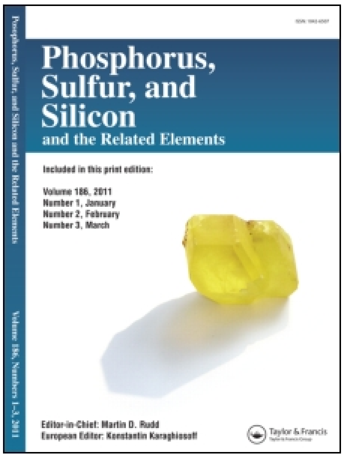

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GAS PHASE REACTIONS OF DIALKOXYDISULFIDES, ROSSOR (R = CH_3 AND CH_3CH_2), WITH ANIONIC NUCLEOPHILES.[1]

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The kinetics and products of a range of reactions between six different nucleophiles of varying gas phase basicities and dimethoxydisulfide and diethoxydisulfide were studied in a flowing afterglow apparatus. Several different types of reactions have been observed, many of which result in the formation of new sulfur containing anions. These reactions include: cleavage of the sulfur-sulfur bond to form ROS^- ions, elimination to give $ROSS^-$ ions and attack at carbon to yield $ROSSO^-$ ions. For some nucleophiles (HA^-), anions of the type HAS^-, $ROSA^-$, and $ROSSA^-$ are also formed. An unified reaction scheme is proposed to account for the formation of each of the product ions and comparisons with the solution phase reactivity of dialkoxydisulfides are made. In addition, the dialkoxydisulfides have been subject to electron impact (EI) in the negative ion mode. The major product ions are the alkoxydisulfide anions, $ROSS^-$. The reactivity of these alkoxydisulfide anions towards several neutral reagents has been probed. Both anions are fairly unreactive, consistent with their low gas phase basicity.

Keywords: Gas Phase Reactivity; Dimethoxydisulfide; Diethoxydisulfide; Flowing Afterglow Technique; Kinetics; Anionic Nucleophiles.

INTRODUCTION

As part of our ongoing interest in the gas phase ion chemistry of sulfur and phosphorus containing species,[2,3] we became interested in developing methods for synthesizing alkoxysulfide anions, ROS^-. The parent system, the hydroxysulfide anion (R = H) can be synthesized via a number of methods including collision induced dissociation (eq. 1) or as a minor product in an ion-molecule reaction between the hydroxide ion and COS (eq. 3) and has been studied in some

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detail.[4-6] Previous attempts to synthesize the methoxysulfide anion via an analogous sulfur atom abstraction reaction (cf. eq. 3) between the methoxide anion and carbonylsulfide failed (eq. 4).[7] Instead the methoxide anion undergoes an inefficient (efficiency = 0.04) hydride transfer reaction (eq. 5).[7]

$$CH_3S(O)CH_2^- \xrightarrow{CID} HOS^- + CH_2{=}CH_2 \quad (1)$$

$$HO^- + COS \begin{cases} \longrightarrow HS^- + CO_2 & (2) \\ \longrightarrow HOS^- + CO & (3) \end{cases}$$

$$CH_3O^- + COS \begin{cases} \cancel{\longrightarrow} CH_3OS^- + CO & (4) \\ \longrightarrow HCOS^- + CH_2O & (5) \end{cases}$$

An alternative route to alkoxysulfide anions is suggested from the work of Grabowski and Zhang on the reactions of dimethyl disulfide with anionic nucleophiles.[8] In several instances, nucleophilic attack at sulfur with resultant cleavage of the sulfur-sulfur bond to form the methylthiolate anion was observed (eg. eq. 6). This paper addresses two main questions: (i) how do anionic nucleophiles react with dialkoxydisulfides, ROSSOR (R = CH_3 and CH_3CH_2), in a FA reactor and (ii) can alkoxy sulfide anions (ROS^-) be synthesized in the gas phase?

$$HO^- + CH_3SSCH_3 \longrightarrow CH_3S^- + CH_3SOH \quad (6)$$

RESULTS AND DISCUSSION

All experiments were performed on a recently modified FA instrument (see experimental section for details). The results of this work are described in five sections: (a) Reactions of anions with ROSSOR; (b) An Unified Gas Phase Anion-Molecule Reaction Model for ROSSOR; (c) Comparisons between the gas phase and solution phase reactions of nucleophiles with ROSSOR; (d) Electron Impact (EI) on ROSSOR and (e) The Gas Phase Reactivity of CH_3OSS^- and $CH_3CH_2OSS^-$.

(a) Reactions of anions with ROSSOR.

The gas phase reactions of six anionic nucleophiles with dimethoxydisulfide are reported in Table I, while those of diethoxydisulfide are reported in Table II.

Both of these tables include the anion proton affinity (APA) of the reactant anion,[9] the product ions, product branching ratios (BR), and the kinetic rate constants for each reaction, the theoretical (k_{ADO}) rate constant[10] and the efficiency of reaction. Before describing an overall mechanistic model for the reactivity of dialkoxydisulfides towards anionic nucleophiles in the gas phase, their reactivity towards the individual anions is described below in six sections.

