thionite (0.03 g, 0.000 22 mol) in deoxygenated water (1 mL) was added, causing precipitation of a white solid. The mixture was shaken occasionally for 5 min before centrifugation. Then, 3.42 μL of the supernatant were added to a UV cell containing deoxygenated ethanol (2.5 mL) and water (0.75 mL) to achieve an approximate concentration of the intermediate of 4×10^{-5} M. The UV range from 220 to 360 nm was then monitored, with a fairly broad absorption with λ_{max} = 260 nm being recorded. With time and with freshly prepared samples from the original stock solution, the absorption gradually diminished and shifted to λ_{max} = 255 nm after about 80 min. No absorption between 310 and 318 nm for the (*E*)-stilbenediol[13,16] was detected. The final spectrum recorded after 80 min compared very well with that of spectrum d of Figure 1 of ref 13.

Electrochemical Investigation of the Intermediate in the Dithionite Reduction of Benzil. A solution of benzil (0.001 M) in ethanol–water (1:1 v/v) with a 0.1 M NaAc–HOAc electrolyte at pH 5[32] was prepared by dissolving benzil (0.021 g, 0.0001 mole) in ethanol (50 mL) and an aqueous solution made up of 35 mL of 0.2 M sodium acetate and 15 mL of 0.2 M acetic acid. The potential range from –1.0 to 0.0 V (Ag–AgCl) was then scanned at 50 mV s^{-1}. The (*E*)- and (*Z*)-stilbenediols were clearly distinguished (Figure 1a) with peak potentials of –0.38 and –0.28 V, respectively. Next, a solution of the dithionite intermediate identical with that described in the UV study above was prepared and centrifuged. An aliquot (0.1 mL) of the supernatant was added to the cell containing the 0.001 M benzil and the potential range scanned again. This time (Figure 1b) the peak for the Z isomer (E_p = –0.28 V) was dramatically increased.

Reduction of Benzil with Sodium Formaldehydesulfoxylate. Benzil (0.50 g, 0.002 38 mol) was dissolved in ethanol (15 mL). Sodium formaldehydesulfoxylate (2.66 g, 0.017 mol) was dissolved in 5 mL of 1.5 N HCl and added to the stirring benzil solution at room temperature. A control reaction was also run at the same time, identical with the above except that the sodium formaldehydesulfoxylate was dissolved in 5 mL of distilled water. Stirring was continued for a total of 3.5 h at room temperature, at which time the reaction mixtures were poured into 100 mL of H_2O, extracted with CH_2Cl_2, dried (Na_2SO_4), filtered, and evaporated to dryness. ^{1}H NMR analysis of the solid residues showed the control to consist solely of benzil, while the reaction mixture produced in the presence of HCl consisted of benzil (58.7%) and benzoin (41.3%).

Reduction of 4-Chlorobenzil. 4-Chlorobenzil (0.25 g, 0.001 mol) was dissolved in 7.5 mL of ethanol. Sodium formaldehydesulfoxylate (1.33 g, 0.011 mol) dissolved in 2.5 mL of 1 N HCl was added with stirring at room temperature. The reaction was monitored by TLC (silica gel with chloroform). Additional solid sodium formaldehydesulfoxylate was added in small portions at 30-min intervals over the next 4 h, and then the mixture was allowed to stir at room temperature overnight. Workup as before produced a pale yellow solid which was shown by ^{1}H NMR to consist of 4-chlorobenzoin (**2a**, 64%) and 4′-chlorobenzoin (**3a**, 36%).

Acknowledgment. We express our appreciation to Drs. R. A. Newmark and S. V. Pathre for their valuable assistance with interpreting the the NMR spectra and to Dr. P. E. Toren for conducting the electrochemical experiments. We also thank Professor A. R. Katritzky and Dr. J. E. Trend for valuable suggestions and discussions. Dr. L. R. Krepski is thanked for providing a sample of 4-hydroxybenzoin.

