(Merck standardized aluminum oxide 90 with pentane as the eluent).

1,2-Dibromo-3-(4-methoxyphenyl)propane. Bromine gas was passed into a stirred solution of 3-(4-methoxyphenyl)propene (1.33×10^{-2} mol) in 10 mL of Me_2SO (used to minimize the formation of 1,3-dibromo-2-arylpropane). After 1 h at room temperature, the reaction mixture was diluted with 100 mL of water and then extracted three times with petroleum ether. The extracts were washed with a solution of $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated; the crude product was then purified by column chromatography as above.

1-Bromo-3-chloro-2-(4-methoxyphenyl)propane. A mixture of equal amounts (1.5×10^{-2} mol) of chlorine and bromine in 1,2-dichloroethane (100 mL) was added to a solution of 3-(4-methoxyphenyl)propene (3×10^{-2} mol) in 1,2-dichloroethane (500 mL). Bromo chloride compounds accounted for 90% of the reaction products, 50% of which was 1-bromo-3-chloro-2-arylpropane. The 1-bromo-2-chloro-3-arylpropane was removed by treatment with zinc in CH_3OH, and the desired product was purified by GLC as above.

2-Bromo-1-chloro-3-(4-methoxyphenyl)propane. 1,2-Dibromo-3-(4-methoxyphenyl)propane (1.5×10^{-3} mol) was added to 10 mL LiCl-saturated DMF. After 40 h at room temperature, the reaction mixture was diluted with water and extracted three times with petroleum ether. After the ether layer was dried and the solvent evaporated, the crude product contained 4% of dibromide, 86% of bromo chloride, and 10% of dichloride. The bromo chloride was purified by GLC. A kinetic calculation indicates that the isolated product consists of 2-bromo-1-chloro-3-(4-methoxyphenyl)propane to the extent of more than 98%.

Other Products. 1,3-Dibromopropane was from Prolabo. 1,2-Dibromodecane was obtained by reaction of bromine with 1-decene. These products were purified by GLC.

Product Identification. Mass spectra were run on a JEOL JMS D100 spectrometer; ^1H NMR spectra were recorded on a JEOL C60 HM spectrometer. The spectra recorded for the 1,3-dihalo-2-arylpropanes were highly characteristic. An additional check on the identification was provided by the conversion of the 1,3-dibromo-2-(4-methoxyphenyl)propane into arylcyclopropane caused by zinc in aqueous alcohol. Unfortunately, there is hardly any difference between the spectra of 2-bromo-1-chloro-3-(4-methoxyphenyl)propane and those of 1-bromo-2-chloro-3-(4-methoxyphenyl)propane [the latter was prepared by reacting BrCl with 3-(4-methoxyphenyl)propene].

Kinetic and Product Studies. A single batch of each tin tetrahalide without further purification was used throughout the entire kinetic study ($SnCl_4$ was a Prolabo RP product; $SnBr_4$ was from Schuchardt).

Each kinetic run was based on ten or more samples subjected to the following treatment. Tin tetrahalide (200 μL) was added to 4 μL of substrate with a reference substance contained in a narrow glass tube. This tube was sealed or quickly capped and then placed in an oil bath at 100 °C for an appropriate length of time; it was then quickly cooled, and its contents were poured into a mixture consisting of 10 mL of HCl (5 N) and 5 mL of pentane. The organic layer was washed with a solution of NaCl and then dried over $MgSO_4$. The pentane was evaporated at room temperature, and the residue was diluted in 200 μL of 1,2-dichloroethane and analyzed by GLC.

When 1,3-dibromopropane is the substrate, a modified procedure, skipping the evaporation of the extraction solvent, was used. The reference substances were *o*-dichlorobenzene, and various 1,2-dichloro-3-arylpropanes [aryl was pentafluorophenyl, (4-trifluoromethyl)phenyl, and 4-chlorophenyl].