TABLE I Reactions of Anions with Dimethoxydisulfide in the Gas Phase at 294 K

Anion (HA⁻)	ΔH_{acid}^{o} $^{(a)}$	*Products*	*BR*	$k_{exp}^{(b)}$	$k_{ADO}^{(c)}$	*Eff.* $^{(d)}$
H_2N^-	403.6	CH_3OS^-	.40	35.2±3.2	23.7	1.00
		CH_3OSS^-	.15			
		CH_3OSSO^-	.45			
HO^-	390.7	CH_3OS^-	.15	40.9±3.6	23.1	1.00
		CH_3OSA^-	.25			
		CH_3OSS^-	.30			
		CH_3OSSO^-	.30			
$CH_2CHCH_2^-$	390.7	CH_3OS^-	.65	17.4±0.8	16.1	1.00
		CH_3OSS^-	.10			
		CH_3OSA^-	.15			
		CH_3OSSO^-	.10			
$PhCH_2^-$	381	CH_3OS^-	.70	9.17±0.44	12.3	.75
		CH_3OSS^-	.05			
		HAS^-	.10			
		CH_3OSA^-	.05			
		CH_3OSSA^-	.10			
$NCCH_2^-$	373	CH_3OSSA^-	1.0	12.0±0.4	16.2	.74
$CH_3C(O)CH_2^-$	369	HAS^-	.10	6.12±0.26	14.3	.43
		CH_3OSA^-	.35			
		CH_3OSSA^-	.55			

(a) The gas phase acidity of H_2A is in kcal mol^{-1} and is taken from ref. 9; (b) The rate constant (k_{exp}) is in units of $10^{-10}cm^3$ $molecule^{-1}$ s^{-1}; (c) k_{ADO} was calculated using the ADO theory of Su and Bowers (ref. 10a) where the polarizability of the dialkoxydisulfides was estimated by the method of Miller and Savichik (ref. 10b) and the dipole moments were calculated from *ab initio* optimized structures (at the HF/6–31G* level of theory). Full details are available from the authors on request; (d) efficiency = k_{exp}/ADO.

TABLE II Reactions of Anions with Diethoxydisulfide in the Gas Phase at 294 K

Anion (HA⁻)	$AH_{acid}O^{(a)}$	*Products*	*BR*	$k_{exp}^{(b)}$	$k_{ADO}^{(c)}$	*Eff.*$^{(d)}$
H_2N^-	403.6	$EtOS^-$	.15	23.6±2.8	27.7	0.85
		$EtOSS^-$	.40			
		$EtOSSO^-$	.45			
HO^-	390.7	$EtOS^-$	.05	36.8±5.1	26.9	1.00
		$HASS^-$	.45			
		$EtOSA^-$	.05			
		$EtOSS^-$	.15			
		$EtOSSO^-$	.20			
$CH_2CHCH_2^-$	390.7	$EtOS^-$	.50	24.9±2.1	18.5	1.00
		$EtOSS^-$	.35			
		$EtOSSO^-$	.15			
$PhCH_2^-$	381	$EtOS^-$	.35	15.2±1.3	13.9	1.00
		$EtOSS^-$	.10			
		HAS^-	.10			
		$EtOSSO^-$	.05			
		$EtOSSA^-$	.30			
		$[M - H]^-$	.10			
$NCCH_2^-$	373	$EtOSSA^-$	.90	26.9±2.8	18.7	1.00
		HAS^-	.10			
$CH_3C(O)CH_2^-$	369	HAS^-	(e)	(e)	(e)	(e)
		$EtOSA^-$				
		$EtOSSO^-$				

(a) The gas phase acidity of H_2A is in kcal mol^{-1} and is taken from ref. 9; (b) The rate constant (k_{exp}) is in units of $10^{-10} cm^3$ $molecule^{-1}$ s^{-1}; (c) k_{ADO} was calculated using the ADO theory of Su and Bowers (ref. 10a) where the polarizability of the dialkoxydisulfides was estimated by the method of Miller and Savichik (ref. 10b) and the dipole moments were calculated from *ab initio* optimized structures (at the HF/6–31G* level of theory). Full details are available from the authors on request; (d) efficiency = k_{exp}/k_{ADO}; (e) Not measured due to low volatility of EtOSSOEt and moderate reactivity of $CH_3C(O)CH_2^-$ (efficiency < 0.5).

i. Amide (H_2N^-)

The amide anion, which is the strongest base used in this study, reacts with high efficiency towards the dialkoxydisulfides to produce three types of product ions:

ROS^- (eq. 7), $ROSS^-$ (eq. 8), and $ROSSO^-$ (eq. 9). When R = CH_3, the branching ratios of these product ions are 0.40, 0.15, and 0.45, while for diethoxydisulfide the branching ratios are 0.15, 0.40, and 0.45 respectively.

$$H_2N^- + ROSSOR \longrightarrow \begin{cases} ROS^- + ROSNH_2 & (7) \\ ROSS^- + R'CHO + NH_3 & (8) \\ ROSSO^- + RNH_2 & (9) \end{cases}$$

$$(R = CH_3 \ \& \ CH_3CH_2;\ R' = H \ \& \ CH_3)$$

Nucleophilic attack at sulfur with concomitant cleavage of the sulfur - sulfur bond accounts for the formation of the alkoxysulfide anions, ROS^- (eq. 7), while elimination (E2) of R'CHO (where R' = H or CH_3) results in the formation of $ROSS^-$ (eq. 8). When R = CH_3, the formation of $ROSSO^-$ is likely to proceed via nucleophilic substitution (S_N2) at carbon (eq. 9). For diethoxydisulfide another possible mechanism for the formation of $ROSS^-$ arises: E2 elimination of $CH_2{=}CH_2$. Since the neutral products are not detected in our experiments, we cannot determine which mechanism (S_N2 vs E2) operates for the formation of these $CH_3CH_2OSS^-$ ions.

