1 mol of MCPBA gives a mixture of 8 and 9. This indicates that for oxidation by MCPBA ($k_{acid}^{ox}/k_{ester}^{ox}$) must be even larger for sulfinic acid 9 and its ester 8 than the factor of ~100 found for sulfenic acid 2 and its ester 3. The reason for this is not known.

Experimental Section

Preparation of 1-Anthraquinonesulfenic Acid (2) and Its Methyl Ester (3). Methyl 1-anthraquinonesulfenate (3) was prepared from 1-anthraquinonesulfenyl bromide in the manner described by Fries.[8a] It was obtained in 78% yield after recrystallization from methanol: mp 189–190 °C (lit.[8a,b] mp 189–190 °C, 189 °C); IR (KBr) 1660, 1570, 1370, 1345, 1275, 985, 700, and 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 7.70–8.38 (m, 7 H); mass spectrum, m/e 270.1 (M^+, 14.5), 239.2 ($M^+ - OCH_3$, 100).

1-Anthraquinonesulfenic acid (2) was prepared from the methyl ester by alkaline hydrolysis, followed by acidification of the reaction solution with acetic acid. To 0.2 g of 3 dissolved in 8 mL of ethanol was added 0.5 mL of a 33% solution of potassium hydroxide in water. The mixture was boiled for about 1 min and then diluted with 30 mL of water. Any insoluble material was filtered off and washed with 20 mL of water, which was added to the filtrate. The filtrate was acidified by the addition of acetic acid until red needles formed. These were then filtered off, washed with cold water, and dried under vacuum at room temperature. They were then recrystallized from benzene, taking care not to let the temperature of the solution get above 60 °C. There was obtained 0.12 g (63%) of 2: mp >300 °C (lit.[8a] mp > 300 °C); IR (KBr) 3200, 1640, 1550, 1310, 1270, and 700 cm^{-1}; mass spectrum, m/e 256.2 (M^+, 35.5), 239.2 ($M^+ - OH$, 100).

Purification of Reagents. m-Chloroperoxybenzoic acid (Aldrich, 85%) was used without further purification. Its active oxygen content was determined by iodometric titration before use. 1-Butanethiol (Aldrich) was purified by fractional distillation, bp 99 °C. All water used in kinetic runs was doubly distilled from glass. All other reagents used were of the highest purity commercially available and were used without further purification.

Reaction of Methyl 1-Anthraquinonesulfenate (3) with 1-Butanethiol. Products. Methyl 1-anthraquinonesulfenate (0.24 g, 0.89 mmol) dissolved in 5 mL of chloroform, 0.15 g of trifluoromethanesulfonic acid, and 0.10 g (1.1 mmol) of 1-butanethiol were mixed together and allowed to stand for 12 h at room temperature. The reaction solution was then poured into 50 mL of water and extracted twice with 5-mL portions of chloroform. The chloroform extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was crystallized from hexane, giving 0.28 g (96%) of n-butyl 1-anthraquinonyl disulfide (5): mp 102–103.5 °C; IR (KBr) 1670, 1570, 1330, 1310, 1270, 955, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H), 1.6 (m, 4 H), 2.86 (t, 2 H), 7.6–8.7 (m, 7 H). Anal. Calcd for $C_{18}H_{16}O_2S_2$: C, 65.82; H, 4.91. Found: C, 65.77; H, 5.19.

Kinetics. A solution of 3 (1×10^{-4} M) in methanol was prepared immediately before use. A 3.5-mL aliquot of this solution was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Beckman Model DU-50 spectrophotometer, and the desired amounts of trifluoromethanesulfonic acid (as a 3–4 M solution in methanol) and 1-butanethiol were then added with good mixing via microsyringe. The progress of the reaction was monitored by following the decrease in the optical density of the solution with time at 450 nm.

