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Displacement Reactions. VIII. A Correlation between the Sulfur–Sulfur Bond Distance and the Activation Energy for a Process Breaking the Bond[1]

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Abstract: An empirical correlation has been found between the activation energy of a displacement reaction and the length of the sulfur–sulfur bond broken in the reaction. Displacement reactions with both cyanide ion and sulfite ion (eq. 1 and 2) are correlated. The correlation can be explained on the basis of current theories of bond-strength concepts. The data are generalized to allow predictions on the rate of cleavage of polythio compounds with varying bond lengths. The oxibase scale is used to predict that hydrosulfide, SH^-, will also follow the empirical relationship. The rate constant and the activation energy of the second-order, bimolecular reaction of cyanide ion with trithionate (eq. 5) have been predicted. The values agree very well with the values measured at 25° in aqueous solution. The value of k_2 is $0.105 \pm 0.004\ M^{-1}$ sec.$^{-1}$ at 25° at infinite dilution and the activation energy is 9.8 kcal./mole. The theoretical value of k_2 is $0.092\ M^{-1}$ sec.$^{-1}$ which is within 8% of the experimental value. The theoretical activation energy is predicted to be 10.0 kcal./mole since the sulfur–sulfur bond in trithionate is 2.15 Å. in length. The reaction of cyanide ion with sodium disulfide (eq. 7) was studied in aqueous solution. The sulfur–sulfur bond has a length of 2.25 Å. and the $E_ar^3 = 99$ kcal./mole Å.^{3} equation predicts an E_a of 8.6 kcal./mole. Experimentally the value is 8.1 ± 0.4 kcal./mole. An estimate of the mean bond strength in the disulfide ion is given as 42 kcal./mole. The experimental error is somewhat uncertain.

The nucleophilic displacement reaction at the carbon atom has played a dominant role in the development of physical organic chemistry. Numerous investigators are now exploring displacement reactions at other atoms. In the present study a correlation between the sulfur–sulfur bond distance and the activation of energy of cleavage of that bond by several nucleophiles has been found. The idea that such a relationship should exist was first discussed in a thesis[3] in 1958. If the correlation is general, it will provide an *a priori* estimate of the rate of reaction. The rate constant of one displacement reaction (of cyanide ion on trithionate) has been predicted using the theory and was found to agree. The reaction of cyanide ion with disulfide ion was also studied. The data are generalized to other polythio compounds.

The Sulfur–Sulfur Bond Distance. The sulfur–sulfur bond distance varies from 1.89 Å. in diatomic sulfur[4] to 2.39 Å. in dithionite.[5,6] The bond lengths have

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(1) Displacement Reactions. VII: R. E. Davis, "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp. 189–238; paper VI: R. E. Davis, *J. Am. Chem. Soc.*, 87, 3010 (1965). An earlier communication (paper IV) reported the data of the present paper: R. E. Davis, A. Cohen, and J. B. Louis, *J. Am. Chem. Soc.*, **85**, 3050 (1963). Earlier papers in this series were entitled Displacement Reactions at the Sulfur Atom.

(2) (a) Alfred P. Sloan Fellow, 1962–1966; (b) National Science Foundation Summer Undergraduate Research Participant, 1962–1963; (c) based in part on a thesis submitted by A. Cohen in partial fulfillment of the requirements for a Master of Science degree, 1962.

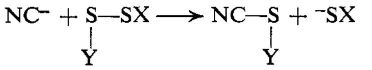
(3) R. E. Davis, Ph.D. Thesis, Harvard University (under P. B. Bartlett), 1958.

(4) K. Ikenoue, *J. Phys. Soc. Japan*, **8**, 646 (1953). It is to be noted that diatomic sulfur, S_2, does not represent a typical sulfur–sulfur bond. This molecule has a triplet ground state like oxygen. As S_2 exists in moderate concentrations in the gas phase at high temperature (1000°K. and greater), the very short bond length will result in no useful solution chemistry at 298°K.

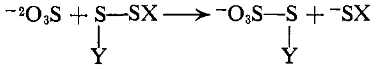
(5) J. D. Dunitz, *Acta Cryst.*, **9**, 579 (1956).