ii. Hydroxide (HO^-)

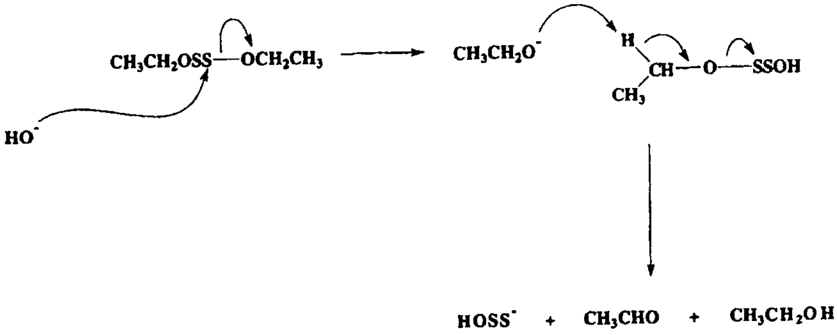
Hydroxide reacts rapidly with both dialkoxydisulfides in a similar fashion to the amide ion, producing the same types of product ions: ROS^- (eq. 10), $ROSS^-$ (eq. 11), and $ROSSO^-$ (eq. 12). An additional product ion ($ROSO^-$) is, however, also observed for HO^- (eq. 13). For diethoxydisulfide, yet another product ($HOSS^-$) is also observed (eq. 14).

$$HO^- + ROSSOR \longrightarrow \begin{cases} ROS^- + ROSOH & (10) \\ ROSS^- + R'CHO + H_2O & (11) \\ ROSSO^- + ROH & (12) \\ ROSO^- + ROSH & (13) \end{cases}$$

$$(R = CH_3 \ \& \ CH_3CH_2;\ R' = H \ \& \ CH_3)$$

$$HO^- + (CH_3CH_2OS)_2 \longrightarrow HOSS^- + CH_3CHO + CH_3CH_2OH \quad (14)$$

The reactions shown in eqs 10–12 are likely to proceed via similar mechanisms to those described above for amide ion. The $ROSO^-$ product ion is related to the ROS^- product ion in that they are likely to originate from the same ion-molecule complex [ROS^- (ROSOH)].[11] Thus dissociation of this ion-molecule complex results in the formation of the products shown in eq. 10, while proton transfer from ROSOH to ROS^- results in the products shown in eq. 13. A possible mechanism for the formation of $HOSS^-$ (eq. 14) is shown in Scheme 1.



SCHEME 1

iii. Allyl Anion ($CH_2CHCH_2^-$)

The allyl anion reacts in a similar fashion to both HO^- and H_2N^- to produce ROS^-(eq. 15), $ROSS^-$ (eq. 16), and $ROSSO^-$ (eq. 17). These reactions are also fast. Only when R = CH_3 is the ion $CH_3OSCHCHCH_2^-$ produced (eq. 18). The mechanism for the formation of this ion is likely to be similar to that described for $ROSO^-$ (eq. 13) above.

$$CH_2CHCH_2^- + ROSSOR \longrightarrow ROS^- + ROSCH_2CHCH_2 \quad (15)$$

$$\longrightarrow ROSS^- + R'CHO + CH_2CHCH_3 \quad (16)$$

$$\longrightarrow ROSSO^- + RCH_2CHCH_2 \quad (17)$$

$$(R = CH_3 \ \& \ CH_3CH_2; \ R' = H \ \& \ CH_3)$$

$$CH_2CHCH_2^- + (CH_3OS)_2 \longrightarrow CH_3OSCHCHCH_2^- + CH_3OSH \quad (18)$$

iv. Benzyl Anion ($PhCH_2^-$)

The benzyl anion reacts rapidly with both dialkoxydisulfides via a number of reaction channels. The three which are in common to both dialkoxydisulfides result in the formation of the following ions: ROS^- (eq. 19), $ROSS^-$ (eq. 20) and $ROSSCHPh^-$ (eq. 21). Each of these reactions have analogies to those of the other anions described above.

$$\mathrm{PhCH_2^- + ROSSOR} \longrightarrow \begin{cases} \mathrm{ROS^- + ROSCH_2Ph} & (19) \\ \mathrm{ROSS^- + R'CHO + PhCH_3} & (20) \\ \mathrm{ROSSCHPh^- + ROH} & (21) \end{cases}$$

$$(\mathrm{R = CH_3\ \&\ CH_3CH_2;\ R' = H\ \&\ CH_3})$$

For dimethoxydisulfide, two additional products are observed $PhCH_2S^-$ (eq. 22) and $CH_3OSCHPh^-$ (eq. 23). Both of these ions can be envisioned as arising via a common intermediate ion-molecule complex as shown in Scheme 2.

