Perhaloalkyl Hypochlorites and Pentafluorosulfur Hypochlorite. II. Preparation of Perfluoro-*t*-butyl Hypochlorite and Related Compounds

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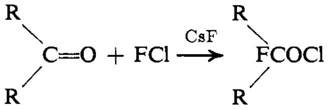
Abstract: The synthesis of the first perfluorinated tertiary alkyl hypochlorite, $(CF_3)_3COCl$, is described along with the new polyfluoroalkyl hypochlorites $CH_3C(CF_3)_2OCl$, $(CF_3)_2CHOCl$, and CF_3CH_2OCl. All were prepared by reaction of the corresponding alcohols with chlorine monofluoride. The new hypochlorites react readily and nearly quantitatively with carbon monoxide and with sulfur dioxide to produce the corresponding chloroformates and chlorosulfates.

We have recently synthesized the first perfluoroalkyl hypochlorites, R_fOCl, and a sulfur analog, SF_5OCl, by the catalytic addition of chlorine monofluoride to the appropriate perfluorinated carbonyl or thionyl compound.[1]



$$F_4S{=}O + FCl \xrightarrow{CsF} F_5SOCl$$

The perhaloalkyl hypochlorites differed significantly from the corresponding fluoroxy compounds in that they underwent facile and characteristic reactions with carbon monoxide or sulfur dioxide to produce chloroformates and chlorosulfates, respectively.[2] Others prepared and reported a few of the hypochlorites and chloroformates somewhat later.[3,4]

Since all of the previous fluoroalkyl hypochlorite syntheses involved addition of the elements of chlorine monofluoride across a carbonyl double bond, they were necessarily restricted to primary and secondary alkyl hypochlorites containing fluorine on the carbon atom bearing the -OCl function (*i.e.*, α fluorine).

In an effort to extend the fluoroalkyl hypochlorite studies to include new members containing no α fluorine, we have examined the reactions of polyfluoroalcohols with chlorine monofluoride. These reactions proceeded smoothly to the desired hypochlorites according to the following equation

$$ROH + ClF \xrightarrow{25^\circ} ROCl + HF$$

where R = $(CF_3)_3C$–, $(CF_3)_2CH$–, $CH_3C(CF_3)_2$–, and CF_3CH_2–.

It is significant that these new compounds extend the hypochlorite series to include not only the first examples of fluorinated tertiary alkyl hypochlorites, but also the first examples of hydrogen-substituted polyfluoroalkyl hypochlorites. As will be shown later, the absence of α fluorine significantly affects the behavior of these hypochlorites, as compared with the earlier members, and often alters the course of subsequent reactions.

These hypochlorites, like their perfluorinated predecessors, readily insert carbon monoxide and sulfur dioxide into the O–Cl bond to produce chloroformates and chlorosulfates.

$$ROCl + CO \longrightarrow ROC(O)Cl$$
$$ROCl + SO_2 \longrightarrow ROSO_2Cl$$

where R = $(CF_3)_3C$–, $(CF_3)_2CH$–, $CH_3C(CF_3)_2$–, and CF_3CH_2–.

The reactions can again be carried out routinely at $-20°$, but in contrast to the earlier work, yields do not suffer at reaction temperatures of 25° or higher.[5]

Experimental Section

Materials and Equipment. Perfluoro-*t*-butyl alcohol and 1,1-bis(trifluoromethyl)ethanol were prepared according to methods described by Filler[6] and Knunyants,[7] respectively. Bis(trifluoromethyl)methanol (Allied Chemical Corporation, Specialty Chemicals Division) and 2,2,2-trifluoroethanol (Matheson Coleman and Bell) were used as received. The *t*-butyl alcohol and *t*-butyl hypochlorite (City Chemical Company) were also used as received.

Vacuum manipulations were carried out in a nickel–Monel system with Kel-F U-traps. Gas-phase infrared spectra were obtained with a Perkin-Elmer Model 137-B or Model 337 spectrophotometer using a Monel infrared cell equipped with silver chloride windows. The ^{19}F nmr spectra were recorded at 56.4 MHz with a Japan Electron Optics Laboratory C60H spectrometer.

