The hydrolysis of any of the previously described perfluorinated hypochlorites would lead to relatively unstable alcohols which would rapidly decompose to carbonyl compounds and HF. These would not then be readily distinguishable from the products evolving in other decomposition modes.

Qualitatively, based on extensive handling experience, it seems that the ease of hydrolysis may be related to the degree of fluorine substitution and is given by the series: $(CF_3)_3COCl > CH_3C(CF_3)_2OCl \sim (CF_3)_2CHOCl > CF_3CH_2OCl \gg (CH_3)_3COCl$.

The ease of carbon monoxide and sulfur dioxide insertion appears to follow the same order as the ease of hydrolysis. Thus, $(CF_3)_3COCl$ readily reacts with carbon monoxide to produce $(CF_3)_3COC(O)Cl$, whereas $(CH_3)_3COCl$ does not. Once again the other new hypochlorites appear to be intermediate in reactivity but much more closely related to $(CF_3)_3COCl$ than $(CH_3)_3COCl$.

The boiling points of the new hypochlorites were not determined owing to the difficulties encountered in trying to isolate and maintain them completely free of their parent alcohols. However, as judged by their behavior during vacuum line fractionation, the volatilities of the hypochlorites appear to be quite close to those of the parent alcohols. This is to be expected since the decrease in hydrogen bonding in going from the alcohol to the hypochlorite will be largely compensated by the increased molecular weight of the resulting hypochlorite.

The new hypochlorites show no tendency to decompose spontaneously at room temperature and are stable to at least 80°. They are probably less stable than CF_3OCl but definitely are much less susceptible to irreversible fragmentation than the other hypochlorites we have described previously. When they do decompose thermally, the products are those which would be predicted by analogy with the scheme already described.[1] As an example, the products of the decomposition of $(CF_3)_3COCl$ are $(CF_3)_2CO$, Cl_2, CF_3Cl, and C_2F_6.

The thermal decomposition of $CH_3C(CF_3)_2OCl$ is a little unusual in that the resulting products are always $CF_3C(O)CH_3$ and CF_3Cl, never $(CF_3)_2CO$ and CH_3Cl.

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Nucleophilic Substitution at Sulfur. Kinetics of Displacement Reactions Involving Trithionate Ion

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Abstract: The kinetics of substitution reactions of trithionate ion, $S_3O_6^{2-}$, have been studied spectrophotometrically in 50 wt % methanol-water at 20.4° and 0.137 *M* ionic strength. For each of the four nucleophiles examined, a rate law of the form $-d[Nu]/dt = k_2[S_3O_6^{2-}][Nu]$ was obtained. It was found that nucleophilic reactivity decreases in the series thioethoxide > thiophenoxide > triphenylphosphine > cyanide. Mechanisms have been formulated which involve substitution at the bridge sulfur with consequent displacement of sulfite ion. The relative reactivities are discussed in terms of the HSAB principle. It is concluded that divalent sulfur in trithionate is a soft-acid center which responds principally to polarizability of the nucleophile, with basicity playing a secondary role.

Nucleophilic substitution at sulfur is a current subject of considerable interest.[1-6] An understanding of the factors which influence reactivity at sulfur centers has been hampered by a lack of quantitative rate data which relate to a single center. We have undertaken an examination of substitution reactions of trithionate ion in an attempt to provide such data for an inorganic sulfur center. The substitution in eq 1 was selected as a generalized model involving

$$Nu + {}^-O_3SS\text{-}SO_3^- \longrightarrow NuSSO_3 + SO_3^{2-} \qquad (1)$$

displacement at the divalent, bridge-sulfur atom of a single leaving group, sulfite ion.

According to the HSAB principle,[7] divalent sulfur is described as being a soft-electrophilic center. Based on a general evaluation of factors which determine nucleophilic reactivity, Edwards and Pearson[8] have suggested that soft, highly polarizable nucleophiles should react especially well at such a center. Qualitative reactivity series for divalent sulfur are in accord with this idea, and suggest also that basicity in the nucleophile is of some importance.[1,5] Recently, Kice and coworkers[4,9] have reported very interesting, quantitative data relative to reactivity at sulfenyl and sulfinyl sulfur centers which also support the HSAB predictions. Previous kinetic studies of trithionate reactions have been limited to cyanide,[10] sulfite,[11] and thiosulfate[12,13]

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as nucleophiles. In this paper we report results for cyanide and three additional nucleophiles in 50 wt % methanol–water.

Experimental Section

Reagents. Potassium trithionate was prepared by the method of Palmer.[14] The crude product was recrystallized from ethanol–water (*ca.* 50%) and vacuum dried over P_2O_5. The final product was 98.7 (±1%) pure, as determined by iodate oxidation, and 99.4% pure, as determined by ignition to constant weight.[14] Aldrich practical grade thiophenol was distilled twice at 50 Torr in a nitrogen atmosphere and stored under nitrogen in the absence of light. Matheson Coleman and Bell practical grade ethanethiol was distilled twice through a 12-in. Vigreux column and used immediately. A purity >99.9% was established by glpc analysis. Matheson Coleman and Bell purified triphenylphosphine was twice recrystallized from methanol–water (*ca.* 50%) and vacuum dried over P_2O_5. Reagent grade Baker and Adamson KCN, $KHCO_3$, and K_2CO_3 were used after drying over P_2O_5. The purity of the KCN was found to be >99% by silver nitrate analysis.

