

Figure 9. Spectrum of 1-methylcytosine-7- ^{15}N hydrochloride in SO_2 at 23° .

the amino lines in Figure 9 as H_a and H_b is consistent with the labeling in formula III.

Attention should also be called to the values of the ^{15}N -H coupling constants in Tables I and II. In IV, for example, the two amino hydrogens are evidently differently hybridized, as indicated by the 2-3-c.p.s. difference in J . There is also a solvent effect of these J 's, the values decreasing in DMSO. Here too there is apparently some rehybridization as a result of solvent effects. (It should be noted that in aniline- ^{15}N , $J(^{15}\text{N}-\text{H})$ increases on hydrogen bond formation, whereas in the cytosine case there is a decrease in going to the hydrogen-bonding solvent DMSO.¹⁷ See further discussion of hydrogen bonding in the next section.)

Discussion of Chemical Shifts

A few points shown in Tables I and II merit comment. Comparison of each of the free bases with its protonated form shows that 5-H and 6-H shift downfield by about 0.5 p.p.m. on protonation. This shift is in accord with some delocalization of charge through the pseudoaromatic ring. There is considerable consistency among all the free bases and among all the salts in the values of $\delta_{5\text{H}}$ and $\delta_{6\text{H}}$ except for the free base 1,3-

(17) E. D. Becker, unpublished work.

dimethylcytosine, where $\delta_{6\text{H}} \approx 7.0$ p.p.m. rather than ca. 7.6, as in the other bases. This must be associated with the change in bonding leading to the exocyclic double bond and probable change in aromatic character of the ring.

The amino hydrogens are, of course, affected markedly in chemical shift by protonation, as shown in Table II. The average downfield shift is about 1.5 p.p.m. The chemical shifts of these protons are also dependent upon solvent, as indicated in the tables and as depicted in Figure 5. Comparison of the room temperature spectra in the two solvents shows that the amino protons are shifted downfield in DMSO by about 1.5 p.p.m. relative to their position in SO_2 . That this results from hydrogen bonding in DMSO is shown by the temperature effects of Figure 5. At 160° the coalesced peak is over 2 p.p.m. at higher field than the average of the peak positions at 30° . This is the direction one expects a hydrogen-bonded proton to shift as the temperature is increased and hydrogen bonds are broken. In SO_2 , on the other hand, there is only a small change in δ_{NH_2} with temperature and it is in the direction opposite to that expected for hydrogen bonding. In XII, the only molecule for which the 3-H peak is discernible in DMSO, there is very little difference between its chemical shift in DMSO and SO_2 . If this result is general for this class of compounds, it would lead to the rather surprising conclusion that the 3-H does not hydrogen bond significantly to the solvent.

Finally, it may be noted from Tables I and II that in X and XI $\delta_{6\text{H}}$ is more dependent upon the geometrical isomerism than $\delta_{5\text{H}}$, even though 5-H is much closer to the methylamino group. This finding may be understood in terms of the effect of solvent redistribution postulated to explain the large entropy difference between the two isomers.

The Dissociation Energy of the Tetrasulfide Linkage

I. Kende,¹ T. L. Pickering, and A. V. Tobolsky

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey. Received July 12, 1965

The thermal decomposition of dimethyl tetrasulfide has been studied using a kinetic technique. It is suggested that the decomposition occurs as follows: $\text{Me-S}_4\text{-Me} \xrightarrow{2k_d f} \text{MeS}_x \cdot + \text{MeS}_{4-x} \cdot$. The radical fragments were scavenged by a stable free radical and the first-order rate constant was found to be given by $2k_d f = 9.55 \times 10^{17} \exp(-36,600/RT)$. It is suggested that the experimental activation energy may be equated to the dissociation energy of the sulfur-sulfur bond in methyl tetrasulfide.

Introduction

The question of the strength of sulfur-sulfur bonds in various systems has been of great interest for many

(1) Ford Foundation Fellow. Central Research Institute for Chemistry of the Hungarian Academy of Science.

years. For example, the value of the dissociation energy for S_2 has been the subject of much controversy² and only recently has a reliable value become available.³⁻⁵ The only other reliably known values for the dissociation energy of sulfur-sulfur bonds are those determined in various disulfide compounds. These values are of the order of 65 to 75 kcal./mole for simple aliphatic disulfides.

In contrast to the dissociation energy of disulfides, which is about 70 kcal./mole, we propose that the dis-

(2) (a) T. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958; (b) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, Ltd., London, 1953.