Preparation of the Hypochlorites. All the hypochlorites were prepared in essentially the same manner. Standard vacuum techniques were used to combine the parent alcohol (10 mmol) and a slight excess of chlorine monofluoride (13 mmol) in a 75-cc stainless steel cylinder fitted with a stainless steel needle valve. The mixture was then agitated at room temperature for 24 hr on a mechanical shaker. Conventional trap-to-trap fractionation on a metal–Kel-F vacuum line through a $-78°$ cold trap was used to remove HF, the excess ClF, and trace impurities from the desired hypochlorite. In the few cases where some unreacted alcohol remained, a small amount of ClF was reintroduced and agitation was resumed for a short period of time.

It was assumed that the reaction was complete whenever characteristic absorptions associated with the parent alcohol were absent in the infrared spectrum of the rectified hypochlorite.

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(2) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, 723 (1969).

(3) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.*, **91**, 2902 (1969).

(4) C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohz, *ibid.*, **91**, 2907 (1969).

(5) When CF_3OCl and CO are allowed to warm from $-196°$ to 25°, the yield of $CF_3OC(O)Cl$ is only about 30%, the major by-products being FC(O)Cl and carbonyl fluoride. When CF_3OCl and SO_2 are allowed to mix at 25°, the reaction products are FSO_2Cl and carbonyl fluoride, and no CF_3OSO_2Cl is formed.

(6) R. Filler and R. M. Schure, *J. Org. Chem.*, **32**, 1217 (1969).

(7) I. L. Knunyants, *et al.*, *Bull. Acad. Sci. USSR*, 650 (1960).

All of the preparations led to nearly quantitative yields of the new hypochlorites, based on the amount of alcohol originally introduced. The materials are pale yellow liquids at room temperature and have boiling points which approximate those of their parent alcohols.

Perfluoro-*t*-butyl Hypochlorite. *Anal.* Calcd for $(CF_3)_3OCCl$: C, 17.74; F, 63.22; Cl, 13.12. Found: C, 17.40; F, 64.91; Cl, 13.84.

Bis(trifluoromethyl)methyl Hypochlorite. *Anal.* Calcd for $(CF_3)_2CHOCl$: C, 17.78; F, 56.29; Cl, 17.53. Found: C, 17.65; F, 55.26; Cl, 17.50.

1,1-Bis(trifluoromethyl)ethyl Hypochlorite. *Anal.* Calcd for $CH_3C(CF_3)_2OCl$: C, 22.17; F, 52.66; Cl, 16.40. Found: C, 21.75; F, 51.50; Cl, 16.48.

2,2,2-Trifluoroethyl Hypochlorite. *Anal.* Calcd for CF_3CH_2OCl: C, 17.84; F, 42.38; Cl, 26.39. Found: C, 17.16; F, 41.00; Cl, 26.06.

Alternative Preparation of Perfluoro-*t*-butyl Hypochlorite. The sodium salt of perfluoro-*t*-butyl alcohol was prepared by reaction of the alcohol with sodium hydride in diethyl ether. The purified salt was allowed to react with excess chlorine monofluoride in a 30-cc stainless steel cylinder fitted with a needle valve. After overnight storage at ambient temperature, an essentially quantitative yield of $(CF_3)_3COCl$ was recovered. Identification of the hypochlorite was made by comparing its infrared spectrum with that of an authentic sample of $(CF_3)_3COCl$.

Attempted Preparation of *t*-Butyl Hypochlorite. *t*-Butyl alcohol (1 mmol) and chlorine monofluoride (1 mmol) were condensed into a 0.25-in. o.d. Kel-F reactor which was fitted with a needle valve. A sharp detonation occurred at about −100° as the mixture was warming slowly from −196°.

Attempted Preparation of $(CF_3)_2C(OCl)C(CF_3)_2OCl$. Perfluoropinacol (*ca.* 1 mmol) was syringed into a Kel-F reactor ($^3/_8$-in. o.d.) which was then capped through Swagelok fittings to a needle valve. Chlorine monofluoride (2 mmol) was then introduced and the mixture was allowed to stand at room temperature for several hours. The only products found were those of degradation, namely, $(CF_3)_2CO$, $CF_3C(O)F$, F_2CO, and CF_3Cl. A repetition of the experiment at −20° led to the isolation of some i-C_3F_7OCl.