(6) The sulfur–sulfur bond of sodium dithionite again cannot be

been tabulated in a recent review[7] and a recent book[8] for nearly 40 polythio compounds. Numerous investigators have been reporting results of kinetic studies of displacement with sulfite ion and cyanide ion on



$$NC^- + \underset{\displaystyle Y}{S}{-}SX \longrightarrow NC{-}\underset{\displaystyle Y}{S} + {}^-SX \qquad (1)$$



$$^{-2}O_3S + \underset{\displaystyle Y}{S}{-}SX \longrightarrow {}^-O_3S{-}\underset{\displaystyle Y}{S} + {}^-SX \qquad (2)$$

various thio compounds. In Table I we present the synthesis of all the revelant data and the correlation with E_a, the activation energy at 25° in *aqueous solution.* The difference in E_a, between sulfite and cyanide, is rather uniform for a constant bond length. Reactions of numerous charge type are correlated. The individual rate constants for the reactions listed in Table I vary by over 10^7-fold at 25°.

Table I. Activation Energies and Sulfur–Sulfur Bond Distances

XSSY	X	Y	r_{SS}, Å.	Ref.	E_a, kcal./mole	Ref.
			$NC^- + XSSY \rightarrow NCSX + {}^-SY$			
$^-SSO_3$	. . .	O_3^-	1.97	*a*	13.0	*b*
S_8	S	S	2.048	*c*	11.7	*d*
$S_4O_6^{-2}$	SO_3^-	SO_3^-	2.02	*c, e*	11.3	*f*
$S_3O_6^{-2}$	SO_3^-	O_3^-	2.15	*g*	9.5	*h*
$^-S{-}S^-$	. . .	. . .	2.25	*e*	8.1	*h*
			$^{-2}O_3S + XSSY \rightarrow {}^-O_3SSX + {}^-SY$			
$^-SSO_3^-$	. . .	O_3^-	1.97	*a*	14.5	*i*
Cystine			2.04	*k*	12.8	*k*
N,N′-Diacetylcystine			2.04	*k*	13.3	*k*
$S_3O_6^{-2}$	SO_3^-	O_3^-	2.15	*g*	10–11.1	*j*

[a] O. Foss and A. Hordnik, *Acta Chem. Scand.*, **11**, 1443 (1957); P. G. Taylor and C. A. Beevers, *Acta Cryst.*, **5**, 341 (1952). [b] R. E. Davis, *J. Phys. Chem.*, **66**, 956 (1962); P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958). [c] S. C. Abrahams, *Acta Cryst.*, **8**, 611 (1955); A. Caron and J. Donohue, *ibid.*, **14**, 548 (1961). [d] P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958), and ref. 6; E_a estimated in pure water from the data in aqueous methanol. [e] O. Foss and A. Hordnik, *Acta Chem. Scand.*, **12**, 1700 (1958). [f] R. E. Davis, *J. Phys. Chem.*, **62**, 1599 (1958). [g] W. H. Zachariasen, *J. Chem. Phys.*, **2**, 109 (1934). [h] This study. [i] D. P. Ames and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 164 (1951). [j] A. Fava and G. Pajaro, *Ann. chim.* (Rome), **44**, 551 (1954). [k] Data are available for the reaction of sulfite ion with cystine and N,N-diacetylcystine with E_a of 12.8 and 13.3 kcal./mole for a bond distance of 2.04 Å. (R. Cecil and J. R. McPhee, *Biochem. J.*, **60**, 496 (1955); L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Am. Chem. Soc.*, **80**, 3855 (1958)). While these fit the r^{-3} relationship quite well, we are not sure how general the rule is for these materials. Work is in progress. [l] H. Foppl, *Angew. Chem.*, **70**, 401 (1958).

Results

The Functional Dependence upon r_{SS}. The activation energy is some inverse proportional function of r_{SS}, the sulfur–sulfur bond distance. The value of n

$$E_a = f\left(\frac{1}{r_{SS}}\right)^n \qquad (3)$$

has been determined by the Student **t** test.[9,10]

In Table II, the mean value of $E_a r^n$ is calculated from some of the data of Table I. Student's t has then been calculated from the range and the classification number.[11] It is obvious from Table II that the best statistical fit to an integer value of n would be $n = 3$ *in both cases.*

Table II. Student's t Test for the Correlation of E_a[a] with r_{SS}

	$E_a r$	$E_a r^2$	$E_a r^3$	$E_a r^4$ [b]
		Sulfite		
Mean[c]	26.1	53.9	110	227
Student's t[d]	2.23	1.79	1.79	9.8
%[e]	8.5	3.0	1.62	4.3
		Cyanide		
Mean	24.4	49.3	99.3	200
Student's t	1.2	1.3	1.5	5.7
%	4.9	2.6	1.5	2.8
E_a[f]	11.3	10.7	10.0	9.3

