

# Exchange of Parts between Molecules at Equilibrium.

## VIII. Dimethyl Polysulfates

John R. Van Wazer, David Grant,<sup>1</sup> and Claude H. Dungan

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Dimethyl (mono)sulfate and sulfur trioxide react to produce a liquid made up of methoxyl-terminated polysulfates,  $\text{CH}_3\text{O}(\text{SO}_3)_i\text{CH}_3$ . Equilibrium mixtures consisting of a size distribution of these straight-chain molecules along with free  $\text{SO}_3$  (present as the monomer and the trimeric ring compound) are produced (using liquid  $\text{SO}_3$ ) within about a day at  $24^\circ$  and an hour at  $50^\circ$ . The equilibria between the variously sized dimethyl polysulfate chain molecules could not be described quantitatively by fewer than four equilibrium constants, in contradistinction to the usual case where one is sufficient. This requirement is interpreted in terms of the influence of atoms (removed by as many as nine intermediate atoms) down the chain on the energy of a given bond. All but one of the total of six pertinent equilibrium constants needed to describe the system were calculated from quantitative proton nuclear magnetic resonance (n.m.r.) measurements which were also employed to obtain some kinetic data. Similar equilibria between variously sized chains were observed quantitatively by  $F^{19}$  n.m.r. in preliminary studies on mixtures of polysulfuryl fluorides.

The system of dimethyl polysulfates offers an excellent example of the use of nuclear magnetic resonance (n.m.r.) end group determinations to a high order of environment<sup>2</sup> and the application of the concept<sup>2a</sup> of a reasonably large reorganization heat order to the calculation of chain-chain and chain-ring equilibrium constants. Several prior papers<sup>3,4</sup> gave a qualitative indication that there might be a family of methoxyl-terminated polysulfates,  $\text{CH}_3\text{O}(\text{SO}_3)_i\text{CH}_3$ , in which an equilibrium could be achieved with respect to exchange of parts between the molecules. There is somewhat more work<sup>5,6</sup> published on the polysulfuryl fluorides,  $\text{F}[\text{SO}_3]_{i-1}\text{SO}_2\text{F}$ , although none of it is quantitative. Similar qualitative work<sup>7</sup> has been done on a few other polysulfate systems.

(1) Postdoctoral fellow from the University of Glasgow, Sept. 1962–1963.

(2) (a) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964); (b) J. R. Van Wazer and D. Grant, *J. Am. Chem. Soc.*, **86**, 1450 (1964).

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(7) H. A. Lehmann, W. Roscher, and K. Wulf, *Z. anorg. allgem. Chem.*, **309**, 71 (1961); H. A. Lehmann and H. Hesselbarth, *ibid.*, **299**, 51 (1959); H. A. Lehmann and W. Holznapel, *ibid.*, **293**, 314 (1958); and R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 658 (1962).

### Experimental

**Reagents.** Dimethyl (mono)sulfate,  $(\text{CH}_3\text{O})_2\text{SO}_2$ , obtained from Eastman Kodak was redistilled under conditions where moisture was carefully excluded and only the center fractions were employed. The anti-mony pentafluoride was produced by the Allied Chemical Co.

The sulfur trioxide was a Baker and Adamson reagent grade sample of Sulfan B, which contains about 0.1% of  $\text{B}_2\text{O}_3$  as a polymerization stabilizer and is described by the makers as having more than 99.5%  $\text{SO}_3$  with a minor amount of sulfuric acid. Unless stated otherwise, this was carefully distilled into a vessel having a polyethylene stopcock and was then transferred into a drybox for further handling. The drybox is one of the type that can be totally evacuated several times to remove moisture. Phosphorus pentoxide was employed as the desiccant. The various preparations of sulfur trioxide were all found to have less than 50 p.p.m. of water, according to an unpublished method.<sup>8</sup> In this method, the infrared spectra in the range of 0.1 to  $2.7 \mu$  are taken with a Cary Model 14 recording spectrophotometer, using a special water-tight inlet for the optical cell. Water in  $\text{SO}_3$  can be quantitatively determined in the range of 5 to 400 p.p.m. from the intensity of the absorption band at  $1.50 \mu$ , using the band at  $1.40 \mu$  as a reference standard. A similar procedure was used for  $\text{B}_2\text{O}_3$ , which, as expected, was absent in the distilled sulfur trioxide.

**Reaction Mixtures and Equilibration.** Various chosen proportions of dimethyl (mono)sulfate and sulfur trioxide were combined in carefully dried, thin-walled, precision-bore, 5-mm. Pyrex n.m.r. tubes (supplied by Varian), which were first closed by means of a tight-fitting plastic stopper and then sealed as soon as possible after removal from the drybox by cooling the contents of the tube with solid  $\text{CO}_2$  and using a needle-flame blowtorch. Kinetic studies were carried out by bringing the samples to temperature ( $0$  to  $72^\circ$ ) in a thermostated n.m.r. probe for the initial part of each run and then removing to outside thermostats when the changes in composition became sufficiently slow that the n.m.r. spectrometer could be employed for other work between measurements on these samples.

