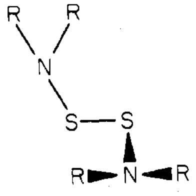
Table I. Nmr Data

Compd	Temp, °C	Type of spectrum	Chem shifts,[a] ppm (from TMS)	Coupling const,[a] Hz	T_c, °C	$\Delta\nu$, Hz	$\Delta G_c^{\ddagger}$, kcal/mol
$S[N(CH_3)_2]_2$	30	A_3	−2.97 (A)				
	−150	A_3	−3.06 (A)				
$S[N(C_2H_5)_2]_2$	30	A_2X_3	−3.07 (A)	7.0 (AX)			
			−1.12 (X)		−61	14.9	10.3
	−120	ABX_3	−2.43 (A), −2.68 (B)	13.0 (AB)			
			−1.12 (X)	7.0 (AX)			
$S[N(C_3H_7)_2]_2$	30	AX_6	−3.49 (A)	6.7 (AX)			
			−1.12 (X)		−61	3.1	11.4
	−80	AX_3Y_3	−3.49 (A)	6.6 (AX)			
			−1.10 (X), −1.12 (Y)	6.8 (AY)			
$S_2[N(CH_3)_2]_2$	30	A_3	−2.56 (A)		−118	5.8	8.1
	−130	A_3B_3	−2.53 (A), −2.58 (B)				
$S_2[N(C_2H_5)_2]_2$	30	$A_2X_3 + C_2Y_3$	−2.75 (A), −2.76 (C)	7.07 (AX)			
			−1.12 (X and Y)	7.11 (CY)	−70	20.5	10.0
	−120	$ABX_3 + CDY_3$	−2.63 (A), −2.74 (B)	7.16 (AX), 7.0 (BX)			
			−2.65 (C), −2.77 (D)	12.5 (AB)			
			−1.12 (X and Y)	6.8 (CY), 7.3 (DY)			
				12.5 (CD)			
$S_2[N(C_3H_7)_2]_2$	30	AX_6	−3.42 (A)	6.6 (AX)			
			−1.17 (X)				
	−110	AX_3Y_3	−3.42 (A)	6.7 (AX)	−82	2.3	10.4
			−1.16 (X), 1.18 (Y)	6.6 (AY)			

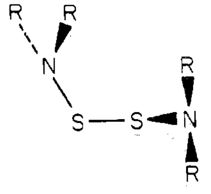
[a] The assignments of coupling constants and chemical shifts were confirmed by double-resonance experiments.

resolution by nmr because in the ambient temperature spectrum of $[(C_2H_5)_2N]_2S_2$ two distinct methylene quartets (separated by less than 1 Hz) are observed. This clearly indicates that in the diethyl derivative and probably in the other two disulfides as well that (since rapid nitrogen inversion would be expected at 30°) either S-N or S-S rotation must already be slow at room temperature.[9] Below 30° the spectra of all these disulfides are temperature dependent, the rate-limiting process being assigned to torsion about a bond rather than nitrogen inversion using arguments similar to those presented above for the bis(amino)sulfides. While it is not possible to determine unambiguously which rotation was observed to slow below ambient temperature and which had already slowed by 30° it is known that in diethoxy disulfide S-S rotation does not become rapid on the nmr time scale until considerably above room temperature.[10] Since the N-S barriers reported above for the bis(amino)sulfides and elsewhere for other S-N barriers[1-3] are near those measured for the exchanges observed below room temperature in $(R_2N)_2S_2$, we tentatively assign the barriers reported in Table I to N-S torsion.

The low-temperature spectrum of $[(C_2H_5)_2N]_2S_2$, which at −120° has become overlapping ABX_3 and CDY_3 spectra, shows not only that the ethyl groups occupy two different sites after N-S and S-S rotation have ceased (but while N inversion is still rapid) but also that the methylene protons on each are diastereotopic. (The low-temperature spectra of the other two disulfides can be interpreted similarly.) The observation of two equally populated alkyl group sites, combined with the nonequivalences of the methylene protons, make a planar N-S-S-N framework unlikely since reasonable structures would either have more or less than two R group sites or the methylene protons would not be diastereotopic. If, on the other hand, the structure is similar to other disulfides[10,11] and is nonplanar, the data can be explained by either of two logical structures



II



III

In II the R_2N planes contain the S-S bond axis while in III this plane is perpendicular to the NSS plane. While no discrimination can be made between these structures on the basis of our data, III may be the more reasonable since the conformation about the S-N bond in it is identical with that in I.

Registry No. $S[N(CH_3)_2]_2$, 2129-20-6; $S_2[N(CH_3)_2]_2$, 928-05-2; $S[N(C_2H_5)_2]_2$, 3768-61-4; $S_2[N(C_2H_5)_2]_2$, 15575-30-1; $S[N(C_3H_7)_2]_2$, 34066-25-6; $S_2[N(C_3H_7)_2]_2$, 38126-23-7.

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[9] Unfortunately $[(C_2H_5)_2N]_2S_2$ decomposes upon heating and we were unable to obtain spectra in the fast-exchange region.