Kinetic Measurements. The reactions of thiophenoxide, thioethoxide, and triphenylphosphine were followed at 260 nm and cyanide at 270 nm using a Beckman Model DU spectrophotometer. All runs were made in 50 wt % methanol–water solvent, prepared from Baker and Adamson absolute methanol. Prior to use, the solvent was boiled and then flushed with prepurified nitrogen while cooling to room temperature in order to remove oxygen. All solutions were used shortly after preparation and were handled under nitrogen. The potassium salts were dissolved in redistilled water, followed by addition of methanol, whereas C_6H_5SH, C_2H_5SH, and $(C_6H_5)_3P$ were dissolved in methanol first. Separate solutions of the nucleophile and trithionate were thermostated at the reaction temperature and then appropriate amounts of each were mixed and transferred to a 1-cm glass-stoppered silica cell. The cells were mounted in a holder thermostated to within ±0.03° of the desired temperature.

A 1:1 mole ratio bicarbonate–carbonate buffer system was used for the thiophenoxide–, cyanide–, and triphenylphosphine–trithionate reactions. Complete conversion of thiophenol to the anion form was verified by observing that the molar absorption coefficient reached a limiting value of ϵ_{260} 1.30 × 10^4 M^{-1} cm^{-1} in a 1:1 carbonate buffer. The free cyanide concentration was estimated from the pH of the carbonate buffer ($[CN^-] \cong 0.97 \cdot [CN^-]_T$). The thioethoxide–trithionate studies were carried out in 0.0667–0.133 *M* NaOH, converting ethanethiol to the anion form as judged by the limiting value of $\epsilon_{260} \simeq 450$ M^{-1} cm^{-1}. $K_2S_3O_6$ is only moderately stable in these highly basic solutions. Although a solution of $K_2S_3O_6$ in 0.1 *M* NaOH showed no change in absorbance over a time interval equal to two half-lives for the $C_2H_5S^-$ reaction, considerable decomposition was observed after 3–4 hr. Blank solutions of the nucleophiles in the buffer solution were stable for the duration of the kinetic runs.

Results

Thiophenoxide–Trithionate Reaction. The stoichiometry of the thiophenoxide–trithionate reaction was found to depend on the concentration of sulfite ion. In the presence of added SO_3^{2-}, S-phenylthiosulfate ion was the product observed.

$$C_6H_5S^- + S_3O_6^{2-} \longrightarrow C_6H_5S\text{-}SO_3^- + S_2O_3^{2-} \qquad (2)$$

In the absence of SO_3^{2-} (removal with HCHO), the product observed was diphenyl disulfide.

$$2C_6H_5S^- + S_3O_6^{2-} \longrightarrow C_6H_5SSC_6H_5 + SO_3^{2-} + S_2O_3^{2-} \qquad (3)$$

Except as noted below, all of the kinetic studies were carried out in the presence of added SO_3^{2-}, corresponding to the consumption of 1 mol of $C_6H_5S^-$ per mole of $S_3O_6^{2-}$.

The stoichiometry in eq 2 was verified by iodimetric analysis. With $[S_3O_6^{2-}] = 1.14 \times 10^{-2}$ *M*, $[C_6H_5S^-] = 6.0 \times 10^{-3}$ *M*, and $[SO_3^{2-}] = 1 \times 10^{-3}$ *M*, 1.06 mol of $S_2O_3^{2-}$ per mole of $C_6H_5S^-$ was produced. In the kinetic runs, infinite-time absorbances were in good agreement (±2.5%) with values predicted from the known molar absorption coefficient of S-phenylthiosulfate, $\epsilon_{260}(C_6H_5S\text{-}SO_3^-)$ 1500 M^{-1} cm^{-1}.[15] There was no evidence for the production of diphenyl disulfide under these conditions in which $[S_3O_6^{2-}] > [C_6H_5S^-]$. However, when the initial conditions are such that $[C_6H_5S^-] > [S_3O_6^{2-}]$, some $C_6H_5SSC_6H_5$ (mp 61°) was observed. Addition of formaldehyde greatly increased the yield of the disulfide due to removal of sulfite to form hydroxymethanesulfonate.[13]

The absence of the disulfide product in the presence of sulfite is not surprising since it is known that SO_3^{2-} reacts with disulfides as shown in eq 4.[16] We have

$$C_6H_5SSC_6H_5 + SO_3^{2-} \rightleftharpoons C_6H_5S\text{-}SO_3^- + C_6H_5S^- \qquad (4)$$

found that the rate constant for the forward reaction in eq 4 (5.2 M^{-1} sec^{-1}) is approximately 300 times greater than the rate constant for reaction of $C_6H_5S^-$ with $S_3O_6^{2-}$ (*vide infra*).