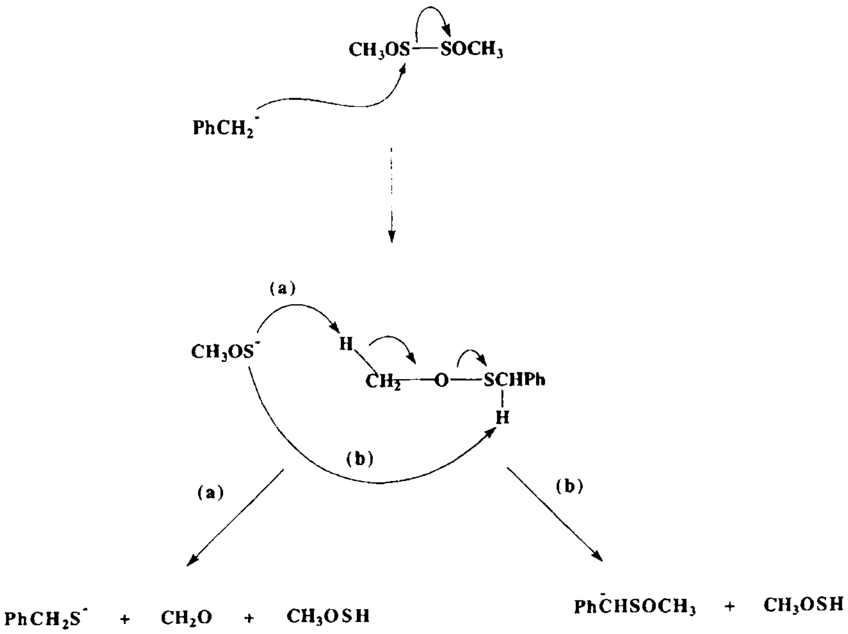
$$\mathrm{PhCH_2^- + (CH_3OS)_2} \longrightarrow \begin{cases} \mathrm{PhCH_2S^- + CH_3OSH + CH_2O} & (22) \\ \mathrm{CH_3OSCHPh^- + CH_3OSH} & (23) \end{cases}$$

For diethoxydisulfide, three additional products are also observed. In this case they are: $PhCH_2S^-$ (cf. eq. 22), $CH_3CH_2OSSO^-$(eq. 24), and a $[M\text{-}H]^-$ ion (eq. 25). In analogy to Grabowski and Zhang's work on CH_3SSCH_3, we have assigned a related mechanism and structure for the formation of this $[M\text{-}H]^-$ ion in Scheme 3.

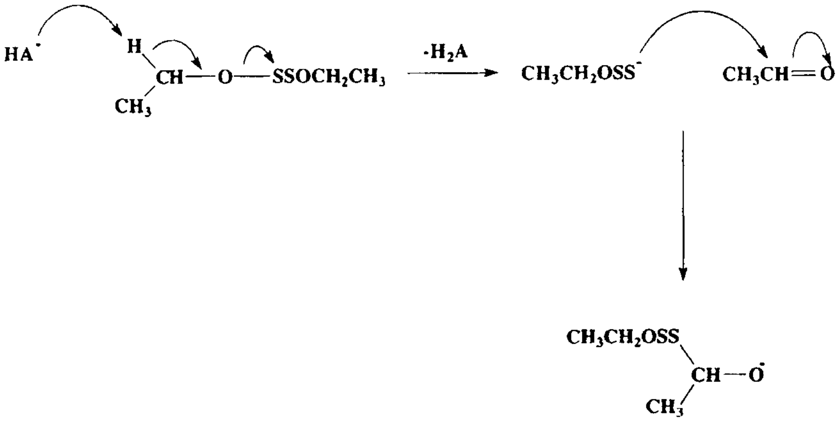
$$\mathrm{PhCH_2^- + (CH_3CH_2OS)_2} \longrightarrow \begin{cases} \mathrm{CH_3CH_2OSSO^- + Ph(CH_2)_2CH_3} & (24) \\ \mathrm{[C_4H_9O_2S_2]^- + PhCH_3} & (25) \end{cases}$$

v. Conjugate Base of Acetonitrile ($NCCH_2^-$)

The $NCCH_2^-$ anion is unique in that it forms the least number of ionic products with the dialkoxydisulfides. Both dialkoxydisulfides react to form $ROSSCHCN^-$ ions (eq. 26). This reaction is similar to that described above for HO^- (eq. 13). For diethoxydisulfide the $NCCH_2S^-$ ion is also observed (eq. 27). This reaction is



SCHEME 2



SCHEME 3

likely to proceed via a similar mechanism to that for the formation of $PhCH_2S^-$, as outlined in Scheme 2. These reactions proceed with high efficiency.

$$NCCH_2^- + ROSSOR \longrightarrow ROSSCHCN^- + ROH \quad (26)$$

$$NCCH_2^- + (CH_3CH_2OS)_2 \longrightarrow NCCH_2S^- + CH_3CH_2OSH + CH_3CHO \quad (27)$$

vi. Acetone Enolate ($CH_3C(O)CH_2^-$)

The weakest base used in this study, the acetone enolate anion, reacted the slowest with both dialkoxydisulfides. This, together with the moderate volatility of diethoxydisulfide, prevented an accurate measurement of the rate and branching ratios of its reaction with diethoxydisulfide. The acetone enolate anion (an ambident anion)[12] reacts with both dialkoxydisulfides to give $CH_3C(O)CH_2S^-$ (eq. 28) and $ROSSCHC(O)CH_3^-$ (eq. 29). For dimethoxydisulfide $CH_3OSCHC(O)CH_3^-$ is also observed (eq. 30), while for diethoxydisulfide $CH_3CH_2OSSO^-$ is also formed (eq. 31).