Registry No. **1a**, 22711-23-5; **1b**, 2431-00-7; **1c**, 22711-21-3; **1d**, 38469-73-7; **2a**, 71292-81-4; **2b**, 2431-02-9; **2c**, 1889-84-5; **2d**, 5230-33-1; **3a**, 39774-18-0; **3b**, 2431-23-4; **3c**, 4254-17-5; **3d**, 54551-71-2; **7**, 42788-50-1; **10a**, 84812-18-0; **10b**, 84812-19-1; **10c**, 84812-20-4; **10d**, 84812-21-5; sodium dithionite, 7775-14-6; sodium formaldehydesulfoxylate, 149-44-0.

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(32) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: London, 1966; p 41.

Mechanism of Oxidation of Trialkylamines by Ferricyanide in Aqueous Solution

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Rates of oxidation of triethylamine, *N*-methylpyrrolidine, and triethanolamine by aqueous ferricyanide have been determined over the range pH 3.7–13.4. Although rates were greater in the more strongly alkaline solutions, no correlation between rate and ratio of unprotonated/protonated amine was found. The oxidations were inhibited in the presence of added ferrocyanide over the entire pH range; correlations of inhibition with ferrocyanide concentration were linear, with the slopes being greater at lower pH. Two rate-determining processes, electron transfer from amine free base (predominant at high pH) and hydrogen transfer from trialkylammonium cation (predominant at intermediate and lower pH), are proposed to account for these observations. Both processes are reversible, and the slopes and intercepts of the inhibition curves may reflect the relative ease of trapping and generating, respectively, intermediates in the two different processes.

Ferricyanide has long been known to react with electron-rich organic compounds by one-electron abstraction processes,[1] and its oxidation of a variety of trialkylamines was investigated mechanistically in a series of papers by Lindsay Smith and co-workers in the 1970s.[2] The characteristics of these amine oxidations by ferricyanide were strikingly similar to those observed for aliphatic amine oxidations by chlorine dioxide (ClO_2), another one-electron oxidant, in aqueous solution.[3] A significant difference, however, was the irreversibility of the rate-determining electron abstraction step (eq 1) reported in the ferricyanide

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(1) Thyagarajan, B. S. *Chem. Rev.* **1958**, *58*, 439–460.

(2) (a) Audeh, C. A.; Lindsay Smith, J. R. *J. Chem. Soc. B* **1970**, 1280–1285. (b) Audeh, C. A.; Lindsay Smith, J. R. *Ibid.* **1971**, 1741–1744. (c) Lindsay Smith, J. R.; Mead, L. A. V. *J. Chem. Soc., Perkin Trans. 2* **1973**, 206–210. (d) Lindsay Smith, J. R.; Mead, L. A. V. *Ibid.* **1976**, 1172–1176.

(3) For a summary see: Rosenblatt, D. H.; Burrows, E. P. In "The Chemistry of Amines, Nitroso and Nitro Groups and Their Derivatives"; Patai, S., Ed.; Wiley: Chichester, England, 1982; Supplement F, pp 1086–1090, 1098–1099.

$$R_3N + Fe(CN)_6^{3-} \xrightarrow{k_1} R_3N^{+\cdot} + Fe(CN)_6^{4-} \qquad (1)$$

case. Thus, while added chlorite retarded oxidation by aqueous ClO_2 (pH 6.6–8.9),[4] suggesting that the analogous rate-determining electron abstraction by ClO_2 is reversible, Lindsay Smith observed no similar effect of added ferrocyanide (in strongly alkaline aqueous *tert*-butylamine).[2a] This observation contrasted with the earlier report[5] that added ferrocyanide retarded the oxidation of triethylamine (TEA) by aqueous ferricyanide at pH 8.8. In an effort to resolve this apparent anomaly and to clarify in detail the mechanism of oxidation of aliphatic amines by ferricyanide, we have studied the kinetics of oxidation of three trialkylamines [TEA, *N*-methylpyrrolidine (NMP), and 2,2′,2″-nitrilotriethanol (triethanolamine, TEOA)] by aqueous ferricyanide in the pH range 3.7–13.4 and have observed a retarding effect of added ferrocyanide over the entire range.