The kinetics of the thiophenoxide–trithionate reaction were studied with $[S_3O_6^{2-}]_0 \gg [C_6H_5S^-]_0$. The reaction was presumed to be overall second-order and all data have been analyzed using eq 5. In a preliminary run with $[C_6H_5S^-]_0 = 5.85 \times 10^{-5}$ *M*, $[S_3O_6^{2-}]_0 = 1.05 \times 10^{-2}$ *M*, and no added SO_3^{2-}, a plot of log $(A - A_\infty)$ *vs.* *t* was nonlinear, the slope decreasing significantly after 40% completion. A value of $k_2 = 3.3\ (\pm 0.2) \times 10^{-2}$ M^{-1} sec^{-1} was obtained using eq 5 and the time-zero limiting slope from the above plot. It was found that initial addition of sulfite ion reduced the amount of curvature in the log plots and that for $[SO_3^{2-}]_0 > 2.5 \times 10^{-4}$ *M*, the curvature was eliminated entirely. As shown in Table I, the second-order rate constants obtained were independent of the concentration of added SO_3^{2-} in the range $(0.50\text{–}7.1) \times 10^{-3}$ *M*, thus ruling out the possibility of an inverse rate-

$$-d[C_6H_5S^-]/dt = k_2[C_6H_5S^-][S_3O_6^{2-}] \qquad (5)$$

Table I. Kinetic Data for the Thiophenoxide–Trithionate Reaction at 20.4° and $\mu = 0.069$ *M*[a]

$10^2[S_3O_6^{2-}]_0$, *M*	$10^3[SO_3^{2-}]_0$, *M*	10^2k_2, M^{-1} sec^{-1}
0.498	0.518	1.66
0.501	0.518	1.69
0.500	0.543	1.60
1.05	0.500	1.59
1.05	1.12	1.60
1.05	1.12	1.63
1.05	4.06	1.62
1.05	5.00	1.56
1.04	7.10	1.58
1.40	1.40	1.63
1.40	1.57	1.51
1.40	1.74	1.51
		Av 1.60 (±0.09)
1.05	1.56	2.71[b]
0.500	0.594	2.79[b]

[a] $[C_6H_5S^-]_0 = 5.85 \times 10^{-5}$ *M*. [b] Ionic strength 0.137 *M*.

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(16) H. Distler, *Angew. Chem., Intern. Ed. Engl.*, **6**, 544 (1967).

dependence on sulfite. The observed rates are independent of the concentration of added thiosulfate as well.

A first-order dependence on trithionate was established by varying $[S_3O_6^{2-}]_0$ in the range (0.50–1.40) $\times 10^{-2}$ M as shown in Table I. (All rate data reported were obtained under conditions in which $[SO_3^{2-}]_0 \geq 5.0 \times 10^{-4}$ M.) At 20.4° and $\mu = 0.069$ M, an average value of $k_2 = 1.60\ (\pm 0.09) \times 10^{-2}$ M^{-1} sec^{-1} was obtained. It should be noted that this value is one-half that obtained from the limiting slope in the curved $\log (A - A_\infty)$ *vs.* t plot. To further characterize the effect of SO_3^{2-}, a run was made in which $[C_6H_5S^-]_0 = 5.85 \times 10^{-5}$ M, $[S_3O_6^{2-}]_0 = 1.05 \times 10^{-2}$ M, and $[HCHO]_0 = 0.04$ M. A plot of $\log (A - A_\infty)$ *vs.* t was linear for two half-lives with a corresponding value of $k_2 = 3.4\ (\pm 0.3) \times 10^{-2}$ M^{-1} sec^{-1}. Thus, under conditions where sulfite is absent (initial stage of the reaction, or with added HCHO), the second-order rate constant is larger by a factor of 2 than it is under conditions in which sulfite is present. We have ruled out the possibility that the greater rate arises from the presence of a tetrathionate impurity in the trithionate. (Qualitative studies have shown that $C_6H_5S^-$ reacts much more rapidly with $S_4O_6^{2-}$ that with $S_3O_6^{2-}$.) The linearity of the first-order plot for the run with added formaldehyde makes it unlikely that $C_6H_5S^-$ is actually reacting with a dilute impurity species, the concentration of which would be comparable with that of $C_6H_5S^-$.

The temperature dependence of k_2 was determined at $\mu = 0.069$ M. At 10.4°, an average value (based on four independent runs) of $k_2 = 0.92\ (\pm 0.04) \times 10^{-2}$ M^{-1} sec^{-1} was obtained. At 29.8°, an average value (based on seven independent runs) of $k_2 = 2.8\ (\pm 0.2) \times 10^{-2}$ M^{-1} sec^{-1} was obtained. Activation parameters, calculated from the equation $\ln (k_2/T) = \ln (k/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$, are reported in Table V.

Thioethoxide–Trithionate Reaction. The stoichiometry of the thioethoxide–trithionate reaction was found to be

$$2C_2H_5S^- + S_3O_6^{2-} \longrightarrow C_2H_5SSC_2H_5 + SO_3^{2-} + S_2O_3^{2-} \quad (6)$$

In a typical experiment involving $[S_3O_6^{2-}] = 1.5 \times 10^{-2}$ M, $[C_2H_5S^-] = 2.46 \times 10^{-2}$ M, and $[OH^-] = 0.10$ M, iodimetric analysis showed that, within 2%, the equivalent of 1 mol of SO_3^{2-} and 1 mol of $S_2O_3^{2-}$ had been produced from 2 mol of $C_2H_5S^-$. A glpc analysis of an ether extract of the product solution showed the presence of a single, volatile component with a retention time equal to that of a known sample of diethyl disulfide. The yield of $C_2H_5SSC_2H_5$ was approximately 95%.