Equilibrium measurements were obtained after thermostating at  $24$  and  $72^\circ$  for periods of time ranging from several days through several months. In no case, however, were data accepted as representing equilibrium conditions unless ten half-lives, as estimated from the kinetic runs, had been passed. The n.m.r. tubes thermostated at  $72^\circ$  were rapidly quenched to room temperature and the n.m.r. measurements were then obtained immediately in order to minimize shifts in the

(8) R. Perry and K. J. Shaver, unpublished report of the Monsanto Co.

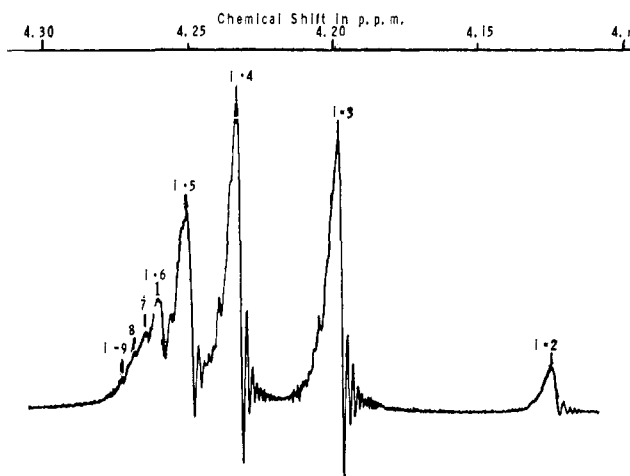
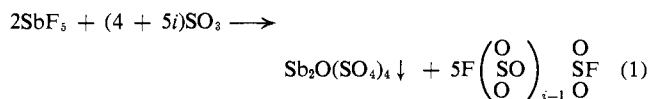


Figure 1. A typical 60-Mc. n.m.r. spectrum showing resonances for  $\text{CH}_3\text{O}(\text{SO}_3)_i\text{CH}_3$  molecules in an equilibrated mixture for which  $R = 0.0487$ . The barely noticeable plateaus for  $i = 7, 8,$  and  $9$  are reproducible and the position of the resonance for  $i = 1$  is off scale (at  $-4.0$  p.p.m.) to the right on this plot. As found previously for other systems, the chemical shifts of the various resonances vary somewhat with  $R$  as expected for changes in bulk magnetic susceptibility.

equilibria owing to lowering of the temperature. It should be noted that the reported decomposition<sup>4</sup> into sulfur trioxide, dimethyl ether, and dimethyl pyrosulfate was not observed for the dimethyl sulfate in our studies. Since the n.m.r. peak corresponding to dimethyl ether was not seen in any of the n.m.r. spectra obtained in this work, we must conclude either that our conditions were not sufficiently severe to allow its formation or that, in a sealed system, the equilibrium  $(\text{CH}_3\text{O})_2\text{SO}_2 = \text{CH}_3\text{OCH}_3 + \text{SO}_3$  or  $2(\text{CH}_3\text{O})_2\text{SO}_2 = \text{CH}_3\text{OCH}_3 + (\text{CH}_3\text{O})_2\text{SOS}(\text{O})_2(\text{OCH}_3)$  is strongly directed toward the  $(\text{CH}_3\text{O})_2\text{SO}_2$ .

The polysulfuryl fluorides were obtained from a more complicated procedure than admixture of  $\text{F}_2\text{SO}_2$  with  $\text{SO}_3$ . The first step of this procedure consisted of allowing sulfur trioxide and antimony pentafluoride to react in fluorocarbon test tubes, according to the stoichiometry of eq. 1. On completion of the reaction,



the liquid phase was equilibrated and examined by  $\text{F}^{19}$  n.m.r. by which it was found to consist of polysulfuryl fluorides, with no  $\text{SbF}_5$  or resonances which could be attributed to species containing Sb-F bonds.

**Analytical Techniques.** The  $(\text{CH}_3\text{O})_2\text{SO}_2\text{-SO}_3$  system was studied by means of proton n.m.r. with a Varian A-60 high resolution spectrometer running at 60.000 Mc., generally using a sweep rate of 0.05 or 0.1 c.p.s./sec. and a sweep width of 25 or 50 c.p.s. for full scale. Quantitative measurement of the various peak areas was made by both electronic integration and cutting out and weighing Xerox copies of each resonance. The  $\text{F}^{19}$  n.m.r. determinations were made with a Varian HR-60 spectrometer running at 56.444 Mc., using a sweep rate of ca. 1 c.p.s./sec. and a range of sweep widths. Sample spinning was not used in the  $\text{F}^{19}$  determinations, but all samples studied by  $\text{H}^1$

n.m.r. were spun in their sealed tubes. Except for overlapping of closely spaced peaks, sharp resonances were always observed in both kinds of spectra.

The various n.m.r. peaks were readily assigned from the fact that, for equilibrated samples, the peak areas were found to maximize in a regular sequence and at the approximate compositions expected, as well as from the fact that the chemical shifts form a sequence which approaches a limiting value, as shown in Figure 1. This figure represents the case of poorest n.m.r. resolution since the relative positions of the various peaks of the equilibrated mixtures varied with composition, coming closer together with decrease in the ratio  $R \equiv \text{total CH}_3/\text{total S}$ . The n.m.r. peak separations varied approximately linearly with  $R$ , being reduced in half when going from  $R = 1.15$  to  $R = 0.05$ .