Experimental Section

Materials. Potassium ferricyanide (Fisher), potassium ferrocyanide (Baker), TEA (Fisher), NMP (Aldrich), and TEOA (MCB) were reagent grade chemicals and were not further purified. Buffers were prepared from sodium mono- and dihydrogen phosphate (Fisher) and potassium hydrogen phthalate (Fisher), and glass-distilled, deionized water was used throughout. Deuterium oxide was 99.8% (Stohler Isotope Chemicals). Measurements of pH were made with a Corning Model 12 pH meter.

General Procedure for Kinetics. Kinetics were followed by measuring the absorbance of ferricyanide at 420 nm with a Beckman UV 5230 recording spectrophotometer equipped with 2-cm cells. In each experiment the absorbance of a solution of aliquots (2.5 mL each) of 0.0005 M $K_3Fe(CN)_6$ and buffer was first recorded, the appropriate volume of TEA or NMP (5–33 μL) to give a solution 0.01–0.05 M in amine was introduced by microliter syringe, the timer was started, and the mixture was shaken thoroughly for 25–30 s. Absorbances were recorded at appropriate intervals starting at 1 min after addition of amine. For TEOA, appropriate volumes of a 3:1 TEOA–H_2O (w/v) mixture were used since the amine alone was too viscous. Only the initial portion of the reaction ($\leq 0.7t_{1/2}$) was followed so as to exclude any retarding effect of ferrocyanide formed. Pseudo-first-order rate constants, k_{obsd}, for these initial reactions were obtained by a linear regression program (Texas Instruments Model 58); correlations were >0.98 when the zero time value (before addition of amine) was omitted. Reactions with added ferrocyanide were studied in a similar manner except that the volume of buffer was decreased so as to make the total volume of buffer plus 0.05 M $K_4Fe(CN)_6$ solution equal to 2.5 mL; e.g., solutions 0.001 M in $K_4Fe(CN)_6$ were prepared by adding buffer (2.4 mL) and 0.05 M $K_4Fe(CN)_6$ (0.1 mL) to 2.5 mL of 0.005 M $K_3Fe(CN)_6$.

Isolation of Acetaldehyde. One drop of TEA was added to solutions of 0.01 M $K_3Fe(CN)_6$ (1 mL) and to 0.01 M $K_3Fe(CN)_6$ (1 mL) containing 1 drop of 0.5 M NaOH. The mixtures were allowed to stand at room temperature until colorless (16 and 3.5 h, respectively) before treatment with 1 drop of 2,4-dinitrophenylhydrazine (DNP) reagent.[6] The precipitate in each case was identified as acetaldehyde 2,4-DNP by silica gel TLC comparison with authentic material (R_F 0.4, 1:1 hexane/ether). The precipitate obtained from reagent blanks (0.01 M $K_3Fe(CN)_6$ and 0.01 M $K_4Fe(CN)_6$) consisted only of DNP reagent.

Table I. Second-Order Rate Constants for Oxidation of Triethylamine by Ferricyanide in Phosphate and Phthalate Buffers

pH	[triethylamine], M	k_{obsd}, min^{-1} (± 0.002)	k_1, M^{-1} min^{-1} (± 0.05)
3.7[a]	0.04	0.028	0.35
3.7–7.0[b]	0.05	0.038	0.38
6.7, 7.0[c]	0.02	0.014	0.35
8.1[c]	0.02	0.023	0.58
9.1[c]	0.02	0.024	0.60
10.0	0.02	0.028	0.70
11.1[c]	0.02	0.028	0.70
12.1[d]	0.02	0.053	1.33

[a] 2.5×10^{-4} M $K_3Fe(CN)_6$, 0.01 M phthalate buffer. [b] 5×10^{-4} M $K_3Fe(CN)_6$. Determinations were made at pH 3.67, 4.33, and 5.39 in 0.01 M phthalate buffer and at pH 6.33 and 6.97 in 0.01 M phosphate buffer. [c] 2.5×10^{-4} M $K_3Fe(CN)_6$, 0.025 M phosphate buffer. [d] 2.5×10^{-4} M $K_3Fe(CN)_6$, 0.05 M phosphate buffer.