The kinetics of the thioethoxide–trithionate reaction were measured by following the change in absorbance at 260 nm with $[C_2H_5S^-]_0 \sim [S_3O_6^{2-}]_0$. At this wavelength most of the change in absorbance arises from the conversion of $C_2H_5S^-$ (ϵ_{260} 4.5×10^2 M^{-1} cm^{-1}) to $C_2H_5SSC_2H_5$ (ϵ_{260} 4.0×10^2 M^{-1} cm^{-1}). The reaction was found to obey the rate law

$$-d[C_2H_5S^-]/dt = k_2[S_3O_6^{2-}][C_2H_5S^-] \quad (7)$$

based on the linearity (to >75% conversion of $C_2H_5S^-$) observed for plots of $\ln ([S_3O_6^{2-}]/[C_2H_5S^-])$ *vs.* t. Kinetic data obtained at 20.4° and 0.069 or 0.137 M ionic strength are shown in Table II. For runs at other temperatures, the average values of the second-order rate constants obtained at $\mu = 0.137$ M were: 1.00 (±0.05) M^{-1} sec^{-1} at 10.4°, 1.73 (±0.03) at 25.2°, and 2.17 (±0.05) at 29.8°. The corresponding activation parameters are reported in Table V.

Table II. Kinetic Data for the Thioethoxide–Trithionate Reaction at 20.4°

$[OH^-]_0$, M	$10^3[C_2H_5S^-]_0$, M	$10^3[S_3O_6^{2-}]_0$, M	k_2, M^{-1} sec^{-1}
	$\mu = 0.069$ M		
0.0667	0.667	1.01	0.84
0.0667	0.763	1.00	0.80
0.0667	0.785	0.495	0.85
0.0667	1.27	1.01	0.86
0.0667	1.32	1.01	0.84
0.0667	1.46	1.02	0.89
0.0667	1.52	1.02	0.86
			Av 0.85 (±0.04)
	$\mu = 0.137$ M		
0.133	0.700	0.965	1.55
0.133	1.52	1.02	1.41
0.133	1.54	1.01	1.46
0.0667	1.22	1.01	1.50
			Av 1.48 (±0.07)

Triphenylphosphine–Trithionate Reaction. Iodimetric analysis of the products of the triphenylphosphine–trithionate reaction confirmed the stoichiometry in eq 8. With $[S_3O_6^{2-}] = 1.7 \times 10^{-2}$ M and $[(C_6H_5)_3P] = 3.0 \times 10^{-3}$ M in a HCO_3^-–CO_3^{2-} buffer, 1 mol (±2%) of SO_3^{2-} per mole of $(C_6H_5)_3P$ was produced. After removal of methanol from the solvent mixture, triphenylphosphine sulfide was recovered in 93% yield. Its melting point (157°) and ir spectrum in carbon disulfide[17] were identical with values reported for the known compound.

$$(C_6H_5)_3P + S_3O_6^{2-} + H_2O \longrightarrow (C_6H_5)_3PS + SO_3^{2-} + SO_4^{2-} + 2H^+ \quad (8)$$

The rate of the triphenylphosphine–trithionate reaction was measured in solutions containing $S_3O_6^{2-}$ in large excess over $(C_6H_5)_3P$. Using absorbance data at 260 nm, plots of $\ln (A - A_\infty)$ *vs.* t were linear for the extent of the reaction covered (one–three half-lives). Variation of the initial excess trithionate concentration revealed a first-order dependence on $S_3O_6^{2-}$, establishing the rate law

$$-d[(C_6H_5)_3P]/dt = k_2[S_3O_6^{2-}][(C_6H_5)_3P] \quad (9)$$

The values of k_2 at 20.4° and $\mu = 0.069$ and 0.137 M are summarized in Table III. Addition of sulfite ion or removal with formaldehyde of sulfite produced in the reaction had no effect on the k_2 values. An increase in ionic strength from 0.069 to 0.137 M resulted in a modest increase in rate for this ion–dipolar molecule reaction. However, the rate enhancement was much less than that observed for the ion–ion reactions, as expected (*cf.* Tables I and II).

The temperature dependence of k_2 was determined at $\mu = 0.069$ M. At 10.4°, an average value (based on four independent runs) of $k_2 = 3.87\ (\pm 0.1) \times 10^{-3}$ M^{-1} sec^{-1} was obtained. At 29.8°, an average value (based on four independent runs) of $k_2 = 9.07\ (\pm 0.15)$

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[17] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, Inc., New York, N. Y., 1964, p 402.