Moreover, on the basis of these assignments, material balances on the equilibrated samples led to a smooth curve for the calculated amount of free  $\text{SO}_3$  (which is not seen in the spectra)—a curve going from zero for the dimethyl (mono)sulfate composition to 100% for the pure  $\text{SO}_3$ . Likewise, reasonable variations with time for any calculated amount of free  $\text{SO}_3$  were obtained for the kinetic runs. N.m.r. referencing was made with respect to tetramethylsilane in the  $\text{H}^1$  spectra and trifluoroacetic acid in the  $\text{F}^{19}$  spectra, with negative shifts being downfield. In both cases, the reference standard was contained in a small, sealed, glass capillary.

Although the resonances for  $i \geq 5$  in Figure 1 show considerable overlapping, this overlap did not lead to unreasonably large absolute or systematic errors in determining the relative amounts of the larger species,  $\text{CH}_3\text{O}(\text{SO}_3)_i\text{CH}_3$  for  $5 \leq i < 9$ . This is demonstrated by the fact that several investigators independently using two different empirical techniques for separating the areas of the overlapping peaks obtained nearly identical relative areas for each given peak. Furthermore, these areas obeyed the following criteria for low error in the technique of area separation. (1) At all points, the separated areas must equal the total unseparated area, and (2) the line shape and width at half-height must be the same for all separated peaks. (3) The relative area of a given resonance must vary smoothly with changing over-all composition, and (4) it should maximize at a specified composition calculable from the chain size and equilibrium constants. Furthermore (5) the material balance based on the separated peak areas must equal closely that calculated from the reagents; or, similarly, any ingredient obtained by difference (see following paragraph) must vary smoothly and in the proper manner with change in over-all composition. Although we were prepared to smooth the data to fit these five criteria, this was not found necessary; and a statistical analysis of replicates showed that the standard error for the relative peak areas of the chains for which  $5 \leq i \leq 9$  was the same (1.5% of the total H) as that of the cleanly resolved peaks ( $i < 5$ ).

## Results and Interpretation

Since in the entire size range from the monosulfate to the infinite chain there are two  $\text{CH}_3$  (or F) groups per chain molecule, the usual normalization of the n.m.r. peaks to 100% gives the mole percentages of the various

**Table I.** Equilibrium Experiments at 72°

Expt. no.	R (CH <sub>3</sub> /S)	Percentage of total CH <sub>3</sub> as the following sulfate esters									Calcd. free SO <sub>3</sub> /100 chains <sup>a</sup>
		Mono C <sub>1</sub>	Di C <sub>2</sub>	Tri C <sub>3</sub>	Tetra C <sub>4</sub>	Penta C <sub>5</sub>	Hexa C <sub>6</sub>	Hepta C <sub>7</sub>	Octa C <sub>8</sub>	Nona C <sub>9</sub>	
1	0.0487		6.1	32.0	27.9	14.4	7.7	5.4	4.0	2.5 <sup>b</sup>	3.67 × 10 <sup>3</sup>
2	0.1428		5.9	35.3	28.3	14.9	7.9	4.5	2.1	1.1 <sup>c</sup>	0.99 × 10 <sup>3</sup>
3	0.1975		5.6	34.8	23.7	16.6	9.4	6.1	2.6	1.2	586.
4	0.2206		5.1	33.2	27.2	15.6	9.8	5.6	2.6	1.0	480.
5	0.4043		11.8	46.8	25.8	10.5	3.5	1.2	0.4		142.
6	0.4173		12.3	46.5	25.8	10.8	2.9	1.1	0.6		128.
7	0.6025	0.3	37.5	47.3	12.5	2.2	0.2				52.9
8	0.6229	0.3	39.7	46.3	11.4	1.6	0.6	0.1			44.6
9	0.7987	2.9	69.2	25.9	2.0						23.4
10	0.8419	3.9	74.7	20.0	1.4						18.6
11	0.9490	12.2	81.2	6.6							16.6
12	1.0243	16.4	78.8	4.8							6.8
13	1.1737	34.2	64.5	1.3							3.3
14	1.1928	37.8	61.4	0.8							4.8
15	1.2208	39.0	60.0	1.0							1.8
16	1.4066	60.2	39.6	0.2							2.2
17	1.6133	77.5	22.5								1.5
18	1.7860	88.6	11.4								0.6

<sup>a</sup> Calculated from eq. 2. <sup>b</sup> Assuming an average chain size of 11 instead of 9. <sup>c</sup> Assuming an average chain size of 9.5 instead of 9.

**Table II.** Data and Equilibrium Constants for Replicate Determinations on an Equilibrated Mixture for Which  $R \equiv (\text{CH}_3/\text{S}) = 0.221$ 