GLC was performed on a Varian 1400 chromatograph (0.125 in. × 10 ft column packed with 15% SE-30 on Chromosorb) equipped with a flame-ionization detector. The temperature of the injector was held below 200 °C to avoid any isomerization during injection. For the different samples resulting from each kinetic run, the chromatographic response for the reference substance did not vary (in overall percentage) as the reaction advanced. The sensitivity of the apparatus was checked as being the same for the 1,2-dihalo-3-arylpropanes as for the 1,3-dihalo-2-arylpropanes, whatever the halogens, thereby indicating a product recovery of ca. 100%.

Products were identified on a JEOL JMS D100 mass spectrometer with a JMA-0231 data analysis system coupled with a JGC 20 K gas chromatograph.

Registry No. 2a, 83333-66-8; **2b**, 83333-67-9; **2c**, 67168-94-9; **2d**, 83333-68-0; **3a**, 37983-33-8; **3b**, 83333-69-1; **3c**, 67168-96-1; $SnBr_4$, 7789-67-5; $SnCl_4$, 7646-78-8; 3-(4-methoxyphenyl)propene, 140-67-0.

Kinetics and Mechanism of the Oxidation of *n*-Dodecanethiol and Pyridine-Substituted Ethanethiols by I_2 in Acetonitrile

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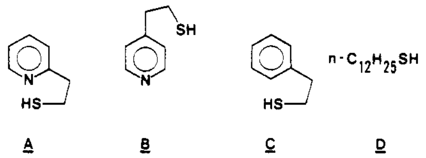
Our investigations of the iodine oxidation of divalent sulfur have been extended to include the thiol group. In acetonitrile the rates of iodine oxidation of thiols can be measured at 25.0 °C by using stopped-flow techniques. The oxidation of the isomeric 2- and 4-(2-pyridyl)ethanethiols (A and B) and two simple sulfides, 2-phenylethanethiol (C) and *n*-dodecanethiol (D), reveals that the rates are extremely sensitive to the basicity of solvent and are maximized for A where the neighboring base is in a position to interact intramolecularly with the thiol. The rates of unsubstituted thiols are also accelerated by added pyridine. Consistent mechanisms of oxidation are proposed.

Thiols can be oxidized to disulfides with iodine in good yield under a variety of conditions.[1] One method is to use a 2:1 molar ratio of thiol and iodine in the presence of a tertiary amine in $CHCl_3$. Another method using aqueous iodine and KI is often satisfactory as well; however, Danehy and co-workers[2] found that "overoxidation" occurs in water when the thiol group is situated three atoms away from a carboxylate ion. It was proposed that a cyclic sulfenic carboxylic acid anhydride intermediate forms, which is further oxidized either to sulfinic or sulfonic acids. Most of their work was qualitative in nature and no kinetic

Chart I



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(1) (a) Klason, P. *Chem. Ber.* **1881**, *14*, 409; **1906**, *39*, 738. (b) Larrouquere, *J. Ann. Chim.* **1961**, *6*, 733. (c) Kharasch, N. "Organic Sulfur Compounds"; Pergamon Press: Oxford, 1961; Vol. I, p 387.

(2) Danehy, J. P.; Oester, M. Y. *J. Org. Chem.* **1967**, *32*, 1491.

0022-3263/82/1947-4860$01.25/0

Table I. Pseudo-First-Order Rate Constants k_{obsd} for the Reaction of A-D with I_3^- in CH_3CN at 25.0 °C[a]

				k_{obsd}, s^{-1}			
line	thiol, M	iodide, M	total pyridine, M	A	B	C	D
1	1.0×10^{-2}	4.0×10^{-2}	1.0×10^{-2}	4.7×10^{1}	8.2	1.1	1.0
2	4.0×10^{-3}	4.0×10^{-2}	4.0×10^{-3}	2.6×10^{1}	9.5×10^{-1}	2.0×10^{-1}	1.6×10^{-1}
3	2.0×10^{-3}	4.0×10^{-2}	2.0×10^{-3}	9.0	3.1×10^{-1}	5.6×10^{-2}	6.0×10^{-2}
4	1.0×10^{-3}	4.0×10^{-2}	1.0×10^{-3}	4.8	8.0×10^{-2}	1.8×10^{-2}	1.1×10^{-2}
5	1.0×10^{-3}	2.2×10^{-2}	1.0×10^{-3}	7.7	1.1×10^{-1}	2.0×10^{-2}	2.7×10^{-2}
6	1.0×10^{-3}	1.5×10^{-2}	1.0×10^{-3}	1.1×10^{1}	1.6×10^{-1}	3.9×10^{-2}	3.5×10^{-2}
7	1.0×10^{-3}	7.5×10^{-3}	1.0×10^{-3}	2.1×10^{1}	3.0×10^{-1}	7.4×10^{-2}	7.0×10^{-2}
8	1.0×10^{-3}	4.0×10^{-3}	1.0×10^{-3}	3.4×10^{1}	5.4×10^{-1}	1.3×10^{-1}	1.1×10^{-1}