Attempted Preparation of CH_3OCl. Methyl alcohol (5 mmol) and ClF (5 mmol) were combined in a 0.25 in. o.d. Kel-F reactor capped with a needle valve. The mixture was then allowed to warm to room temperature and react. Although reaction occurred nonexplosively to give products that were not completely identified, no evidence was found for CH_3OCl.

Preparation of the Chloroformates. The method for the preparation of chloroformates was similar to that previously described.[2] However, the reactions could also be performed at higher temperatures (25°) without loss of yield through side reactions.

Generally, the hypochlorite (10 mmol) was combined with excess carbon monoxide in a stainless steel cylinder at −196°. The reactor was then allowed to warm to room temperature and was mechanically agitated for several hours. After this period the container was again cooled to −196°, and the excess carbon monoxide was pumped away leaving a nearly quantitative yield of the chloroformate. The material was normally quite pure (if the starting hypochlorite was pure) and exhibited a characteristic infrared absorption band in the 1810–1840-cm^{-1} region associated with the carbon stretching mode. Minor impurities were usually removed by fractionation through a −78° cold trap on a conventional glass vacuum line. The chloroformates are clear, colorless liquids.

Perfluoro-*t*-butyl Chloroformate. *Anal.* Calcd for $(CF_3)_3COC(O)Cl$: C, 20.10; F, 57.28; Cl, 11.88. Found: C, 20.16; F, 56.78; Cl, 11.91.

Bis(trifluoromethyl)methyl Chloroformate. *Anal.* Calcd for $(CF_3)_2CHOC(O)Cl$: C, 20.82; F, 49.46; Cl, 15.40. Found: C, 20.92; F, 49.30; Cl, 14.94.

1,1-Bis(trifluoromethyl)ethyl Chloroformate. *Anal.* Calcd for $CH_3C(CF_3)_2OC(O)Cl$: C, 24.54; F, 46.64; Cl, 14.52. Found: C, 23.77; F, 45.10; Cl, 14.06.

2,2,2-Trifluoroethyl Chloroformate. *Anal.* Calcd for $CF_3CH_2OC(O)Cl$: C, 22.15; F, 35.08. Found: C, 22.10; F, 34.90.

Attempted Preparation of *t*-Butyl Chloroformate. The normal preparative procedure for the chloroformates was followed using $(CH_3)_3COCl$ (7 mmol) and CO (7 mmol). No reaction was observed to occur between these two substances over the temperature range −20° to +80°.

Preparation of the Chlorosulfates. The method for the preparation of chlorosulfates has been previously described[2] and was followed quite closely except that reactions were allowed to proceed at room temperature rather than −20°.

The nearly quantitative yields of chlorosulfates were separated from minor impurities and excess SO_2 by fractionation through a −45° trap. The chlorosulfates are clear, colorless liquids and were initially identified by the characteristic bands in the infrared associated with the asymmetric sulfuryl stretching frequency (1444–1455 cm^{-1}).

Perfluoro-*t*-butyl Chlorosulfate. *Anal.* Calcd for $(CF_3)_3COSO_2Cl$: C, 14.35; F, 51.12; S, 9.57. Found: C, 14.28; F, 50.98; S, 9.44.

Bis(trifluoromethyl)ethyl Chlorosulfate. *Anal.* Calcd for $(CF_3)_2CHOSO_2Cl$: C, 13.51; F, 42.78; Cl, 13.32. Found: C, 13.30; F, 42.09; Cl, 13.20.

1,1-Bis(trifluoromethyl)ethyl Chlorosulfate. *Anal.* Calcd for $CH_3C(CF_3)_2OSO_2Cl$: C, 17.11; F, 40.65; Cl, 12.65. Found: C, 17.06; F, 40.50; Cl, 12.28.

2,2,2-Trifluoroethyl Chlorosulfate. *Anal.* Calcd for $CF_3CH_2OSO_2Cl$: C, 12.08; F, 28.70; Cl, 17.87. Found: C, 12.15; F, 28.13; Cl, 17.50.

Infrared absorptions and nmr data for the hypochlorites and their derivatives are listed in Table I.

