(10 g) was dissolved in 80 ml of methanol. Brucine (containing $2H_2O$, 21.3 g) was added and the solution was left overnight, whereby a brucine salt had crystallized. The salt was recrystallized twice from methanol and the diacid liberated by treatment with dilute hydrochloric acid, $[\alpha]_{578}^{20}$ +37.6° (*c* 0.1 ethanol). Two further recrystallizations of the brucine salt from methanol gave diacid samples with $[\alpha]_{578}^{20}$ 39.5 and 38.7°, respectively, showing that the resolution was complete.

Diisopropylmaleic Anhydride (15). *meso*-2,3-Diisopropylsuccinic acid[36] (5 g) was dissolved in acetyl chloride (10 ml) and allowed to stand overnight. Excess acetyl chloride was evaporated and the anhydride was purified by distillation. Bromine (3 g) was then added slowly to the anhydride (3.7 g) at 120°. When the bromine color had disappeared the reaction mixture was dissolved in aqueous sodium hydroxide. The solution was acidified with hydrochloric acid and the resulting precipitate was filtered off and recrystallized from ethanol–water: mp 123–124°; nmr (δ in CCl_4) 3.01 (1, heptuplet, $CH(CH_3)_2$, J = 7.0 Hz), 1.28 (6, d, $CH(CH_3)_2$, J = 7.0 Hz); ir (KBr) 1830, 1760 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.9; H, 7.74; O, 26.3. Found: C, 66.0; H, 7.70; O, 26.2.

3,6-Diethylphthalic Anhydride (22). 2,5-Diethylfuran[49] (10 g) was added to a solution of maleic anhydride (7.9 g) in ether (10 ml). After stirring for 4 hr, the mixture was cooled to −20° and the crystals were filtered off. The product (which slowly reverts to starting materials on standing at room temperature) was immediately transferred to a beaker containing 90% sulfuric acid (150 ml) cooled to −5°. The solution was stirred for 30 min at −5 to 0° and then poured onto ice. The precipitate was filtered and dissolved in aqueous sodium hydroxide (6 g in 120 ml of water). Addition of acetic acid (10 ml) precipitated some oily impurities which were filtered off. Final acidification of the filtrate gave the anhydride (12% yield) which was purified by sublimation and recrystallization from hexane, mp 124–125° (lit.[50] 122–125°).

Kinetic Measurements. Rate constants for the solvolysis of anhydrides (k_{-1}) were determined by the pH-stat method used previously.[51] At temperatures $\leq 30°$ the Radiometer G 202 B glass electrode was employed, whereas the high-temperature electrode G 202 CH was used at 60°. Rate constants for attaining equilibrium (eq 1) from the diacid side ($k_1 + k_{-1}$) were determined spectrophotometrically (Cary 15 spectrophotometer, with the cuvette housing thermostated by circulating water from an external thermostat). The reaction was followed by a suitable wavelength on a solution prepared by rapid addition of a solution of the salt of the diacid to 0.1 *M* hydrochloric acid.

For systems with difficultly soluble anhydrides (**10** and **11**) the following method was used. An accurately weighed amount (about 10 mg) of the diacid was dissolved in an acetic acid–acetate (0.1 *M*) buffer solution (250 ml) and the solution was kept in a well-stoppered flask at 60.0° for several weeks for equilibration. After this period 100 ml of the solution was withdrawn by a pipet and quickly cooled to about +5° in an ice bath. The solution was neutralized by sodium carbonate (to a pH of 8) and then it was extracted by ether (two 20-ml portions). The amount of anhydride in the ether solution was then determined by glc (internal standard, 2 m × 0.3 mm 10% DC-30 column).

Equilibration of Succinic Anhydrides. Solutions of the anhydrides (20 mg in 1 ml of dioxane) were filled into ampoules and the ampoules were equilibrated in an oven for 2 weeks. The temperature of the oven[52] was kept at 170.0 ± 0.2°. The equilibrium mixture of anhydrides was analyzed directly on a 2 m × 0.3 mm 5% SE-30 on Chromosorb P column. No equilibration took place at the temperatures used (less than 100° on both injector and column) during these analyses.

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Kinetics of Sulfur–Sulfur Bond Cleavage in Methylated Methyl Disulfide by Nuclear Magnetic Resonance

Stephen H. Smallcombe and Marjorie C. Caserio* [1]

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. Received February 1, 1971

Abstract: The sulfenyl compound $(CH_3)_2S^+SCH_3BF_4^-$ reacts rapidly and reversibly with both methyl sulfide and methyl disulfide by cleavage of the S–S bond. The rates and activation parameters for these reactions in CH_3NO_2 have been determined by nmr techniques. The position of equilibrium in the reaction $(CH_3)_2S^+SCH_3 + CH_3SSCH_3 \rightleftarrows (CH_3)_2S + CH_3S^+(SCH_3)_2$ has been found to lie far to the left with $K = k_2/k_3 = 7.4 \times 10^{-4}$. Equilibrium is rapidly established ($k_2 = 1.06 \times 10^4\ M^{-1}\ sec^{-1}$ and $k_3 = 1.4 \times 10^7\ M^{-1}\ sec^{-1}$) and is responsible for the pronounced catalytic effect observed for $(CH_3)_2S^+SCH_3BF_4^-$ in the interchange of organic disulfides. The enthalpy and entropy of the disulfide–salt equilibrium and the rates of cleavage of $CH_3S^+(SCH_3)_2$ with methyl sulfide and methyl disulfide have been determined. The results indicate that the reactivity of the S–S bond toward nucleophilic attack is enhanced by a factor in excess of 10^6 by methylation and S-methylation at sulfur.

The ease with which the S–S bond of dimethylthiomethylsulfonium salts **1** are cleaved by nucleophilic reagents was first documented by Helmkamp and coworkers in their work on the preparation of **1** and its addition to alkenes and alkynes.[2] These reactions and the related studies of Meerwein[3] indicate that compounds of type **1** may be regarded as sulfenyl derivatives and a potential source of alkylsulfenyl ions,

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(1) The authors gratefully acknowledge support received for this work from the National Science Foundation (GP-7485 and GP-12828).

(2) (a) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964); (b) G. K. Helmkamp, B. A. Olsen, and D. J. Pettitt, *ibid.*, 30, 676 (1965); (c) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *ibid.*, 30, 933 (1965); (d) G. K. Helmkamp, B. A. Olsen, and J. R. Kaskinen, *ibid.*, 30, 1623 (1965).

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RS^+.[4-6] More recently, Kice and Favstritsky[7] reported an interesting reaction between **1** (as the trinitrobenzenesulfonate salt) and methyl sulfide (eq 1). Al-

$$\underset{\mathbf{1}}{(CH_3)_2\overset{+}{S}SCH_3} + S(CH_3)_2 \overset{k_1}{\rightleftarrows} (CH_3)_2S + \underset{\mathbf{1}}{CH_3S\overset{+}{S}(CH_3)_2} \quad (1)$$

though the reactants and products are chemically indistinguishable, the reaction is observable by nmr techniques and was found to be so fast as to preclude accurate measurement of its rate. A lower limit for the specific rate was set at $10^5\ M^{-1}\ sec^{-1}$.