Reaction of 1-Anthraquinonesulfenic Acid (2) with 1-Butanethiol. Products. 1-Anthraquinonesulfenic acid (0.13 g, 0.5 mmol) was dissolved in 35 mL of acetonitrile, and 0.5 mmol of trifluoromethanesulfonic acid dissolved in 5 mL of water, plus 0.11 g (0.6 mmol) of 1-butanethiol in 5 mL of acetonitrile, was added. This solution was allowed to stand at room temperature for 18 h. It was then worked up by pouring the solution into a large excess of water, extraction of the resulting mixture several times with chloroform, drying of the chloroform extracts, and removal of the solvent under reduced pressure. Recrystallization of the residue from hexane gave 0.154 g (94%) of 5, mp 102–103 °C, identical in all respects with the compound obtained from the reaction of the thiol with 3.

Kinetics. A solution of 2 (1×10^{-4} M) in 50% acetonitrile was prepared immediately prior to use. The procedure for carrying out the kinetic runs was the same as for the reaction of the thiol with 3, except that the progress of the reaction was followed at 462 nm, rather than 450 nm.

Oxidation of 3 by m-Chloroperoxybenzoic Acid. Products. To 0.24 g (0.89 mmol) of 3 dissolved in 5 mL of chloroform was added a solution of 0.89 mmol of MCPBA in 5 mL of the same solvent. The reaction mixture was allowed to stand at room temperature for 2 h, and the solvent was then removed under reduced pressure. The residue was dissolved in ether, washed first with 5% sodium bicarbonate, and then once with water. The ether solution was dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure. The residue was purified by column chromatography on silica gel using first carbon tetrachloride, and then chloroform, as eluent. Removal of the chloroform gave a solid that was recrystallized by dissolving it in carbon tetrachloride and then precipitating it by addition of hexane or heptane. There was obtained 0.215 g (84%) of methyl 1-anthraquinonesulfinate (6): mp 144–145 °C; IR ($CHCl_3$) 1680 (C=O), 1120 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H), 7.2–7.7 (m, 7 H). Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52. Found: C, 62.25; H, 3.71.

In a second experiment 0.24 g of 3 was oxidized with 1.98 mmol of MCPBA under the same conditions. The reaction mixture was allowed to stand overnight at room temperature and was then worked up in the same manner as in the previous experiment.

(15) Kice, J. L.; Chiou, S. J. Org. Chem. 1986, 51, 290.
(16) Reich, H. J. Oxidation in Organic Chemistry; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, p 12.
(17) With ozone, O_3, as the oxidizing agent, on the other hand, there is a large difference in rate, with the sulfide being oxidized over 50 times slower than the selenide.[16,18]
(18) Ayrey, G.; Barnard, D.; Woodbridge, D. T. J. Chem. Soc. 1962, 2089.

The product was purified by precipitating it from a chloroform solution by addition of carbon tetrachloride. This gave 0.216 g (81%) of methyl 1-anthraquinonesulfonate (7): mp 209–210 °C; IR ($CHCl_3$) 1690 (C=O), 1370 and 1170 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.07 (s, 3 H), 7.65–8.71 (m, 7 H). Anal. Calcd for $C_{15}H_{10}O_5S$: C, 59.60; H, 3.33. Found: C, 58.98; H, 3.28.

Kinetics. The procedure was the same as previously outlined for the reaction of 3 with *n*-BuSH, except that a solution of MCPBA in methanol, rather than a solution of the thiol, was used. The reaction was followed at 450 nm.

Oxidation of 2 by MCPBA. Products. 1-Anthraquinonesulfenic acid (0.26 g, 1 mmol) was dissolved in 10 mL of acetone, 2 mmol of MCPBA was added, and the mixture was allowed to stand at room temperature for 48 h. The solvent was removed under reduced pressure, and the residue was dissolved in hot 5% sodium bicarbonate. The pH of the resulting solution was then adjusted to 3.5 by careful addition of 6 N HCl from a buret. This led to the precipitation of *m*-chlorobenzoic acid, which was filtered off. The pH of the filtrate was then decreased to 0.0 by the addition of more 6 N HCl. At that point sodium 1-anthraquinonesulfonate (0.25 g, 81%) precipitated and was filtered off, mp >300 °C. Comparison of its infrared spectrum, IR (KBr) 2480, 1680, 1570, 1415, 1310, 1280, 1210, 1050, 950, 805, 700, and 610 cm^{-1}, with that of an authentic sample of this salt (Kodak) showed the two to be identical.