(3) J. Berkowitz and J. B. Marquart, *J. Chem. Phys.*, **36**, 275 (1963).

(4) L. Brewer, *ibid.*, **31**, 1143 (1959).

(5) R. Colin, P. Goldfinger, and M. Juenehomme, *Nature*, **187**, 408 (1960).

Table I

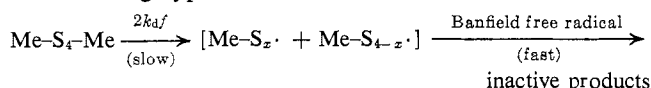
(B) × 10 ³ moles/l. ^a	Time, min.	Temp., °C.	(S), mole/l. ^b
3.52	0		
2.68	15		
1.97	25	78.9	0.0607
1.35	33		
0.75	48		
3.88	0		
3.23	20		
2.60	35	68.9	0.175
1.97	50		
1.32	65		
0.88	80		
3.22	0		
3.02	15		
2.97	20		
2.85	30		
2.78	30	58.9	0.438
2.58	45		
2.42	50		
2.27	60		
1.58	95		
1.26	115		
7.52	0		
5.44	51		
4.36	78	70.3	0.178
3.42	92		
2.62	108		
2.35	125		
1.98	0		
1.82	10.3		
1.66	20.8	52.0	0.682
1.63	32.2		
1.47	42.9		
1.36	53.5		
1.23	90.0		

^a (B) is the concentration of the Banfield free radical. ^b (S) is the concentration of methyl tetrasulfide.

sulfide of 0.5 sec. at 170°, the injector temperature used in previous studies.

Results

In treating our data the following scheme was adopted as a working hypothesis.



Using the usual approximations, the following equation can be derived

$$(B)_t = (B)_0 - 2k_{df}(Z)t$$

where (B)_t and (B)₀ are the Banfield stable free-radical concentrations at time *t* and at time *t* = 0, respectively; *f* is the cage factor, *k_d* is the specific rate constant for decomposition of methyl tetrasulfide, and (Z) is the concentration of the tetrasulfide. Our conditions were chosen such that the concentration of tetrasulfide was always at least two orders of magnitude greater than the concentration of the Banfield free radical. Preliminary e.s.r. investigations showed that the concentration of thiyl radicals in our temperature range was less than 10⁻⁶ mole/l. Thus we feel any recombination process involving two thiyl radicals is negligible compared to combination with the Banfield stable free radical. The data are presented in Table I and the rate constants, derived from a least-squares analysis of the data, are presented in Table II, along with the activation parameters. The Arrhenius graph is given

Table II. Rate Constants for Decomposition of Me-S₄-Me^a

2 <i>k_df</i> × 10 ³ sec. ⁻¹	Temp., °C.
16.4 ± 0.08	78.9
4.07 ± 0.20	70.3
3.70 ± 0.10	68.9
0.68 ± 0.02	58.9
0.203 ± 0.08	52.0

^a Δ*H** = 36 ± 3.6 kcal./mole; Δ*S** = 22.4 e.u.

in Figure 1. The rate of decomposition is given by

$$2k_{df} = 9.55 \times 10^{17} \exp(-36,600/RT)$$

Discussion

The thermochemical bond strength^{1,15,16} of the sulfur-sulfur bond (in disulfides, polysulfides, and sulfur) is known to be about 63 kcal./mole.¹⁷⁻²¹ The values arrived at by several workers are presented in Table III.

Table III. Thermochemical Bond Energy of S-S Bonds

<i>E</i> (S-S), kcal./mole	Ref. compd.	Ref.
63.66	S ₈	19
63.2	H ₂ S _n ^a	20
62.8	S ₈	17
64.0	RSSR	21

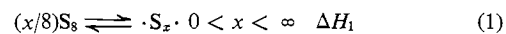
^a *n* = 2-6.

The value of the bond dissociation energy of the sulfur-sulfur bond appears to have been determined only for disulfides. Franklin and Lumpkin²² found the bond dissociation energy to be around 70 kcal./mole for simple aliphatic disulfides. These values have recently been corrected by Mackle²³ and are given in Table IV.