[a] The E_a values of $S_3O_6^{-2}$ and S^{-2} with cyanide were not used to derive the relationship in this paper or in paper IV.[1] [b] Noninteger values would be harder to treat in a theoretical manner. The *Anova* has been computed by the range techniques rather than by variance procedures. [c] Mean value of the product of E_a times some power of r_{SS}. [d] Student's t, ref. 9. [e] Correlation per cent; the lower this number the better the fit of the data to the given function. [f] Predicted E_a for CN^- with $S_3O_6^{-2}$ (kcal./mole) for each value of n.

$$E_a = f\left(\frac{1}{r_{SS}}\right)^3 = \frac{C}{r_{SS}{}^3} \qquad (4a)$$

$$E_a = \frac{99}{r^3}\ \frac{\text{kcal.}}{\text{mole}}\ \text{(cyanide)} \qquad (4b)$$

$$E_a = \frac{110}{r^3}\ \frac{\text{kcal.}}{\text{mole}}\ \text{(sulfite)} \qquad (4c)$$

Discussion

The correlation is to be expected on the basis of current theoretical developments. The sulfur–sulfur bond is a useful one in which to expect such a dependence between the activation energy and the bond length. The sulfur–sulfur bond can be varied from 1.97 to 2.25 Å. with little change in the hybridization or bond type. The theoretical justifications are discussed within two frameworks, one of electrostatics and the other in terms of bond strength.

The electrostatic free energy, ΔF^*_{el}, of a reaction can be calculated for an ionic reaction if reasonable assumptions are made about the microscopic dielectric constant and the distance of closest approach.[12-14] The ΔF^*_{el} of an ion–ion reaction depends upon $1/r^*$ and

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assumed to be a typical sulfur–sulfur bond. Dunitz[6] has suggested the unusual explanation that the bond is formed by overlap of dp orbitals tilted 30° to explain the fact that the SO_2^- groups lie in planes inclined 30° to one another. The sulfur–sulfur bond is quite weak.

(7) S. C. Abrahams, *Quart. Rev.* (London), **10**, 424 (1956).

(8) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 16–27.

(9) W. S. Gosset, *Biometrika*, **6**, 1 (1908).

(10) E. L. Bauer, "A Statistical Manual for Chemists," Academic Press Inc., New York, N. Y., 1960.

(11) L. H. C. Tipett, *Biometrika*, **17**, 364 (1925); H. A. David, *ibid.*, **38**, 393 (1951).

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 145–152.

(13) M. Born, *Z. Physik*, **1**, 45 (1920).

(14) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939); **2**, 351 (1934).

would be only 2.1 kcal./mole if $r^* = 2$ Å. for univalent ions[13] in water at 25°.

For reactions of ions with neutral molecules with a dipole moment, ΔF^*_{el} depends upon the inverse square[14] of the critical distance, r^*. The values of ΔF^*_{el} are again small compared to the ΔF^* of reactions reported in Table I. Perhaps only for extremely rapid reactions ΔF^* would be equal to ΔF^*_{el}.

Bond Strength. Numerous authors have suggested that there is a relationship between the strength of a bond and the activation energy required for bond rupture.[15] Some empirical rules exist which have limited application but do work well in a series of very closely related reactions. The empirical relationships between the force constant and the bond distance are also well known.[16,17] The use of the Gordy rule and a potential function with both square terms and cubic terms (representing the first anharmonic term) to represent the potential along the reaction coordinate predicts $E_a = f(1/r)^n$ with n from 2 to 3. This represents a satisfactory explanation for the data of Table I.

Bond Lengths and Bond Strengths. In 1954 Pauling[18] published tabulations suggesting a square relationship between bond energy and the equilibrium internuclear distance. In 1957, Feilchenfeld,[19] extending these investigations and those of Glockler,[20] suggested that the carbon–hydrogen bond and the carbon–carbon bond energies were inversely proportional to the *cube* of the bond length. The *best statistical fit* was for the r^{-3} dependence: $E_{\text{CH}} = 128.21/r_{\text{CH}}^3$ kcal./mole; $E_{\text{CC}} = 312.33/r_{\text{CC}}^3$ kcal./mole. More recently McKelvie[21] has generalized the work of Feilchenfeld to consider numerous other types of bonds and has expressed the r^{-3} equation in terms of

$$\log Er_{\text{AB}}^3 = \log C$$

(where C is a constant) because an error of ±0.01 Å. in r shows up as an error of about 0.01 in the value of log Er^3. The Er^3 values show consistent patterns as bonds between first-row elements have log Er^3 values of about 2.50. Thus the value for the carbon–carbon single bond is 2.50; for the double bond, 2.50; and for the carbon–carbon triple bond, 2.49. The B–B, C–C, B–N, and B–O bonds each have values of 2.50. The log Er^3 values for first-row elements bonded to hydrogen vary from 1.99 to 2.11 with a mean of 2.04.

