pearance of 1 was monitored by absorption spectroscopy as was the appearance of 3. Typically, a conversion of about 10% of starting material was used in the quantum-yield determinations.

General Photolysis Method. A suspension of 10 mg of 1 or 4 in 25 mL of aqueous or alcoholic 1 M acid was vibrated in an ultrasonic bath for 10 min. The resulting suspension was transferred to Pyrex test tubes sealed with serum caps. Such suspensions were either irradiated directly or were deoxygenated by a 30-min purge with dry argon. The process of the reaction was monitored by absorption spectroscopy after withdrawing an appropriate aliquot and diluting. Light source for the irradiation was either a circular array of 350-nm phosphor-coated low-pressure mercury arcs, natural sunlight, or a water-cooled 200-W GE Sunlamp.

Stability of 2 and 3. The photolysis mixtures obtained from 1 by the above procedure were wrapped in foil and stored in the dark in a desk drawer or in the refrigerator. The intense blue color of a 50:50 mixture of 1–photoproducts had completely disappeared overnight. If air was bubbled slowly through the resulting yellow suspension for 2 h, quinone 1 was the sole recoverable product after chromatography on silica gel (EtOAc eluant).

After five cycles (irradiation–fading) in water essentially the same results were obtained, except that poorer (>80%) mass balance in the recovery of 1 was obtained. A yellow-colored side product(s) eluting more slowly from the column gave elemental analysis with oxygen contents 50–200% higher that that required for 1.

Electrochemistry of 1. Cyclic voltammograms were obtained in a previously described three-compartment cell employing a silver wire quasi-reference electrode[17] or with a saturated calomel electrode separated from the electrolysis cell by a glass frit. The experiments were conducted with a PAR (Princeton Applied Research Corp.) Model 173 potentiostat and Model 175 universal programmer. An X-Y recorder (Houston Instruments) was used to record current-potential curves. The curves obtained for 1 and 3 are shown in Figures 2 and 3.

"Photocurrent" measurements were obtained by monitoring current between a glassy carbon anode and a platinum cathode with a microammeter (Keithley Model 177 multimeter) while the potential was maintained at –0.75 eV with a PAR Model 173 potentiostat. The entire thermostatted electrochemical cell was inserted into the circular cavity of a Rayonet photochemical reactor equipped with 350-nm phosphor-coated low-pressure mercury lamps. The anodic current was monitored as a saturated solution of 1 in 0.1 M ethanolic H_2SO_4 containing 0.1 M $NaSO_4$ was irradiated. The blue color which developed upon irradiation was accompanied by an anodic current (0–0.3 mA). This color faded immediately upon the injection of 10 mL of a 0.01 M aqueous solution of benzoquinone.

Flash Photolysis. A N_2 laser (≤5 mJ/pulse) was used to excite a saturated solution of 1 in 0.1 M ethanolic H_2SO_4 after a 3-min nitrogen purge. Transients were observed in the range from 380–700 nm. Data analysis was conducted with a previously described system.[18]

Acknowledgment. We are grateful for financial support for this research by the U.S. Department of Energy and the Robert A. Welch Foundation. M. A. F acknowledges support as an Alfred P. Sloan Foundation Research Fellow (1980–82). The flash spectroscopic measurements were conducted with the assistance of Dr. M. A. J. Rodgers at the Center for Fast Kinetics Research, a facility sponsored by the National Institutes of Health and the University of Texas at Austin. We are especially grateful to Professor Roland Pettit for bringing this problem to our attention and for helpful comments during the course of the work.

Registry No. 1, 76447-82-0; 2, 76447-83-1; 3, 76447-85-3; 4, 25174-63-4; 5, 258-67-3.

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[17] Fox, M. A.; Kabir-ud-Din; Bixler, D.; Allen, W. S.; *J. Org. Chem.* **1979**, *44*, 3208.

[18] Rodgers, M. A. J.; Foyt, D. C.; Zimek, Z. A. *Rad. Res.* **1978**, *75*, 296.