Table IV. Bond Dissociation Energy of Some S-S Bonds

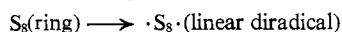
Compound	<i>D</i> (S-S), kcal./mole
Me-S-S-Me	67 ± 6
Et-S-S-Et	69 ± 6
<i>n</i> -Pr-S-S-Pr- <i>n</i>	68 ± 6

Powell and Eyring²⁴ sought to explain the results of Bacon and Fanelli²⁵ in terms of an equilibrium between S₈ rings and polymeric sulfur chains, as represented in eq. 1. They found that Δ*H*₁ for reaction 1 was about 28 kcal./mole and noted that this value was in discrepancy with the accepted value of 63 kcal./mole for the sulfur-sulfur bond strength.



- (15) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, London, 1962, pp. 1-10; see also ref. 1 and 16.
 (16) M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).
 (17) H. Mackle, private communication.
 (18) H. Mackle, *Tetrahedron*, **19**, 961 (1963).
 (19) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).
 (20) F. Feher and G. Winkhaus, *Z. anorg. allgem. Chem.*, **292**, 210 (1957).
 (21) H. Mackle and R. G. Mayrich, *Trans. Faraday Soc.*, **58**, 238 (1962).
 (22) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).
 (23) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).
 (24) R. E. Powell and H. Eyring, *J. Am. Chem. Soc.*, **65**, 648 (1943).
 (25) R. F. Bacon and R. Fanelli, *ibid.*, **65**, 639 (1943).

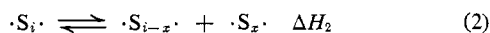
It is essential to note that a comparison of ΔH_1 to a thermochemical bond strength is invalid. The fundamental process involved, in all likelihood, is



Thus, the process is more strictly analogous to dissociation of one sulfur-sulfur bond in the S_8 molecule, and ΔH_1 should be compared to a bond dissociation energy. It is well-known that most free radical recombination reactions take place with little or no activation energy.¹¹ The reverse of reaction 1 should therefore require no activation energy and the ΔH_1 is probably equal to the dissociation energy of the sulfur-sulfur bond in the S_8 ring.

However, comparison of this value to the known bond dissociation energies of disulfides (see Table IV) still leaves a large discrepancy.

Several years after Bacon and Fanelli's article appeared, Gee²⁶ presented a comprehensive theoretical treatment of the liquid sulfur system. In it an expression for the degree of polymerization of the sulfur chains in terms of the heat of reaction 2 was derived.



This ΔH_2 was used as an adjustable parameter to fit Bacon and Fanelli's data. Gee obtained a value of 35 kcal./mole for ΔH_2 . Subsequently several other workers²⁷⁻³⁰ have used ΔH_2 in the same way to fit other types of data on the liquid sulfur system. The values obtained by these workers are presented in Table V.

Table V. $\cdot S_i \cdot \rightleftharpoons \cdot S_{i-x} \cdot + \cdot S_x \cdot \quad \Delta H_2$

ΔH_2	Data fitted	Ref.
31.7	Magnetic susceptibility and electron spin resonance	27
34.6-34.9	Magnetic susceptibility	28
35	Viscosity	26
35	Heat capacity	29
28	Viscosity	24

Similar results have been found by workers studying the vulcanization of rubber. Many studies have been done in systems containing only rubber and sulfur. In these systems activation energies of about 35 kcal./mole are invariably found. Most workers feel that the rate-determining step involves opening of the S_8 ring.³¹⁻³³ Some of these values are presented in Table VI. Again, we feel these values are to be associated with the bond dissociation energy of the sulfur-sulfur bond in S_8 .

Our results shown that the bond dissociation energy of a sulfur-sulfur bond in methyl tetrasulfide is about 36 kcal./mole. The inference that the important process in the polymeric sulfur system is a bond-dissociation step is thus given indirect experimental verification. It would appear that the dissociation energy of the sul-

(26) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

(27) J. A. Poulis and W. Derbyshire, *ibid.*, **59**, 559 (1963).

(28) J. A. Poulis, C. H. Massen, and P. v. d. Leeden, *ibid.*, **58**, 474 (1962).

(29) G. Gee, F. Fairbrother, and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955).

(30) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

(31) M. Gordon, *J. Polymer Sci.*, **5**, 485 (1951).

(32) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(33) W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).

