

covered by the signals of the aromatic protons. The extreme low-field shift of the signals might be due to a special sterical arrangement of the four highly hindered aromatic rings. A ^{13}C NMR signal at δ 87.1 (CDCl_3) for C_2 and C_5 is supporting the structure.

Anal. ($\text{C}_{32}\text{H}_{32}\text{O}_5$) C, H.

Anodic Oxidation of DMOS in Acetonitrile/Methanol. DMOS (1.2 g, 5.0 mmol) in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ (3:1, 100 mL) containing LiClO_4 (0.2 M) was subjected to anodic oxidation at a platinum electrode (7 cm^2) at a controlled potential of +0.67 V vs. Ag/AgNO_3 (0.1 M) and a current of 10 mA in an undivided cell under N_2 atmosphere. DMOS was only partially soluble in the solvent but went into solution during the course of the reaction. After consumption of 490 A s (5 mF) the current dropped to 1 mA and the electrolysis was stopped. The solvent was removed under vacuum, and the residue was dissolved in small amounts of dichloromethane and three times washed with 30 mL of H_2O to remove LiClO_4 . The organic phase was dried (MgSO_4) and the solvent evaporated. The residue (1.5 g) was analyzed by GLC/MS coupling. Current yields (quantitative GLC, 4% SE-30) follow: **3** (75%), **4** + **5** (7.5%), **6** (2.5%). Compound **3** was isolated from the crude product by preparative TLC (petroleum ether/ether, 2:1) and purified by recrystallization from CCl_4 and subsequent sublimation. **3**: mp 234–237 °C; IR (KBr pellet) 1608, 1502, 1460, 1304, 1242, 1174, 1092, 1034, 882, 830, 814, 786 cm^{-1} ; ^1H NMR (CCl_4 , Me_4Si) δ 2.84 (s, 6 H), 3.28 (s, 2 H), 3.63 (s, 6 H), 3.74 (s, 6 H), 3.84 (s, 2 H), 6.4–6.8 (s + m, 16 H); ^{13}C NMR (CDCl_3) δ 55.0, 55.4, 56.7, 83.0, 112.7, 127.7, 131.4, 131.7, 133.5, 158.0; mass spectrum (70 eV) *m/e* (rel intensity) 542 (0.3), 479 (0.3), 478 (0.6), 359 (2.0), 346 (1.0), 271 (4), 240 (10), 227 (10), 225 (9), 152 (43), 151 (100), 136 (10), 135 (22), 121 (8), 108 (5), 91 (3), 75 (4).

Anal. ($\text{C}_{34}\text{H}_{38}\text{O}_6$) C, H.

Compounds **4**, **5**, and **6** could not be isolated because of the small yields. They were identified by mass spectra (70 eV): **4** *m/e* (rel intensity) 270 (8), 255 (5), 227 (9), 151 (100), 135 (22), 75 (13); **5** *m/e* (rel intensity) 270 (12), 255 (5), 227 (12), 151 (100), 135 (17), 75 (20); **6** *m/e* (rel intensity) 270 (60), 255 (25), 227 (60), 135 (12), 119 (17), 113 (12), 75 (100).

Kinetic Study. The instrumentation has previously been described^{1a} but instead of a Ag/AgCl reference electrode a pseudoreference silver wire was inserted into the solution next to the working electrode to minimize uncompensated resistance effects. The optical signal was subjected to signal averaging by a Princeton Applied Research TDH

9 Waveform Eductor to optimize the signal to noise ratio. The electronic circuit to disconnect the working electrode in the OCR experiment has been described elsewhere.²² The solvents were dried over alumina and solvents and solutions were transferred to the volumetric flasks and the spectroelectrochemical cell by use of gas-tight syringes. Solutions not containing methanol were stored over neutral alumina.

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Formation of Dithioether Dications in the Anchimerically Assisted Reduction of Monosulfoxides of Mesocyclic and Acyclic Dithioethers

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Abstract: The reduction of the mesocyclic sulfoxide, 1,5-dithiacyclooctane 1-oxide (**1**) by iodide in aqueous acid proceeds $\sim 10^6$ times more rapidly than simple sulfoxides. The rate is essentially independent of iodide and shows a second-order dependence on acid concentration. The accelerated rate of reduction is attributed to an anchimeric assistance by the transannular thioether group which leads to an intermediate dithioether dication, **3**. This same dithioether dication has been isolated previously in the oxidation of 1,5-dithiacyclooctane (**2**) in nonaqueous solvents. 2,6-Dithiaheptane 2-oxide (**6**) is the acyclic analogue of **1**. The rate of reduction with HI is also zero order in iodide, suggesting that neighboring-group participation also occurs in an acyclic compound to give a five-membered-ring dithioether dication (**7**). In contrast to **1** and **6**, 1,4-dithiane 1-oxide behaves like a simple sulfoxide. Thus, the rapid formation of dithioether dications in the reactions of **1** and **6** suggests that these species should be considered as possible intermediates in reactions where a positive charge is induced on a sulfur atom in the proximity of a thioether group.