Neighboring-Group Participation in Organic Redox Reactions: Effect of Tertiary Amine and Pyridine Groups on the Kinetics and Mechanism of Thioether–Sulfoxide Interconversions

Joyce Takahashi Doi,* W. Kenneth Musker, David L. deLeeuw, and Albert S. Hirschon

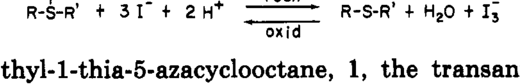
Department of Chemistry, University of California, Davis, California 95616

Received October 28, 1980

The effect of neighboring tertiary amine, quaternary ammonium, and pyridine substitution on both the oxidation of thioethers by aqueous I_2 and the reduction of sulfoxides by aqueous HI has been evaluated. The millionfold acceleration in the rates of the reactions of 5-methyl-1-thia-5-azacyclooctane and its sulfoxide is unique. The rates of the lower homologues and acyclic analogues are not accelerated and at a given acid concentration the rates of oxidation of amine sulfides follow the rate law $d[RSR']/dt = -k_{ox}[RSR'][I_2][I^-]^{-1}$. The rates of reduction of the amine sulfoxides follow the rate law $d[RSR']dt = k_{red}[RR'S{-}O][I^-]$. The pH profiles of the I_2 oxidation of 6-methyl-2-thia-6-azaheptane and 2-[2-(methylthio)ethyl]pyridine demonstrate neighboring-group participation and suggest N–S interacted intermediates.

Introduction

As part of our studies of intramolecular catalysis of organic oxidation and reduction reactions, the effect of neighboring tertiary amine, quaternary ammonium, and pyridine substitution on both the oxidation of thioethers by aqueous I_2 and the reduction of sulfoxides by HI (eq 1) has been evaluated. We previously had shown that in



$$R\text{-}\overset{O}{S}\text{-}R' + 3I^- + 2H^+ \underset{oxid}{\overset{redn}{\rightleftharpoons}} R\text{-}S\text{-}R' + H_2O + I_3^- \qquad (1)$$

5-methyl-1-thia-5-azacyclooctane, 1, the transannular tertiary amine group catalyzes both the oxidation of the

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Table I. Oxidation of Amine Sulfides with Aqueous Iodine at 26 °C

compd	pH	$[KI]_0$	$[KCl]_0$	k_2,[a] $M^{-1}\ s^{-1}$	$\Delta \log k_2/(\Delta \log [KI]_0)$
5-methyl-1-thia-5-azacyclooctane, **1**	7.0	0.060		ca. 10^5 [c]	-0.8 ± 0.1[b]
	8.0	0.060		ca. 10^6 [c]	
4-methyl-1-thia-4-azacycloheptane, **2**	8.0[d]	0.060	-	1.17 ± 0.06	−1.8
$(CH_3)_2N(CH_2)_3SCH_3$, **3**	6.9[d]	0.060	-	0.20 ± 0.03	−1.7
	8.0[d]	0.060	-	1.7 ± 0.2	−1.9
	9.0[e]	0.060	-	2.90 ± 0.05	−1.8
$(CH_3)_3N^+(CH_2)_3SCH_3I^-$, **4**	8.0[d]	0.060	-	0.20 ± 0.01	−1.7
$(CH_3)_2N(CH_2)_2SCH_3$, **5**	8.0[d]	0.060	-	ca. 0.19	-
2-[2-(methylthio)ethyl]pyridine, **6**	4.0[f]	0.050	0.050	0.055 ± 0.003	−1.7
	5.0[f]	0.050	0.050	0.213 ± 0.007	−1.7
	6.0[f]	0.050	0.050	0.56 ± 0.03	−1.7
	6.0[d]	0.050	0.050	0.570 ± 0.003	−1.7
	7.0[d]	0.050	0.050	0.87 ± 0.02	−1.8
	8.0[d]	0.050	0.050	1.12 ± 0.04	−1.8

[a] Second-order rate constants, k_2, calculated by dividing the pseudo-first-order rate constant, k_1, by [RSR′]. Error is the result of replicate determinations. [b] Determined at pH 3.5. [c] Extrapolated from data at pH 3.5–5.3.[1a] [d] 0.0125 M phosphate buffer. [e] 0.0125 M borate buffer. [f] 0.0125 M acetate buffer.