Reaction time at 72°, hr.	Sulfate ester chain molecules									Free SO <sub>3</sub> /100 chains
	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	
132	0.0	5.6 <sup>a</sup>	36.3 [0.10] <sup>b</sup>	23.0 [1.2]	17.0 [0.7]	8.7 [1.2]	5.5 [0.8]	2.8 [1.5]	1.1 [0.029]	484.
228	0.0	5.3	38.5 [0.09]	26.3 [0.9]	15.4 [0.9]	7.9 [1.1]	4.4 [0.7]	1.8 [1.1]	0.4 [0.053]	501.
324	0.0	5.8	28.8 [0.20]	28.1 [0.7]	19.9 [0.6]	8.4 [1.6]	5.8 [0.5]	2.2 [2.4]	1.0 [0.024]	477.
348	0.0	4.7	31.1 [0.14]	28.0 [0.5]	12.7 [2.0]	11.3 [0.8]	8.1 [0.5]	3.1 [1.7]	1.0 [0.034]	468.
396	0.0	5.0	33.3 [0.13]	29.7 [0.4]	11.4 [2.3]	9.9 [0.8]	7.1 [0.5]	2.7 [1.8]	0.9 [0.035]	481.
468	0.0	4.4	29.7 [0.14]	27.7 [0.5]	14.0 [1.9]	13.6 [0.4]	4.7 [2.4]	3.9 [1.2]	2.0 [0.021]	460.
492	0.0	5.1	34.6 [0.12]	27.3 [0.9]	18.8 [0.7]	8.8 [0.8]	3.4 [1.1]	1.5 [1.5]	0.5 [0.035]	495.

<sup>a</sup> Percentage of chain molecules, as normalized over total chains. <sup>b</sup> Chain-chain constant,  $*K_i = c_{i-1}c_{i+1}/c_i^2$ , as in Table III. <sup>c</sup> Constant for equilibrium of chains with free SO<sub>3</sub>, eq. 5, as in Table IV.

chain molecules with respect to the total chains. The free SO<sub>3</sub> (not in chains) is obtained by difference from the material balance. By expressing the over-all composition in terms of a mole ratio  $R \equiv \text{total CH}_3/\text{total S}$ , it is obvious that the total CH<sub>3</sub> equals twice the number of chain molecules and the total S equals the sulfur in the chains plus that in the free SO<sub>3</sub>. This means that the free SO<sub>3</sub> expressed in terms of the mole percentage of total chains is

$$(\text{free SO}_3)/(\text{100 chains}) = [200 - R \sum_i ic_i]/R \quad (2)$$

where  $c_i$  is the mole percentage of the chains having  $i$  sulfur atoms as normalized over the total number of chains so that  $\sum_{i=1}^{\infty} c_i = 100$ .

#### Equilibria between Methoxyl-Terminated Chains at 72°.

The experimental data are presented in Table I, where the directly measured concentration of the variously sized dimethyl sulfate chains ranging from the monosulfate through the nonasulfate are presented along with the amount of free SO<sub>3</sub> calculated from the  $R$  value. Each experiment reported in Table I corresponds to the average of several replicate determinations of the n.m.r. peak areas on the same sample, with replicates being measured on different days. The largest number of replicate determinations were obtained on experiment no. 4 of Table I, as reported in Table II.

All reactions between unbranched chain molecules to give unbranched chains as products should exhibit<sup>9</sup>

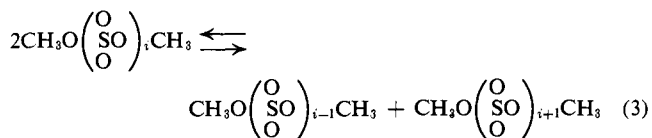
(9) D. W. Scott, *J. Am. Chem. Soc.*, **68**, 2294 (1946). The statement made in this reference that  $*K_i = 1$  is based on "a statistical mechanical

**Table III.** Chain-Chain Equilibrium Constants from Data of Table I

Expt. no.	$*K_i = c_{i-1}c_{i+1}/c_i^2$ for $i =$						
	2	3	4	5	6	7	8
18	0.02 (0.11) <sup>a</sup>						
17	0.02 (0.03)						
16	0.02 (0.03)						
15	0.02 (0.02)						
14	0.026 (0.008)						
13	0.024 (0.006)						
12	0.014 (0.005)	0.6 (0.6)					
11	0.016 (0.008)	0.4 (0.3)					
10	0.01 (0.04)	0.21 (0.04)	0.6 (0.5)	3. (8.)	0.9 (0.1)		
9	0.01 (0.04)	0.20 (0.03)	0.7 (0.5)	1. (8.)			
8		0.14 (0.03)	0.8 (0.2)	0.6 (0.4)	1.4 (2.3)	3. (11.)	
7		0.14 (0.03)	0.7 (0.2)	0.8 (0.4)	1.0 (1.5)	2. (9.)	
6		0.13 (0.04)	0.7 (0.1)	1.1 (0.3)	0.9 (0.4)	0.8 (0.6)	2. (3.)
5		0.11 (0.03)	1.0 (0.2)	0.8 (0.2)	1.1 (0.4)	0.7 (0.5)	2. (4.)
4		0.13 (0.04)	0.7 (0.1)	1.0 (0.3)	1.1 (0.5)	0.8 (0.8)	2. (4.)
3		0.16 (0.05)	0.6 (0.1)	1.0 (0.3)	1.3 (0.6)	1.1 (0.7)	1.7 (1.6)
Weighted av.	0.020 (0.003) <sup>a</sup> (0.009) <sup>b</sup>	0.153 (0.01) (0.04)	0.70 (0.06) (0.12)	0.91 (0.12) (0.18)	1.1 (0.2) (0.2)	0.8 (0.3) (0.2)	1.8 (1.2)

<sup>a</sup> Standard deviation calculated on the assumption that the error in each n.m.r. value of Table I is 1.5% of the total CH<sub>3</sub>. <sup>b</sup> Standard deviation computed from weighted distribution of constants.

an equilibrium constant of unity, when the equilibrium distribution of chain sizes is statistically random with respect to sorting<sup>10</sup> of the monofunctional [(CH<sub>3</sub>O)-SO<sub>2</sub>(O<sub>1/2</sub>-)] and difunctional [(-O<sub>1/2</sub>)SO<sub>2</sub>(O<sub>1/2</sub>-)] groups. In order to minimize experimental error, the most satisfactory reaction of this type involves neighboring chains in the series, e.g.