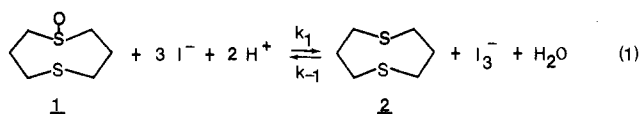
A transannular interaction in the mesocyclic dithioether, 1,5-dithiacyclooctane (**2**) has been suggested to explain its mass spectrum,¹ its electrochemistry,² and its facile oxidation

to the dithioether dication (**3**) in nonaqueous solvents.³ Mechanistic studies on the HI reduction of monosulfoxides^{4–9} have indicated that reaction proceeds through a protonated

Table I. The Pseudo-First-Order Rate Constant k_1 for the Reaction between $\sim 10^{-4}$ M 1,5-Dithiacyclooctane 1-oxide (**1**) and I^- in $HClO_4$ at 25.6 °C

Run	$HClO_4/M$	NaI/M	$NaClO_4/M$	k_1, s^{-1}
a	0.20	0.30		10.5 ± 0.2
b	0.20	0.15	0.15	9.0 ± 0.4
c	0.10	0.30		1.73 ± 0.06
d	0.050	0.30		0.52 ± 0.03
e	0.00734	0.30		$(6.1 \pm 0.3) \times 10^{-3}$
f	0.00636	0.30		$(4.33 \pm 0.02) \times 10^{-3}$
g	0.00489	0.30		$(2.5 \pm 0.2) \times 10^{-3}$
h	0.00342	0.30		$(1.20 \pm 0.02) \times 10^{-3}$
i	0.00293	0.30		$(8.02 \pm 0.06) \times 10^{-4}$
j	0.00489	0.15	0.145	$(2.16 \pm 0.04) \times 10^{-3}$
k	0.00489	0.205	0.101	$(2.17 \pm 0.02) \times 10^{-3}$

sulfoxide and that neighboring groups can provide anchimeric assistance to the reduction. Furthermore, the thioether group has been reported to act as an internal nucleophile^{10,11} in reactions of mesocyclic compounds, but no kinetic studies have been reported. The reduction of the mesocyclic sulfoxide 1,5-dithiacyclooctane 1-oxide (**1**) by HI (reaction 1) is ex-



tremely rapid. The rate of reduction is 10^6 times that of dimethyl sulfoxide,⁴ more than 100 times the rate of any sulfoxide previously reported,⁴⁻⁹ and essentially independent of iodide concentration. Thus, the rapid rate of reaction 1 suggests anchimeric assistance via the dication **3**.

Results and Discussion

1,5-Dithiacyclooctane 1-Oxide. Using published rate constants for dimethyl sulfoxide,⁴ tetrahydrothiophene 1-oxide,⁴ and β -propylsulfinylpropionic acid⁶ and extrapolating against the acidity functions used by the original investigators, it is possible to calculate that **1** is reduced more rapidly in aqueous solution than any other sulfoxide previously reported.¹² At 2 M $HClO_4$ (the usual condition for sulfoxide reduction), the conversion of **1** to **2** and its precipitation as the iodine complex of **2** is complete instantaneously.

The kinetics of reaction 1 were studied spectrophotometrically at 400 nm in a stopped-flow apparatus at 25.6 °C with solutions 0.05–0.2 M $HClO_4$ (runs a–d, Table I). Under these conditions, the reaction goes essentially to completion and is first order in **1**, at least through 83% reaction. At lower acid concentrations, (runs e–k) the kinetics were followed at 353 nm in a Cary 17 spectrophotometer, but equilibrium is established when only 12–38% of **1** has been reduced. Data at low acidity were treated according to the equation derived for the general equilibrium type¹³ $A = B + C$ since $HClO_4$ and NaI were present in a 50–3000-fold excess and were invariant during the course of a reaction. The equilibrium constant for reaction 1 at 25.6 °C is 14.5 ± 0.6 . Under either of the above conditions the amount of I_3^- present is an accurate indication of the extent to which reaction 1 has occurred and its absorption at 353 nm ($\epsilon 2.3 \pm 0.1 \times 10^4$) and at 400 nm was followed. The concentration of the products was sufficiently low to prevent precipitation of the iodine complex of **2**.