We have investigated the kinetics of a closely related reaction, namely the reversible cleavage of **1** (as the fluoroborate salt) with methyl disulfide (eq 2). For

$$\underset{\mathbf{1}}{(CH_3)_2\overset{+}{S}SCH_3} + CH_3SSCH_3 \underset{k_3}{\overset{k_2}{\rightleftarrows}} (CH_3)_2S + \underset{\mathbf{2}}{CH_3\overset{+}{S}(SCH_3)_2} \quad (2)$$

completeness, we have also studied the kinetics of reaction of **1** with methyl sulfide, and the results and implications of our work are described in this paper.

Kinetic Studies

Methyl Disulfide with Dimethylthiomethylsulfonium Fluoroborate. The nmr spectrum of dimethylthiomethylsulfonium fluoroborate (**1**) in nitromethane is comprised of two sharp singlets with a relative intensity of 2:1 at 3.22 and 2.86 ppm, respectively, as shown in Figure 1a. Addition of methyl disulfide causes a profound change in the line shape and chemical shift of the three-proton SCH_3 resonance of **1** which broadens and shifts progressively upfield with increasing concentration of CH_3SSCH_3 (Figure 1b). In contrast, the line shape and chemical shift of the six-proton $(CH_3)_2S^+$ resonance are only slightly affected (Figure 1c) and no resonance corresponding to that expected for CH_3SSCH_3 in nitromethane (2.3 ppm) is evident. This behavior signifies that a fast reaction occurs between **1** and CH_3SSCH_3 to cause only an average chemical shift to be apparent for the SCH_3 protons of the disulfide and the salt. The reaction given in eq 2 is consistent with the nmr evidence; the salt initially transfers S^+CH_3 to methyl disulfide to form (dithiomethyl)-methylsulfonium fluoroborate (**2**) and methyl sulfide. In the reverse reaction, S^+CH_3 is transferred from **2** to methyl sulfide and, because of the symmetry of **2**, there is an equal chance that the S^+CH_3 group transferred will have originated from CH_3SSCH_3 as from **1**. This may be more obvious from eq 3 in which the pertinent methyl groups are distinguished by the symbolism CH_3 and Me. The net result of the reaction is to exchange the *S*-methyl groups of **1** with those of methyl disulfide (eq 4)

The position of equilibrium in eq 2 must be far to the left since the chemical shift of the $(CH_3)_2S^+$ resonance changes only slightly with $[CH_3SSCH_3]$ (Figure 1c) implying that the population of methyl sulfide must be very low. The equilibrium must also be rapidly established since the appearance of only *one* resonance for the SCH_3 protons means that exchange is rapid on the nmr time scale.

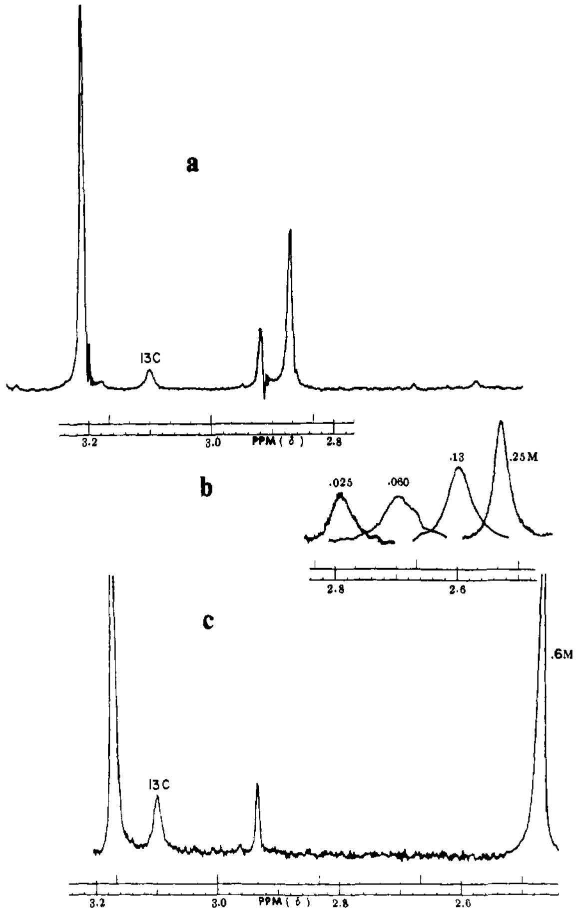
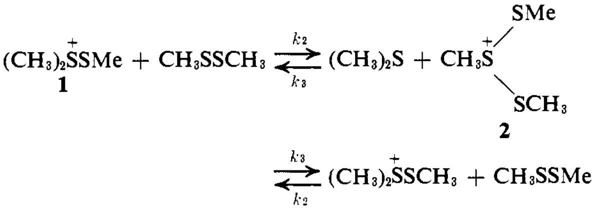


Figure 1. (a) Nmr spectrum of **1** (0.246 *M*) in nitromethane; the main solvent signal is not shown but the ^{13}C side band is evident; the sharp singlet downfield of the SCH_3 resonance of **1** is due to trimethylsulfonium fluoroborate which was present as a minor impurity (see Discussion). (b) Nmr spectrum of **1** in nitromethane showing effect of added CH_3SSCH_3 (0.025–0.25 *M*) on the SCH_3 resonance. (c) Nmr spectrum of **1** in nitromethane containing 0.6 *M* CH_3SSCH_3.



$$\underset{\mathbf{1}}{(CH_3)_2\overset{+}{S}SMe} + CH_3SSCH_3 \underset{k_3}{\overset{k_2}{\rightleftarrows}} (CH_3)_2S + \underset{\mathbf{2}}{CH_3\overset{+}{S}(SMe)(SCH_3)}$$

$$\underset{k_2}{\overset{k_3}{\rightleftarrows}} (CH_3)_2\overset{+}{S}SCH_3 + CH_3SSMe \quad (3)$$

$$(CH_3)_2\overset{+}{S}SMe + CH_3SSCH_3 \overset{k_A}{\rightleftarrows} (CH_3)_2S^+SCH_3 + CH_3SSMe \quad (4)$$

Although the trisulfide salt **2** which is postulated as an intermediate in the exchange process of eq 2 and 3 is not a known compound, related structures have been proposed as intermediates in the reactions of disulfides with sulfenyl chlorides[8] and sulfinic acids.[9]

Kinetics of Disulfide Exchange. The first objective of the kinetic study was to determine the specific rate k_2 for the reaction of methyl disulfide with **1**. The nmr method permits the measurement of the mean

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(4) G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Amer. Chem. Soc.*, **90**, 1635 (1968); D. C. Owsley and G. K. Helmkamp, *ibid.*, **89**, 4558 (1967).

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(6) R. E. Benesch and R. Benesch, *J. Amer. Chem. Soc.*, **80**, 1666 (1958).

(7) J. L. Kice and N. A. Favstritsky, *ibid.*, **91**, 1751 (1969).

(8) C. G. Moore and M. Porter, *J. Chem. Soc.*, 2890 (1958).

(9) (a) J. L. Kice and E. H. Morkved, *J. Amer. Chem. Soc.*, **86**, 2270 (1964); (b) J. L. Kice and K. W. Bowers, *ibid.*, **84**, 2384 (1962).