The equilibrium constants,<sup>11</sup>  $*K_i$ , corresponding to treatment of the data of Table I according to eq. 3 are presented in Table III.

treatment [which] applies to the limiting case of long-chain molecules and would not necessarily be expected to apply to the very smallest species of a polymer series" has been resolved. It has been mathematically demonstrated<sup>2a</sup> that  $*K_i = 1$  for all sizes of chains, down through the smallest ones.

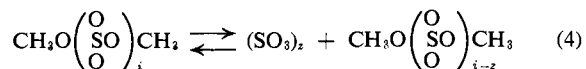
(10) This corresponds to a reorganization heat order of unity according to the theoretical presentation of ref. 2a. It is also equivalent to what Flory has called the "principle of equal reactivity of functional groups": see P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 102, 103.

(11) The statistical treatment of the chain-chain equilibrium data is similar to that given by L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964). A computer program is used in calculating the constants.

It is apparent from the values of Table III that many of the experimentally derived equilibrium constants,  $*K_i$ , for the various sizes,  $i$ , of chains differ greatly from unity. Moreover, the deviation from unity is seen to decrease as  $i$  increases. On a theoretical basis, the observed deviations from unity in the values of  $*K_i$  are attributable to either of two causes: (1) solution nonideality<sup>12</sup> (i.e., interactions between the various molecules forming the liquid phase) or (2) a rather large value for the reorganization heat order<sup>2a</sup> (i.e., the effect of distant atoms in a chain on thermodynamic or other properties attributable to a given site in the chain—in this case, the free energy of the reaction of eq. 3). On the assumption that the observed deviations from unity in the equilibrium constants of Table III are due to solution nonideality, a regular trend in the constants with  $R$  value would be expected. Indeed, the radical changes in the over-all composition of the mixture corresponding to the range of  $R$  values employed should lead to a larger solution-nonideality variation in the equilibrium constants with varying  $R$  value than with chain size at a given  $R$  value. Furthermore, the equilibrium constants shown in Table II for replicate n.m.r. determinations on a given experimental sample exhibit about the same amount of variation with time of measurement after equilibrium was achieved as do the various equilibrium constants of Table III with  $R$  value. We must therefore conclude that the cause of the deviations from unity in the equilibrium constants of Table III is a reorganization heat order greater than unity.

Inspection of the weighted-average equilibrium constants shown at the bottom of Table III indicates that the reorganization heat order,  $\rho$ , in the system of methyl polysulfates is probably 3, or perhaps even 4. Since the equilibrium constants corresponding to eq. 3 involve three different sizes of chains, it is more appropriate to use an equilibrium constant based on a single-sized graph<sup>2a</sup> in order to estimate properly the reorganization heat order. This has been done, using the constant described in eq. 28 of ref. 2a with  $j = k = l = 1$  and  $g_C = g_D$ . From this operation, we can conclude only that  $\rho \geq 4$ . Therefore, the equilibria between chain molecules in the family of dimethyl polysulfates must be described by a minimum of four equilibrium constants for  $\rho = 4$ ; and one group of such constants consists of the set of average values for  $*K_i$  with  $i = 2, 3, 4$ , and 5—values which are presented at the bottom of Table III. It is understood that  $*K_i$  has the random value of unity for  $*K_i$  with  $i \geq 6$ .

*Equilibrium between the Chains and Free SO<sub>3</sub> at 72°.* Now that the equilibria between chains has been quantitatively evaluated, we must consider the equilibria between the chains and free SO<sub>3</sub>.



where  $z = 1$  or 3 and  $i > (z + 1)$ . The Raman data on SO<sub>3</sub><sup>13</sup> indicate that at 72° in the liquid state, the equilib-

(12) H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 724 (1965).

(13) G. E. Walrafen, *J. Chem. Phys.*, **40**, 2326 (1964); also see R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2189 (1961), and G. E. Walrafen and T. F. Young, *Trans. Faraday Soc.*, **56**, 1419 (1960), as well as R. W. Lovejoy, J. H. Colwell, D. F. Eggers, and G. D. Halsey, *J. Chem. Phys.*, **36**, 612 (1962). For the equilibrium constant in gase-

Table IV. Equilibrium Constants Relating the Free SO<sub>3</sub> to the Dimethyl Polysulfates<sup>a</sup>