The rate of reduction increases with increasing $HClO_4$, and a plot of $-\log k_1$ against pH at lower concentrations is linear with a slope of 2.1. A plot of $-\log k_1$ against H_0''' at higher concentrations¹⁴ is also linear with a slope of 1.8.

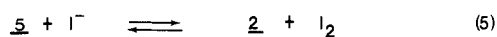
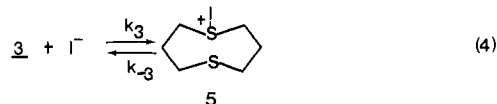
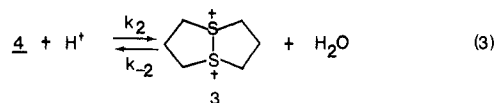
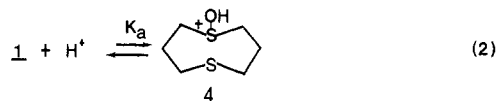
At constant ionic strength, the rate of reduction decreases only slightly with decreasing iodide. From runs a and b and runs g, j, and k, it is observed that a decrease of $[I^-]$ of 50% causes a decrease in rate of only 12–14%. While rates of re-

duction of simple sulfoxides show a first-order dependence on iodide,^{4,5,7} anchimerically assisted rates of reduction are considerably less sensitive to the concentration of iodide^{6,7} as also observed here.

The reactivity of compound **1** is not due to an unusual basicity of the sulfoxide. The value of $pK_a = -1.9$, as determined by plotting¹⁴ $A_{210} - A_{220}$ against H_A by the method of Davis and Geissman¹⁵ is close to the values of -1.54 to -2.7 reported for dimethyl sulfoxide.^{16,4} Unlike the plots of Landini et al., the horizontal portion of the curve does not extend to 10^{-7} M H^+ ; however, in the original paper by Davis and Geissman that is not a requirement.

The kinetic behavior of **1** is consistent with Scheme I.

Scheme I



Using a steady-state approximation for [3] and neglecting the k_{-3} term at high $[I^-]$,^{6,7} the following expression is obtained:

$$\text{rate} = \frac{k_2 k_3 K_a [\mathbf{1}] [H^+]^2 [I^-]}{k_3 [I^-] + k_{-2}} \quad (7)$$

Equation 7 predicts iodide independence at high $[I^-]$ and a fraction order (< 1) in $[I^-]$ at lower concentrations. Alternatively, if the reaction represented by k_2 is the rate-determining step,

$$\text{rate} = K_a k_2 [\mathbf{1}] [H^+]^2$$

the rate would be independent of iodide at all concentrations. Anchimeric assistance to form dication **3** is suggested in either case because of the role of k_2 in the rate expression. The

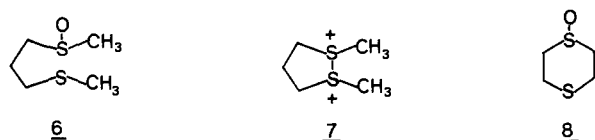
Table II. The Pseudo-First-Order Rate Constants k_1 for the Reaction between **6** and **8** with I^- in $HClO_4$ at 25.6 °C

Run	Compd	$HClO_4/M$	NaI/M	$NaClO_4/M$	k_1, s^{-1}
l	6	0.96	0.30		$(2.7 \pm 0.1) \times 10^{-4}$
m	6 ^a	0.96	0.30		$(3.0 \pm 0.5) \times 10^{-4}$
n	6	0.96	0.15	0.15	$(2.8 \pm 0.2) \times 10^{-4}$
o	6 ^a	0.96	0.15	0.15	$(2.5 \pm 0.4) \times 10^{-4}$
p	8 ^b	5.84	0.30		$(1.03 \pm 0.05) \times 10^{-4}$
q	8 ^b	5.84	0.15	0.15	$(0.51 \pm 0.01) \times 10^{-4}$

^a Titrimetric rates; at $\sim 5 \times 10^{-3}$ M **6** the reaction did not go to completion and the constant was calculated as given in ref 13. ^b Titrimetric rates, at $\sim 5 \times 10^{-3}$ M **8**; the reaction did proceed essentially to completion.

steady-state approximation for this reaction is parallel to the treatment of neighboring carboxyl in the reduction of sulfoxides.^{6,7}

2,6-Dithiaheptane 2-Oxide and 1,4-Dithiane 1-Oxide. Because of the dramatic acceleration in **1**, explainable in terms of the formation of the dithioether dication (**3**), the acyclic analogue, 2,6-dithiaheptane 2-oxide (**6**) was studied for evidence of formation of the dicationic intermediate **7**. As an



example of a monosulfoxide of a cyclic dithioether in which transannular interaction of the sulfur atoms is minimal, 1,4-dithiane 1-oxide (**8**) was also studied.