[a] All runs made in triplicate. Precision of replicate runs is ±5%.

studies of thiol oxidation with a two-electron oxidizing agent such as iodine has ever been reported. We had previously shown kinetically[3] that the pyridine nitrogen interacts with a neighboring thioether sulfur during the oxidation of methyl 2-(2-pyridyl)ethyl sulfide with aqueous iodine and KI to give an intermediate having an N^+–S^+ bond. Because of this nitrogen sulfur interaction we decided to examine the involvement of the pyridine nitrogen in the oxidation of the corresponding thiol, 2-(2-pyridyl)ethanethiol (A, Chart I). We were also motivated by the recent report[4] that in papain, the nucleophilicity of the thiol group of cysteine-25 toward a carbonyl group is enhanced by the imidazole group of histidine-197. A similar effect of pyridine may facilitate thiol oxidation in A. Either one of the synergistic mechanisms could result in a rate enhancement in the oxidation of A over its isomer, 2-(4-pyridyl)ethanethiol (B). Unfortunately, the reaction of A with aqueous iodine and KI was too fast to follow with stopped-flow techniques. However, when the solvent was changed to acetonitrile, the reaction could be followed easily. Acetonitrile was selected because it is a dipolar aprotic solvent[5] and because the concentration of iodine can be maintained at very low concentrations in solutions of $(n\text{-Bu})_4NI$ ($K_{I_3^-} = 7.1 \times 10^6$).[6] To rule out any through-bond effects of the pyridine ring and also to examine standard thiols for comparison, we also investigated the I_2 oxidations of 2-phenylethanethiol (C) and *n*-dodecanethiol (D), a relatively nonvolatile and odorless thiol.

Results

The oxidation kinetics were studied spectrophotometrically by following the decrease in absorbance of the triiodide in acetonitrile at 362 nm with a stopped-flow spectrophotometer. The amount of triiodide present at any time is indicative of the extent to which oxidation has occurred. Rate constants, k_{obsd}, were determined over 2 half-lives, using 10–12 data points, beginning arbitrarily when the optical density equalled 0.6 in the 2.0-cm quartz cell. The reactions are first order in triiodide.

Iodide solutions varied in initial concentration from 4×10^{-2} to 4×10^{-3} M and were maintained at constant ionic strength by addition of tetrabutylammonium tetrafluoroborate (Table I, lines 4–8). Solid iodine was added to these iodide solutions until the triiodide absorbance reached optical density 0.6–1.0 in the 2.0-cm quartz cell.

Table II. Pseudo-First-Order Rate Constants k_{obsd} for the Reaction of D with I_3^- in CH_3CN in the Absence of Pyridine at 25.0 °C[a]

line	thiol, M	k_{obsd}, s^{-1}
1	1×10^{-2}	1.8×10^{-1}
2	4×10^{-3}	7.4×10^{-2}
3	2×10^{-3}	3.6×10^{-2}
4	1×10^{-3}	1.9×10^{-2}

[a] All runs made in triplicate. Precision of replicate runs is ±5%. $[I^-] = 4 \times 10^{-3}$ M.