Expt. no.	Equilibrium constants								
	<sup>o</sup> K <sub>1,6</sub>	<sup>o</sup> K <sub>1,7</sub>	<sup>o</sup> K <sub>1,8</sub>	<sup>o</sup> K <sub>1,9</sub>	<sup>o</sup> K <sub>2,6</sub>	<sup>o</sup> K <sub>2,7</sub>	<sup>o</sup> K <sub>2,8</sub>	<sup>o</sup> K <sub>2,9</sub>	
Equilibration at 72°									
1	0.039	0.030	0.028	0.033					
2	0.029	0.027	0.033	0.029					
3	0.022	0.019	0.029	0.026					
4	0.018	0.020	0.024	0.029					
5	0.016	0.016	0.016						
6	0.019	0.013	0.009						
7	0.031								
Av.	0.025	0.021	0.023	0.029					
Std. dev. of av.	0.002	0.004	0.004	0.001					
		<sup>o</sup> K <sub>1</sub> <sup>1</sup> = 0.024 ± 0.002							
Equilibration at 24°									
19	0.021	0.014	0.014	0.011	0.075	0.024	0.023	0.011	
20	0.014	0.018	0.014	0.020	0.020	0.051	0.024	0.063	
21	0.021	0.009	0.017	0.012	0.072	0.007	0.038	0.013	
22	0.017	0.008			0.042	0.005			
23	0.015	0.012			0.027	0.014			
24	0.015	0.014			0.025	0.023			
25	0.007				0.002				
26	0.019				0.074				
27	0.020				0.066				
Av.	0.017	0.013	0.015	0.014	0.045	0.021	0.028	0.029	
Std. dev. of av.	0.003	0.002	0.001	0.003	0.031	0.007	0.005	0.017	
		<sup>o</sup> K <sub>1</sub> <sup>1</sup> = 0.015 ± 0.001					<sup>o</sup> K <sub>2</sub> <sup>3</sup> = 0.033 ± 0.005		

<sup>a</sup> See eq. 5 and 6.

rium between monomeric and trimeric sulfur trioxide is shifted essentially completely to the monomer. Since the presence of the chain molecules has the effect of dilution of the SO<sub>3</sub>, it is even more certain that all of the free SO<sub>3</sub> is monomeric at this temperature. Since the chain molecules in this system exhibit a reorganization heat order of 4, we must employ an equation corresponding to ρ = 4 (see eq. 35 of ref. 2a) to describe the equilibrium with free SO<sub>3</sub>. This equation has the following form for the reaction shown in eq. 4

$${}^oK_{z,i} = \frac{{}^oc_z}{(\text{molecular volume term})} \left( \frac{c_{i-1}}{c_i} \right)^z \quad (5)$$

where  $c_{i-1}$  and  $c_i$  refer to the relative amounts of chain molecules present as the  $(i - 1)$  and  $i$  chains, respectively, and  ${}^oc_z$  refers to the number of moles of free SO<sub>3</sub> present as the  $z$ -mer, as normalized over the total number of molecules.

A molecular volume term appears in eq. 5 because the chemical reaction shown as eq. 4 corresponds to the formation of two molecules from one. To the approximation that the density of the CH<sub>3</sub>O(SO<sub>3</sub>) <sub>$i$</sub> CH<sub>3</sub> molecules is equal to the average density of  $1(\text{CH}_3\text{O})_2\text{SO}_2$  plus  $(i - 1)\text{SO}_3$ , it can be shown that, in order to express  ${}^oK_{z,i}$  in terms of moles of molecules/l.

$$\text{molecular volume term} \equiv V = (41.7 + 25.8R)(f_m + f_t + \sum_i ic_i) \quad (6)$$

where  $f_m$  and  $f_t$  are the SO<sub>3</sub> units per 100 molecules in the monomeric and trimeric sulfur trioxide, respectively.

The equilibrium constants hand-calculated from eq. 5 and 6 are shown in Table IV. It should be noted

ous sulfur trioxide, see R. W. Lovejoy, J. H. Colwell, D. F. Eggers, and G. D. Halsey, *J. Chem. Phys.*, **36**, 612 (1962).

that for the values in this table,  $i$  in  ${}^oK_{z,i}$  is always greater than 5 because the smallest chain containing a sequence of four middle groups (required for ρ = 4) is the dimethyl hexasulfate. According to stochastic graph theory,<sup>2a</sup> the equilibrium constants,  ${}^oK_{z,i}$  should exhibit values which are independent of the size  $i$  but not of  $z$  for any given temperature. The 72° data of Table IV are in accord with this theoretical requirement.

*Equilibria at 24°.* Data obtained from equilibrium measurements at room temperature are presented in Table V along with the respective calculated values of the chain-chain equilibrium constants,  ${}^*K_i$ . These data all correspond to single n.m.r. determinations and have a good probability of belonging to the same statistical population as the equilibrium data obtained at 72°. The average values of  ${}^*K_i$  for the various values of  $i$  less than 6 which are given in Table V agree quite well with the equivalent values of Table III.

Calculation of the equilibrium constants relating the free SO<sub>3</sub> to the dimethyl polysulfate is considerably more complicated at 24° than at 72°, since at the lower temperature there is a measurable equilibrium between monomeric SO<sub>3</sub> and that present in the form of the trimeric ring molecule. According to Walrafen,<sup>13</sup> 26.6% of the molecules making up liquid sulfur trioxide at room temperature consist of the trimeric ring, with the remainder being the monomer. From this, we calculate the following value for the equilibrium constant interrelating the two molecular species appearing in the free SO<sub>3</sub> at 25°.

$${}^oK = [\text{SO}_3]^3/[\text{S}_3\text{O}_9] = 3.65 \times 10^{-4} \text{ (moles of molecules)}^2/\text{l.}^2 \quad (7)$$

where the brackets [], refer to molecular concentrations in moles/l. Applying eq. 5 through 7 to the data of Table V, we obtain the equilibrium constants reported