Of more interest to the present investigation is the finding of McKelvie that the sulfur–sulfur bond has a log Er^3 value of 2.71: $\log E_{\text{SS}}r_{\text{SS}}^3 = 2.71$; or $E_{\text{SS}} = 513/r_{\text{SS}}^3$. The immediate conclusion is that *the activation energy of cleavage of the sulfur–sulfur bond by cyanide ion or by sulfite ion is directly proportional to the bond energy, E_{SS}, of the bond being broken in the rate-determining step.* In particular, $E_{a_{\text{CN}^-}} = 0.19E_{\text{SS}}$, and $E_{a_{\text{SO}_3{}^{2-}}} = 0.21E_{\text{SS}}$; the activation energies are about one-fifth of the bond energy. It will be of interest to determine the generality of these equations.

An Interpretation Using LCAO–MO Theory. MO theory can also be used to make a prediction as to the effect of the sulfur–sulfur bond length upon the energy of activation. In each case the bonding between each sulfur atom has been assumed to be essentially the same. The greater stability and shorter length of an S–S bond implies a greater *instability* of the sulfur *antibonding* acceptor orbital. As cyanide approaches, the NC–S, bond forming is weaker and more energy would be required to form this new bond and break the old one.[22] The suggestion can be made *that the electrons on the nucleophile enter the antibonding orbital of the sulfur–sulfur bond* and that the activation energy is related to the energy difference between the antibonding acceptor orbital and its bonding orbital.

New Data. The Reaction of Cyanide with Trithionate. The usefulness of eq. 4 is illustrated by the calculation of a rate constant and then comparing it with experiment. The reaction of cyanide with trithionate was selected.

$$\text{CN}^- + {}^-\text{O}_3\text{S—S—SO}_3{}^- \xrightarrow[\text{slow}]{k_2} \text{SO}_3{}^{-2} + {}^-\text{O}_3\text{SSCN} \tag{5}$$

$$\text{H}_2\text{O} + {}^-\text{O}_3\text{SSCN} \xrightarrow{\text{fast}} 2\text{H}^+ + \text{SO}_4{}^{-2} + \text{SCN}^- \tag{6}$$

ΔH^* can be estimated[13] using Table II. One must then estimate ΔS^*. The usual estimate of ΔS^*_{el} is $-10Z_AZ_B$ gibbs for an ion–ion reaction in water at 25° with $r = 2$ Å. This would predict a value of −20 gibbs. The reaction of tetrathionate[23] with cyanide ion has $\Delta S^* = -22$ gibbs, while the reaction of cyanide ion with thiosulfate has a ΔS^* of −39 gibbs. However, ΔS^*_{el} is a function[12] of $1/r^*$. In the present case we have used the change in distance from the negative charge in the ion to that of the oxyanion; ΔS^* for the trithionate reaction is then estimated to be −25 gibbs. The second-order rate constant, k_2, has been calculated using a digital computer and is presented in Table III using several values of ΔH^* and ΔS^*. From relationship 4 and the estimate of ΔS^*, the calculated value of k_2 is 0.092 M^{-1} sec.$^{-1}$ at $\mu = 0$. This value is only 8% lower than the experimental value. The near agreement may be fortuitous or may be due to the fact that the extrapolations from the other systems are small. Certainly the reactions of cyanide ion with thiosulfate, trithionate, and tetrathionate are extremely analogous.

The rate of reaction can be conveniently measured by noting the change in the ultraviolet absorption spectrum of the reaction system as a function of time. The rate expression is found to be

$$\text{rate} = k_2[\text{CN}^-][\text{S}_3\text{O}_6{}^{-2}]$$

when the cyanide concentration has been varied from 0.001 to 0.20 M and the trithionate concentration varied from 0.001 to 0.40 M. The concentration of cyanide

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(15) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(16) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

(17) W. Gordy, *ibid.*, **14**, 304 (1946).

(18) L. Pauling, *J. Phys. Chem.*, **58**, 662 (1954).

(19) H. Feilchenfeld, *ibid.*, **61**, 1133 (1957).

(20) G. Glockler, *J. Chem. Phys.*, **21**, 1242 (1953).

(21) N. McKelvie, private communications, CCNY, 1964 and 1965.