Table III. Kinetic Data for the Reaction of Triphenylphosphine and Trithionate at 20.4°

$10^5[(C_6H_5)_3P]_0$, M	$10^2[S_3O_6^{2-}]_0$, M	10^3k_2, M^{-1} sec^{-1}
	$\mu = 0.069\ M$	
5.30	1.90	6.13
5.30	1.50	5.98
5.30	1.50	5.95
5.30	1.05	5.99
5.37	1.05	6.03
5.30	0.513	6.05
5.37	0.502	6.36
		Av 6.1 (±0.3)
	$\mu = 0.137\ M$	
5.37	0.500	7.12
5.37	1.05	7.13
		Av 7.1 (±0.3)

$\times\ 10^{-3}\ M^{-1}$ sec^{-1} was obtained. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table V.

Cyanide–Trithionate Reaction. The stoichiometry

$$CN^- + S_3O_6^{2-} + H_2O \longrightarrow SCN^- + SO_3^{2-} + SO_4^{2-} + 2H^+ \quad (10)$$

of the cyanide–trithionate reaction has been reported previously.[10,18] The reaction was followed at 270 nm with $\epsilon(S_3O_6^{2-})$ 13.9, $\epsilon(CN^-)$ 1.4, $\epsilon(SCN^-)$ 0.85, and $\epsilon(SO_3^{2-})$ 0.9 M^{-1} cm^{-1}. Experimental values of A_∞ were in reasonable agreement with ones calculated from these absorption coefficients. Because the reaction was very slow, only a few kinetic runs were made. Trithionate is subject to hydrolysis in highly basic solution. However, trithionate blank solutions in carbonate–bicarbonate buffers were stable for 3–4 days. A rate law of the form

$$-d[CN^-]/dt = k_2[S_3O_6^{2-}][CN^-] \quad (11)$$

was assumed. Plots either of $(A_0 - A_\infty)/(A - A_\infty)$ or $\ln([S_3O_6^{2-}]/[CN^-])$ *vs.* t were linear for the extent of reaction examined (*ca.* one half-life). The data are summarized in Table IV.

Table IV. Kinetic Data for the Cyanide–Trithionate Reaction at 20.4° in 50 Wt % Methanol–Water, $[S_3O_6^{2-}]_0 = 2.00 \times 10^{-2}\ M$

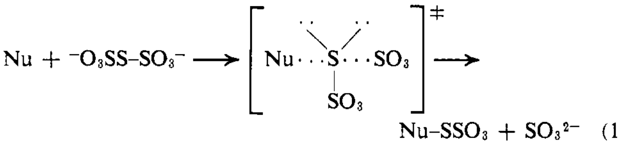
$10^2[CN^-]_0$, M^a	$[CO_3^{2-}] = [HCO_3^-]$, M	μ, M	10^4k_2, M^{-1} sec^{-1}
1.98	0.013	0.137	5.0 (±0.5)
1.44	0.0157	0.137	5.1 (±0.5)
2.00	0.0200	0.160	6.6 (±0.6)
2.00	0.0200	0.147	45 (±3)^b

^{a} Free [CN$^-$] allowing for approximately 3% hydrolysis of total cyanide. ^{b} In water.

The second-order rate constant obtained in 50 wt % CH_3OH-H_2O, $k_2 = 5.0 \times 10^{-4}\ M^{-1}$ sec^{-1} ($\mu = 0.137$), is an order of magnitude smaller than the same constant obtained by us in water, $k_2 = 45 \times 10^{-4}\ M^{-1}$ sec^{-1} ($\mu = 0.147$). A solvent effect of this nature is anticipated from the difference in dielectric constants involved.[19] The k_2 values reported by Davis, *et al.*,[10] are considerably larger. For example, at 20.9° and $\mu = 0.1$ in water, $k_2 = 0.26\ M^{-1}$ sec^{-1}.[10] The discrepancy is such that it seems unlikely that both results apply to the reaction in eq 10. We are unable to explain this difference. However, based on the chemical analyses performed and the stoichiometric results obtained with the other nucleophiles, we believe that our results were obtained with reliably pure samples of $K_2S_3O_6$.

Discussion

As a general model, we propose that each of the four systems studied proceeds *via* a direct, bimolecular nucleophilic displacement on the bridge sulfur in trithionate (eq 12). The second-order rate law obtained

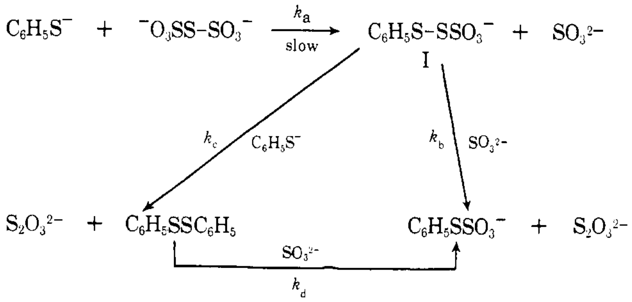


(12)

for each reaction is consistent with this proposal. Of the two potential sites for nucleophilic attack, the bridge (sulfenyl) sulfur is far more reactive than is the end (sulfonate) sulfur.[2,21,22] Sulfonate sulfur is subject to attack only by hydroxide ion or other hard bases.