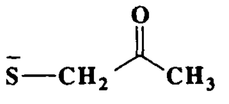
$$CH_3C(O)CH_2^- + (ROS)_2 \longrightarrow CH_3C(O)CH_2S^- + ROSH + R'CHO \quad (28)$$

$$CH_3C(O)CH_2^- + (ROS)_2 \longrightarrow ROSSCHC(O)CH_3^- + ROH \quad (29)$$

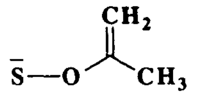
$$CH_3C(O)CH_2^- + (CH_3OS)_2 \longrightarrow CH_3OSCHC(O)CH_3^- + CH_3OSH \quad (30)$$

$$CH_3C(O)CH_2^- + (CH_3CH_2OS)_2 \longrightarrow CH_3CH_2OSSO^- + [C_5H_{10}O] \quad (31)$$

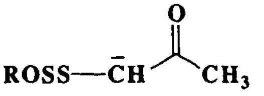
The mechanisms for the formation of these ions are related to those described above for other anions. We note, however, that due to the ambidency of the acetone enolate anion, our assignment of the structures of the product ions of the reactions shown in eqs. 28–30 is tenuous. If these reactions proceed through carbon attack, then the product ion structures will be (**A**), (**B**) and (**C**) for eqs. 28, 29 and 30, while if oxygen attack occurs structures (**D**), (**E**) and (**F**) will result.



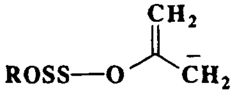
(A)



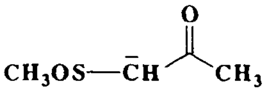
(D)



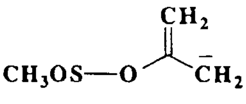
(B)



(E)



(C)

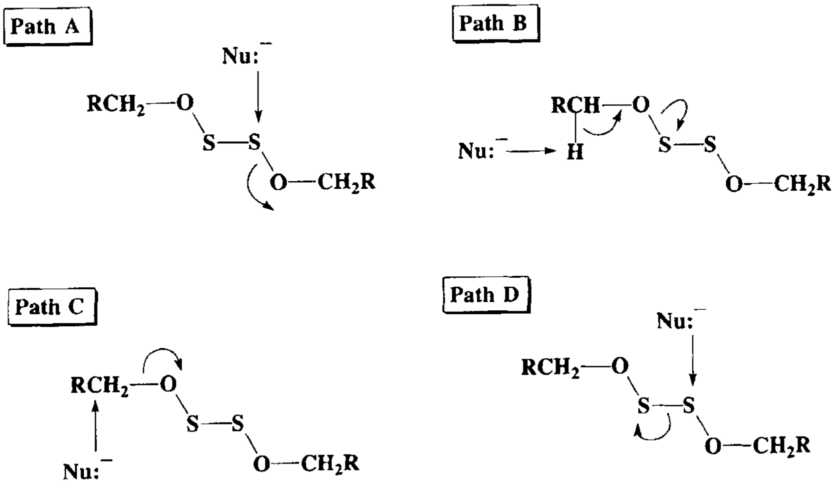


(F)

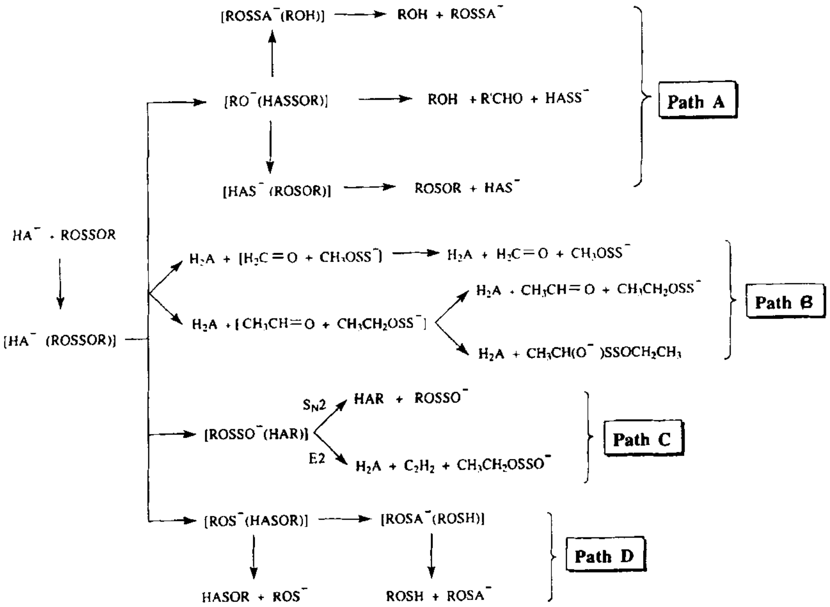
(b) An Unified Anion-Molecule Reaction Model for ROSSOR.