(22) In LCAO–MO theory the energy of an electron in the lower MO of a homonuclear bond is given by $E_+ = (\alpha + \beta)/(1 + S)$ where α is the Coulomb integral, β is the energy of an electron in the field of both nuclei (the bond integral), and S is the overlap integral. For nonorthogonal atomic orbitals used in bonding, β decreases as S decreases. Both β and S decrease with increasing distance between the bonded nuclei. The antibonding (or acceptor) orbital has an energy, $E_- = (\alpha - \beta)/(1 - S)$. Thus the energy difference between E_+ and E_- decreases with increasing r. The overlap integrals of (3pσ, 3pσ) for a homonuclear system have been computed by R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff (*J. Chem. Phys.*, **17**, 1248 (1949)). The value of S can best be described as dropping in an exponential manner with r or in a power series expansion.

(23) R. E. Davis, *J. Phys. Chem.*, **62**, 1599 (1958).

Table III. Calculated Second-Order Rate Constants for the Reaction of Cyanide with Trithionate at 25° Using a Digital Computer (k_2, M^{-1} sec.,$^{-1}$ as a Function of ΔH^*, n, and ΔS^*)

Function	ΔH^{*d}	ΔS^*, gibbs -20^a	 -25^b	 -30	 -35	 -40^c
		k_2, M^{-1} sec.$^{-1}$				
E_ar	10.7	1.27×10^{-1}	1.02×10^{-2}	8.31×10^{-4}	6.71×10^{-5}	5.42×10^{-6}
E_ar^2	10.1	3.51×10^{-1}	2.83×10^{-2}	2.29×10^{-3}	1.84×10^{-4}	1.49×10^{-5}
E_ar^3	9.4	1.14	9.23×10^{-2}	7.45×10^{-3}	6.02×10^{-4e}	4.86×10^{-5}
E_ar^4	8.7	3.72	3.01×10^{-1}	2.43×10^{-3}	1.96×10^{-3}	1.58×10^{-4}

[a] Calculated from $\Delta S^*_{\mathrm{el}} = -10Z_AZ_B$ gibbs. [b] Calculated for trithionate. [c] Value of ΔS^* for thiosulfate and cyanide. [d] ΔH^*, kcal./mole. [e] The use of the semiempirical rules developed by Cobble would predict a S of about -35 ± 4 gibbs for the reaction of cyanide ion and the trithionate ion. The estimated rate constant would then be about 6×10^{-4} M^{-1} sec.$^{-1}$. The important point is not the absolute value of the prediction but the fact by comparison with other rather closely related systems the rate constant of this reaction can be calculated to within a factor of 10^2 in rate: J. Cobble, private communications, Purdue University, 1965.

was also adjusted by the use of buffer solutions (pH 9 to 10.5). See Table IV.

Table IV. Experimental Data on the Rate of Reaction of Cyanide with Trithionate

CN^-, M $\times 10^3$	$S_3O_6^{-2}$, $M \times 10^3$	Temp., °C.	$\mu^{1/2}$	k_2, M^{-1} sec.$^{-1}$
		25.00	0^a	0.105 ± 0.004
2.03^b	0.761		0.05^c	0.141
2.50	2.47		0.10	0.165
1.50	2.50		0.10	0.167
2.30	1.67		0.103	0.166
10.0	10.0		0.21	0.258
6.7	12.9		0.20	0.250
5.0	11.6		0.20	0.251
63.0	10.3		0.31	0.360
75.3	5.4		0.31	0.370
110	22.0		0.43	0.481
123	10.3		0.43	0.487
114	20.7		0.43	0.491
105	105		0.63	0.70
130	105		0.69	0.76
		20.92	0	0.0780 ± 0.004
10.1	10.2		0.22	0.187
76.5	5.72		0.32	0.265
		9.97		
			0	0.0423 ± 0.006
3.04	1.00		0.12	0.0594
1.03	3.05		0.12	0.0603
5.21	10.1		0.20	0.0986
10.7	9.83		0.20	0.0990
120	11.2		0.43	0.19
		0.03		
11.3	10.7		0.20	0.0500
83.1	15.3		0.43	0.0930
130	102		0.69	0.130

[a] Extrapolated. [b] Free cyanide ion concentration. [c] The square root of the ionic strength computed from the sum of the ionic strengths of KCN, $K_2S_3O_6$, and any buffer salt present.

The reaction is sensitive to changes in the ionic strength (μ) of the solution. A plot of log k/k_0 *vs.* $\mu^{1/2}$ has a limiting slope of +2 at 25°, the product of the charges of the ions forming the activated complex. The rate constants were determined at 25.00, 20.92, 9.97, and 0 ± 0.03°. The empirical activation energy is 9.8 ± 0.3 kcal./mole at an ionic strength (μ) of 0.1 and 9.6 ± 0.3 at $\mu = 0$. The rate constant at 25° is 0.105 ± 0.004 M^{-1} sec.$^{-1}$ at $\mu = 0$.