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Disproportionation of Dithionate

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Aqueous dithionate is known to disproportionate in a slow acid-catalyzed reaction at high temperatures[1]

$H^+ + {}^-O_3S\text{-}SO_3^- \rightarrow SO_2 + HSO_4^-$

We report here our observation that the same reaction takes place smoothly at room temperature in 7-10 *M* sulfuric acid.

Table I

$[H_2SO_4]$, *M*	Pseudo-first-order rate constant × 10^4, sec^{-1}	$[H_2SO_4]$, *M*	Pseudo-first-order rate constant × 10^4, sec^{-1}
7.15	0.418	9.28	8.26
7.78	0.820	9.73	19.4
8.30	1.72	10.18	32.0
8.81	4.00	10.52	65.5

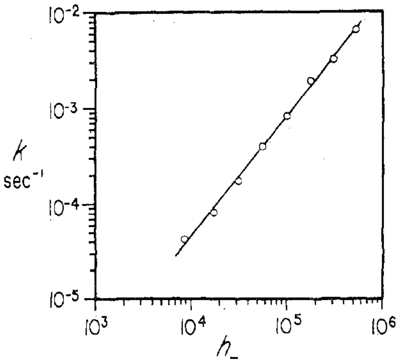

Figure 1. Dependence of the rate on acidity.

Experimental Section

$Na_2S_2O_6 \cdot 2H_2O$ was synthesized by the literature method.[2] Sulfuric acid solutions were made up by mixing appropriate portions of 7 *M* with 11 *M* reagent grade H_2SO_4, in each case checked by titration. Each sulfuric acid solution was precooled slightly before adding the dithionate stock solution, so that all final solutions were at 23 ± 1°. The final concentration of dithionate was approximately 0.003 *M*. The reaction was followed with a Cary 14 spectrophotometer, using the SO_2 absorption at 2790 Å. All rates were first order with respect to dithionate for at least 4 half-lives. The pseudo-first-order rate constant, evaluated graphically, is probably reliable to within about ±2%.

Results and Discussion

The pseudo-first-order rate constant, *k*, has the values given in Table I, at the stated acid concentration. The dependence of *k* on the indicator acidity, h_-,[3] is shown in Figure 1. The indicator acidity h_- is reasonable to use, since the protonation of one end of a dithionate ion probably affects the hydration of the other end only slightly. In any event, the indicator acidity function H_{2-} has not been tabulated for these acidic solutions. The slope of the line in Figure 1 is 1.26. The discrepancy between the observed slope and unity is probably without mechanistic significance,[5] indicating merely a slight difference between the hydration of the transition state and of the indicators used to establish the H_- scale. We conclude that the transition state is singly protonated from dilute solutions[1] to the highest acidity reached in this study. We note in passing that the data in Figure 1 show no tendency to level off at high acidities, indicating that dithionic acid is a completely strong diprotic acid up to the highest acidity reached.

In order to compare our second-order rate constant with the literature values at high temperatures, we had to extrapolate our data to infinite dilution. There is no generally accepted way to make this extrapolation. In 1961, Bunnett[4] recommended a log-log plot of k/h *vs.* water activity, extrapolated to unity water activity. By 1966 he had changed his mind, he and Olsen[5] recommending a log-log plot of k/h *vs.* $h/[H^+]$, extrapolated to unity value of the latter. We have applied both methods to our data, obtaining good straight lines with both

$$k/h_- = 10^{-8.92}(a_{H_2O})^{-1.0}\ sec^{-1}\ M^{-1}$$

$$k/h_- = 10^{-9.22}(h_-/[H^+])^{+0.27}\ sec^{-1}\ M^{-1}$$

We take the extrapolated value at 23° to be $10^{-9.07 \pm 0.15}$ sec^{-1} M^{-1}. Figure 2 is an Arrhenius plot of our data with those of Meyer,[1d] which seem to be the best, also extrapolated slightly to infinite dilution. As was already pointed out[1c,d] the Arrhenius plot is curved, but our data are quite compatible with the earlier data. The slope of the curve at 25° corresponds to $\Delta H^{\ddagger} = 52$ kcal and $\Delta S^{\ddagger} = +74$ cal deg^{-1}.

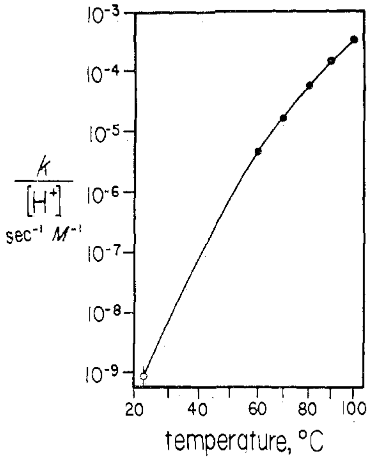

Figure 2. Arrhenius plot of the second-order rate.

Registry No. $Na_2S_2O_6 \cdot 2H_2O$, 10101-85-6.

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Electrophilic Acceleration by Bromine of the Elimination of Bromide Ion from $[Co^{III}(EDTA)Br]^{2-}$

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The ring-closure reactions of mixed halide-aminopolycarboxylate complexes of cobalt(III) have been studied by several workers.[1-5] It has been found that a number of

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