Table II. Second-Order Rate Constants for Oxidation of 0.01 M *N*-Methylpyrrolidine by 0.000 25 M Ferricyanide in Phosphate and Phthalate Buffers

pH	k_{obsd}, min^{-1}	k_1, M^{-1} min^{-1}
3.7[a]	0.0076 ± 0.0004	0.38 ± 0.02
6.7[b]	0.0086 ± 0.0004	0.43 ± 0.02
8.1[b]	0.0395 ± 0.0015	1.98 ± 0.07
9.1[b]	0.0505 ± 0.0015	2.52 ± 0.07
10.0[b]	0.0496 ± 0.0015	2.48 ± 0.07
11.1[b]	0.0484 ± 0.0015	2.42 ± 0.07
12.1[c]	0.0894 ± 0.0015	4.47 ± 0.05
12.1[c,d]	0.0288 ± 0.0015	1.44 ± 0.07

[a] 0.01 M phthalate buffer. [b] 0.025 M phosphate buffer. [c] 0.05 M phosphate buffer. [d] 0.05 M phosphate buffer, 0.001 M added ferrocyanide.

Table III. Second-Order Rate Constants for Oxidation of 0.04 M Triethanolamine by 0.000 25 M Ferricyanide in Phosphate and Phthalate Buffers

pH	k_{obsd}, min^{-1} ($\pm 0.000\,25$)	k_1, M^{-1} min^{-1} (± 0.006)
3.7[a]	0.000 895	0.011
6.7[b]	0.001 75	0.022
9.1[b]	0.003 63	0.045
11.1[b]	0.004 06	0.051
11.9[c]	0.039 3	0.492
11.9[c,d]	0.029 5	0.369

[a] 0.01 M phthalate buffer. [b] 0.025 M phosphate buffer. [c] 0.05 M phosphate buffer. [d] 0.05 M phosphate buffer, 0.002 M added ferrocyanide.

Results and Discussion

Second-order rate constants were obtained according to the expression $k_1 = k_{obsd}/2[\text{amine}]$, which takes into account the consumption of a second equivalent of ferricyanide in a fast reaction. Results are summarized in Tables I–III. It is noteworthy that alkaline solutions are not necessary for rapid oxidation of these completely water-miscible amines. Indeed, TEA is oxidized only twice as fast at pH 11 as at pH 7, and both TEA and NMP continue to be oxidized at the same rate in acidic solution as the pH is lowered to 3.7, the minimum value studied. Oxidation at pH 7 and below does not appear to depend on the nature or concentration of the buffer or, at these low ionic strengths, on the presence of buffer at all. Thus, rates of oxidation of TEA in 0.01 and 0.025 M sodium phosphate buffers at pH 7, in 0.01 M potassium phthalate buffer at pH 3.7, and in glass-distilled deionized water alone were not distinguishably different (Table I). For verification that the overall course of the reaction at lower pH is the same as that of the well-studied reaction in alkaline solution, i.e., oxidative dealkylation,[3] the carbonyl

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[4] Hull, L. A.; Davis, G. T.; Rosenblatt, D. H.; Williams, H. K. R.; Weglein, R. C. *J. Am. Chem. Soc.* **1967**, *89*, 1163–1170.

[5] Hull, L. A.; Davis, G. T.; Rosenblatt, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 6247–6250.

[6] Fieser, L. F. "Experiments in Organic Chemistry"; 3rd ed.; D. C. Heath: Boston, 1955; p 284.