Table VI. $S_8 \rightleftharpoons \cdot S_8 \cdot$

ΔH^* or E_a	A , sec. ⁻¹	Ref.
35	$10^{16.1a}$	<i>b</i>
35-36	...	<i>c</i>
30.5-35	$10^{12.5-10^{14.5}}$	31
34.8	$10^{14.9}$	<i>d</i>
35.6	$10^{15.1}$	<i>e</i>
35.2	$10^{14.3}$	<i>f</i>
37	...	<i>g</i>
37.8	...	17
34-35	$10^{14.2}$	33
32.8 ^b	$10^{18.1c}$	<i>j</i>

^a Calculated from their data. See footnote *b*. ^b E. Echte, W. Scheele, and S. Sonnenberg, *Rubber Chem. Technol.*, **33**, 1059 (1960). ^c D. Spence and J. Young, *Kolloid-Z.*, **11**, 28 (1911). ^d R. Ludwig, *Rubber Chem. Technol.*, **33**, 1029 (1960). ^e P. K. Chatterjee and A. K. Sircar, *Indian J. Technol.*, **2**, 259 (1964). ^f P. K. Chatterjee and A. K. Sircar, *ibid.*, **2**, 190 (1964). ^g G. W. Ross, *J. Chem. Soc.*, 2856 (1958). ^h ΔH^* . ⁱ Calculated from ΔS° using the equation $\log A = \log kT/h + [(\Delta S^\circ + R)/(2.303R)]$ with $T = 300^\circ$. ^j A. V. Tobolsky and A. Eisenberg, *J. Colloid Sci.*, **17**, 49 (1962).

fur-sulfur bond in all polysulfides, except possibly a trisulfide, is about 36 kcal./mole.

We cannot say which of the three possible bonds in our system is broken. However, the middle bond is the most logical one to which to attribute the primary cleavage process. Abrahams³⁴ has found that the central bond in a tetrasulfide is longer than the other two sulfur-sulfur bonds, and thus presumably weaker.³⁵

We would also offer our results as evidence that the reaction of sulfur with olefins is at least partly radical in nature.³⁶ At the time the work of the British Rubber Producers Group was done there were no thoroughly documented cases of homolytic cleavage of sulfur-sulfur bonds in disulfides or polysulfides. This work clearly demonstrates that polysulfide bonds can and do undergo such cleavage. Further, we can predict that the rate of this process will be quite high at the temperatures usually used in such investigations (140-160°).

The physical reason for the lower value of the dissociation energy in polysulfides from which fragments containing at least two consecutive sulfur atoms are formed, as opposed to disulfides, remains unclear. Such results are usually explained in terms of some electronic effect such as resonance stabilization.

Gee's^{29,37} three-electron bond formulation has been widely used to explain the results found in Tables V and VI. There can be no question that fragments such as R-S-S· are unreactive. Sulfur is known to inhibit the polymerization of vinyl acetate³⁸ and styrene.^{39,40} We have found that methyl tetrasulfide

(34) S. C. Abrahams, *Acta Cryst.*, **7**, 413 (1954).

(35) R. E. Davis, A. Cohen, and J. A. Louis, *J. Am. Chem. Soc.*, **85**, 3050 (1963), report that there is a good correlation between sulfur-sulfur bond length and ease of nucleophilic attack on the bond.

(36) In 1958 workers at the British Rubber Producers' Research Association Laboratory published their results of an intensive re-examination of the reaction of sulfur with olefins. They felt that a completely ionic mechanism was in better accord with their data than the previously accepted radical mechanism. See footnote *g* (Table I) and work cited therein. For a critical discussion of this work see ref. 32, pp. 100-108.

(37) G. Gee, *Sci. Progr.* (London), **43**, 193 (1955).

(38) P. D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, **74**, 3969 (1952).

(39) P. F. Lyons of these laboratories has also found that sulfur inhibits the autoxidation of natural rubber, ethylene-propylene terpolymer, and poly(propylene oxide).

(40) P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 457 (1956).

shows no change in its ultraviolet spectrum after >50 hr. at 80° in cyclohexane or cyclohexene. Thus R-S-S· apparently does not add to the double bond or abstract hydrogen under these mild conditions.⁴¹ In contrast, disulfides are known to be chain-transfer agents. Thus RS· fragments add to active double bonds quite readily and reinitiate polymerization at 60–80°.⁴² However, e.s.r. investigations,^{30,43} while inconclusive, have given no indication of delocalization of the odd electron in polythiyl radicals.

Bergson, in some semiempirical molecular orbital cal-

(41) It is possible in the cyclohexene case that a small amount of addition takes place. If species such as RS₂R, etc., are also formed, however, no change in the ultraviolet spectrum would be anticipated. Further studies are planned to elucidate this problem.