Table III. Pseudo-First-Order Rate Constants k_{obsd} for the Reaction of A, B, and D with I_3^- in CH_3CN in the Presence of Excess Pyridine at 25.0 °C

	total pyridine,	k_{obsd}, s^{-1}		
line	M	A	B	D
1	0			1.9×10^{-2}
2	1.0×10^{-3}	4.6×10^{1}	5.4×10^{-1}	1.1×10^{-1}
3	1.5×10^{-3}	4.3×10^{1}	5.2×10^{-1}	1.5×10^{-1}
4	2.0×10^{-3}	4.8×10^{1}	5.5×10^{-1}	1.8×10^{-1}
5	4.0×10^{-3}	5.0×10^{1}	6.7×10^{-1}	3.3×10^{-1}
6	8.0×10^{-3}	5.3×10^{1}	8.2×10^{-1}	6.2×10^{-1}

[a] All runs made in triplicate. Precision of replicate runs is ±5%. [Thiol] = 1.0×10^{-3} M, $[I^-] = 4.0 \times 10^{-3}$ M.

With use of the published equilibrium constant for the formation of triiodide in acetonitrile, the initial concentration of triiodide is calculated to vary from 1.2×10^{-5} to 2.0×10^{-5} M. The extinction coefficient of triiodide in 100% acetonitrile at 362 nm and 25.0 °C was determined experimentally by preparing six iodine and iodide solutions and found to be $(2.4 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}.

Thiol solutions varied in initial concentration from 1×10^{-2} to 1×10^{-3} M (as shown in Table I, lines 1–4). Under these conditions, there exists a 500–50-fold excess of thiol relative to the oxidizing agent. The excess thiol serves to ensure good pseudo-first-order kinetic conditions, and in the case of A and B the pyridine moiety absorbs the HI liberated during the course of the reaction. For compounds C and D, a mixture of thiol and pyridine was generally used and in the concentrations listed in Tables I and II. In Table I, [pyridine] = [D] or [C] in order to more closely duplicate the conditions that exist for A and B. Thiol solutions were prepared immediately before use, although samples left standing for 24 and 48 h oxidized at rates essentially identical with fresh samples. Control runs made with solutions thoroughly degassed with argon were, within experimental error, identical with runs made under normal conditions. Subsequent runs were made without argon degassing. All glassware in contact with the thiol solutions was flame-dried prior to use.

n-Dodecanethiol (D) reacts with I_2 in CH_3CN even with no added pyridine (Table III, line 1). In contrast, when I_2 and D are mixed in CH_2Cl_2, no reaction could be observed. There was no change in the rate of oxidation of D when glacial acetic acid (0.1 and 1.0 equiv) was added

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[3] Doi, J. T.; Musker, W. K.; deLeeuw, D. L.; Hirschon, A. S. *J. Org. Chem.* **1981**, *46*, 1239.

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[5] Popovych, O.; Tomkins, R. P. T. "Nonaqueous Solution Chemistry"; Wiley: New York, 1981; p 60.

[6] Barraqûe, C.; Vedel, J.; Trêmillon, B. *Anal. Chem. Acta* **1969**, *46*, 263.

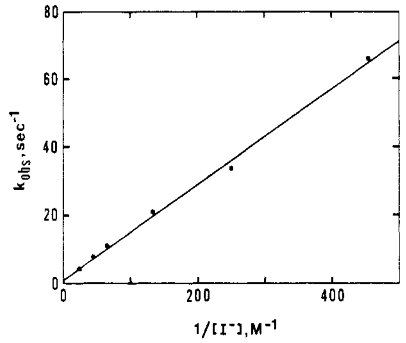


Figure 1. Iodide dependence on oxidation rate of A by I_2. The solid line indicates the best least-squares fit on the data points. A log–log plot yields a line of slope −0.9. [RSH] = 1 × 10^{-3} M.

to the reaction mixture. The presence of 0.1 equiv of triethylamine causes the reaction rate to increase more than 160-fold relative to a similar quantity of pyridine. A more precise value was not obtained because the rate exceeds the response time of the stopped-flow spectrometer.

The data in Figure 1 Table I show that all the reactions are inverse first order in iodide (lines 5–8). From the data on the thiol dependence of the rate (lines 1–4, Tables I and II) it can be shown that the reactions of A and D are first order in thiol and compound B is second order in B. The thiol dependence of C was not determined.