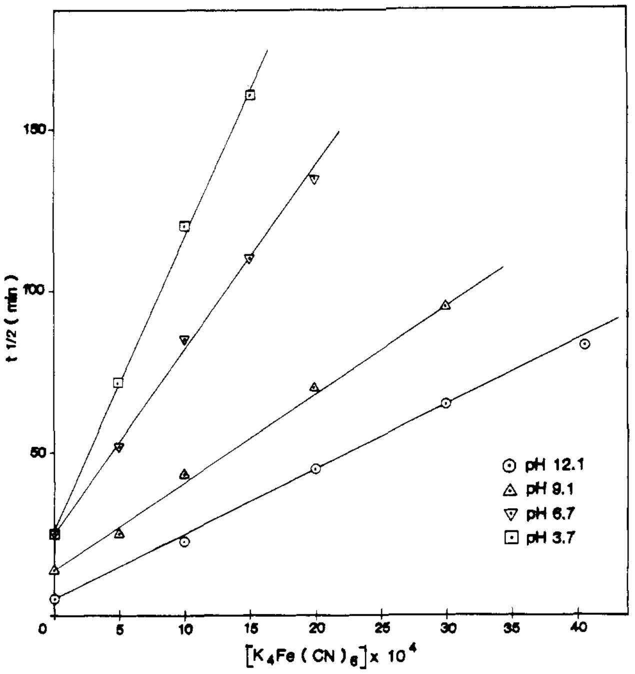


Figure 1. Retardation of oxidation of 0.04 M triethylamine by 0.000 25 M ferricyanide in the presence of added ferrocyanide.

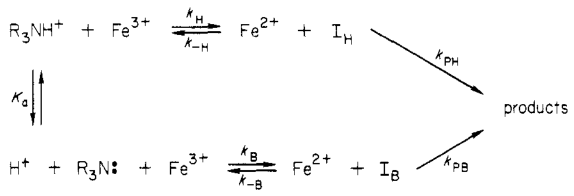
products of TEA in water alone and in aqueous NaOH were isolated. Only acetaldehyde was found in each case.

It can be seen that, while rates of oxidation of NMP (Table II) were higher relative to those of TEA (Table I) at and above pH 6.7, the two were oxidized at the same rate at pH 3.7. That the latter observation was fortuitous and that oxidation rates at or below neutral pH may also vary with the structure of the amine was shown by the oxidation of TEOA (Table III). Not unexpectedly, in view of its electron-withdrawing substituents,[2d] this amine at pH 11 and below was less than one-tenth as reactive as TEA. The ten-fold increase in rate of oxidation of TEOA between pH 11 and 12 may be attributed to a faster electron-transfer reaction of the alkoxide ion. Shukla and co-workers[7] have studied the oxidation of TEOA in aqueous sodium hydroxide and observed first-order dependence on ferricyanide, hydroxide ion, and amine.

We have examined the effect of added ferrocyanide on the rates of oxidation of TEA at four different pHs; the results are displayed in Figure 1. In each case, substantial retardation of the pseudo-first-order rates was observed, and there was a linear correlation of inhibition (plotted as increase in half-life) with concentration of added ferrocyanide. In addition, the retardative effect appeared to be somewhat greater as the pH was lowered, e.g., with no added ferrocyanide any difference in rate between pH 6.7 and 3.7 was too small to measure, but the addition of equal amounts of ferrocyanide resulted in significantly greater inhibition at the lower pH. Under the conditions of Figure 1 the rate of reaction of TEA at pH 13.4 was too fast to allow more than semiquantitative estimation ($t_{1/2} < 4$ min), but in the presence of 0.004 M ferrocyanide a half-life of 10 min was observed.

Data for similar inhibition in the presence of added ferrocyanide for NMP and TEOA are included in Tables II and III. The data for TEOA do not substantiate the report of ferrocyanide-*accelerated* oxidation of TEOA in 0.001 M aqueous NaOH.[7] Since the concentrations of both ferricyanide (0.002 M) and ferrocyanide (0.0125, 0.025 M) in those experiments were approximately 10 times greater than ours, the known large cationic salt effect[2a,5] might be expected to obscure the smaller effect of a reversible step. In addition, there is no support for the proposed prior complexation of amine and ferricyanide.[7] The small rate enhancement reported[2a] for oxidation of methyldi-*sec*-butylamine by 0.0018 M ferricyanide in the presence of 0.000 18 M added ferrocyanide is not readily explained, but our experiments indicate that such a low concentration of ferrocyanide would not result in measurable retardation.