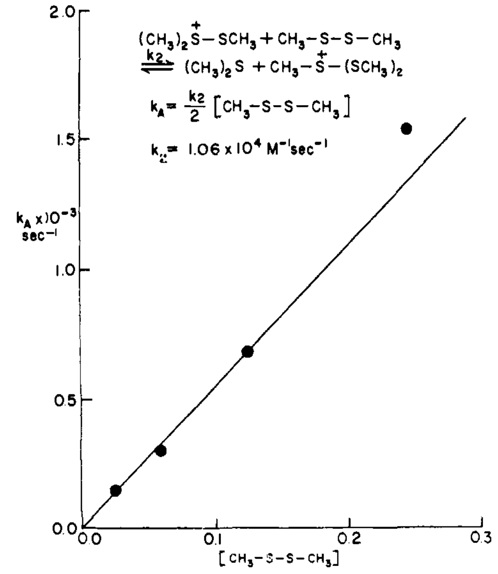


Figure 2. Kinetics of SCH_3 exchange between **1** and CH_3SSCH_3. Plot of k_A against $[CH_3SSCH_3]$ for solutions 0.246 M in **1** in nitromethane at 40°.

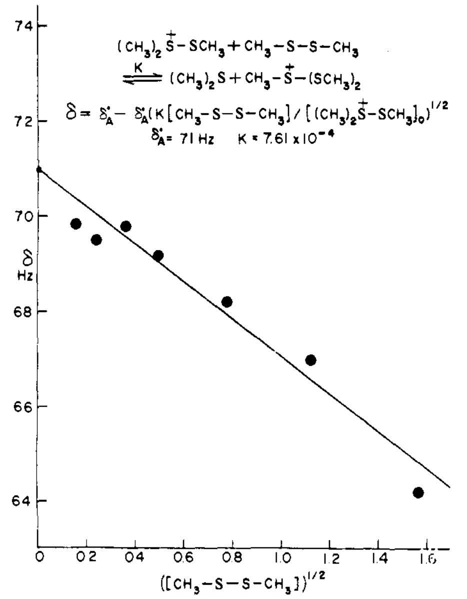


Figure 3. Determination of the equilibrium constant of eq 2 from a plot of the chemical shift of the $S(CH_3)_2$ resonance of **1** against $[CH_3SSCH_3]^{1/2}$ for solutions 0.246 M in **1** in nitromethane at 40°

lifetime τ_A of the SCH_3 protons in **1** (site A), where τ_A is related to the specific rate k_A of SCH_3 exchange by $k_A = 1/\tau_A$. The relationship between k_2 and k_A is given in the following equation

$$\frac{-d[\text{salt}]}{dt} = k_2[\text{salt}][CH_3SSCH_3] = 2k_A[\text{salt}] \quad (5)$$

where $2k_A = k_2[CH_3SSCH_3]$. The factor of *two* appears in eq 5 because only one-half of all the molecules of **2** formed from **1** revert to give **1** with exchanged *S*-methyl groups (see eq 3). That is to say, the rate of reaction of methyl disulfide with **1** is twice the rate of *S*-methyl exchange.

The kinetic expression for a rapid two-site exchange process is given in eq 6 where the subscript A refers

$$k_A = \frac{1}{\tau_A} = \frac{4\pi p_A p_B{}^2(\delta_A - \delta_B)^2}{\Delta\delta\nu_{1/2}} \quad (6)$$

to site A (the SCH_3 protons of **1**) and B refers to site B (the SCH_3 protons of methyl disulfide); p_A and p_B are the relative populations of sites A and B with the condition that $p_A + p_B = 1$; δ_A and δ_B are the nonexchanging chemical shifts of the SCH_3 protons in sites A and B, respectively; the term $\Delta\delta\nu_{1/2}$ is the line-broadening term and is equal to the line width of the exchanging resonance less the line width of the resonance in the absence of exchange (which was assumed to be equal to the line width of trimethylsulfonium fluoroborate in the reaction mixture). Justification for eq 6 is given in Appendix A.

The specific rate of exchange k_A was determined at various concentrations of disulfide by monitoring the exchanging SCH_3 chemical shift δ_{SCH_3} and the line-broadening $\Delta\delta\nu_{1/2}$ measured at half-height. The populations p_A and p_B were calculated from eq 7 which relates

$$\delta_{SCH_3} = p_A\delta_A + p_B\delta_B \quad (7)$$

lates δ_{SCH_3} to the populations and nonexchanging chemical shifts of the two sites, and the values obtained were used to determine k_A from eq 6. According to eq 5, a plot of k_A against $[CH_3SSCH_3]$ should be linear and of slope $0.5k_2$. A plot of the experimental data for solutions 0.246 M is **1** and up to 0.597 M in CH_3SSCH_3 in nitromethane at 40° is given in Figure 2. The rate of exchange is evidently linear in $[CH_3SSCH_3]$ up to about 0.15 M but is faster than predicted by eq 5 at higher concentrations. The specific rate constant k_2 for the reaction of disulfide with **1** was estimated from the slope of the line shown in Figure 2 as $k_2 = 1.06 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at 40°. The reasons why the exchange rate increases nonlinearly at high concentrations of disulfide are discussed in a later section.

Determination of the Equilibrium Constant. As noted previously, the chemical shift of the *S*-dimethyl resonance of **1** ($\delta_{S(CH_3)_2}$) changes relatively little on addition of methyl disulfide (Figure 1c). However, the change is significant and is related to the equilibrium constant K for the reaction of disulfide with **1** by the expression

$$\delta_{S(CH_3)_2} = \delta_A' - (\delta_A' - \delta_B') \times (K/[\text{salt}]_0)^{1/2}[CH_3SSCH_3]^{1/2} \quad (8)$$

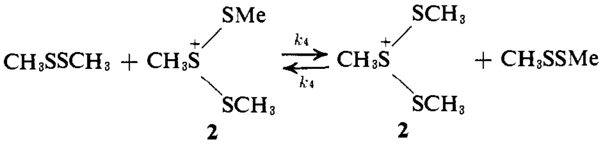
where δ_A' and δ_B' are the nonexchanging chemical shifts of the $S(CH_3)_2$ resonance of **1** and methyl sulfide, respectively. The derivation of eq 8 is given in Appendix B. On referring to the chemical shifts relative to site B (*i.e.*, $\delta_B = 0$), eq 8 simplifies to

$$\delta_{S(CH_3)_2} = \delta_A' - \delta_A'(K/[\text{salt}]_0)^{1/2}[CH_3SSCH_3]^{1/2} \quad (9)$$

which predicts that a plot of $\delta_{S(CH_3)_2}$ against $[CH_3SSCH_3]^{1/2}$ should be linear. A plot of the data, shown in Figure 3, is roughly linear with an intercept of $\delta_A' = 71$ Hz and a slope of $3.95 = \delta_A'(K/[\text{salt}]_0)^{1/2}$ from which a value of $K = 7.6 \times 10^{-4}$ was calculated for solutions initially 0.246 M in **1**.