The Reaction of Cyanide Ion with Disulfide. Cyanide will react with sodium disulfide to produce sulfide and thiocyanate. The yellow color of the disulfide allows the rate to be studied using a spectrophotometer. The data are listed in Table V.

Table V. Reaction of Potassium Cyanide with Sodium Disulfide in Water[a]

KCN, M $\times 10^2$	Na_2S_2, $M \times 10^2$	Temp., °C.	μ	k_2, M^{-1} sec.$^{-1}$
1.25	1.25	24.7	0.05	0.0790
3.75	2.25	24.7	0.07	0.0824
1.25	1.25	39.8	0.05	0.151
1.25	1.00	39.8	0.05	0.150
1.00	1.00	39.8	0.05	0.151
1.25	1.25	39.8	0.05	0.163

[a] E_a at $\mu = 0.05$ is 8.1 ± 0.4 kcal./mole.

The reaction is second order, first order in each reactant. While not as many kinetic experiments were performed as with trithionate, the value of E_a of 8.1 ± 0.4 kcal./mole seems quite consistent with the data.

$$\mathrm{NC^- + {}^-S{-}S^- \xrightarrow{k_2} NCS^- + S^{-2}} \tag{7}$$

$$r = k_2[\mathrm{CN^-}]\,[\mathrm{S_2^{-2}}]$$

The weak sulfur–sulfur bond is broken quite quickly. Using the empirical relationship $E_{\mathrm{SS}} = E_a/0.19$, the bond energy of the sulfur–sulfur bond in disulfide is estimated to be only 42 kcal./mole. The experimental uncertainty is large and more conventional methods ought be used to establish the bond strength.

Extensions. Bond Alteration and Reactivity of Polythio Compounds. In Table VI the bond lengths of several polythio compounds are tabulated. It is of

Table VI. Sulfur–Sulfur Bond Distances (Å.) in Polythio Compounds[a]

Compound	Ref.	S_1–S_2	S_2–S_3	S_3–S_4	S_4–S_5	S_5–S_6
$(CH_3SO_2)_2S_2$	*b*	2.10	2.06	2.10		
$BaS_4O_6 \cdot 2H_2O$	*c*	2.11	2.04	2.11		
$BaS_4 \cdot H_2O$	*d*	2.02	2.07	2.02		
$BaS_5O_6 \cdot 2H_2O$	*e*	2.14	2.04	2.04	2.14	
Cs_2S_6	*f*	1.99	2.10	2.03	2.12	2.03
$K_2Ba(S_6O_6)_2$	*g*	2.10	2.04	2.04	2.04	2.10

[a] Average experimental errors are ±0.03 A. [b] H. Sorum, *Acta Chem. Scand.*, **7,** 1 (1953). [c] O. Foss, S. Furberg, and H. Zachariasen, *ibid.*, **8,** 459 (1954). [d] S. C. Abrahams, *Acta Cryst.*, **7,** 423 (1954). [e] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, **9,** 1016 (1955). [f] S. C. Abrahams, R. L. Collin, and W. N. Lipscomb, *Acta Cryst.*, **4,** 15 (1951). [g] O. Foss, A. Hordvik, and K. H. Palmork, *Acta Chem. Scand.*, **12,** 1339 (1958); O. Foss, *Advan. Inorg. Chem. Radiochem.*, **2,** 237 (1960).

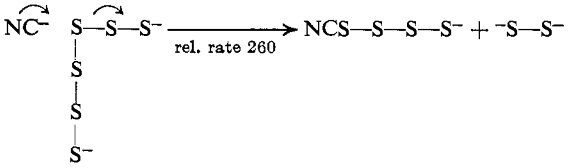
interest to use the new empirical relationship to predict which bond of such a compound would break most easily with a nucleophilic thiophile such as cyanide. At present no experimental technique can discriminate between the positions of attack of cyanide on hexasulfide ion. The general rule would be that *the longer bond would break with the lower activation energy.* The problem remains to evaluate the ΔS^* for each position for the hexasulfide reaction with cyanide ion. The longest bond is between atoms 2 and 3. This bond should break with the lowest activation energy. The attack of atom 3 should be faster as the distance between the negative changes is greater and ΔS^* would be more favorable.

$$\underset{2.01}{{}^-S_1 - S_2} \underset{2.11}{- S_3 ——} \underset{2.03\ \text{Å}.}{S_3 - S_2 - S_1^-}$$