At a first glance, the numerous types of product ions observed in the reactions of the dialkoxydisulfides towards anionic nucleophiles in the gas phase suggest that they arise from a series of unrelated mechanistic sequences. It seems likely, however, that these different products are likely to arise from only a few entrance channels (paths), which in turn are related to the initial sites of attack of the nucleophile onto the dialkoxydisulfide. Indeed if we consider Scheme 4, we note that there are really only four initial paths: path A involves nucleophilic attack at sulfur with S-O bond cleavage; path B involves attack at carbon, proceeding via an elimination reaction which results in S-O bond cleavage; path C involves nucleophilic attack (or elimination for EtOSSOEt) at carbon with C-O bond cleavage and path D involves nucleophilic attack at sulfur with S-S bond cleavage. By taking Scheme 4 as a starting point, it is convenient to rationalize the formation of many of the final product ions as proceeding via the intermediacy of several key ion-molecule complexes, including [RO^- (HASSOR)] and [ROS^-(HASOR)]. Thus we have represented the modes of reactivity of the dialkoxydisulfides towards anionic nucleophiles in the gas phase via the general model shown in Scheme 5.

By comparing the mechanistic sequences shown in scheme 5 with the data given in Tables I and II, certain trends emerge regarding the reactivity of both dimethoxydisulfide and diethoxydisulfide towards anionic nucleophiles. It appears that as the basicity (or alternatively, the anion proton affinity) decreases, the relative amount of products arising from sulfur attack with cleavage of the S-O bond (i.e. path A) increases, while the relative amounts of products arising carbon attack with either S-O bond cleavage (i.e. path B) or C-O bond cleavage (i.e. path C) decreases.[13] Products due to S-S bond cleavage (i.e. path D), although observed in all cases (except that of $NCCH_2^-$) do not seem to be solely influenced by the nucleophile's APA. Some of these trends are consistent with similar observations made in the literature. For example, DePuy and co-workers have noted that as the APA of the nucleophile decreases, its reactivity in S_N2 and E2 reactions decreases.[14] In contrast, Grabowski and Zhang have noted that cleavage of the S-S bond in dimethyldisulfide is not solely influenced by the nucleophile's APA.[8]



SCHEME 4



SCHEME 5

(c) Comparisons between the gas phase and solution phase reactions of nucleophiles with ROSSOR.

How do our gas phase results on the reactions of anionic nucleophiles with dialkoxydisulfides compare with their solution phase reactivity? The only direct comparisons between the reactivity of ROSSOR towards anionic nucleophiles in the gas phase and solution that we have been able to find is the reaction of hydroxide ion.[15c] Meuwsen rationalized the formation of the products in the reaction between dialkoxydisulfides and KOH as arising from cleavage of the sulfur sulfur bond (eq. 32),[15c] which is consistent with our gas phase results described above (cf eqs. 10 and 13).

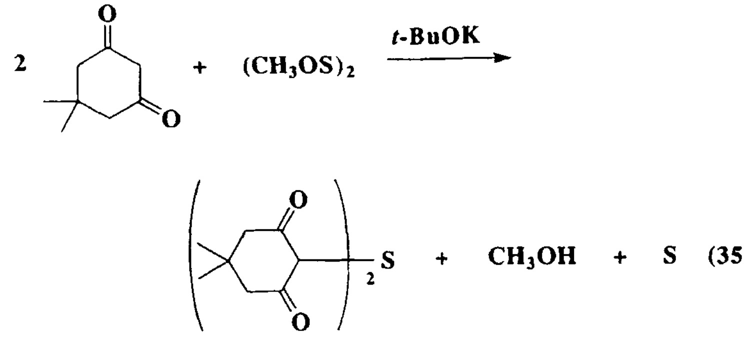
$$\mathbf{KOH + ROSSOR \longrightarrow ROSK + ROSOH} \quad \mathbf{(32)}$$

In addition there have been reports on the solution phase reactions of dialkoxydisulfide with other anionic nucleophiles such as alkoxide ions (eq. 33),[15d] alkyllithium reagents (eq. 34)[15d] and enolates (eq. 35). In each of the cases, cleavage of the sulfur-sulfur bond occurs, which is once again consistent with many of our gas phase results (cf. eqs.7, 15 and 19).

$$\mathbf{RONa + ROSSOR \longrightarrow ROSNa + (RO)_2S} \quad \mathbf{(33)}$$

$$\mathbf{4BuLi + (PhCH_2OS)_2 \longrightarrow 2(Bu)_2S + 2PhCH_2OLi} \quad \mathbf{(34)}$$

Several studies have also examined the reactions of neutral nucleophiles with dialkoxydisulfides.[15e-g] Thiols and secondary amines react via attack at sulfur with concomitant elimination of the alkoxygroup (eq. 36), while primary amines undergo a similar reaction, although the resultant product undergoes an intramolecular elimination of alcohol (eq. 37).[15e] It is interesting to note that these solution phase reactions also bear a resemblance to some of our gas phase results (cf eqs. 21, 26 and 29).



(35)

$$\text{XH} + \text{ROSSOR} \longrightarrow \text{ROSSX} + \text{ROH} \quad (36)$$

$$\text{R'NH}_2 + \text{ROSSOR} \longrightarrow \text{R'NSS} + 2\text{ROH} \quad (37)$$

(d) Electron Impact (EI) on ROSSOR.