The effect of added pyridine on the reaction rate is shown in Table III. While A and B show small, nonlinear increases, D shows a markedly enhanced rate. When k_{obsd} is plotted against [pyridine], the data fit the equation

$$k_{obsd} = [(3.4 \times 10^{-2}) + (7.3 \times 10^{1})][\text{pyridine}] \quad (\text{s}^{-1})$$

Kinetic Scheme

The inverse-first-order dependence in $[I^-]$ shown by the oxidation rates of A–D is due to the equilibrium

$$I_3^- \rightleftharpoons I_2 + I^- \tag{1}$$

and indicates that the reaction is first order in I_2

$$-(d[I_3^-]/dt) = k_{obsd}([I_3^-]/[I^-])$$

but

$$([I_3^-]/[I_2][I^-]) = 7.1 \times 10^6$$

and

$$\frac{[I_3^-]}{[I^-]} = (7.1 \times 10^6)[I_2]$$

thus

$$-(d[I_3^-]/dt) = k_{obsd}(7.1 \times 10^6)[I_2]$$

For A, the kinetic scheme is

$$I_2 + A \xrightarrow{k_a}$$

and

$$-(d[A]/dt) = (7.1 \times 10^6)[I_2][A]$$

For B, the kinetic scheme is

$$B + B \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} B{\cdot}B \xrightarrow{[I_2]k_b}$$

and

$$-(d[B]/dt) = (7.1 \times 10^6)[B]^2(k_B/k_{-B})[I_2]k_b$$
$$= (7.1 \times 10^6)(k_B/k_{-B})k_b[I_2][B]^2$$
$$k_{obsd} = [B]^2(k_B/k_{-B})k_b$$

For D, the kinetic scheme has two paths as indicated by the equation

$$-\frac{d[D]}{dt} = [(3.4 \times 10^{-2}) + (7.3 \times 10^1)][\text{pyr}][D][I_2]$$

The pyridine independent path would involve the reaction

$$D + I_2 \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} D{\cdot}I_2 \xrightarrow{k_d}$$

$$-\frac{d[D]}{dt} = [D][I_2]k_Dk_d$$

The pyridine dependent path involves an additional step

$$D + \text{pyr} \underset{k_{-P}}{\overset{k_P}{\rightleftharpoons}} D{\cdot}\text{pyr} \xrightarrow{[I_2]k_p}$$

and

$$-\frac{d[D]}{dt} = [D][\text{pyr}]\frac{k_P}{k_{-P}}[I_2]k_p$$
$$= [D][I_2][\text{pyr}]\frac{k_P}{k_{-P}}k_p$$

Alternative mechanisms that involve the formation of a thiyl radical were eliminated since no evidence of thiyl radical formation was observed by ESR.

In order to assess the extent of hydrogen bonding in A and B, we examined the infrared spectra. At high concentrations (≥1 M) in CCl_4, B showed a peak at 2573 cm^{-1} and a broad peak at 2473 cm^{-1}. Upon dilution, the 2473-cm^{-1} peak decreased in intensity relative to the higher energy peak. These data are consistent with B exhibiting intermolecular hydrogen bonding. Compound A gave a peak in the infrared spectrum at 2575 cm^{-1} with a shoulder at 2485 cm^{-1}. Both peaks decreased proportionately upon dilution. These data are consistent with but not conclusive evidence for intramolecular hydrogen bonding. At lower concentrations in CCl_4 and in CH_3CN at all concentrations, no hydrogen-bonding effects could be seen for either A or B.