Table V. Equilibrium Experiments at 24°

Expt. no.	R (CH <sub>3</sub> /S)	Percentage of total CH <sub>3</sub> as the following sulfate esters									Calcd. free SO <sub>3</sub> /100 chains
		Mono C <sub>1</sub>	Di C <sub>2</sub>	Tri C <sub>3</sub>	Tetra C <sub>4</sub>	Penta C <sub>5</sub>	Hexa C <sub>6</sub>	Hepta C <sub>7</sub>	Octa C <sub>8</sub>	Nona C <sub>9</sub>	
19	0.1617		2.5	20.8	30.2	23.8	9.6	5.8	4.3	3.0 <sup>b</sup>	881.
				[0.2] <sup>a</sup>	[0.5]	[0.5]	[1.5]	[1.2]	[0.8]	[1.]	
20	0.1975		3.2	22.3	35.6	19.1	11.2	4.9	2.3	1.4	566.
				[0.2]	[0.34]	[1.1]	[0.7]	[1.]	[3.]		
21	0.2047		3.3	24.0	30.9	21.8	8.2	6.9	3.0	1.9	523.
				[0.18]	[0.55]	[0.5]	[2.]	[0.5]	[3.]		
22	0.3961		10.0	46.6	28.8	10.0	2.9	1.7			151.
				[0.13]	[0.6]	[0.8]	[4.]				
23	0.4043		10.6	42.1	30.5	11.7	3.6	1.5			135.
				[0.18]	[0.5]	[0.8]	[3.]				
24	0.4133		12.3	43.0	28.5	11.5	3.5	1.2			129.
				[0.19]	[0.6]	[0.8]	[2.]				
25	0.6025		28.7	54.8	14.1	1.8	0.6				41.2
				[0.13]	[0.5]	[5.]					
26	0.6049		26.5	55.7	14.7	2.8	0.3				35.9
				[0.13]	[0.7]	[1.]					
27	0.6240		32.2	54.6	11.6	1.4	0.2				37.7
				[0.13]	[0.6]	[2.]					
28	0.7987	1.8	61.2	34.0	3.0						23.0
			[0.02]	[0.3]							
29	0.8009	1.3	61.0	34.1	3.6						9.7
			[0.01]	[0.2]							
30	0.8419	2.7	68.6	27.1	1.6						10.0
			[0.016]	[0.3]							
31	0.9490	11.2	79.0	9.8							12.1
			[0.035]								
32	0.9673	6.4	80.8	12.8							0.3
			[0.012]								
33	0.9840	7.5	82.3	10.2							0.5
			[0.023]								
34	1.0243	15.5	77.5	7.0							3.7
			[0.036]								
35	1.1737	33.1	64.8	2.1							1.4
			[0.03]								
36	1.1928	34.9	62.2	2.9							0.0
			[0.05]								
37	1.2208	39.8	58.9	1.3							2.3
			[0.03]								
38	1.4066	59.9	39.9	0.2							1.9
			[0.02]								
39	1.6133	73.8	26.2								0.0
40	1.7860	88.9	11.1								0.9
Weighted Averaged Equil. const.			[0.027] (0.011) <sup>c</sup>	[0.141] (0.026)	[0.048] (0.18)	[0.6] (0.2)	[1.0] (0.3)	[0.7] (0.3)	[0.9] (0.7)	[1.]	
			(0.010) <sup>d</sup>	(0.024)	(0.17)	(0.2)	(0.6)	(0.2)			

<sup>a</sup> Equilibrium constants  $*K_i$ , where  $*K_i = c_{i-1}c_{i+1}/c_i^2$ . <sup>b</sup> Of this value, 0.4 is assigned to the deca. <sup>c</sup> Standard deviation calculated on the assumption that the error in each n.m.r. value of Table I is 1.5% of the total CH<sub>3</sub>. <sup>d</sup> Standard deviation computed from weighted distribution of constants.

in Table IV for a temperature of 24°. The equilibrium constants,  ${}^{\circ}K_{1,i}$  relating monomeric SO<sub>3</sub> to the various sizes of dimethyl sulfate chains are again seen to be constant regardless of the value of  $i$ , with little variation between the various members of the set of experimentally derived values. However, there is considerable scatter of data for the equilibrium constant,  ${}^{\circ}K_{3,i}$ , relating trimeric SO<sub>3</sub> to the chain species. In spite of this scatter, we can reasonably conclude that the value of  ${}^{\circ}K_{3,i}$  is independent of the value of  $i$ .

**Kinetic Measurements.** When carefully purified liquid sulfur trioxide was mixed with various proportions of dimethyl sulfate at room temperature and the changes in composition were determined by proton n.m.r., using great precaution to avoid contamination by moisture, it was found that the relative areas (measured from their respective equilibrium values) of the

various n.m.r. peaks increased or decreased essentially logarithmically with time; *i.e.*, the kinetics of these systems appear to be pseudo-first-order. In the range of  $R$  values from 0.2 to 0.8, the half-life for the decrease in the amount of dimethyl (mono)sulfate was found to be 80 min. at 24°. At  $R = 1$ , a larger half-life, *ca.* 300 min., was observed at this temperature. In some preliminary experiments at 50°, in which the unpurified Sulfan brand of stabilized sulfur trioxide was employed, the amounts of the dimethyl polysulfate chains larger than the disulfate were observed to go through maxima within the first half-life, which was considerably longer than the values reported above for room temperature. Although a great deal of effort was expended on them, the bulk of our kinetic studies were plagued with problems of irreproducibility and inconsistencies so that the only data which we believe

are reasonably reliable are reported in the first three sentences of this paragraph.