Kinetics. A solution of 2 (10^{-4} M) in 15% CH_3CN–85% H_2O was prepared immediately prior to use. After a measured aliquot had been placed in the thermostated spectrophotometer cell the reaction was initiated by the addition from a microsyringe of a measured amount of a solution of MCPBA. When used, trifluoromethanesulfonic acid was also added in the same manner. The reaction was monitored by observing the decrease in the absorbance of the solution at 462 nm.

Determination of the pK_a of 2. To 3.5 mL of 15% acetonitrile–85% water, contained in a 1-cm spectrophotometer cell, was added 60 μL of a 0.007 M solution of 2 in acetonitrile. The UV–visible absorption spectrum of this solution was recorded. Sufficient 1.0 N sodium hydroxide was then added by microsyringe to give a solution containing 0.02 N OH^-, and the spectrum for the anion of 2 (4) was recorded. In 15% acetonitrile 2 has its long-wavelength maximum at 462 nm; its anion shows its λ_{max} at 676 nm.

To determine the pK_a of 2 0.350 mL of one of a series of tris buffers of pH 7.5–8.5, prepared as outlined by Bates and Bower,[9] was added to 3.5 mL of a 10^{-4} M solution of 2 in 15% acetonitrile, and the optical density of the solution was immediately determined at the wavelengths corresponding to the long-wavelength absorption maxima of both the sulfenic acid (462 nm) and its anion (676 nm). The concentration ratio $[ArSO^-]/[ArSOH]$ was estimated for that particular buffer from the absorbance of the solution at the two wavelengths and the extinction coefficients for $ArSO^-$ and ArSOH at these two wavelengths.

Photocyclization of Terthiophenes

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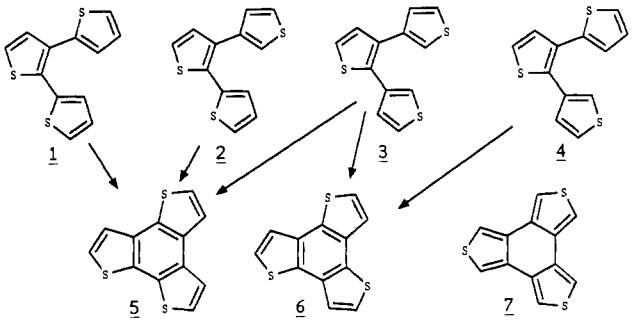
The terthiophenes in which thienyl groups are attached to the 2- and 3-positions of a central thiophene ring undergo oxidative photocyclization to benzotrithiophenes. A single product, unsymmetrical benzotrithiophene 5, was obtained from 2,2′:3′,2″- and 2,2′:3′,3″-terthiophenes, and its symmetrical isomer 6 from 2,3′:2′,3″-terthiophene. However, a mixture of these two products was produced by irradiation of 3,2′:3′,3″-terthiophene, indicating that a rearrangement of a β- into an α-substituted thiophene had occurred. This is a very rarely encountered photochemical rearrangement.

Introduction

Two of the seven possible benzotrithiophenes, 6 and 7 (Scheme I), have been reported. Through sequential treatment of hexakis(bromomethyl)benzene with Na_2S and DDQ, Hart and Sasaoka synthesized benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene, 7, an "exocyclic benzene" with D_{3h} symmetry which contains only 3,4-disubstituted (*c*-fused) thiophene rings.[1] Three other benzotrithiophene isomers containing one or two *c*-fused thiophene rings are possible; none has been reported to date.

The remaining two isomers contain only *b*-fused thiophene rings. Benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene 6, with C_{3h} symmetry, has been described.[2] However, it is not very conveniently available, particularly on a large scale, since it was produced from γ-thiobutyrolactone at 170–200 °C under 15–20 kbar pressure.

Scheme I



Since its isolation from marigold (*Tagetes erecta*) blossoms by Zechmeister in 1943, there has been much interest in α-terthienyl, 2,2′:5′,2″-terthiophene, one of the most highly phototoxic substances known. In a related study, two of us (N.J., J.K.) recently reported the first synthesis of α-terthienyl isomers 1 to 4,[3] which may be

(1) Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326–4327.
(2) Proetzsch, R.; Bieniek, D.; Korte, F. *Tetrahedron Lett.* **1972**, 543–544.

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