Table II. Reductions of Amine Sulfoxides with Aqueous HI at 25.8 °C

compd	$[HClO_4]$	$10^4 k_1$, s^{-1} [c] 0.30 M NaI	concn range, M, NaI[b]	$\frac{\Delta \log k_1}{\Delta [NaI]}$[d]
5-methyl-1-thia-5-azacyclooctane 1-oxide, **7**	5.84[a]	50000[a]	-	2.0[a]
5,5-dimethyl-1-thia-5-azoniacyclooctane 1-oxide iodide, **8**	5.84	0.61 ± 0.12	-	-
4-methyl-1-thia-4-azacyclohexane 1-oxide, **9**	5.84	0.20 ± 0.01	0.15–0.30	0.99 ± 0.06
4-methyl-1-thia-4-azacycloheptane 1-oxide, **10**	5.84	2.6 ± 0.3	0.15–0.30	0.90
$(CH_3)_2NCH_2CH_2CH_2S(O)CH_3$, **11**	5.01	3.1 ± 0.2	0.10–0.30	0.8 ± 0.3
$(CH_3)_2NCH_2CH_2S(O)CH_3$, **12**	5.01	1.22 ± 0.13	0.15–0.30	1.0
	5.84	5.23 ± 0.05	-	-
$((CH_3)_3NCH_2CH_2S(O)CH_3)^+I^-$, **13**	5.84	6.0 ± 0.5	0.08–0.30	0.89 ± 0.03
$((CH_3)_3NCH_2CH_2S(O)CH_3)^+PF_6^-$, **14**	5.84	5.1 ± 0.5	0.08–0.30	1.02 ± 0.07
2-(2-methylsulfinylethyl)pyridine, **15**	5.01	17.3	0.08–0.30	1.09 ± 0.05
$(CH_3)_2SO$[e]	4.85	4.3		
	5.82	24		

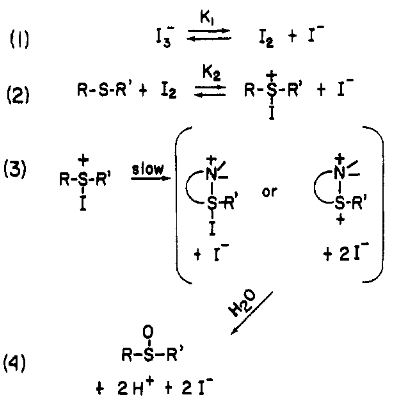
[a] Data for **7** have been published.[16] The value listed here is an extrapolated value. [b] These rates were run in 7.92 M $HClO_4$ for **9**, 5.84 M $HClO_4$ for **10**, **13**, and **14**, and 5.01 M $HClO_4$ for **11**, **12**, and **15**. [c] Pseudo-first-order rate constants based on I_3^- production in excess NaI and $HClO_4$. [d] Ionic strength maintained by addition of $NaClO_4$. [e] Reference 6b.

mesocyclic thioether **1**[1a] and the reduction of its sulfoxide **7**[1b] by a factor of 10^5–10^6 relative to simple analogues. The speed and the unusual rate laws observed for these reactions were satisfactorily interpreted in terms of the facile formation of an intermediate sulfurane $R_3N^+S(R)_2I$ or dication $R_3N^+S^+R_2$. Similar intermediates are also generated when other neighboring groups with lone-pair electrons interact with an oxidized thioether group.[2]

The lower homologues and acyclic analogues of **1** and **7** were studied. The results are summarized in Tables I and II. Unlike the eight-membered-ring system, these compounds have been found to react at rates resembling those of the corresponding simple thioethers and sulfoxides, in spite of the full positive charge on the quaternary ammonium compounds. However, the pH profiles of the I_2 oxidation of 6-methyl-2-thia-6-azaheptane, **3**, and 2-[2-(methylthio)ethyl]pyridine, **6**, demonstrate neighboring-group participation and suggest N–S interacted intermediates.

Primary and secondary amines were not included because these compounds undergo N–H bond cleavage to form isothiazolidinium salts,[3] thereby complicating the detection of N–S dication intermediates.

Scheme I



Steps (1) and (2) are GENERAL for **2**–**6**.
Steps (3) and (4) are SPECIFIC for **3** and **6**.

Results and Discussion

Aqueous I_2 Oxidation of Thioethers. The thioethers are oxidized by a limiting quantity of iodine in buffered aqueous KI solutions. The rate of oxidation is followed by monitoring the absorbance of I_3^- at 353 nm. Rela-

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[1] (a) J. Takahashi Doi and W. K. Musker, *J. Am. Chem. Soc.*, in press; (b) W. K. Musker, A. S. Hirschon, and J. Takahashi Doi, *J. Am. Chem. Soc.*, **100**, 7754 (1978).

[2] (a) W. Takagi, M. Ochiai, and S. Oae, *Tetrahedron Lett.* 6131 (1968); (b) S. Allenmark, *Int. J. Sulfur Chem*, **8**, 127 (1973); H. Johnson and S. Allenmark, *Chem. Scr.*, **8**, 216 (1975); (c) J. Takahashi Doi and W. K. Musker, *J. Am. Chem. Soc.*, **100**, 3533 (1978).

[3] (a) K.-H. Gensch and T. Higuchi, *J. Pharm. Sci.* **56**, 177–184 (1967); (b) P. R. Young and L.-S. Hsieh, *J. Am. Chem. Soc.*, **100**, 7121 (1978); (c) D. O. Lambeth and S. W. Swank, *J. Org. Chem.*, **44**, 2632 (1979).