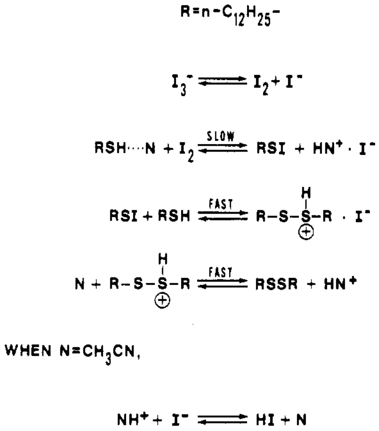
Electrochemical oxidations of A, B, and D were carried out by cyclic voltammetry at a platinum electrode in acetonitrile to determine whether a correlation exists between the oxidation rates and the peak potentials of first oxidation peaks. A 100-mV/s scan rate, 0.100 M tetra-*n*-butylammonium perchlorate supporting electrolyte, and Ag|0.1 M $AgNO_3(CH_3CN)$ reference electrode were used. Compound A exhibited a peak potential at 1.14 V, B at 1.08 V, and C at 1.35 V. Whereas A and B have oxidation rates that vary by several 100-fold, their peak potentials are similar. B and C are similar kinetically, yet have peak potentials that differ by 0.27 V. Thus, no direct correlation between peak potentials and oxidation rates is apparent.

Discussion

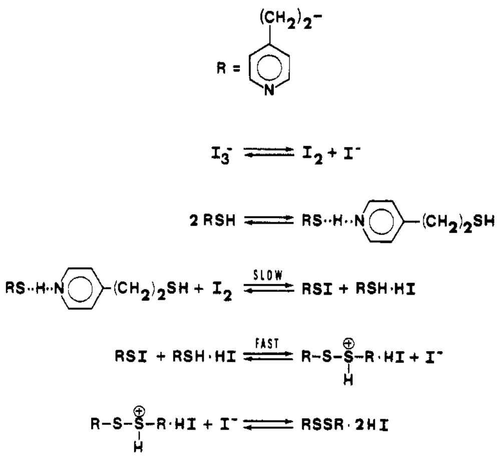
The results demonstrate the use of stopped-flow techniques to measure the rates of reaction of I_2 with a variety of thiols in CH_3CN to give disulfides. The rate of triiodide loss is directly proportional to $[I_3^-]/[I^-]$ (Table I) and is usually interpreted as resulting from the equilibrium $I_3^- \rightleftharpoons I_2 + I^-$ prior to the oxidation by iodine. The absence of higher inverse terms in iodide indicates that the intermediates formed do not dissociate to iodide ion prior to the rate-determining step. This equilibrium is shown as the first step in Schemes I–III.

For dodecanethiol (D) the reaction is first order in D and the results show that the reaction will proceed even in the absence of added base. The acceleration of the rate by

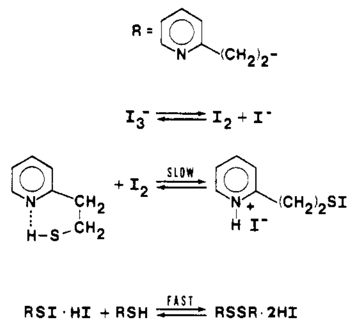
Scheme I. Mechanism of the Oxidation of D with I_2 in CH_3CN (N = CH_3CN or Pyridine)



Scheme II. Mechanism of the Oxidation of B with I_2 in CH_3CN



Scheme III. Mechanism of the Oxidation of A with I_2 in CH_3CN



pyridine has been measured, but the acceleration of the rate by the more basic triethylamine was too large to be measured by stopped-flow techniques. Thus, acetonitrile itself must function as a weak base, polarizing the S–H bond and enhancing the nucleophilic character of the thiol sulfur. More basic compounds can compete favorably with the acetonitrile to accelerate the rate. It should be pointed out that dodecanethiol does not react with iodine in nonbasic solvents such as dichloromethane or glacial acetic acid. In Scheme I, N is either CH_3CN or pyridine and R is n-$C_{12}H_{25}$. The reaction of the polarized thiol with iodine is rate determining. In the case where N is pyridine, the polarization may be hydrogen bonding as was observed by Bicca de Alencastro and Sandorfy[7] between propanethiol and pyridine. The structures are drawn as ion pairs because anion solvation is poor in acetonitrile. The next steps lead to the disulfide product and were selected to be consistent with microscopic reversibility. The mechanism of the disulfide cleavage has been discussed by Pappas and others.[8]

2-Phenylethanethiol (C) is oxidized in a similar manner. 2-(4-Pyridyl)ethanethiol (B) also could have a similar mechanism, and its second-order dependence on B is interpreted in Scheme II where there is an intermolecular interaction between the thiol functionality of one molecule and the pyridine functionality of the second prior to the rate-determining step. Although we were unable to determine whether there was intermolecular hydrogen bonding of B in acetonitrile, it was observed in >1 M B in CCl_4.