The kinetics of the reduction of **6** and **8** were followed either spectrophotometrically (runs l and n, Table II) or titrimetrically with sodium thiosulfate (runs m, o, p, q). For **6** at 1 M $HClO_4$, at titrimetric concentrations of **6**, equilibrium is established at 44–71% and the data has been treated accordingly.¹³ The equilibrium constant for the reduction of **6** at 25.6 °C is 0.52 ± 0.06 . At constant ionic strength the rate of reduction of **6** is essentially iodide independent (runs l–o, Table II), whereas for **8** there is a first-order dependence on iodide (runs p, q).

The mechanism shown in Scheme I also applies to the reduction of **6** to 2,6-dithiaheptane. The intermediate dithioether dication (**7**) would be formed in the second step of the reaction. The conformational heterogeneity of **6** compared with that of **1** would contribute to its modestly accelerated rate of reaction which is only about 300 times faster than an extrapolated value for dimethyl sulfoxide.⁵ Compound **6** is reduced at essentially the same rate as β -propylsulfanylpropionic acid described by Allenmark.⁶ The reduction of both compounds are zero order in iodide. The kinetics of the reduction of β -propylsulfanylpropionic acid is believed to proceed by anchimeric assistance by the carboxylic acid group, giving a five-membered-ring intermediate in the rate-determining step. Thus, thioether and carboxylate participation are similar.

Compound **8** is reduced at essentially the same rate as thiane 1-oxide (thiacyclohexane 1-oxide) at ~ 6 M $HClO_4$.⁴ The rate of reduction of **8** is first order in $[I^-]$ as are the reported rates of simple sulfoxides.^{5,7} This would indicate that the rate-determining step in these reductions is the attack on a protonated sulfoxide by iodide. In **8** the reaction at the sulfoxide (S-1) appears to be independent of the thioether group (S-4).

An interconversion between a thioether and a sulfoxide has been postulated as a viable redox system in biochemical processes.^{17,18} However, such processes must be rapid and efficient to provide a useful biochemical path. In this study we have shown that sulfoxide reduction can be extremely rapid when a suitably disposed neighboring group is present. Whether methionine and methionine sulfoxide specifically can be interconverted rapidly is still unknown, but in the folded protein

there are many neighboring groups which might provide the assistance needed to facilitate electron transfer processes.

Experimental Section

Materials and Solvents. 1,5-dithiacyclooctane (**2**)^{19,20} and 2,6-dithiaheptane^{21,22} were synthesized as described elsewhere. 1,4-Dithiane (Aldrich Co.), 2,6-dithiaheptane and **2** were oxidized by $NaIO_4$ in CH_3OH-H_2O or by *m*-chloroperbenzoic acid in $CHCl_3$ to yield the essentially pure monosulfoxides²³ as determined by NMR and thin layer chromatography.

Sodium iodide and perchloric acid were Mallinckrodt Analytical Grade. The sodium perchlorate monohydrate was G. Frederick Smith reagent grade and used without further purification. The perchloric acid was diluted with conductivity water which had been refluxed and cooled under N_2 . The resulting solutions were standardized by titration with standardized NaOH solutions.

Stopped-flow Kinetic Measurements. Measurements were taken with a Durrum Model D-40 stopped-flow apparatus fitted to a Beckman UV spectrophotometer.

Titrimetric Kinetic Measurements. Separate solutions of the sulfoxide in $HClO_4$ and the NaI (or NaI and $NaClO_4$) in $HClO_4$ were mixed in a volumetric flask and the volume made up to the mark. The solution was placed in a constant-temperature bath at 25.6 °C and flushed with N_2 . A constant atmosphere of N_2 was maintained during the course of the reaction. Aliquots taken of the solution at given time intervals were titrated with standardized $Na_2S_2O_3$.

Spectrophotometric Kinetic Measurements. Equal volumes of separate solutions of the sulfoxide in water and the NaI (or NaI and $NaClO_4$) were simultaneously injected into a thermostated 1-cm quartz cell in the Cary 17 spectrophotometer. Absorbance at 353 nm was recorded during the course of the reaction. The initial concentrations of sulfoxide were $\sim 10^{-4}$ M. The rate constants were calculated using a least-squares plot of 6–12 points.