The small value of K confirms the qualitative observation made from the nmr spectrum of disulfide-salt mixtures that the equilibrium of eq 2 lies far to the left. Since $K = k_2/k_3$, and using the value of $k_2 = 1.06 \times 10^4\ M^{-1}\ \text{sec}^{-1}$, the specific rate of the back reaction is calculated to be $k_3 = 1.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ at 40°. Thus, methyl sulfide reacts with $CH_3S^+(SCH_3)_2$ approximately 10^3 times faster than methyl disulfide reacts with $(CH_3)_2S^+SCH_3$.

Methyl Disulfide with (Dithiomethyl)methylsulfonium Fluoroborate. A plausible explanation for the observation that the rate of SCH_3 exchange of **1** occurs faster than predicted by eq 5 at high disulfide concentration is that exchange of CH_3SSCH_3 with **2** becomes significant under these conditions (eq 10). There are, therefore,



$$CH_3SSCH_3 + CH_3\overset{+}{S}(SMe)(SCH_3) \underset{k_4}{\overset{k_4}{\rightleftharpoons}} CH_3\overset{+}{S}(SCH_3)(SCH_3) + CH_3SSMe \quad (10)$$

two pathways by which the SCH_3 groups of methyl disulfide may exchange with **1**, and these are represented by eq 2 (or 3) and 10. In the limit, when the rate of eq 10 greatly exceeds the rate of the back reaction of eq 2 (*i.e.*, $k_4[CH_3SSCH_3] \gg k_3[CH_3SCH_3]$, each molecule of CH_3SSCH_3 that reacts to form **2** will have its SCH_3 groups completely exchanged by the process of eq 10 *before* the back reaction of eq 2 takes effect. Under these conditions, the specific rate of exchange k_A is related to the specific rate of displacement k_2 by the expression

$$k_A = k_2[CH_3SSCH_3] \quad (11)$$

Equation 11 may be rewritten in the more general form of eq 12 where α is defined as the fraction of **2** that

$$k_A = \frac{1}{2}k_2[CH_3SSCH_3](1 + \alpha) \quad (12)$$

reacts by eq 10 and $(1 - \alpha)$ is the fraction that reacts by eq 2. In the limit, when $\alpha = 0$, then $k_A = {}^1/_2k_2[CH_3SSCH_3]$; when $\alpha = 1$, $k_A = k_2[CH_3SSCH_3]$ The relative rates of the two pathways for the destruction of **2** are

$$\alpha/(1 - \alpha) = k_4[CH_3SSCH_3]/k_3[CH_3SCH_3]$$

and substituting for $[CH_3SCH_3] = \{K[CH_3SSCH_3][\text{salt}]\}^{1/2}$ gives

$$\alpha/(1 - \alpha) = k_4[CH_3SSCH_3]^{1/2}/k_3\{K[\text{salt}]\}^{1/2} \quad (13)$$

The objective was to determine k_4 from eq 13. To do so, a value of α was first calculated from eq 12 using a measured value of k_A at a given disulfide concentration. The data for two determinations are given in Table I from which it is clear that the agreement in k_4 is poor. However, the data establishes the order of magnitude of k_4, and for the purposes of further calculations we will use an average value of $k_4 = 2 \times 10^5\ M^{-1}\ \text{sec}^{-1}$.

Table I. Kinetics of Exchange of Methyl Disulfide with (Dithiomethyl)methylsulfonium Fluoroborate at 40° in Nitromethane

k_A, 10^{-3} sec^{-1}	[CH$_3$-SSCH$_3$], M	[Salt],[a] M	α[b]	k_4,[c] 10^{-5} sec^{-1}
1.53	0.246	0.246	0.177	0.83
4.65	0.597	0.246	0.472	2.2

[a] Concentration of 1. [b] Calculated from eq 12 using $k_2 = 1.06 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. [c] Calculated from eq 13 using $k_3 = 1.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ and $K = 7.6 \times 10^{-4}$.

Temperature Dependence of Disulfide Exchange. The change in k_A with temperature was determined from the line shape and chemical shift of the SCH_3 resonance of solutions 0.296 M in **1** and 1.13 M in methyl disulfide in nitromethane over the temperature range −60 to +35°. The expression used to calculate τ_A and hence k_A is given in eq 14, which holds over the temperature range employed encompassing regions of both fast and slow exchange.[10] The negative sign in eq 14 is applicable in the region of fast exchange and the positive sign in the region of slow exchange. The k_A values obtained using eq 14 were used to calculate k_2

$$\tau_A = \frac{1}{k_A} = p_A \times \frac{(\delta_A - \delta_B) \pm \{p_A^2(\delta_A - \delta_B)^2 - 4(\Delta\delta\nu_{1/2})^2\}^{1/2}}{2(\delta_A - \delta_B)\Delta\delta\nu_{1/2}} \quad (14)$$

from the expression $2k_A = k_2[CH_3SSCH_3]$.[11] The temperature dependence of k_2 is expressed by the Arrhenius equation $\ln k_2 = -E_a/RT + \ln A$. A plot of $\ln k_2$ *vs.* $1/T$ was linear and gave $E_a = 8.27$ kcal/mol and $A = 7.4 \times 10^9$. The enthalpy and entropy of activation were calculated from these data such that $\Delta H^{\ddagger} = E_a - RT = 7.68$ kcal/mol and $\Delta S^{\ddagger} = R[\ln(hA/kT) - 1] = -15.1$ eu.

A more satisfactory method of determining the activation parameters involves direct use of the Eyring equation which may be expressed as in eq 15.[12] A plot of $\ln(k_2/T)$ against $10^3/T$ is shown in Figure 4.

$$\ln(k_2/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(k/h) \quad (15)$$

The slope of the line gave $\Delta H^{\ddagger} = 7.5$ kcal/mol, which value was used to calculate $\Delta S^{\ddagger} = -16$ eu using $k_2 = 1.06 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at 40°

Temperature Dependence of Equilibrium Constant. The objective was to determine the enthalpy and entropy for the equilibrium of eq 2 and to use these values with the activation parameters determined for the forward reaction to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the back reaction. To do this, the equilibrium constant K was calculated from eq 8 by measuring $\delta_{S(CH_3)_2}$ at various temperatures in solutions 0.29 M in **1** and 1.13 M in CH_3SSCH_3 in nitromethane. A plot of $\ln K$ *vs.* $10^3/T$ was roughly linear (Figure 5, and eq 16) and gave $\Delta H = 2.4$ kcal/mol and $\Delta S = -6.7$ eu.

$$\ln K = -\Delta H/RT + \Delta S/R \quad (16)$$

Subtracting the thermodynamic parameters from the activation parameters for the forward reaction gives $\Delta H^{\ddagger} = 5.1$ kcal/mol and $\Delta S^{\ddagger} = -9.3$ eu for the back reaction, which is the reaction of **2** with methyl sulfide.

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(10) C. S. Johnson, Jr., *Advan. Magn. Resonance*, 1, 33 (1965).