2-(2-Pyridyl)ethanethiol (A) reacts with I_2 more rapidly than do thiols B–D. The reaction is first order in A and added pyridine does not compete to create a second path for the oxidation reaction as it does with D (Table III, lines 1–6). In Scheme III the molecules that have intramolecular hydrogen bonding between the thiol and pyridine groups are proposed to be the reactive species. The accelerated rate of oxidation may be due to both the higher concentration of hydrogen-bonded molecules in A vs. the intermolecular hydrogen-bonded molecules in B, or to an enhancement of the nucleophilicity of the thiol due to intramolecular hydrogen bonding.

The parallel mechanisms shown in Schemes I–III for compounds A, B, and D are consistent with the observed rate laws. Because of the different rate laws, the degree of acceleration of the oxidation of A depends on the concentration of thiol in solution. When [thiol] = 1.0×10^{-3} M, [I^-] = 4.0×10^{-3} M, the relative rates of oxidation are A/B/(D + 1 equiv of pyridine)/D = 1800:28:6:1. In the oxidation of simple thiols by iodine it appears that the rate is extremely sensitive to the basicity of solvent and to added base. The rate is maximized when a neighboring base is in a position to interact intramolecularly with the thiol.

The kinetic results for A do not reflect any direct intramolecular interaction between the pyridine nitrogen and the thiol sulfur prior to the rate-determining step. However, a nucleophilic displacement of iodide ion from the sulfenyl iodide by pyridine subsequent to the rate-determining step would give and N^+–S bonded intermediate if proton loss from pyridine occurs. Although at the moment such a path would only be speculative, we are conducting further experiments on other model systems to detect these intermediates if they are formed.

Experimental Section

Materials and Solvents. 2-(2-Pyridyl)ethanethiol (A) and 2-(4-pyridyl)ethanethiol (B) were synthesized by the method of Chia et al.[9] 2-Phenylethanethiol (C) was purchased from ICN Pharmaceuticals, Inc. *n*-Dodecanethiol (D) was purchased from Aldrich Chemical Co. Compounds A and B were purified by two successive vacuum distillations and then checked by NMR and GC techniques. Compounds C and D were determined to be essentially pure by NMR, GC, and TLC techniques. They were used without additional purification.

Stopped-Flow Kinetics. Measurements were taken with a Durrum Model D110 stopped-flow spectrophotometer. The photomultiplier output was converted to absorbance via an internal logarithmic amplifier and displayed on a Tektronix 5103N storage oscilloscope. The oscilloscope trace was then displayed

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[7] Bicca de Alencastro, R.; Sandorfy, C. *Can. J. Chem.* **1973**, *51*, 985.

[8] Pappas, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2926.

[9] Chia, P. S. K.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1966**, *19*, 1835, synthesis via method 2.

as absorbance at 362 nm as a function of time. After three superimposible traces were recorded, a Polaroid photograph of the oscilloscope screen was taken. Pseudo-first-order rate constants were calculated from these photographs by using a least-squares line fitting computer program.

One reservoir syringe of the spectrophotometer was filled with a solution of thiol and pyridine (if any) in acetonitrile. The other syringe was filled with a solution of tetrabutylammonium triiodide and tetrabutylammonium tetrafluoroborate in the same solvent. The two solutions were simultaneously injected into a 2.0-cm path length cell. Maximum mixing time with this cell is 2 ms. The syringes, mixing chamber, and cell were thermostated at 25.0 ± 0.1 °C with a Brinkmann Instrument Lauda Type K-2/R thermostat.