Scheme I



Thus, we have documented two salient features of the oxidation of trialkylamine by ferricyanide in aqueous solution; neither was anticipated in view of the earlier investigations. First, alkaline solutions were not a requisite; indeed, oxidation took place at pHs as low as 3.7, and only a very modest pH dependence which did not correlate with concentration of free amine was observed. Second, inhibition of the oxidation was linear with concentration of ferrocyanide added and was somewhat greater as the pH was lowered.

In mechanistic assessment, it is clear that both electron transfer from amine free base to ferricyanide ion (eq 1, reversible), and some other reductive process involving the protonated amine, can be important rate-determining processes. We suggest hydrogen transfer from ammonium ion to ferricyanide ion (eq 2) as the most probable pathway

$$R_3N^+{:}H + Fe(CN)_6^{3-} \rightleftarrows R_3N^{+\cdot} + HFe(CN)_6^{3-} \qquad (2)$$

for reaction at pHs appreciably below pK_a of the ammonium ion. The kinetic isotope effects observed for the unbuffered oxidations of TEA and NMP (k_H/k_D 1.8 ± 0.2 and 1.7 ± 0.2, respectively) are in accord with N-H bond involvement in the rate-determining process.

A simple phenomenological scheme summarizing our findings and consistent with eq 1 and 2, is given in Scheme I, where k_H, k_{-H} and k_B, k_{-B} are forward and reverse rates of formation of intermediates I_H and I_B from protonated and unprotonated amine, respectively, and k_{PH} and k_{PB} are rates of formation of products from the two respective intermediates. Thus over the entire pH range the second-order rate constant may be expressed as eq 3. For

$$k_1 = \frac{1}{(K_a + [H^+])}\left[\frac{k_H k_{PH}[H^+]}{k_{-H}[Fe^{2+}] + k_{PH}} + \frac{k_B k_{PB} k_a}{k_{-B}[Fe^{2+}] + k_{PB}}\right] \qquad (3)$$

the simplest cases, reactions at very low and very high pH, the expression, written inversely so as to relate directly to the inhibition studies (Figure 1), reduces to eq 4 and 5,

$$\frac{1}{k_1} = \frac{k_{-H}[Fe^{2+}]}{k_H k_{PH}} + \frac{1}{k_H} \qquad (4)$$

$$\frac{1}{k_1} = \frac{k_{-B}[Fe^{2+}]}{k_B k_{PB}} + \frac{1}{k_B} \qquad (5)$$

respectively. Although at intermediate pH the situation is more complex, it is evident that the intercepts of the curves (half-lives without added ferrocyanide) may reflect

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[7] Shukla, K. S.; Mathur, P. C.; Bansal, O. P. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1301-1307.

the relative ease of formation of the intermediates ($I_B > I_H$), while the slopes (greater at lower pH) may reflect the relative ease of trapping of the two intermediates.

Acknowledgment. We are grateful to Professor Richard L. Schowen for reading the manuscript and providing valuable comment on the significance of the inhibitions.

Registry No. TEA, 121-44-8; NMP, 120-94-5; TEOA, 102-71-6; potassium ferricyanide, 13746-66-2; potassium ferrocyanide, 13943-58-3.

Reaction of Methoxide Ion with Dibenzo[*ce*]-1,2-dithiin 1,1-Dioxide: Surprising Behavior in the Reaction of an Aryl Thiolsulfonate with an Alkoxide

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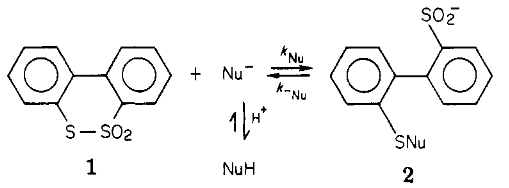
Received August 30, 1982