(11) The use of the limiting form of eq 12 may at first appear surprising since it may be calculated from eq 13 using $k_3 = 1.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, $k_4 = 2 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, and $K = 7.6 \times 10^{-4}$, that $\alpha = 0.5$ in solutions 0.296 M in 1 and 1.13 M in CH_3SSCH_3. However, provided the term $(1 + \alpha)$ in eq 12 remains constant with temperature the slope of an Arrhenius plot and hence E_a (or $\Delta H^{\ddagger}$) will be independent of α. A calculation in which α was varied between the limits $\alpha = 0$ to $\alpha = 1$ was found to give a maximum error of 10% in the value of $\ln k_2$ and a probable maximum error in $\Delta H^{\ddagger}$ of 0.2 kcal/mol. The errors introduced by neglecting the temperature dependence of α are probably much less than indicated and are considered insignificant relative to the overall experimental error.

(12) G. Binsch, *Top. Stereochem.*, 3, 97 (1969).

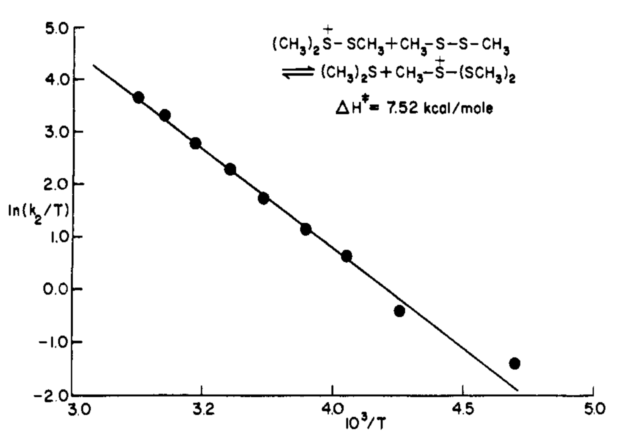


Figure 4. Activation parameters determined for SCH_3 exchange from a plot of ln (k_2/T) against $10^3/T$ for solutions 0.296 M in **1** and 1.13 M in CH_3SSCH_3 in nitromethane.

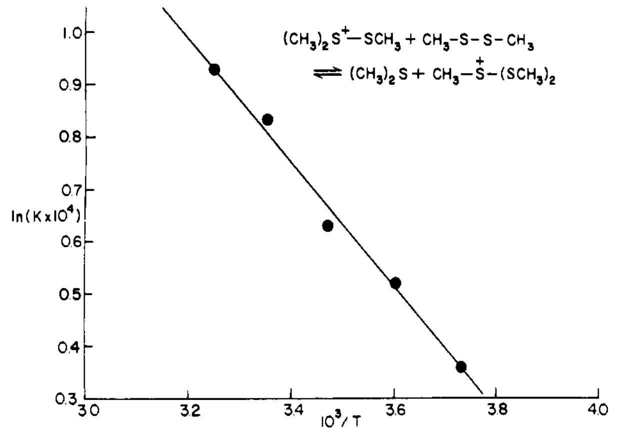


Figure 5. Thermodynamic parameters for equilibrium of eq 2 from a plot of ln $(K \times 10^4)$ against $10^3/T$ for solutions 0.296 M in **1** and 1.13 M in CH_3SSCH_3 in nitromethane.

Methyl Sulfide with Dimethylthiomethylsulfonium Fluoroborate. We have noted that CH_3SSCH_3 exchanges with the SCH_3 group of **1**. In contrast, methyl sulfide exchanges with the $S(CH_3)_2$ group of **1** (eq 17).

$$\underset{\mathbf{1}}{(CH_3)_2\overset{+}{S}SCH_3} + Me_2S \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1}}{Me_2\overset{+}{S}SCH_3} + (CH_3)_2S \qquad (17)$$

This has the effect of shifting the $S(CH_3)_2$ resonance of **1** upfield on the addition of methyl sulfide without producing a change in the magnetic or chemical environment of the SCH_3 resonance.

As reported by Kice and Favstritsky[7] the reaction of CH_3SCH_3 with **1** is extremely fast. We have attempted to measure the rate, however, using low concentrations of reagents and low temperatures. In the region of fast exchange eq 6 applies and the specific rate of exchange k_A is related to the specific rate of displacement k_1 by eq 18. The factor of 2 in eq 18 arises from the

$$1/\tau_A = k_A = 2k_1[CH_3SCH_3] \qquad (18)$$

fact that the reaction in question is symmetrical and produces exchange in both directions. The rate of $S(CH_3)_2$ exchange is therefore twice as fast as the rate of reaction between methyl sulfide and **1**.

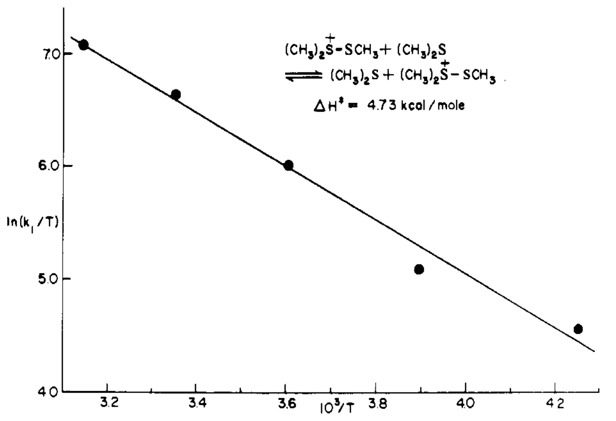


Figure 6. Activation parameters for the reaction of methyl sulfide with **1** from a plot of ln (k_1/T) against $10^3/T$ for solutions 0.0645 M in **1** and 0.106 M in methyl sulfide in nitromethane.

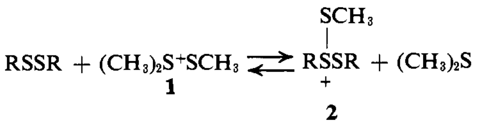
A plot of k_A *vs.* $[CH_3SCH_3]$ for solutions 0.0532 M in **1** in nitromethane at 5° should be linear according to eq 18. The experimental data, however, showed a high degree of scatter which precluded an accurate determination of k_1. The "best" value of k_1 was determined at $1.5 \times 0.5 \times 10^5\ M^{-1}\ sec^{-1}$ at 5°. The temperature dependence of k_A over the range −35 to 45° was measured with better precision using solutions 0.0645 M in **1** and 0.106 M in methyl sulfide. An Arrhenius plot of ln k_1 *vs.* $10^3/T$ was linear and gave E_a = 5.52 kcal/mol. Using this value of E_a and $k_2 = 1.5 \times 10^5\ M^{-1}\ sec^{-1}$ at 5°, the frequency factor was calculated as $A = 3.3 \times 10^9$. The values of E_a and A were converted to $\Delta H^{\ddagger}$ = 4.93 kcal/mol and $\Delta S^{\ddagger}$ = −16.8 eu at 25° The activation parameters were also determined more directly from a plot of ln (k_1/T) *vs.* $10^3/T$ (Figure 6). The slope gave $\Delta H^{\ddagger}$ = 4.73 kcal/mol and the intercept gave $\Delta S^{\ddagger}$ = −17.6 eu. These parameters were used to calculate $k_1 = 4.5 \pm 1 \times 10^5\ M^{-1}\ sec^{-1}$ at 40°. It should be noted that this value agrees with the lower limit of $10^5\ M^{-1}\ sec^{-1}$ predicted by Kice and Favstritsky[7] for the specific rate of reaction between methyl sulfide and **1**.