*Polysulfuryl Fluorides.* Only preliminary studies were carried out on this system; but they and the literature<sup>5,6,14</sup> indicate that the chain-chain equilibrium constants for the polysulfuryl fluorides are probably not much different than those for the system involving chain termination with methoxyl groups. The liquid phase resulting from the reaction of eq. 1 was seen by  $F^{19}$  n.m.r. to consist of mixtures of regularly decreasing amounts of the successively larger polysulfuryl fluorides bigger than the monosulfuryl fluoride. Indeed the  $F^{19}$  n.m.r. pattern for several polysulfuryl fluoride mixtures was very similar to the  $H^1$  pattern for equivalent dimethyl polysulfate mixtures. Distillation at  $45^\circ$  and atmospheric pressure of a mixture of polysulfuryl fluorides having an  $R$  value of *ca.* 0.5 gave a distillate consisting of pyrosulfuryl fluoride (the di chain) and free sulfur trioxide plus a small amount (*ca.* 2% of the total molecules) of trisulfuryl fluoride. The residue from this distillation contained a solid along with a liquid phase which was seen by n.m.r. to consist of a mixture of polysulfuryl fluorides. From stoichiometric requirements, the solid phase must have consisted of very long-chain polysulfuryl fluoride molecules of a structure comparable to asbestos-like  $SO_3$ .

## Discussion

*Thermodynamic Considerations.* By comparing the measured equilibrium constants with the values corresponding to completely random sorting of the molecules, a free energy term,  $\delta(\Delta F^\circ)$ , is obtained which gives a measure of the deviation from randomness. For the equilibrium constants between neighboring chains (see eq. 3), the following values are computed for  $\delta(\Delta F^\circ)$ : 1.3 kcal. for  $*K_2$ , 0.6 for  $*K_3$ , and 0.1 for  $*K_4$ . We are amazed to find such a small value as 1.3 kcal. for the  $\delta(\Delta F^\circ)$  associated with  $*K_2$  in a system which exhibits a value of  $\rho$  as large as 4.

To the approximation that  $\delta(\Delta F^\circ) \approx \Delta H$ , we can conclude that the heat of the various reactions between dimethyl sulfate chains must exhibit a relatively small enthalpy ( $\leq 1.3$  kcal.). The small ratio (2:3)

(14) R. J. Gillespie, J. V. Oubridge, and E. A. Robinson, *Proc. Chem. Soc.*, 428 (1961).

of the values of  ${}^\circ K_{1,i}$  measured at  $24$  and  $72^\circ$  shows that the reaction (of the form of eq. 3) relating monomeric sulfur trioxide to the dimethyl polysulfate chains also has a small enthalpy (*ca.* 2 kcal.). On the other hand, measurements<sup>13,15</sup> on the equilibrium between monomeric and trimeric sulfur trioxide indicate a large enthalpy for this reaction. This means that the heat of the reaction shown in eq. 3, where  $z = 3$ , must have a large positive value.

*Stabilized Liquid Sulfur Trioxide.* Much of the published work on  $SO_3$  since 1956 has been concerned with the stabilization of sulfur trioxide in liquid form. In addition to a large patent literature, there have been several reviews on this subject.<sup>16</sup> Although previous authors have assumed that the stabilizing agents act to remove or tie up the water which catalyzes the formation of the long-chain crystalline species ( $\beta$  form of  $SO_3$ ) from liquid  $SO_3$ , our work indicates that the effect may be due merely to the incorporation of other structure-building units (ends or branches) into the polysulfate chain system composed of a large number of  $SO_3$  middle groups plus a few hydroxyl-terminated ends formed by the pickup of water. Indeed, a small amount of dimethyl sulfate is a very effective stabilizer<sup>17</sup> for liquid  $SO_3$ . Presumably, the hydroxyl end groups can readily be fitted into the crystal lattice of the  $\beta$  form of  $SO_3$  because of their small size. Incorporation of end groups which are more bulky than (or chemically quite different from) the OH group and/or incorporation of branch groups (as by adding  $B_2O_3$ ) to the liquid  $SO_3$  contaminated by small amounts of water are envisaged as causing difficulty in fitting the resulting polysulfate chains into the long-chain crystal lattice, so that the nucleation and growth of  $\beta$ - $SO_3$  crystals are inhibited.

*Acknowledgment.* We wish to thank Dr. Leo C. D. Groenweghe for a number of helpful discussions concerning the interpretation of the equilibrium data. We also employed in this work several computer programs (for the IBM 7040) which he developed.

(15) G. E. Walrafen, private communication in which the statement is made that "the monomeric  $SO_3$  concentration increases very rapidly with temperature. (Indeed, the equilibrium is about as sensitive to temperature as any I know)."

(16) C. F. P. Bevington and J. L. Pegler, Special Publication No. 12, The Chemical Society, London, 1958, p. 283; A. T. Royle, *Chem. Ind.* (London), 1140 (1959).

(17) British Patent 735,836 and French Patent 1,065,022.