[4] (a) R. J. Angelici, "Synthesis and Technique in Inorganic Chemistry", W. B. Saunders Co., Philadelphia, PA, 1969; (b) D. D. Perrin, "Dissociation Constants of Organic Bases", Plenum Press, New York, 1965.

tionships between ln A and time are linear up to 60–80% of the reaction. The pseudo-first-order rate constant is calculated from eq 2.[1a] The rate constant k_{obsd} is divided

$$\frac{d[I_3^-]}{dt} = -k_{\text{obsd}}[I_3^-] = -\frac{d[RR'S]}{dt} \qquad (2)$$

by the thioether concentration to give the pseudo-second-order rate constants reported in Table I.

The iodide dependence of the rates was determined by measuring the rate of oxidation of each compound, using three or more different iodide concentrations. These values are listed in column 6 in Table I. For compounds **2** through **6** the rate is directly proportional to the inverse of the square of the iodide concentration. The rate law is $d[RR'S]/dt = d[I_3^-]/dt = -k'_{\text{ox}}[I_3^-][RR'S][I^-]^{-2}$. Consistent with this dependence is the mechanism in Scheme I in which there is equilibration between the species in steps 1 and 2 which precede the rate-determining step. Thus a comparison of the rate laws for compound **1**[1a] and compounds **2–6** reveals that different mechanisms are required.

The seven-membered-ring thioether, **2**, reacts about 10^6 times slower than the eight-membered-ring thioether, **1**. The pH dependence of the rate of oxidation of **2** was studied by oxidizing it in solutions buffered with 0.0125 M borate at pH 7.7, 9.0, 9.7, and 10.1. The plot of log k vs. pH is linear with a slope of 1.01 and a correlation coefficient of 0.997, suggesting that these rates involve nucleophilic attack of hydroxide on the iodosulfonium ion[5] rather than intramolecular catalysis of free amine. Thus, the transannular interaction which is the dominant feature in the oxidation of the eight-membered-ring amine–thioether is not detectable in the seven-membered-ring. At pH 8.0 the rates of oxidation of **2** and the acyclic compound $(CH_3)_2N(CH_2)_3SCH_3$, **3**, are about equal. When the chain length of **3** has been shortened by one methylene group as in **5**, the rate is decreased. When the γ-amine group of **3** has been quaternized as in **4**, the rate is also decreased. These decreases in rate could be due to the inductive effect of a positive charge β vs. γ to the cationic sulfur in the iodosulfonium ion in **5** and to the loss of the lone-pair electrons on the nitrogen γ to the iodosulfonium group in **4**. The latter would suggest that an N–S bonded intermediate is important in the reaction of **3**. If the N–S bonding is important, the reactions should depend on pH due to the equilibrium $R_3N\text{–}H^+ + B^{-N} \rightleftarrows R_3N{:} + HB^{-N+1}$. The rate would level off at a pH about equal to the pK_a for the protonated amine[3a] group in the iodosulfonium intermediate formed in the equilibrium, K_2. The exact pK_a value cannot be determined but would be slightly smaller than the pK_a of the corresponding amine thioether. Compound **3** has a pK_a value of 9.8 ± 0.2 as measured by the titration method,[4a] and compound **6** would have about the same basicity as 2-ethylpyridine (pK_a = 5.97).[4b] The theoretical curves for the pH dependence of the fraction of free amine for compounds with pK_a = 5.2 and 9.2 have been drawn in Figure 1.

The rate data plotted in Figure 1 have been extrapolated to zero buffer concentration when **3** or **6** is oxidized at pH ≥7 in phosphate or carbonate buffers. Buffer concentration does not affect the rates of oxidation of **3** in borate, of **3** in pH 8 phosphate, or of **6** in acetate. The log k vs. pH curves for **3** and for **6** (Figure 1) correspond to the theoretical curves based on intramolecular catalysis. This kind of behavior has been reported for the oxidation of methionine.[3a] (The product of that oxidation is the cyclized dehydromethionine.) Similarly, the rates of I_2 oxidation of 2-methylthiobenzoic acid[2a] increased with increasing pH in the region where the carboxylic acid groups are largely unionized, but are pH insensitive once the carboxylate anion is formed. In Scheme I the oxidations of **3** and **6** are shown with neighboring-group participation. The rate-determining step involves formation of N–S bonded intermediates which are hydrolyzed to the sulfoxides.