Discussion

The hypochlorites described above represent a significant extension of the new class of compounds, fluoroalkyl hypochlorites. All previous fluorine-substituted hypochlorites (R_fOCl) are structurally related to known fluoroxy compounds (R_fOF), although, as we have demonstrated, the two types of materials differ significantly in their chemical behavior.[1,2] Of the new compounds presented here, only one corresponding fluoroxy compound, $(CF_3)_3COF$, was known prior to this work.[8] Further, it has been reported that fluoroxy compounds containing hydrogen in the alkyl portion of the molecule are explosively unstable and cannot be isolated.[9–11] In contrast, we have experienced no decomposition of the hydrogen-substituted fluoroalkyl hypochlorites during normal handling.

It is also surprising that treatment of fluoro alcohols containing carbon–hydrogen bonds with such a powerful oxidizing agent as chlorine monofluoride did not produce extensive degradation. Considering the fact that $(CH_3)_3COH$ reacted explosively with ClF, it is interesting to note the degree of fluorine substitution required in the parent alcohol to permit the chlorine monofluoride oxidation to proceed smoothly to the hypochlorite.

In the series CH_3OH, CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$, where hydrogen atoms are progressively replaced by trifluoromethyl groups, the last three members react readily and nonviolently with chlorine monofluoride to produce excellent yields of the corresponding hypochlorite. Methyl alcohol was degraded when combined with ClF and did not produce CH_3OCl.

This is also consistent with the behavior in the series $(CH_3)_3COH$, $CH_3C(CF_3)_2OH$, and $(CF_3)_3COH$. Even though *t*-butyl alcohol detonates in the presence of ClF, replacement of methyl by trifluoromethyl groups in the latter two cases leads to excellent yields of the corresponding hypochlorites. We therefore conclude that one trifluoromethyl group in the α position of an alcohol is all that is necessary to allow preparation of the corresponding hypochlorite by reaction with chlorine monofluoride. We made no attempt to study

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Table I. Infrared and Nmr Data for the Hypochlorites and Their Derivatives

Compound	Infrared absorptions, cm^{-1}	Nmr[a]
$(CF_3)_3COCl$	1282 (vs), 1232 (ms), 1190 (mw), 1108 (s), 1003 (s), 983 (s), 788 (w), 758 (m), 732 (s)	^{19}F, +70.1 (singlet)
$(CF_3)_2CHOCl$	3013 (w), 1360 (s), 1300 (s), 1265 (s, shoulder), 1250 (s), 1218 (s), 1160 (m), 1120 (s), 1085 (m), 1010 (m), 970 (m), 910 (ms), 885 (ms), 782 (m), 720 (m), 690 (s)	^{19}F, +72.5 (doublet) ^{1}H, −4.25 (septet) J_{FH} = 5.6 Hz
$CH_3C(CF_3)_2OCl$	1460 (m), 1392 (mw), 1308 (s), 1215 (vs), 1163 (ms), 1137 (s), 1092 (s), 952 (w), 930 (m), 882 (mw), 780 (w), 740 (w), 704 (ms)	^{19}F, +74.5 (quartet) ^{1}H, −1.77 (septet) J_{FH} = 1.2 Hz
CF_3CH_2OCl	3000 (w), 1465 (w), 1410 (mw), 1285 (s), 1180 (s), 1060 (m), 968 (m), 840 (w), 763 (w), 675 (w)	^{19}F, +73.4 (triplet) ^{1}H, −3.84 (quartet) J_{FH} = 8.0 Hz
$(CF_3)_3COC(O)Cl$	1838 (s),[b] 1280 (vs), 1200 (w), 1121 (s), 1060 (s), 1012 (s), 990 (s), 1060 (s), 1012 (s), 990 (s), 830 (ms), 732 (ms)	^{19}F, +70.0 (singlet)
$(CF_3)_2CHOC(O)Cl$	3020 (w), 1812 (s),[b] 1486 (ms), 1464 (m), 1303 (s), 1270 (ms), 1243 (s), 1212 (s), 1128 (vs), 1070 (w), 1015 (w), 920 (m), 820 (m), 730 (m), 698 (m)	^{19}F, +72.8 (doublet) ^{1}H, −5.65 (septet) J_{FH} = 6.0 Hz
$CH_3C(CF_3)_2OC(O)Cl$	1820 (s),[b] 1468 (w), 1400 (w), 1315 (s), 1238 (vs), 1170 (m), 1138 (s), 1112 (s), 918 (w), 897 (w), 830 (ms), 703 (m), 680 (w)	^{19}F, +74.1 (quartet) ^{1}H, −2.03 (septet) J_{FH} = 1.2 Hz
$CF_3CH_2OC(O)Cl$	3015 (w), 1810 (s),[b] 1449 (w), 1410 (m), 1300 (s), 1190 (s), 1170 (s), 1138 (vs), 980 (m), 902 (w), 860 (w), 817 (m), 691 (w)	^{19}F, +75.5 (triplet) ^{1}H, −4.57 (quartet) J_{FH} = 7.5 Hz
$(CF_3)_3COSO_2Cl$	1455 (s),[c] 1282 (vs), 1228 (m), 1210 (m), 1090 (s), 985 (s), 836 (s), 732 (s), 618 (s),[d] 515 (m)	^{19}F, +69.5 (singlet)
$(CF_3)_2CHOSO_2Cl$	2995 (vw), 1448 (s),[c] 1363 (s), 1299 (s), 1266 (s), 1249 (vs), 1218 (s), 1195 (s), 1119 (s), 1065 (s), 908 (m), 887 (ms), 834 (s), 739 (w), 690 (ms), 620 (s),[d] 518 (m)	^{19}F, +73.2 (doublet) ^{1}H, −5.37 (septet) J_{FH} = 5.4 Hz
$CH_3C(CF_3)_2OSO_2Cl$	1450 (s),[c] 1300 (s), 1236 (vs), 1204 (m), 1170 (w), 1131 (ms), 1112 (s), 1095 (s), 951 (s), 878 (w), 822 (m), 706 (m), 649 (m), 610 (s),[d] 518 (m)	^{19}F, +74.5 (quartet) ^{1}H, −2.20 (septet) J_{FH} = 1.2 Hz
$CF_3CH_2OSO_2Cl$	2970 (w), 1444 (s),[c] 1410 (m), 1285 (s), 1180 (vs), 1042 (s), 960 (mw), 860 (m), 822 (m), 610 (ms),[d] 530 (mw)	^{19}F, +74.7 (triplet) ^{1}H, −4.48 (quartet) J_{FH} = 7.5 Hz