Thiophenoxide Mechanism. The overall mechanism suggested is shown in Chart I. The k_a step is rate determining and is not significantly reversible since (i) there is no rate dependence on SO_3^{2-} concentration, and (ii) there is no evidence for a greater than first-order dependence on $C_6H_5S^-$. Thus, k_2(obsd) = k_a. Intermediate I is subject to attack either by thiophenoxide or by sulfite. The site of attack is very likely to be the sulfur atom farthest removed from the negatively charged sulfonate group in I.[2,22] In the presence of added sulfite ion, the k_b path is favored on the basis of $[SO_3^{2-}] \gg [C_6H_5S^-]$. However, the greater sulfur nucleophilicity of $C_6H_5S^-$ (*vide infra*) and a lower charge type favor the k_c path. If diphenyl disulfide were produced *via* the k_c path, it would be converted very rapidly by SO_3^{2-} to the S-phenylthiosulfate product. Therefore, regardless of which path is taken, the net change is that expressed by eq 2.

Chart I. Thiophenoxide–Trithionate Mechanism



Added formaldehyde eliminates the k_b and k_d paths, leading to diphenyl disulfide as the observed product (eq 3). Since two $C_6H_5S^-$ are consumed in the k_c step, but only one in the k_b step, the rate of disappearance of

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(18) "Gmelins Handbuch der Anorganischen Chemie," E. Pietsch, Ed., 8 Auflage, Teil B2, "Sulfur," Verlag Chemie, Weinheim, 1960, p 990.

(19) The dielectric effect can be estimated qualitatively using the equation $\ln(k/k_{D=\infty}) = -z_Az_Be^2/kTrD$ (ref 20) in which D is the dielectric constant of the medium and r is the distance between ions A and B in the activated complex. Assuming $r = 2.15$ Å (approximated by comparison with the S–S bond length in $S_3O_6^{2-}$, 2.15 Å), $\log(k_{H_2O}/k_{CH_3OH-H_2O}) \sim 1.0$ at 20°. Because of the uncertainties in applying the equation above, the result has only order-of-magnitude significance.

(20) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, Inc., New York, N. Y., 1966, p 4.

(21) A. Fava and A. Illiceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958).

(22) O. Foss, *Acta Chem. Scand.* **12**, 959 (1958).

$C_6H_5S^-$ is twice as great in the presence of added formaldehyde as it is in the presence of added sulfite. When neither SO_3^{2-} nor HCHO is added, the reaction proceeds at first *via* the k_c path. Thus, the *initial* k_2 value is $3.3 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$, which is essentially the same as the second-order rate constant obtained with added HCHO, $k_2 = 3.4 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. As the reaction proceeds, the sulfite ion concentration increases and the reaction stoichiometry changes from eq 3 to eq 2, resulting in a decrease in the observed k_2 value. When sulfite is added, $k_2 = 1.60 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ over the entire range of reaction. Presumably, it is this value of k_2 (obsd) which corresponds to the rate-determining conversion of 1 mol of $S_3O_6^{2-}$.

Thioethoxide Mechanism. Under the kinetic conditions employed ($[S_3O_6^{2-}]_0 \sim [C_2H_5S^-]_0$), the stoichiometry is that expressed by eq 6. The simplest mechanism in accord with this stoichiometry and the rate law is

$$C_2H_5S^- + {}^-O_3SS\text{–}SO_3^- \xrightarrow[\text{slow}]{k_a} C_2H_5S\text{–}SSO_3^- + SO_3^{2-} \qquad (13)$$

$$C_2H_5S\text{–}SSO_3^- + C_2H_5S^- \xrightarrow{k_c} C_2H_5SSC_2H_5 + S_2O_3^{2-} \qquad (14)$$

for which $k_2(\text{obsd}) = k_a$.

Triphenylphosphine Mechanism. The following mechanism is proposed for the triphenylphosphine–trithionate reaction.

$$(C_6H_5)_3P + {}^-O_3SS\text{–}SO_3^- \xrightarrow[\text{slow}]{k_a} (C_6H_5)_3P^+SSO_3^- + SO_3^{2-} \qquad (15)$$

$$(C_6H_5)_3P^+SSO_3^- + H_2O \xrightarrow{k_b} (C_6H_5)_3PS + SO_4^{2-} + 2H^+ \qquad (16)$$

The reverse of the k_a step is much less important than reaction 16 since neither addition of sulfite nor its removal by formaldehyde has any effect on the rate. In the basic solutions involved, reaction 16 probably involves OH^- attack on sulfonate sulfur in the intermediate. However, OH^- does not participate in the slow step, so that $k_2(\text{obsd}) = k_a$. Initial attack of $(C_6H_5)_3P$ on the end (sulfonate) sulfur can be ruled out for this reaction since $S_2O_3^{2-}$ is not observed as a product. In addition, the $(C_6H_5)_3P\text{–}SO_3$ species produced would be expected to hydrolyze to $(C_6H_5)_3P$ and SO_4^{2-}. The absorbance changes observed are not consistent with regeneration of triphenylphosphine.