Linear regression of the effect of changes in [I^-] and k_{obsd} (Table I, lines 5–8) yields the following correlations: A, slope = −0.9, coefficient of correlation = 0.998; B, slope = −0.9, coefficient of correlation = 0.995; C, slope = −0.9, coefficient of correlation = 0.98; D, slope = −1.0, coefficient of correlation = 0.990. These reactions are thus inverse first order in iodide. Linear regression of the thiol dependence of k_{obsd} (Table I, lines 1–4; Table II, lines 1–4) yield the following: A, slope = 1.0, coefficient of correlation = 0.98; B, slope = 2.0, coefficient of correlation = 0.997; D, slope = 1.0, coefficient of correlation = 0.99993. The reactions of A and D are first order in thiol. Compound B is second order in B. The thiol dependence of C was not studied.

Infrared Measurements. Measurements were made with a Perkin-Elmer Model 180 spectrophotometer.

Electrochemical Oxidations. Electrochemical oxidations were carried out by cyclic voltammetry. A Princeton Applied Research Model 173 potentiostat, Model 175 universal programmer, Model 178 electrometer, and Model RE 0074 X–Y recorder were used. Sample preparation was carried out under a nitrogen atmosphere in a Kewaunee Scientific Equipment drybox. Kodak electrochemical grade tetrabutylammonium perchlorate was the supporting electrolyte in acetonitrile (Burdick and Jackson Laboratories, Inc.).

A three-compartment electrochemical cell consisted of two outer compartments containing a silver reference electrode (Ag|0.1 M $AgNO_3$ in CH_3CN) and a platinum counterelectrode. The platinum working electrode was cleaned in 10 M HNO_3, heated in a flame, and oven-dried before each experiment.

Reaction Products. Products were determined by titration of 5 mmol of thiol in 50 mL of CH_3CN with 2.6 mmol of I_2 in 50 mL of CH_3CN. The titration continued until the I_2 had been consumed by the thiol. The end point was determined by the slight retention of the yellow color from excess iodine.

The resulting solutions were extracted three times into $CHCl_3$ following neutralization of the pyridinium salts with an aqueous solution of 1 M NaOH. The solvent was removed with a rotary evaporator, yielding the products. Mass spectra and data obtained from a Varian 90 MHz NMR spectrometer are consistent with disulfides being the reaction products in each case.

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Gas-Phase Dieckmann Ester Condensation Characterized by Mass Spectrometry/Mass Spectrometry

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Negative-ion mass spectra obtained by chemical ionization show signals which correspond in mass-to-charge ratio to the products of the title reaction. Collision-induced dissociation of these ions and comparison of the resulting spectra with those of authentic compounds confirm this assignment. Charge-inversion spectra and isotopic labeling both provide further evidence for analogous mechanisms for the Dieckmann reaction in the gas phase and in solution. A closely related gas-phase reaction, not observed in solution, is cyclization of diesters bearing α-alkyl substituents by elimination of a molecule of dialkyl ether. This apparently represents a new type of fragmentation reaction in closed-shell negatively charged ions. The newer mass spectral methods used here not only provide a rapid means of uncovering such variants in the course of reaction but also allow the direct characterization of species which occur only as transient reaction intermediates in the condensed phase.

Because ionic species have long been known to be the reactive intermediates responsible for the conversion of nonionic reactants to nonionic products in many condensed-phase organic reactions, gas-phase analogues of well-known organic reactions have frequently been a target for investigation by mass spectrometry. Typical of early electron-impact studies of this nature were those on anchimeric assistance in processes analogous to solvolytic reactions,[1] intramolecular cyclizations which amount to nucleophilic aromatic substitution,[2] Wagner–Meerwein rearrangements,[3] and rearrangement reactions which correspond to thermolytic processes.[4] These studies were limited in two particular ways: first, the great body of reactions which are not unimolecular was excluded from examination, and second, evidence for the structures of the ions under study was indirect and relied on a considerable knowledge of fragmentation behavior under electron-impact conditions. These two limitations have subsequently been lifted: first, ion/molecule reactions can be investigated by various experimental means, including chemical ionization (CI),[5] flowing afterglow,[6] and ion cyclotron

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