Disulfide Interchange. A suspension of about 5 mg of **1** in 10 ml of an equimolar mixture of methyl disulfide and ethyl disulfide (no solvent) caused immediate interchange of the disulfides. Within 30 min the mixture had reached equilibrium (K = 4).

$$CH_3SSCH_3 + C_2H_5SSC_2H_5 \xrightleftharpoons{(CH_3)_2S^+SCH_3} 2CH_3SSC_2H_5$$

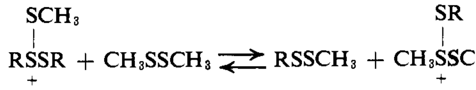
Two-component mixtures of methyl disulfide, ethyl disulfide, phenyl disulfide, and *tert*-butyl disulfide were observed to interchange with each other when any given symmetrical pair and **1** were dissolved in nitrobenzene to be 5 M in each disulfide and 10^{-2} M in **1**. Although no quantitative measurements were made under these conditions, interchange involving *tert*-butyl disulfide was notably slower than exchange between CH_3SSCH_3 and $C_2H_5SSC_2H_5$. Also, addition of methyl sulfide to a mixture of CH_3SSCH_3 and *tert*-BuSS-*tert*-Bu slowed the rate of interchange appreciably.

The catalytic action of **1** is undoubtedly due to the combination of reactions 19 and 20. In eq 19, the catalyst **1** converts one disulfide partner to the active intermediate **2** which, if captured by the second disulfide partner, results in interchange (eq 20). The inhibiting



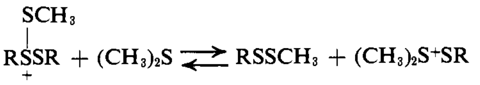
$$RSSR + (CH_3)_2S^+SCH_3 \rightleftarrows R\overset{SCH_3}{\underset{+}{S}}SR + (CH_3)_2S \qquad (19)$$

$$\mathbf{1} \qquad\qquad \mathbf{2}$$



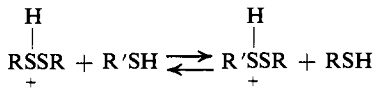
$$R\overset{SCH_3}{\underset{+}{S}}SR + CH_3SSCH_3 \rightleftarrows RSSCH_3 + CH_3\overset{SR}{\underset{+}{S}}SCH_3 \qquad (20)$$

effect of methyl sulfide can now be understood as a competing reaction of methyl sulfide for the active intermediate **2** (eq 21). Based on the data obtained in

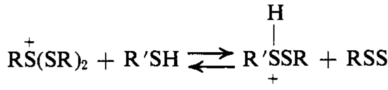


$$R\overset{SCH_3}{\underset{+}{S}}SR + (CH_3)_2S \rightleftarrows RSSCH_3 + (CH_3)_2S^+SR \qquad (21)$$

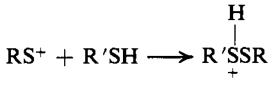
this work, the specific rate of eq 21 is about 70 times faster than eq 20 with the position of equilibrium in eq 21 lying far to the right. Clearly, large concentrations of $(CH_3)_2S$ will so reduce the concentration of **2** and compete so effectively with RSSR for **2** as to effectively inhibit disulfide interchange. In this connection, the reported inhibition of acid-catalyzed disulfide interchange by thiols[6,13] can be understood as the removal of the ionic intermediates RHS^+SR and $RS^+(SR)_2$ by thiol (eq 22 and 23) rather than by the removal of RS^+ by thiol (eq 24) as has been suggested.[6]



$$R\overset{H}{\underset{+}{S}}SR + R'SH \rightleftarrows R'\overset{H}{\underset{+}{S}}SR + RSH \qquad (22)$$



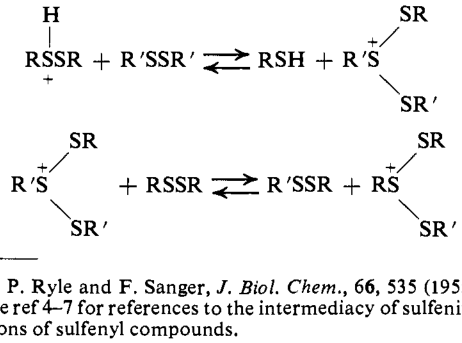
$$R\overset{+}{S}(SR)_2 + R'SH \rightleftarrows R'\overset{H}{\underset{+}{S}}SR + RSSR \qquad (23)$$



$$RS^+ + R'SH \longrightarrow R'\overset{H}{\underset{+}{S}}SR \qquad (24)$$

Discussion

The reactions of **1** with methyl sulfide and with methyl disulfide are both bimolecular processes each being first order in the concentration of sulfide or disulfide. A reaction mechanism involving rate-controlling dissociation of **1** into methylsulfenium ions CH_3S^+ is therefore excluded.[14] Both reactions are best formulated as SN2 processes in which the sulfide or disulfide behaves as a nucleophile and attacks the electrophilic sulfenyl sulfur of **1** to displace methyl sulfide. In view of these results, it seems very unlikely that acid-catalyzed disulfide interchange occurs by way of sulfenium ions as has been suggested.[6] The process is most reasonably formulated as proceeding by displacement of the protonated disulfide by neutral disulfide to form a trisulfide species related to **2** as the key intermediate.



$$R\overset{H}{\underset{+}{S}}SR + R'SSR' \rightleftarrows RSH + R'\overset{+}{S}(SR)(SR')$$

$$R'\overset{+}{S}(SR)(SR') + RSSR \rightleftarrows R'SSR + R\overset{+}{S}(SR)(SR')$$

Table II. Kinetics of Displacement of Sulfenyl Salts with Methyl Sulfide and Methyl Disulfide[a]

Reaction	k,[b] M^{-1} sec^{-1}	$\Delta G^{\ddagger}$,[b] kcal	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
CH_3SSCH_3 + **1**	1.1×10^4	12.5	7.5	−16.1
CH_3SCH_3 + **1**	4.5×10^5	10.2	4.7	−17.6
CH_3SSCH_3 + **2**	2×10^5	11		
CH_3SCH_3 + **2**	1.4×10^7	8.1	5.1	−9.3

[a] In nitromethane. [b] At 40°.

The kinetic data obtained in this work are summarized in Table II. It is apparent from the data that methyl sulfide is about 40 times more reactive than methyl disulfide toward **1** and about 70 times more reactive than methyl disulfide toward **2**. Methyl sulfide may be said, therefore, to be the stronger nucleophile. These results are consistent with the related work of Kice and Morkved[9a] on the reaction of disulfides with sulfinic acids; it may be determined from their data that di-*n*-butyl sulfide is some 250 times more reactive than di-*n*-butyl disulfide toward the intermediate (RSS^+R)-$S(O)Ar$. The data of Table II also establish that **2** is some 30 times more reactive than **1** toward CH_3SCH_3 and some 20 times more reactive than **1** toward CH_3SSCH_3. Accordingly, **2** may be said to be the stronger electrophile. The reactions in question can also be treated by Pearson's theory of hard and soft acids and bases[15] according to which the exceptional reactivity of methyl sulfide toward **2** reflects the affinity of a soft base (CH_3SCH_3) for a soft acid, $CH_3S^+(SCH_3)_2$. The kinetic data place methyl sulfide as a softer base than methyl disulfide, and **2** as a softer acid than **1**.