Cyanide Mechanism. The following mechanism has been proposed.[10]

$$CN^- + {}^-O_3SS\text{–}SO_3^- \xrightarrow[\text{slow}]{k_a} SO_3^{2-} + {}^-O_3S\text{–}SCN \qquad (17)$$

$${}^-O_3S\text{–}SCN + H_2O \xrightarrow{k_b} SCN^- + SO_4^{2-} + 2H^+ \qquad (18)$$

End attack of CN^- on $S_3O_6^{2-}$ can be ruled out as there would be no reasonable way in which to explain the appearance of SCN^- as a product.

Comparison of Nucleophilic Reactivities. There is reasonable evidence that each of the reactions above involves rate-determining substitution at the bridge sulfur in trithionate. A quantitative measure of sulfur nucleophilicity at divalent sulfur can be obtained by a comparison of the second-order rate constants observed. The kinetic data, including activation parameters, are summarized in Table V. Since the reactions[11–13] in aqueous solution, eq 19 and 20, have beens hown to

$$^*SO_3^{2-} + {}^-O_3SS\text{–}SO_3^- \longrightarrow SO_3^{2-} + {}^-O_3SS\text{–}^*SO_3^- \qquad (19)$$

$$^*SSO_3^{2-} + {}^-O_3SS\text{–}SO_3^- \longrightarrow S_2O_3^{2-} + {}^-O_3S^*SSO_3^- \qquad (20)$$

proceed *via* displacement on the bridge sulfur, data for these reactions are included also. (Reaction 20 involves $S_4O_6^{2-}$ as an intermediate which is attacked by SO_3^{2-}, subsequent to the initial, slow step.) Only a range of k_2 values is given for reactions 19 and 20 because of the uncertainty in converting rate data between solvents of different dielectric constant (*cf.* footnote 19). Regardless of the uncertainty in k_2 values for SO_3^{2-} and $S_2O_3^{2-}$, it is clear that the reactivity order is: $C_2H_5S^- > C_6H_5S^- > (C_6H_5)_3P > CN^- > SO_3^{2-} > S_2O_3^{2-}$.

Table V. Nucleophilic Reactivity toward Trithionate in 50 Wt % Methanol–Water

Nucleophile	10^3k_2, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$C_2H_5S^-$	740[a,b]	6.3 (±0.3)	−36 (±2)
$C_6H_5S^-$	28[a]	9.4 (±0.3)	−35 (±2)
$(C_6H_5)_3P$	7.1[a]	6.9 (±0.4)	−45 (±2)
CN^-	0.5[a]		
SO_3^{2-}	0.02–0.003[c]	9.5	−43
$S_2O_3^{2-}$	<0.003[d]		

[a] Determined at 20.4° and $\mu = 0.137\ M$. [b] Obtained by dividing the observed value by two, since the observed rate refers to the reaction of two $C_2H_5S^-$ per $S_3O_6^{2-}$. [c] Estimated (range) k_2 value at 20° and $\mu = 0.137\ M$ in 50 wt % $CH_3OH\text{–}H_2O$ from ref 11. [d] Estimated (upper limit) k_2 value at 20° and $\mu = 0.137\ M$ in 50 wt % $CH_3OH\text{–}H_2O$ from ref 12 and 13.

In HSAB terminology, it appears that the bridge sulfur in trithionate is best described as a soft center. All of the above nucleophiles fall into the soft, polarizable category.[7] Hard bases of low polarizability and high electronegativity, such as OH^- or $(C_2H_5)_3N$, are much less reactive toward trithionate. However, among the soft nucleophiles, those which possess a greater proton basicity display a greater reactivity toward divalent sulfur (Table VI). The correlation is quite rough and, together with the lack of accurate thermodynamic data in methanol–water, precludes any attempt to apply the Edwards equation.[23] Although the Edwards equation (oxibase scale[24]) has been applied successfully for some systems,[23,24] proton basicity appears to be unsuitable for correlating substitution at divalent sulfur. It should be noted that the relative rates found in this study stand in the same order as that given by Parker[25] for equilibrium displacement at divalent sulfur (in 90% $C_2H_5OH\text{–}H_2O$): $C_6H_5S^- > CN^- > OH^- > SO_3^{2-} > S_2O_3^{2-}$.

Table VI. Basicity and E_n Values of Nucleophiles

	$C_2H_5S^-$	$C_6H_5S^-$	$(C_6H_5)_3P$	CN^-	SO_3^{2-}	$S_2O_3^{2-}$
pK_a[a]	10.6	7.5		9.3	7.3	1.9
E_n[b]		2.9		2.79	2.57	2.52

[a] Of the conjugate acid in H_2O at 25°. [b] $E_n = E° + 2.60$ V for $2Nu^- \rightleftharpoons Nu_2 + 2e^-$ in the Edwards equation, $\log (k/k_0) = \alpha E_n + \beta H$.

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[23] J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

[24] R. E. Davis, "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press, Inc., New York, N. Y., 1964, p 189.

[25] A. J. Parker, *Acta Chem. Scand.*, **16**, 855 (1962).