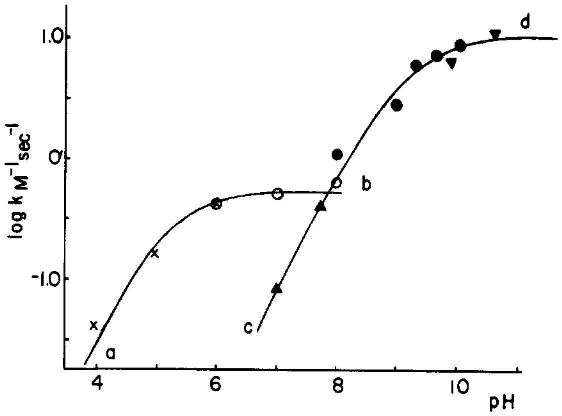

Figure 1. Effect of pH on the rates of oxidation, 0.060 M KI, (2–5) × 10^{-5} M I_2, (4–7) × 10^{-4} M thioether: (×) **6**, 0.0125 M acetate; (○) **6**, phosphate; (▲) **3**, phosphate; (●) **3**, 0.0125 M borate; (▼) **3**, carbonate. Curves were calculated by using $k \propto K_a/(K_a + [H^+])$: curve a-b, K_a = 5.2; curve c-d, K_a = 9.2.

Aqueous HI Reduction of Sulfoxides. The acceleration of the aqueous HI reduction of 5-methyl-1-thia-5-azacyclooctane 1-oxide, **7**, is attributed to stabilization of the cationic sulfur center by the lone pair on the transannular tertiary amine group.[1b] The anchimeric assistance is especially surprising since the amine is protonated in the strongly acid solution used for this reaction and only the very small fraction of amine which exists as the free base is responsible for the 10^6-fold acceleration.

The general mechanism for the HI reduction of sulfoxides proceeds by diprotonation of the sulfoxide oxygen and attack by iodide ion on the cationic sulfur. The rate law (eq 3) is generally first order in iodide.[6] Exceptions

$$I^- + RR'SOH_2^{2+} \xrightarrow{\text{rd}} RR'SI^+ + H_2O \qquad (3)$$

of this observation have been explained in terms of neighboring-group participation by heteroatoms with lone-pair electrons.[2] The compounds in Table II are acyclic and cyclic homologues of **7**. The presence of any nitrogen–sulfur interaction in the reduction reaction may be detected by an examination of the relative rate of reduction and a zero-[2c] or second-order[1b] dependence of the rates on iodide. The last column lists the orders in iodide of the rates as determined by the rates in solutions of at least three different iodide concentrations. The order in iodide is approximately one for compounds **9–15**.

The quaternary ammonium salt **8** is reduced approximately 10^6 times slower than **7** (Table II). Compound **8** has a full positive charge transannular to the sulfoxide group and is probably the closest possible model on which to base the degree of anchimeric assistance seen in **7**. The rates of reduction of **8** and the lower cyclic homologues of **7** correlate with ring size in a manner similar to those in other series.[7] Reduction of the six-membered-ring sulf-

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[5] T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 5486 (1966).

[6] (a) V. Miotti, G. Modena, and L. Sedea, *J. Chem. Soc. B* 802 (1970); (b) D. Landini, G. Modena, F. Montanari, and G. Scorrano, *J. Am. Chem. Soc.*, **92**, 7168 (1970).

oxide 9 occurs about 10 times slower than that of the seven-membered-ring sulfoxide 10.

The acyclic amine sulfoxide 12 behaves like the seven-membered-ring 10. When the acyclic chain is extended by one methylene as in 11, the rate is increased, reflecting the decrease in the inductive effect of the protonated nitrogen. The behavior of 11 contrasts sharply with that of the corresponding thioether sulfoxide, 2,6-dithiaheptane 2-oxide,[3c] which has an accelerated rate of reduction and a rate law which is zero order in iodide. These results show that in acyclic compounds a protonated sulfoxide is more likely to interact with a thioether group than with a tertiary amine group.

The rate of reduction of $(CH_3)_2N(CH_2)_2S(O)CH_3$, 12, compared to that of dimethyl sulfoxide shows about a 5-fold decrease. We considered it is possible that this decreased rate could be attributed to two factors which are a deceleration due to the inductive effect and an acceleration by an internal proton bridging the nitrogen and the sulfoxide oxygen atom via a six-membered ring. The proton bridging cannot occur in the corresponding quaternary ammonium salts 13 and 14. The rates of reduction of 12–14 at 0.30 M NaI and 5.84 M $HClO_4$ are almost indistinguishable from each other, suggesting that no special bridging in $12{\cdot}H^+$ occurs and that the deceleration is simply due to the inductive effect of the protonated amine group.