[a] The nmr spectra of the hypochlorites were obtained from samples in heat-sealed spinning Kel-F tubes of approximately 5-mm o.d. The fluorine-19 nmr spectra were measured in ppm relative to $CFCl_3$ internal standard, and the proton spectra measurements are in ppm relative to TMS internal standard. Coupling constants obtained from ^{19}F and from ^{1}H spectra agreed to within ±0.2 Hz. [b] C=O stretching frequency. [c] Asymmetric S=O stretching frequency. [d] S—Cl stretching frequency.

either the effect of other electronegative substituent groups or the effect of substituting trifluoromethyl groups in positions other than the α position.

The absence of α-fluorine atoms in these hypochlorites and in their derivatives is especially important, and the higher yields of the chlorosulfates described herein compared to those we prepared earlier is attributed to just this factor. Fluorine atoms in the α position provide a convenient pathway for elimination of chlorine monofluoride in hypochlorites or for transfer of fluorine to the sulfur atom in chlorosulfates. In either case the side reaction yields the same products, *i.e.*, FSO_2Cl and a fluorocarbonyl compound. Since none of the perfluoroalkyl chlorosulfates decomposes spontaneously at the reaction temperature,[2] we feel that only the former pathway is operable to decrease yields. However, we have observed, in systems which will be the subjects of subsequent papers of this series, that the latter mechanism is not an unusual one.

An interesting discovery was that the new hypochlorites are extremely susceptible to hydrolysis. This is particularly surprising when it is considered that a standard preparation for ordinary alkyl hypochlorites involves aqueous media.[12] The fluorinated hypochlorites react so readily with water that it is sometimes difficult to handle them, even in vacuum systems considered to be moisture-free, without generating hydrolysis products (parent alcohols). In retrospect, it appears that all the polyfluoroalkyl hypochlorites are probably quite susceptible to hydrolysis, and this fact is recognized clearly only in these latter cases because the parent alcohol is a stable and readily identifiable compound.

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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

$$\text{Nu} + {}^-O_3SS\text{-}SO_3^- \longrightarrow \text{NuSSO}_3 + SO_3^{2-} \qquad (1)$$

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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