The dialkoxydisulfides were subjected to EI conditions in the flowing afterglow in order to investigate whether cleavage of the disulfide bond occurs to form alkoxysulfide anions. Although ROS^- anions were not produced under these EI conditions, several other ions were formed. In each instance, the dominant product ions were the alkoxydisulfide anions, $ROSS^-$. Other minor product ions included $ROSSO^-$, OSS^-, and SS^-.

(e) The Gas Phase Reactivity of CH_3OSS^- and $CH_3CH_2OSS^-$

With an efficient method for producing $ROSS^-$ anions (via EI), we embarked on an investigation of their gas phase reactivity. In particular, their reactivity towards neutral molecules containing an acidic proton as well as those which do not contain an acidic proton was determined.

Both CH_3OSS^- and $CH_3CH_2OSS^-$ deprotonate acetic acid ($\Delta H^{\circ}_{acid}(CH_3CO_2H) = 349$ kcal mol^{-1}) but not 2,2-dimethyl ethyl mercaptan ($\Delta H^{\circ}\text{acid}((CH_3)_3CSH) = 352$ kcal mol^{-1}). Thus the acidities of the conjugate acids (which are assumed to have the structure ROSSH) are estimated to be 350 kcal mol^{-1}.

A qualitative study of the reactivity of CH_3OSS^- and $CH_3CH_2OSS^-$ with neutral molecules containing no acidic protons was also investigated. In general, these anions are quite unreactive, with no reaction (i.e. the efficiency of reaction < 0.0001) being observed for N_2O, CO_2, and SF_6. Adduct formation, which was observed for both CS_2 (eq. 38) and SO_2 (eq. 39), is likely to occur via three body association reactions with the helium buffer gas. The general lack of reactivity of these $ROSS^-$ ions is consistent with that observed previously for the related CH_3SS^- ion.[16]

$$\text{ROSS}^- + \text{CS}_2 \longrightarrow \text{ROSS}^-.\text{CS}_2 \quad (38)$$

$$\text{ROSS}^- + \text{SO}_2 \longrightarrow \text{ROSS}^-.\text{SO}_2 \quad (39)$$

In conclusion, the gas phase anion-molecule reactions of dialkoxydisulfides reveal a rich chemistry, including cleavage of the sulfur-sulfur bond, elimination to give $ROSS^-$ ions and attack at carbon to yield $ROSSO^-$ ions. For some nucleophiles (HA^-), anions of the type HAS^-, $ROSA^-$, and $ROSSA^-$ are also formed. The first reaction type, which results in the hitherto elusive alkoxysulfide anions ROS^- ions, occurs mainly for the highly basic anions (NH_2^-, HO^-, $CH_2CHCH_2^-$ and $PhCH_2^-$). Thus these reactions provide new synthetic routes to novel sulfur containing anions[17] which could be investigated via tandem mass spectrometry techniques (such as the FA-SIFT).[5, 16]

EXPERIMENTAL

All experiments were carried out at 294±3 K using a recently modified flowing afterglow reactor which has been previously described.[3] Anionic nucleophiles were prepared by allowing the appropriate neutral precursor to react with a reagent anion (NH_2^- or HO^-), which in turn were prepared by electron impact (rhenium filament operating at 200 mA and 300 eV) on the appropriate precursor gases (NH_3 or a 2:1 mixture of CH_4 and N_2O). All ions and neutrals are entrained in a stream of helium buffer gas (at a pressure of 0.35 to 0.40 torr and flowing with a velocity of 195.9 $cm^3\ s^{-1}$), confined in a 1-m long × 7.6-cm i.d. stainless steel tube. At the end of the flow tube, the plasma is sampled through a 1-mm diameter orifice into a low-pressure region where the ions are separated in a quadrupole mass filter and detected by an electron multiplier.

To study the kinetics of the reactions between the anionic nucleophile and the dialkoxydisulfide, a known flow of ROSSOR is added at varying distances along the flow tube through a series of seven fixed inlets. Flow rates of ROSSOR were determined by monitoring the pressure increase with time in a calibrated volume. Each reported rate constant is the average of at least three independent measurements at different flow rates of ROSSOR. The experimental precision of each rate constant is ±10%. Product ions were monitored as a function of reaction distance and product branching ratios are reported as extrapolations to zero reaction distance to eliminate any effects of differential diffusion among the ions and of secondary reactions. An attempt to correct for mass discrimination was made by reducing the resolution of the mass analyzer. Branching ratio measurements are estimated to be accurate to ±30%.

All reagents were obtained from commercial sources and were of the following purities: He (>99.99%), N_2O (99.99%), CH_4 (99.99%), NH_3 (99.99%), and $CH_3CH{=}CH_2$ (>99%). All other compounds were of reagent grade obtained commercially and were used without further purification. Both dimethoxydisulfide and diethoxydisulfide which were synthesized via reported procedures,[15a] were purified via vacuum distillation and gave ^1H NMR spectra identical to those reported in the literature.[18] The helium buffer gas was passed through a liquid-nitrogen cooled molecular sieve trap before entering the flow tube.

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References

[1] Part of the M.S. thesis of J.D. Smith, Kansas State University, 1996.