Although the six-membered cyclic thiolsulfonate dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (1) reacts with such nucleophiles as RS^-, CN^-, or SO_3^{2-} at a rate only slightly slower than they react with an acyclic aryl thiolsulfonate ($PhSSO_2Ph$), it reacts with methoxide ion *over 10^4 times slower* than does $PhSSO_2Ph$, and in methanol the equilibrium constant for the reaction of 1 with CH_3O^- to form the ring-opened sulfenate ester **2a** (eq 3) is so small that at equilibrium only a few percent of 1 is converted to **2a**, even at quite high methoxide concentrations. The equilibrium constant for the conversion of 1 to **2a** is, as might be expected, much larger in dimethyl sulfoxide (Me_2SO)–methanol, and the rate constants for both the forward and reverse steps of the equilibrium can be determined in 70–90% Me_2SO by stopped-flow spectrophotometry. The rate for the conversion of 1 to **2a** is found to increase markedly with an increase in the Me_2SO content of the medium, but the rate of the reverse reaction (**2a** → 1 + MeO^-) *is not significantly dependent* on solvent composition. It is shown that all these results can seemingly be satisfactorily explained only if the reaction of 1 with methoxide to form **2a** is assumed to take place by a stepwise mechanism (eq 8) in which a hypervalent sulfur species (**6a**) is present on the reaction coordinate as an intermediate which lies in a potential well of sufficient depth that there is a substantial ΔG^* for collapse of **6a** to **2a**. Because of the six-membered ring in **6a**, ΔG^* for **6a** going to **2a** is 5–6 kcal/mol larger than ΔG^* for the collapse of the equivalent intermediate (**6o**) to $PhSOCH_3$ plus $PhSO_2^-$ in the reaction of $PhSSO_2Ph$ with methoxide. In the reactions of RS^-, CN^-, or SO_3^{2-} with 1, the free energy of **6b**, the intermediate analogous to **6a**, is substantially higher, so much so that ΔG^* for collapse of **6b** to ring-opened products is in no case more than 1–2 kcal/mol. For this reason there is little difference for these nucleophiles in the rates for 1 vs. $PhSSO_2Ph$. The preceding explanations are all in accord with expectations based on the findings of Martin and co-workers[10,11] regarding the relative stability of isolable hypervalent sulfur species containing apical ligands of differing electronegativity and the influence of a ring on the stability of such species.

The cyclic thiolsulfonate dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (1) reacts readily in aqueous dioxane with such nucleophiles as cyanide, sulfite, or thiolate ions (step k_{Nu}, eq 1) to form ring-opened substitution products **2** (Nu = CN, SO_3^-, or SR).[1,2] The rate constants, k_{Nu}, at which 1 reacts with these nucleophiles are 2.5–8 times smaller than the rate constants[3] for the reactions of the same nucleophiles with the acyclic aryl thiolsulfonate $PhSSO_2Ph$. Acidification of the final reaction solutions with a carboxylic acid buffer sufficiently acidic to protonate the nucleophiles to their conjugate acids (NuH) causes **2** to revert (step k_{-Nu}, eq 1) rapidly and quantitatively to 1, and the rate constants, k_{-Nu}, for these processes can also be measured.[1,2]



1 2 (1)

Another nucleophile that reacts readily with the acyclic thiolsulfonate $PhSSO_2Ph$ is methoxide ion (eq 2).[3] We

$$CH_3O^- + PhSSO_2Ph \xrightarrow[\text{(in } CH_3OH,\ k'_{MeO} = 400\ M^{-1}\,s^{-1})]{k'_{MeO}} PhSOCH_3 + PhSO_2^- \quad (2)$$

therefore anticipated that 1 should react readily with CH_3O^- in methanol (eq 1, $Nu^- = CH_3O^-$) to give **2a** (Nu = OCH_3) and that acidification of the final reaction solution would cause the reversion of the sulfenate ester **2a** to 1. Surprisingly, 1 does not react readily in methanol with methoxide, even when the latter is present at high concentration (0.2 M), and acidification of the solution at the completion of the very slow reaction that does occur fails to regenerate 1. On the other hand, in dimethyl sulfoxide (Me_2SO)–methanol mixtures containing at least 80% Me_2SO, 1 does react rapidly with methoxide ion, and, under appropriate conditions, prompt acidification of the final reaction solution leads to rapid regeneration of 1.

The present paper reports the details of a kinetic study of the reaction of 1 with methoxide ion in both methanol

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[1] Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1978**, *43*, 914.
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