Table VII. A Comparison of Nucleophilic Reactivity at Divalent Sulfur, sp³ Carbon, and Platinum(II)

Values of 10^3k_2, M^{-1} sec^{-1} for nucl	Subst at $S_3O_6{}^{2-}$ (eq 12)[a]	Subst at sp³ carbon (eq 21)[b]	Subst at Pt(II) (eq 22)[b]
$C_2H_5S^-$	740		
$C_6H_5S^-$	28	1070	6,000
$(C_6H_5)_3P$	7.1	1.3	249,000
CN^-	0.5	0.65	4,000
$SO_3{}^{2-}$	0.02–0.003	44	250
$S_2O_3{}^{2-}$	<0.003	114	9,000

[a] See footnotes in Table V. [b] Values at 25° in methanol solvent, from ref 27.

That polarizable nucleophiles react with particular advantage at the bridge sulfur in trithionate is readily understood by considering the effect of the two lone pairs and two bond pairs of electrons present on that center.[8] The electrophilic character of the bridge sulfur resembles that of peroxide oxygen[26] and sulfenyl sulfur.[9] Although polarizability is the dominant factor, basicity is also important, more so, it would appear, than at peroxide oxygen or sulfenyl sulfur. This behavior in trithionate may arise from a greater degree of bond breaking in the transition state, resulting in a greater positive charge on the bridge sulfur.

$$^{-}O_3SS^{\delta+}\cdots SO_3{}^{(1+\delta)-}$$

Thus, nucleophiles which are good proton bases are likely to be more effective in displacing the rather basic $SO_3{}^{2-}$ ion.[7]

It is of interest to compare reactivity at the bridge sulfur in trithionate with that found for substitution at sp³ carbon in methyl iodide (eq 21) and at Pt(II) in *trans*-$Pt(py)_2Cl_2$ (eq 22).[27] Rate data for nucleophiles

$$CH_3I + Nu^- \longrightarrow CH_3Nu + I^- \qquad (21)$$

$$trans\text{-}Pt(py)_2Cl_2 + 2Nu^- \longrightarrow trans\text{-}Pt(py)_2Nu_2 + 2Cl^- \qquad (22)$$

in common are presented in Table VII. The three centers are similar in their general response to polarizability in the nucleophile. However, they clearly do not share any overall order of reactivity. The bridge-sulfur center resembles more closely the medium-soft sp³ carbon than it does the very soft Pt(II). Reactions at divalent sulfur, like those at sp³ carbon, are subject to steric hindrance.[2] Thus, the reactivity of triphenylphosphine at these centers may be considerably reduced (*cf.* triphenylphosphine at platinum). It is surprising that the lower rate for $(C_6H_5)_3P$ appears to arise from an entropy effect (Table V). In comparing reactivities at these three centers, account must be taken of the effect of the difference in charge type. The inherent reactivities of negatively charged nucleophiles, especially those of $SO_3{}^{2-}$ and $S_2O_3{}^{2-}$, are partially masked in reaction with the $S_3O_6{}^{2-}$ ion. The large, negative $\Delta S^{\ddagger}$ values (Table V) indicate the magnitude of this electrostatic effect on the rate.

Acknowledgment. We are grateful to Dr. Brian Saville for stimulating discussions concerning HSAB. This study was supported, in part, by National Science Foundation Grant No. 7981.

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Kinetics of Water Exchange between Solvent and Aquobipyridylnickel(II) Complexes

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Abstract: Water exchange rates with $Ni(H_2O)_6{}^{2+}$, $Ni(H_2O)_4bipy^{2+}$, and $Ni(H_2O)_2(bipy)_2{}^{2+}$ in 10^{-3} *M* HCl are reported. The k_1 (25°, sec^{-1}) values (per H_2O) are 3.2×10^4, 4.9×10^4, and 6.6×10^4, respectively. The corresponding ΔH^* and ΔS^* values are 12.1 ± 0.5, 2.6 ± 2; 12.6 ± 0.5, 5.1 ± 2; and 13.7 ± 0.5, 9.2 ± 4 kcal mol^{-1}, eu. Scalar coupling constants (A/h) in the same order are 2.1×10^7, 1.6×10^7, and 3.8×10^7 cps. A summary of data on $Ni(H_2O)_6{}^{2+}$ is given.

In previous studies[2] on nickel complexes we have reported labilizing effects on water molecules in aquo complexes as a result of substitution of water by various ligands. Rablen and Gordon[3] found that terpyridine substitution, on the contrary, caused only a small change in water exchange rates. We wish to report here studies on 2,2′-bipyridyl complexes of nickel where similarly only a slight change in water exchange behavior occurs.

Experimental Section

The nmr equipment and techniques used have been described.[4] A Varian 24.6-kG magnet was employed and the ^{17}O resonance ordinarily observed at 14.19 MHz.

The water used was obtained from YEDA R and D Co. Ltd., Rehovoth, Israel, and contained *ca.* 7 atom % ^{17}O (normal H content). It was distilled *in vacuo* for reuse. Other reagents were Mallinckrodt AR $Ni(NO_3)_2 \cdot 6H_2O$, HCl, and 2,2′-bipyridyl purified by sublimation or recrystallization from water.

Solutions were prepared from measured amounts of all reagents. Hydrochloric acid was used to give a pH of 2.9 to reduce possible

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(1) This work supported by USAEC contract No. AT(45-1)-2040 and is report No. RLO-2040-17.

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