2-(2-Methylsulfinyl)pyridine (15) is reduced more rapidly than dimethyl sulfoxide in ≤5.84 M $HClO_4$. The first-order dependence on iodide indicates that iodide and not the pyridine nitrogen is the nucleophile in the rate-determining step. The high concentration of acid required in the reduction reaction causes the amine to be highly protonated and lowers the concentration of free base required for any N–S interaction. Thus, the large change in pH between the oxidation and reduction reactions has drastically altered the concentration of the free amine so that the N–S interaction which is responsible for acceleration in the oxidation reaction at pH 4–6 appears to be, at best, a minor factor in the reduction reaction in 5 M $HClO_4$. A similar argument also applies to the dimethylamino catalysis in the oxidation of $(CH_3)_2N(CH_2)_3SCH_3$, 3.

Using relative reaction rates and iodide dependence as criteria, it appears that among the amine sulfoxides studied, only the eight-membered-ring amine sulfoxide 7 undergoes reduction via neighboring-group participation.

Experimental Section

Materials. 5-Methyl-1-thia-5-azacyclooctane, 1,[8] 5-methyl-1-thia-5-azacyclooctane 1-oxide, 7,[8] 4-methyl-1-thia-4-azacyclohexane 1-oxide, 9,[9] 5-methyl-2-thia-5-azahexane, 5,[10] 2-[(2-methylthio)ethyl]pyridine, 6,[11] and 6-methyl-2-thia-6-azaheptane, 3,[12] were prepared by the literature references indicated. The structures of these and all new compounds were checked by ^1H NMR (Varian EM-360) and infrared (Beckman IR 8 or IR 12) spectroscopy.

Thioethers were converted to sulfoxides by sodium periodate.[13]

***N,N*-Dimethyl-2-(methylsulfinyl)ethylamine, 12.** Anal. Calcd for $C_5H_{13}NOS$: C, 44.5; H, 9.70. Found: C, 44.3; H, 9.85.

***N,N*-Dimethyl-3-(methylsulfinyl)propylamine, 11:** bp 73 °C (1.0 mm) [lit.[12] bp 97–98 °C (1.8 mm)].

2-[2-(Methylsulfinyl)ethyl]pyridine, 15. Anal. Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.53; H, 6.59; N, 8.12; S, 18.88.

Quaternary ammonium alkyl sulfides and sulfoxides were prepared by the standard procedure.[12]

5,5-Dimethyl-1-thia-5-azoniacyclooctane 1-oxide iodide, 8: ^1H NMR (D_2O) δ 3.5 (br, 4), 3.2 (m, 2), 3.0 (s, 6), 2.7 (m, 4).

***N,N,N*-Trimethyl-2-(methylsulfinyl)ethylammonium Iodide, 13.** Anal. Calcd for $C_6H_{16}NOSI$: C, 26.0; H, 5.78. Found: C, 25.9; H, 5.78.

***N,N,N*-Trimethyl-2-(methylsulfinyl)ethylammonium Hexafluorophosphate, 14.** Anal. Calcd for $C_6H_{16}NOSPF_6$: C, 24.4; H, 5.42. Found: C, 24.2; H, 5.47.

6,6-Dimethyl-2-thia-6-azoniaheptane iodide, 4: ^1H NMR (D_2O) δ 3.6–2.9 (m, 2), 3.1 (s, 9), 2.7 (t, 2), 2.3–1.9 (m, 2), 2.1 (s, 3).

4-Methyl-1-thia-4-azacycloheptane, 2. A mixture of 5.2 g (50 mmol) of 1-thiacyclohexan-4-one, 3.5 g (50 mmol) of $NH_2OH{\cdot}HCl$, and 4.1 g (50 mmol) of sodium acetate in 70 mL of 95% ethanol was refluxed 2–3 h[14a] and then allowed to stir overnight. The ethanol was removed under vacuum, water was added, and the oxime was extracted into CH_2Cl_2. The organic extracts were dried and the crude oxime was obtained on evaporation. Beckmann rearrangement of the oxime[14b] yielded 3.0 g (23 mmol) of 1,4-thiazepin-5-one. In a drybox $(CH_3)_2S{\cdot}BH_3$ (2 M) was added dropwise over 20 min to the amide crystals in 10 mL of diethyl ether. During the addition the tan solid dissolved. The mixture was stirred for 24 h. A saturated HCl/diethyl ether solution was added cautiously (gas evolution) dropwise until the solution was strongly acidic. The reaction was stirred for 24 h and the solvent was removed by rotary evaporation. The amine salt was treated with 10% NaOH, extracted into CH_2Cl_2, and dried.[14c] Evaporation of the solvent yielded about 1 g of a viscous liquid which was treated with 2.6 g (51 mmol) of formic acid[15] and 4.14 g (51 mmol) of formaldehyde, refluxed for 15 h, acidified with aqueous HCl, and evaporated to dryness.[13] The residue was redissolved in H_2O, made basic with NaOH, and extracted into dichloromethane. Distillation yielded 0.30 g of a colorless liquid: bp 79 °C (30 mm); mass spectrum, *m/e* calcd 131.0770, found 131.0748.