[2] J.D. Smith and R. A. J. O'Hair, *Phos. Sulf. Silicon Rel. Elements,* **1996**, *119*, in press.

[3] J.D. Smith and R. A. J. O'Hair, *Eur. Mass Spectrom.*, **1996**, *2*, 225.

[4] J.H. Bowie, M.B. Stringer and R.N. Hayes, *Rapid Commun. Mass Spectrom.* **1990**, *4*, 129.

[5] R. A. J. O'Hair, C. H. DePuy and V. M. Bierbaum, *J. Phys. Chem.*, **1993**, *97*, 7955.

[6] M. Iraqi, N. Goldberg and H. Schwarz, *J. Phys. Chem.*, **1994**, *98*, 2015.

[7] The gas phase reaction of CH_3O^- with CS_2 has been studied in a flowing afterglow selected ion flow tube (R.A.J. O'Hair and C.H. DePuy, unpublished observations, 1993) at 298K. The rate constant is 6.4 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, while the theoretical Langevin rate constant is calculated to be 1.47 x 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.

[8] J.J. Grabowski and L. Zhang, *J. Am. Chem, Soc.*, **1989**, *111*, 1193.

[9] Gas phase acidities and other thermochemistry are taken from: NIST Standard Reference Database 19B: NIST Negative Ion Energetics Database Version 2.07, Program written/ Data compilation by: John E. Bartmess, Department of Chemistry,University of Tennessee, Knoxville TN 37996-1600. This compilation is based on original data from: "Gas-phase Ion and Neutral Thermochemistry" : Lias S.G.; Bartmess, J.E.; Liebman, J.F.; Holmes, J.L.; Levin R.D., W.G. Mallard *J. Phys. Chem. Ref. Data*, Vol. 17, 1988; Suppl. 1.

[10] (a) T. Su and M.T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **12**, 347 (1973); (b) K.J. Miller and J.A. Savichik, *J. Am. Chem. Soc.*, **101**, 7206 (1979).

[11] For an excellent review of ion-molecule complexes (sometimes called ion-neutral complexes) in the gas phase see: R.D. Bowen, *Acc. Chem. Res.*, **24**, 364 (1991).

[12] For previous gas phase chemical probes of "O" versus "C" reactivity of ambident enolate anions see: (a) M.D. Brickhouse and R.R. Squires, *J. Phys. Org. Chem.*, **2**, 389 (1989); (b) I.L. Freriks, L.J. de Koning and N.M.M. Nibbering, *J. Am. Chem. Soc.*, **113**, 9119 (1991); (c) B.D. Wladkowski, J.L. Wilbur, M. Zhong and J.I. Brauman, *J. Am. Chem. Soc.*, **115**, 8833 (1993).

[13] A reviewer has asked us to describe these relationships between the relative rates of reactions and the type of nucleophiles in more detail. Once such way is to express the relative amount of products arising from each of the different pathways via a relative reaction efficiency, which can be calculated by multiplying the branching ratio with the overall reaction efficiency. For example, the relative reaction efficiency for the formation of **all** products which proceed via pathway A in the reaction of $PhCH_2^-$ with MeOSSOMe would be calculated by multiplying 0.2 (the sum of branching ratios for the formation of 2 products HAS^- and $MeOSSA^-$) with 0.75 (the overall reaction efficiency) to give a relative reaction efficiency of 0.15). The relative reaction efficiencies can then be plotted as a function of the anion proton affinity (APA); see for example: R. Damrauer, C.H. DePuy and V.M. Bierbaum, *Organometallics*, **1**, 1553 (1982). Given that the rates of only six nucleophiles whose APAs span a range of less than 35 kcal mol^{-1} we measured for each dialkoxydisulfide, we believe that the results of such an analysis would be tenuous.

[14] C.H. DePuy, S. Gronert, A. Mullin and V.M. Bierbaum, *J. Am. Chem. Soc.*, **112**, 8650 (1990).

[15] (a) Q.E. Thompson, M.M. Crutchfield, M.W. Dietrich and E. Pierron, *J. Org. Chem.*, **1965**, *30*, 2692; (b) A. Meuwsen and H. Gebhardt, *Ber. B.*, **1935**, *68*, 1011; (c) A. Meuwsen, *Ber. B.*, **1936**, *69*, 935; (d) A. Meuwsen and H. Gebhardt, *Ber. B.*, **1936**, *69*, 937; (e) H. Kagami and S. Motoki, *J. Org. Chem.*, **1977**, *42*, 4139; (f) H. Kagami and S. Motoki, *Bull. Chem. Soc. Jpn.*,

1979, *52*, 3463; (g) H. Kagami, T. Hanzawa, N. Suzuki, S. Yamaguchi, M. Saito and S. Motoki, *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 3658.

[16] K.M. Downard, J.H. Bowie, R.A.J. O'Hair, M. Krempp and C.H. DePuy, *Int. J. Mass Spectrom. Ion Proc.*, **1992**, *120*, 217.

[17] V. M. Bierbaum, J.J. Grabowski and C. H. DePuy, *J. Phys. Chem.*, **1984**, *88*, 1389.

[18] R. Borghi, L. Lunazzi, G. Placucci, G. Cerioni and A. Plumitallo *J. Org. Chem.*, **1996**, *61*, 3327.