Reaction Products. In all cases the reaction products were extracted into $CHCl_3$ from the solution following reduction of the generated I_3^- with $Na_2S_2O_3$ and neutralization of the acid with $NaHCO_3$. The dithioethers were identified by comparison of the NMR spectra with those of known samples.²³

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Neutral Products from Deprotonation of Tertiary Cations in the Gas Phase

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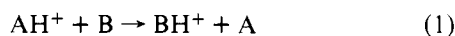
Abstract: The products of gas-phase proton transfer from cations with chemically nonequivalent acidic protons have been examined experimentally. The neutral products of deprotonation of 1-methylcyclopentyl cation (**1**) and of *tert*-amyl cation (**2**) have been collected using an electron bombardment flow (EBFlow) reactor. The cations were generated by 70-eV electron impact on bromocyclohexane and isoamyl bromide, respectively, at pressures of 4×10^{-4} Torr in the presence of 2×10^{-4} Torr triethylamine. The products from **1**, 1-methylcyclopentene and methylenecyclopentane, are recovered in a ratio of 1.2:1, which is closer to the statistical value of 4/3 than it is to the equilibrium value $\sim 10^3$. Analysis of the products from **2** requires the use of deuterium-labeled isoamyl bromides to exclude the products of dehydrohalogenation of the molecular ions. When the products of EBFlow radiolysis of $(\text{CH}_3)_2\text{CDCH}_2\text{CH}_2\text{Br}$ and of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$ are compared, the ratio of 2-methyl-1-butene to 2-methyl-2-butene from **2** is estimated to be 2.5:1. Both results support the notion that statistical effects predominate in deprotonations of *tert*-alkyl cations by triethylamine. Generation of **2** by addition of isopropyl cation to ethylene in the presence of di-*n*-propyl ether affords 2-methyl-1-butene and 2-methyl-2-butene in a ratio of 1.2:1, which implies that thermodynamic effects play more important roles in deprotonations by weaker bases.

Proton transfer in the gas phase, reaction 1, represents a prototype for Brønsted acid-base chemistry. Despite widespread interest in this reaction, only a few investigations have probed the identities of the neutral products (A) produced by gas-phase proton transfer.¹ One question, in particular, has received scant attention: what is the distribution of isomers of A when proton transfer may yield more than one neutral product? There are at least three different surmises which predict different outcomes when two acidic sites in the same ion compete for reaction with a gaseous base:

(1) Proton transfer is dominated by statistical effects. The product distribution reflects the number of protons which can be removed to give each product.

(2) Ion and molecule form a long-lived complex in which the proton is exchanged between A and B many times before the products separate from one another. Under such conditions thermodynamic control is expected, and an equilibrium distribution of products should be formed.

(3) The more weakly bound protons are preferentially transferred, by analogy to hydrogen abstractions by recoil tritium atoms.² This surmise predicts that even under kinetic control reaction 1 may yield the thermodynamically more stable product.



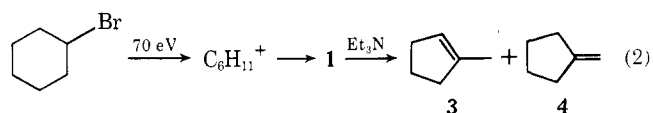
The tertiary cations **1** and **2** represent two of the simplest examples of ions with nonequivalent acidic protons. Analysis of the neutral products from their deprotonations can distinguish among the surmises regarding reaction 1. Two considerations dominate the contemplation of such a neutral product study: ion currents on the order of microamperes are required for adequate yields of neutrals to be recovered within a rea-

sonable time, and the products of reaction 1 must be distinguishable from other reaction products. Electron impact at 70 eV is well known as an efficient method of generating cations from neutral substrates in the gas phase.³ The construction of an electron bombardment flow (EBFlow) reactor for collection of neutral products from reactions of ions in the gas phase



provides the capability to realize the yields necessary for such an experiment.⁴

Electron bombardment can efficiently generate excited neutrals as well as cations. Therefore, it is necessary to choose neutral substrates from which the products of nonionic pathways are distinct from the products of cationic pathways. For this reason, electron bombardment of *tert*-methylcyclopentyl compounds ought not to be used to generate ion **1**, since 1-methylcyclopentyl radicals could give the same products, **3** and **4**, as deprotonation of **1**. Bromocyclohexane was chosen instead as a source of **1**, since the stable $\text{C}_6\text{H}_{11}^+$ cation generated from



this compound in solution has been reported to be **1**.⁵ The $\text{C}_6\text{H}_{11}^+$ cation is the base peak in the mass spectrum of bromocyclohexane, composing at least one-third of the total ionization at 70 eV. Other conceivable ionic sources of **3** and **4** are produced in negligible quantities.⁶