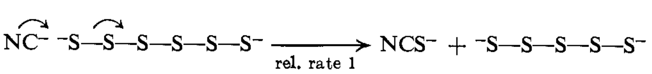
A semiquantitative estimate can be given by computing the $\Delta\Delta E_a$ for each bond and then computing the $\Delta\Delta S^*_{el}$ and taking a constant C–S bond distance in the activated complex. Defining $k_{S,1,1-2}$ as the rate of displacement of cyanide ion on the sulfur atom number one and breaking bond 1–2, one can calculate the relative rate for each cleavage reaction (Table VII). The fastest reaction would be

Table VII. Relative Rate of Displacement on Hexasulfide Ion by Cyanide Ion

Cleavage	Theoret. rel. rate
S_1, 1–2	1
S_2, 1–2	4.7
S_2, 2–3	94
S_3, 2–3	260
S_3, 3–3	13



the reaction cleaving the longest bond and having the two sulfide negative charges the farthest apart from the cyanide ion. The slowest reaction would be



Work is in progress to estimate the rates of cyanide ion with the polysulfide ions.

Rate Effects with Sulfur Allotropes. The allotropes of elemental sulfur have different bond lengths. Indeed, the longer the sulfur–sulfur bond the faster the reaction (Table III) with triphenylphosphine *in benzene.*

$$(C_6H_5)_3P + S_8 \xrightarrow[\text{slow}]{\text{rate-determining step}} (C_6H_5)_3{}^+P\text{-}S_8^-$$

However, since ring size of the sulfur allotropes causes *strain* and *dihedral* angle effects, the relief of strain also provides an additional driving force not observed in the reactions discussed in Table I.

Prediction of Reaction Mechanisms Using Eq. 4 and the Oxibase Scale. In each reaction reported in Table I a powerful thiophile[24] such as cyanide ion or sulfite ion cleaves the sulfur bond. Examination of the E and H table[1] listed in paper VII[1] of the present group shows what other ions would also be good thiophiles at 25°. Iodide ion (E = 2.06 and H = −7.7) is a very poor thiophile because the E value is low compared to the E value of most RS⁻ leganions and because the H of iodide is so low. Thiosulfate is a poor thiophile, not because of its E value of 2.52, but because of its low H of only 3.60. The ions listed in Table IX are generally considered good thiophiles. The new value of E for ⁻CN is certainly more consistent with the behavior of cyanide ion.

Table VIII. Rates of Reaction of Triphenylphosphine with Various Elemental Sulfurs in Benzene at 7.35°

Allotrope	S–S, Å.	k_2, M^{-1} sec.$^{-1}$ [a]
S_8	2.048[b]	7.54×10^{-4}
S_6	2.06[c]	19.1
S_x (polymeric)	2.08[d]	Too fast to measure

[a] P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961). [b] Table I. [c] J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961). [d] N. S. Gingrich, *J. Chem. Phys.*, **8**, 29 (1940).

Table IX. Oxibase Scale. E and H Values at 25° in Water for Several Excellent Thiophiles[a]

Ion	E, v.[b]	H[c]
SO_3^{-2}	2.57	9.00
HS^-	2.60	8.70
CN^-	2.79	10.88
S^{-2}	3.08	14.66

[a] Values from R. E. Davis, "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp. 189–238; see pp. 204 and 217. [b] ϵ + 2.60 v. for $2X^{-n} \rightleftharpoons X_2^{-2n+2} + 2e^-$. [c] $H = pK_a + 1.74$ for $X^{-n} + H^+ \rightleftharpoons HX^{-n+1}$.

Since hydrosulfide ion is a good thiophile we could predict, using the oxibase scale and the bond energy concepts, that the activation energy for sulfur–sulfur bond cleavage would also follow the r^{-3} equation.

$$HS^- + RS\text{—}SR \longrightarrow HSSR + {}^-SR \qquad (8)$$

$$E_a = \frac{C}{r_{SS}{}^3}$$

The similar E and H values of the ions listed in Table IX would suggest similar thiophilic mechanisms. For example thiosulfate will react with both cyanide ion and sulfite ion (data of Table I).

$$NC^- + S\text{—}SO_3^{-2} \longrightarrow NCS^- + SO_3^{-2}$$

$${}^{-2}O_3S + S\text{—}\overset{*}{S}O_3^{-2} \longrightarrow {}^{-2}O_3SS + \overset{*}{S}O_3^{-2}$$

and the oxibase equations[1] can be written at 25°

$$\log \frac{k_{CN^-}}{k_{H_2O}} = 2.79\alpha + 10.88\beta$$

$$\log \frac{k_{SO_3^{-2}}}{k_{H_2O}} = 2.57\alpha + 9.08\beta$$

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(24) P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, 80, 2513 (1958).