Compound 2 was oxidized with $NaIO_4$[13] and the sulfoxide, 10, was crystallized from methanol–ether as the perchlorate salt. The N–H stretch of the perchlorate salt[8] occurs in the infrared (KBr pellet) at 2610 (s), 2500 (m, sh) cm^{-1}.

Kinetic Measurements. Procedures have been described previously.[1a,2c] The contribution to the loss of I_2 due to reaction with the tertiary amine moiety of these amine sulfides was measured. These rates were slow at pH 8.0: ca. 0.06 $M^{-1}\ s^{-1}$ at 0.06 and 0.03 M KI in solutions 1.4×10^{-3} M in amine. This rate is less than the experimental error in the rates reported in Table I. However, because of this possible competing reaction, only limited data on the reduction of $(CH_3)_2N(CH_2)_2SCH_3$, 5, are reported since its rate of oxidation at pH 8.0 is about one-tenth the rate of 3 and the side reaction could contribute to the observed rate. The rate of oxidation of 3 was not accelerated by the addition of an equivalent amount of triethylamine at pH 8.0.

The rates of oxidation of all compounds were essentially first order in amine–thioether when the amine–thioether concentrations were in the range of $(0.4\text{–}1.2) \times 10^{-3}$ M and when respective buffers were used within 0.5 pH units of their pK_a. The concentrations of the buffers were kept at 0.0125 M to minimize nucleophilic reactions of the buffers with the reactants; exceptions are noted. The rate of compounds 3, 6 and quaternary salt 4 in acidic solutions deviated most from integral dependence on $1/[I^-]$ (Table I). In these solutions, the reactant is cationic and it is possible that in these cases some reaction occurs within an ion pair by the

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[7] (a) S. Tamagaki, M. Mizuno, H. Yoshida, H. Hirota, and S. Oae, *Bull. Chem. Soc. Jpn.*, **44**, 2456 (1971); (b) R. Curci, F. DiFuria, A. Levi, G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 408 (1975).

[8] N. J. Leonard and A. E. Yethon, *Tetrahedron Lett.* 4259 (1965); A. E. Yethon, Ph.D. Thesis, University of Illinois, Urbana, IL, 1968.

[9] W. E. Lawson and E. E. Reid, *J. Am. Chem. Soc.*, **47**, 2821 (1925).

[10] G. Tsatsas, G. Sandris, and D. Kontonassios, *Bull. Soc. Chem. Fr.*, **10**, 2160 (1963).

[11] P. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1835–45 (1966).

[12] F. K. Kirchner, A. E. Soria, and C. Cavallito, *J. Am. Chem. Soc.*, **77**, 4599 (1955).

[13] P. B. Roush and W. K. Musker, *J. Org. Chem.*, **43**, 4295 (1978).

[14] (a) C. Barkenbus, J. F. Diehl, and G. R. Vogel, *J. Org. Chem.*, **20**, 871 (1955); (b) C. A. Grob and J. Ide, *Helv. Chim. Acta*, **57**, 2562 (1974); (c) C. F. Lane, M. L. Myatt, J. Daniels, and H. B. Hopps, *J. Org. Chem.*, **39**, 3052 (1974).

[15] W. K. Musker, Ph.D. Thesis, University of Illinois, Urbana, IL, 1959.

reaction of the ammonium thioether with the triiodide ion itself.

Reaction Products. Procedures have been described previously.[1a,2c]

Acknowledgment. This research was supported by a Faculty Research Grant to J.T.D. and by National Science Foundation and National Institutes of Health Grants to W.K.M.

Registry No. 1, 5932-57-0; 2, 76429-53-3; 3, 16220-69-2; 4, 44826-69-9; 5, 35332-10-6; 6, 14143-85-2; 7, 5947-17-1; 8, 76429-54-4; 9, 38280-81-8; 10, 76429-55-5; 10 perchlorate, 76429-56-6; 11, 76429-57-7; 12, 76429-58-8; 13, 76429-59-9; 14, 76429-61-3; 15, 76429-62-4; 1-thiacyclohexan-4-one, 1072-72-6; 1-thiacyclohexan-4-one oxime, 6309-59-7; 1,4-thiazepin-5-one, 2896-98-2.