We noted with interest that no observable reaction takes place on the nmr time scale between **1** and methyl ether which must reflect in large part the "hardness" of methyl ether as a base relative to methyl sulfide.

$$(CH_3)_2\overset{+}{S}SCH_3 + (CH_3)_2O \underset{\longleftarrow}{\not\longrightarrow} (CH_3)_2S + (CH_3)_2\overset{+}{O}SCH_3$$

Comparing the activation parameters for the reactions of **1** with CH_3SCH_3 and CH_3SSCH_3 (the first two reactions listed in Table II) shows that the entropies of activation are very nearly the same although the enthalpies of activation differ significantly. In contrast, the reactions of CH_3SCH_3 with **1** and **2** have comparable activation enthalpies but different activation entropies. The relative reactivities of CH_3SCH_3 and CH_3SSCH_3 with **1** (and by inference with **2** also) are determined therefore by differences in $\Delta H^{\ddagger}$ values, while the relative reactivities of **1** and **2** with CH_3SCH_3 (and by inference with CH_3SSCH_3 also) are determined by differences in $\Delta S^{\ddagger}$ values. The question of interest is whether these differences are primarily ground-state or transition-state effects. That ground-state effects are probably important can be seen from the equilibrium of eq 2 which lies far to the left with $\Delta H = 2.4$ kcal and $\Delta S = -6.7$ eu. The free energy of the products (CH_3SCH_3 + **2**) therefore lies 4.4 kcal above that of the reactants (CH_3SSCH_3 + **1**). Furthermore, the ΔH value of 2.4 kcal is closely similar to $\Delta\Delta H^{\ddagger} = 2.8$ kcal for the reactions of **1** with CH_3SCH_3 and CH_3SSCH_3, and the ΔS value of −6.7 eu is similar to $\Delta\Delta S^{\ddagger} = -8.3$ eu for the reactions of CH_3SCH_3 with **1** and **2** (Table II). We suggest, therefore,

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[13] A. P. Ryle and F. Sanger, *J. Biol. Chem.*, 66, 535 (1955).

[14] See ref 4–7 for references to the intermediacy of sulfenium ions in the reactions of sulfenyl compounds.

[15] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 89, 1827 (1967); J. O. Edwards and R. G. Pearson, *ibid.*, 84, 16 (1962).

that the relative reactivities of the reactions of Table II are determined primarily by ground-state effects. Specifically, the greater reactivity of CH_3SCH_3 toward **1** or **2** compared to CH_3SSCH_3 may be attributed to the greater stability of CH_3SSCH_3 manifested as an enthalpy effect, and the greater reactivity of **2** relative to **1** may be due to the greater stability of **1** manifested as an entropy effect. Stabilization of methyl disulfide over methyl sulfide may be attributed to electron delocalization of nonbonding electrons on sulfur by (3p–

$$CH_3\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}CH_3 \longleftrightarrow CH_3\overset{-}{\underset{\cdot\cdot}{\ddot{S}}}=\overset{+}{\underset{\cdot\cdot}{S}}CH_3 \longleftrightarrow CH_3\overset{+}{\underset{\cdot\cdot}{S}}=\overset{-}{\underset{\cdot\cdot}{\ddot{S}}}CH_3$$

3d) π bonding. Delocalization of this type has long been discussed as a possible explanation of the bonding, spectral, and chemical properties of disulfides.[16–19]

Stabilization of **1** over **2** by an entropy effect is less readily explained although solvation effects are probably responsible. Thus, the greater reactivity of **2** could result from its being more highly solvated which would serve to lower its entropy in solution (raise its free energy) placing it closer to the reaction transition state.

Finally, it is informative to compare the reactivity of the sulfenyl sulfur of **1** with other electrophilic groups. We have studied the behavior of the dimethylmethoxysulfonium cation **3** with methyl sulfide

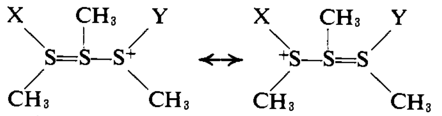
$$\underset{\mathbf{3}}{(CH_3)_2\overset{+}{S}OCH_3} + Me_2S \rightleftarrows (CH_3)_2S + \underset{\mathbf{3}}{CH_3O\overset{+}{S}Me_2}$$

and found the reaction to be immeasurably slow by nmr standards. This sets an upper limit on the rate of about 1 M^{-1} sec^{-1} although it is probably much slower, if it occurs at all. Compared, therefore, to the SCH_3 group, the OCH_3 is far less reactive—less electrophilic—a "harder" acidic group. In fact, alkoxysulfonium salts such as **3** generally react with nucleophiles by attack at either carbon or sulfur rather than oxygen.[20,21] Similarly, the reaction of $(CH_3)_2S^+NH_2$ with iodide is thought to occur by way of attack at sulfur rather than nitrogen.[22]

No reaction took place (on the nmr time scale) between trimethylsulfonium fluoroborate and methyl sulfide in nitromethane, and it can be estimated that methyl sulfide attacks the sulfenyl sulfur of **1** 10^9 or

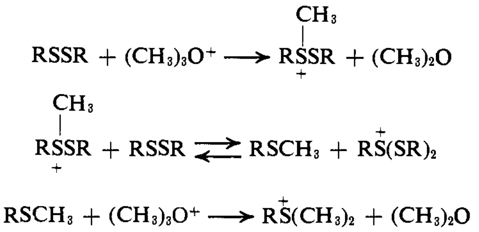
$$(CH_3)_2\overset{+}{S}CH_3 + Me_2S \rightleftarrows (CH_3)_2S + CH_3\overset{+}{S}Me_2$$

more times as rapidly as it attacks carbon in trimethylsulfonium salts.[7] This enormous difference in reactivity would seem to be related to an exceptional stabilization of the transition states for reactions involving sulfenyl sulfur. The electron-accepting properties of sulfur may be responsible for this stabilization. The reactions of methyl sulfide and methyl disulfide with **1** and **2** can each be formulated in terms of a transition state or intermediate **4** in which the positive charge is effectively delocalized over at least three sulfur atoms by way of (3p–3d) π bonding.