(42) W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

(43) A. G. Pinkus and L. H. Piette, *J. Phys. Chem.*, **63**, 2086 (1959).

culations,⁴⁴ has found that there should be an increase in stability of species such as R-S_n· with *n*. He attributes this stability to the fact that the odd electron can occupy an antibonding π orbital formed from 3pπ orbitals. He estimates that this stabilization should be worth about 30 kcal./mole in a trisulfide compared to a disulfide. This is the same order of magnitude as we find for a tetrasulfide. Investigations on methyl trisulfide are under way to see if its dissociation energy is intermediate between that of disulfides and tetrasulfides.

Acknowledgment. The authors wish to acknowledge many fruitful discussions with Dr. W. J. MacKnight of these laboratories. We wish to thank the Air Force Office of Scientific Research and the Sulfur Institute for partial support of this work.

(44) G. Bergson, *Arkiv Kemi*, **18**, 409 (1961).

Kinetic Studies of Group VI Metal Carbonyl Complexes. I. Substitution Reactions of Dipyridyl Complexes of Chromium Hexacarbonyl¹

Robert J. Angelici and James R. Graham

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa. Received August 9, 1965

The reaction of Cr(CO)₄(X-X) (where X-X = dipyridyl or 4,4'-dimethyldipyridyl) with phosphites, L (where L = P(OC₂H₅)₃, P(OCH₂)₃CCH₃, and PO₃C₆H₉), to yield cis-Cr(CO)₃(L)(dipy) proceeds according to a first-order rate law at temperatures of 35 to 60° in various organic solvents. The 4,4'-dimethyldipyridyl complex reacts faster than does that of dipyridyl. In contrast to the very slow rates of reaction of Cr(CO)₆ and its phosphine derivatives, these dipyridyl complexes are relatively labile, and the labilizing abilities of these and other ligands are discussed in terms of "hard" and "soft" bases. Activation parameters and solvent effects for the reactions have also been evaluated.

The kinetic inertness of Cr(CO)₆ has been demonstrated by the following observations: it shows no exchange with ¹⁴CO in toluene in 3 weeks at 30°;^{2a} and phosphines are able to replace CO groups from it only at relatively high temperatures.^{2b} Replacement of two CO groups in Cr(CO)₆ by a dipyridyl ligand to form Cr(CO)₄(dipy) would presumably increase chromium π bonding to the remaining four CO groups rendering them more inert than those in Cr(CO)₆.³ However, there was some indication that the CO groups in Cr(CO)₄(dipy) would not be as inert as expected since Mo(CO)₄(dipy) is known to react with ligands, L (where L = pyridine, triphenylphosphine, and diphenyl

sulfide), to form cis-Mo(CO)₃(L)(dipy) at temperatures of 120–160° in the absence of a solvent.⁴ Despite the rather rigorous conditions, it was a surprising result since the CO groups of Mo(CO)₆ can be substituted by phosphines only at rather high temperatures.⁵

In order to determine whether the CO groups in Cr(CO)₄(dipy) are indeed more labile than in Cr(CO)₆, a kinetic investigation of the reactions of Cr(CO)₄(dipy) with phosphites was undertaken.

Experimental Section

Preparation and Purification of Materials. The complexes Cr(CO)₄(X-X) (where X-X = 2,2'-dipyridyl and 4,4'-dimethyldipyridyl) were prepared from chromium hexacarbonyl and the desired dipyridyl as described in the literature⁶ and identified by their infrared spectra.³ The bicyclic phosphite ligands, 4-methyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH₂)₃CCH₃, and 1-phospha-2,8,9-trioxaadamantane, PO₃-C₆H₉, were obtained by refluxing P(OCH₃)₃ with the appropriate triol.⁷ Triethyl phosphite was purchased from Matheson Coleman and Bell and used without further purification. Purification of 1,2-dichloroethane was effected by fractional distillation. Chlorobenzene and nitrobenzene were dried over P₂O₅ and fractionally distilled, while reagent grade acetone was used directly.

Determination of Rates. All rates of reaction were determined by following the disappearance of the high-

(4) M. H. B. Stiddard, *J. Chem. Soc.*, 756 (1963).

(5) R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962).

(6) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

(1) Presented before the Division of Inorganic Chemistry at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) (a) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); (b) T. A. Magee, C. N. Mathews, T. S. Wang, and J. H. Wotiz, *ibid.*, **83**, 3200 (1961).

(3) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).