Substituent Effect on the Electrochemical Oxidation of Trityl Anions. 2. Effect of an Electron-Withdrawing Group

Shelton Bank,* Clifford L. Ehrlich, Mark Mazur, and Jon A. Zubieta

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

Received October 27, 1980

The reversible one-electron oxidations of triarylmethyl anions and the irreversible second oxidative processes were examined for a series of sequentially substituted *p*-trimethylsilyl anions. The cycle voltammograms of the lithium salts prepared in dimethoxyethane reveal that the reversible potentials depend upon the substituent in the para positions. In contrast the second oxidative process is only slightly affected. Comparison with similarly substituted methyl triarylmethyl anions leads to estimates of the effect of a trimethylsilyl group on carbanion, radical, and cation stability.

In a previous study[1] we obtained and utilized electrochemical data to provide information about the several equilibria among triarylmethyl anions, radicals, and cations as shown in eq 1.

$$R^- \underset{e}{\rightleftarrows} R\cdot \underset{e}{\rightleftarrows} R^+ \qquad (1)$$

The reversible one-electron oxidation of lithium triarylmethyl anions and the irreversible second oxidative process were examined for a series of sequentially substituted *p*-methyl anions. The substituent effect on stability of the several species was assessed and compared with other estimating methods.

The electron-donating properties of the methyl group have a larger stabilizing effect on the energy of cations than the destabilizing effect on the energy of anions which in turn was larger than the moderate stabilizing effect on the energy of radicals. Additionally, sequential substitution revealed the effect for a single methyl group to be different for the two oxidative processes. For the reversible anion to radical oxidation the single methyl substitution brought about the smallest change. In contrast the radical oxidation process reveals the greater change for substitution by a single methyl group.

These effects are consonant with the known propeller geometry of the aryl rings in these species.[2] Of great interest for the anion, the twist angles for the phenyl rings are 19.7°, 30.6°, and 44.8°, respectively.[2a] Thus there is significant differential in the degree of conjugation of the several rings. For the electron-deficient cation the greatest stabilizing effect is realized when the donor methyl group is in the maximally conjugated ring. Similarly for the electron-rich anion the great stabilizing effects are achieved when the maximally conjugated ring is unsubstituted. This analysis is based on the electron-donor properties of methyl and the differential ring conjugation.

Differential ring conjugation is inherent in the geometrical requirements of the triaryl methyl system but maximum preference should be determined by substituent. In fact an electron-withdrawing group should reverse the pattern of sequential substituent effect; thus for the anion greater stabilization would be realized when a substituted ring is maximally conjugated. For the cation the prediction is exactly opposite.

The trimethylsilyl group was selected as representative of electron-withdrawing groups. Accordingly this study concerns a quantitative assessment of the effect of the trimethylsilyl group on the reversible and irreversible oxidation potentials of a series of para-substituted anions. The method permits direct comparison with the previous study of a representative electron-donor group. Additionally, the results can be compared to related studies of trimethylsilyl groups to delocalization energies and restricted rotation in diarylmethyl anions.[3]

Results and Discussion

The triarylmethanes Id, IId, and IIId were obtained via Grignard syntheses. The lithium anions Ia, IIa, and IIIa were prepared from the reaction of the corresponding triarylmethane and *n*-butyllithium in dimethoxyethane (DME). Freshly prepared anion solutions were generated and transferred to the electrochemical cell in a No-Air system.

Improvements in reversibility and reproducibility of the voltammograms were realized by a change to a nonaqueous reference electrode. The voltammogram of Ia depicted in Figure 1 reveals the one-electron oxidation at −1.068 V and the irreversible oxidation at +0.516 V. For direct comparison the reversible anion oxidation of the triphenylmethyl anion was obtained with this reference electrode.

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(1) S. Bank, C. L. Ehrlich, and J. A. Zubieta, *J. Org. Chem.*, 44, 1454 (1979).

(2) (a) J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 94, 7333 (1972); (b) H. Gomes de Mesquito, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, 18, 437 (1965); (c) P. Andersen and B. Klewe, *Acta. Chem. Scand.*, 21, 2599 (1967).

(3) S. Bank, J. S. Sturges, D. Heyer, and C. H. Bushweller, *J. Am. Chem. Soc.*, 102, 3982 (1980).

0022-3263/81/1946-1243$01.25/0