4a, X = Y = CH_3
b, X = Y = SCH_3
c, X = CH_3,
Y = SCH_3

The reactivity of **1** may also be compared to neutral disulfides which also undergo S–S cleavage by nucleophilic attack at sulfur.[23] However, cleavage of disulfides by thiolate ions is approximately 10^6 times slower than cleavage of **1** by methyl sulfide. Clearly, methylation, S-methylation, and protonation[6] of disulfides greatly enhances the reactivity of the S–S bond toward nucleophiles. Unfortunately, attempts to alkylate disulfides often result in extensive formation of trialkylsulfonium salts rather than dialkylthioalkylsulfonium salts,[2c] and this may now be understood in terms of the following reactions. Thus the sulfide



$$RSSR + (CH_3)_3O^+ \longrightarrow R\overset{CH_3}{\underset{+}{S}}SR + (CH_3)_2O$$

$$R\overset{CH_3}{\underset{+}{S}}SR + RSSR \rightleftarrows RSCH_3 + R\overset{+}{S}(SR)_2$$

$$RSCH_3 + (CH_3)_3O^+ \longrightarrow R\overset{+}{S}(CH_3)_2 + (CH_3)_2O$$

that is formed reversibly by the reaction of the alkylated disulfide with unreacted disulfide is effectively trapped by the alkylating agent to give (irreversibly) a trialkylsulfonium salt. In the preparation of **1**, we consistently observed the formation of small amounts of trimethylsulfonium fluoroborate (Figure 1a). Clearly, preparation of higher dialkylthioalkylsulfonium salts by alkylation of disulfides will be successful only if formation of monosulfides can be avoided.

Experimental Section

All nmr spectra and kinetic data were recorded using Varian HA-60 and A-60 nmr spectrometers. Tetramethylsilane was employed as an internal reference for chemical shift.

Dimethylthiomethylsulfonium fluoroborate was prepared by methylation of methyl disulfide with trimethyloxonium fluoroborate[24] by a procedure similar to that described by Helmkamp and coworkers.[2] On adding a suspension of the oxonium salt in nitromethane (or acetonitrile) to an equimolar amount of methyl disulfide in nitromethane (or acetonitrile) followed by excess dry ether to precipitate the product led to the coprecipitation of approximately 5–10% trimethylsulfonium fluoroborate impurity. The impurity was minimized by a procedure in which methyl disulfide in acetonitrile was added dropwise to an equimolar amount of trimethyloxonium fluoroborate suspended in acetonitrile at 0°. After stirring the mixture for approximately 1 hr at 0°, dry ether was added to precipitate dimethylthiomethylsulfonium fluoroborate, which had mp 58–59°.

Dimethylmethoxysulfonium salt was prepared as the benzenesulfonate by the reaction of methyl benzenesulfonate with dimethyl sulfoxide.

Acknowledgment. We greatly appreciate the technical assistance of Mr. David Ralston whose initial observations on the nature of disulfide methylation led to the work described in this paper.

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Appendix A

The line width ($1/T_2$) in radians per second of an observed resonance that is broadened by rapid exchange between two sites A and B is given by[25]

$$\frac{1}{T_2} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + p_A^2 p_B^2(\omega_A - \omega_B)^2(\tau_A + \tau_B) \quad (25)$$

Assuming that the transverse relaxation times T_{2A} and T_{2B} are equal, and using $p_A + p_B = 1$ and $p_A/p_B = \tau_A/\tau_B$, then eq 25 reduces to

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + p_A p_B^2(\omega_A - \omega_B)^2\tau_A$$

Substituting $\tau_A = 1/k_A$ gives

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{p_A p_B^2(\omega_A - \omega_B)^2}{k_A} \quad (26)$$

According to eq 26, the observed line width ($1/T_2$) is equal to the natural line width ($1/T_{2A}$) plus the exchange-broadened line width $p_A p_B^2(\omega_A - \omega_B)^2/k_A$. Expressing chemical shift and line width in hertz (*i.e.*, $\omega = 2\pi\nu$) gives

$$\frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{4\pi^2 p_A p_B^2(\delta_A - \delta_B)^2}{k_A} = \pi\Delta\nu_{1/2}$$

or

$$\Delta\nu_{1/2} = \frac{4\pi p_A p_B^2(\delta_A - \delta_B)^2}{k_A}$$

where $\Delta\nu_{1/2}$ is the line width due to exchange in hertz.

Appendix B

The equilibrium constant for eq 2 may be written as

$$K = k_2/k_3 = \frac{[CH_3S^+(SCH_3)_2][CH_3SCH_3]}{[(CH_3)_2S^+SCH_3][CH_3SSCH_3]} = \frac{[CH_3SCH_3]^2}{[salt][CH_3SSCH_3]}$$

or

$$[CH_3SCH_3] = (K[salt][CH_3SSCH_3])^{1/2} \quad (27)$$

The concentration of methyl sulfide is also related to the exchanging chemical shift $\delta_{S(CH_3)_2}$ by way of the populations p_A and p_B and nonexchanging chemical shifts δ_A' and δ_B' of sites A and B. Thus

$$\delta_{S(CH_3)_2} = p_A\delta_A' + p_B\delta_B' \quad (28)$$

$$p_B = \frac{[CH_3SCH_3]}{[CH_3SCH_3] + [salt]} = \frac{[CH_3SCH_3]}{[salt]_0}$$

where $[salt]_0$ is the initial concentration of **1**. Substituting for p_B in eq 28 and using $p_A + p_B = 1$ gives

$$\delta_{S(CH_3)_2} = \delta_A' + \frac{[CH_3SCH_3]}{[salt]_0}(\delta_B' - \delta_A') \quad (29)$$

Substituting eq 27 in eq 29 and setting $\delta_B' = 0$ gives

$$\delta_{S(CH_3)_2} = \delta_A' - \delta_A'(K/[salt]_0)^{1/2}[CH_3SSCH_3]^{1/2} \quad (9)$$

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[25] S. Meiboom, Z. Luz, and D. Gill, *J. Chem. Phys.*, 27, 1411 (1957); J. A. Pople, H. J. Bernstein, and W. G. Schneider, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

Electron Spin Resonance Study of Nitroxides Formed in the Reaction of Nitrogen Dioxide and Nitrogen Oxide with Styrenes

Leffert Jonkman,* Hans Muller, and Jan Kommandeur

Contribution from the Laboratory of Physical Chemistry, The University of Groningen, Bloemsingel 10, Groningen, The Netherlands.

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Abstract: When NO_2 reacts with styrenes in the presence of nitrosobenzene, phenyl(1-aryl-2-nitroethyl) nitroxides (**3**) are formed through the reaction of β-nitroalkyl radicals **2** with nitrosobenzene. In the reaction of NO_2–NO mixtures with styrenes, bis(1-aryl-2-nitroethyl) nitroxides (**5**) are formed by the reaction of **2** with the α-nitroso-β-nitro addition products **4** of the styrenes. Both diastereomers of **5** (meso, and *d,l*) were observed with all styrenes investigated, except for those with ortho substituents. Dissociation of the dimer of **4** is found to be accompanied by decomposition of **4** into NO and the radical **2** with subsequent formation of the nitroxide **5**.

When nitrogen oxides react with olefinic substances, radicals are almost always formed. These radicals have in the past been interpreted to be charge-transfer complexes.[1-3] In a recent note[4] we have argued that these radicals are nitroxides and we reported the structure of a nitroxide formed in the reaction of NO_2 with styrene. We now present a more detailed account of the nitroxide formation in the reaction of NO_2 and NO with various styrenes of the general type **1**, in which Ar means a substituted phenyl nucleus.

We will first discuss the nitroxide formation in the reaction of NO_2 with styrenes in the presence of nitrosobenzene. Our experiments show that NO_2 reacts with styrenes to give a radical intermediate **2**; this β-nitroalkyl radical is trapped by nitrosobenzene to give the nitroxide **3** (Scheme I).

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