or

$$\log \frac{k_{CN^-}}{k_{SO_3^{-2}}} = 0.22\alpha + 1.88\beta$$

then

$$\log \frac{k_{SH^-}}{k_{SO_3^{-2}}} = 0.03\alpha - 0.30\beta$$

This equation predicts (1) that the rate of reaction of hydrosulfide ion would be within an order of magnitude or so within the sulfite rate and (2) that the mechanism of the thio sulfur exchange would be

$$HS^- + \overset{*}{S}{-}SO_3^{-2} \xrightarrow{\text{slow}} HS\overset{*}{S}^- + SO_3^{-2}$$

$$HS\overset{*}{S}^- \rightleftharpoons {}^-S\overset{*}{S}H$$

$$H\overset{*}{S}S^- + SO_3^{-2} \longrightarrow H\overset{*}{S}^- + SSO_3^{-2}$$

Presently, Pryor[25] is studing the ratio-sulfur exchange reaction with sulfide and thiosulfate and predictions 1 and 2 are borne out by his results.

Reactions Not Obeying Eq. 4. One system was known at the time of our earlier investigations that did not fit the inverse cubic relationship 4, the reaction of cyanide ion with the amino acid disulfide, cystine. Yet the reaction of cystine and sulfite ion has an activation energy which fits the inverse cubic relationship 4c. Either the cyanide datum with cystine was in error *or* another type of mechanism is operative. In the next paper (paper IX) in this series[26] the cyanide–cystine reaction is considered in greater detail. A different mechanism is operative.

In another paper[27] the reaction of cyanide ion with tetramethylthiuram disulfide was studied in methanol. Using the activation energy in methanol and the $Er^3 = 99$ relationship (which is only for water solution at 25°), a sulfur–sulfur bond length of 2.12 ± 0.04 Å. was suggested. Foss[28] has obtained a preliminary X-ray value of 2.03 Å. It was thought at the time[27] that water and methanol are so similiar that the Er^3 relationship ought have nearly the same value in both solvents. Apparently this is not true. Examination of our Table I in that paper[27] does show that the activation energy increases somewhat as water is added to the methanol. We did not have enough data to extrapolate to pure water. The system is under reinvestigation.

Experimental Section

All numeral calculations were done on a Royal McBee RPC-4000 digital computer using the PINT (*P*urdue *Int*erpreter) method of programming. The assistance of Mr. S. P. Molnar and Mr. R. Yantis is appreciated.

Kinetics. Potassium cyanide solutions were freshly prepared from freshly opened bottles and titrated against silver nitrate.[24] Potassium trithionate solutions were prepared and used within a few hours.

The optical density was recorded at 230, 250, and 270 mμ in several sets of experiments on the cyanide–trithionate reaction depending upon the concentration of reagents. Both 1.00- and 10.00-cm. cells were used with both a Cary Model 14 and a Beckman DU spectrophotometer. The Beckman cell compartment was thermostated[24] to ±0.02° or better by circulating water. The Cary cell compartment was also thermostated but not as effectively. The 10-cm. cells and the two solutions were prethermostated in a constant temperature bath and then mixed.

Sodium disulfide was prepared by dissolving a ratio of 1 g.-atom of sulfur to 1 mole of sodium sulfide in a minimum amount of water and stirring under nitrogen in total darkness. The sample was then diluted, thermostated, and then allowed to react with cyanide.

The reaction of potassium cyanide with sodium disulfide was studied at 370 mμ in distilled and then deionized water using 1.00-cm. quartz cells in the Beckman DU spectrophotometer.

The second-order rate constants and standard deviations were calculated from the raw data using the RPC digital computer using the method of least squares.

Materials. Potassium trithionate was recrystallized three times from a small volume of aqueous methanol or ethanol. The material was dried *in vacuo.* Oxidation with hydrogen peroxide formed sulfate which has determined as barium sulfate. *Anal.* Calcd.: 35.77. Found: 35.53, 35.56, 35.59.

The potassium cyanide solutions were prepared, analyzed by titration with silver nitrate, and used within a few hours. Conductivity water was used as the solvent in all experiments. Aqueous buffer solutions of phosphate, borate, and carbonate were used to vary the pH from 9 to 11. Various salts, as sodium and potassium chloride, were used to vary the ionic strength.

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(25) J. E. Ciuffarin and W. A. Pryor, *J. Am. Chem. Soc.*, **86,** 3621 (1964); W. A. Pryor, personal communications, 1963–1965.

(26) E. S. Wagner and R. E. Davis, **88,** 7 (1966).

(27) R. E. Davis and A. Cohen, *ibid.*, **86,** 440 (1964).

(28) O. Foss and K. Maroy, private communications, June 1965.