°C (overnight), the solvent was removed, the residue was basified with 20% sodium hydroxide, and the mixture was extracted with ether. The ether extract was dried (sodium sulfate) and analyzed by gas chromatography for imine **11**. None was detected. The ether was removed to give a yellow solid, which was identified as rearranged **10** (50%).[24]

Acknowledgment. We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for partial support of this work.

Registry No. **1**, 80953-41-9; **2**, 96040-82-3; **3**, 96040-83-4; **4**, 85462-15-3; **5**, 96040-84-5; **6**, 96040-85-6; **7**, 96040-86-7; **8**, 96040-87-8; **9**, 3338-03-2; **10**, 96040-89-0; **11**, 62150-62-3; $PhCH_2NH$, 100-46-9; $PhCH(CH_3)NH_2$, 98-84-0; Ph_2CHNH_2, 91-00-9; t-$BuNH_2$, 75-64-9; $CH_3(CH_2)_5CH(NH_2)CH_3$, 693-16-3; $CH_3(CH_2)_5C(CH_3)_2NH_2$, 2626-63-3; $PhN{=}CH_2$, 100-62-9; $PhCH{=}NH$, 16118-22-2; $PhN{=}CHCH_3$, 6052-11-5; $PhC(CH_3){=}NH$, 13280-20-1; $PhCH{=}NCH_3$, 622-29-7; $PhCH{=}NPh$, 538-51-2; $Ph_2C{=}NH$, 1013-88-3; $(CH_3)_2C{=}NCH_3$, 6407-34-7; n-$C_6H_{13}C(CH_3){=}NH$, 64030-07-5; n-$C_6H_{13}N{=}CHCH_3$, 96040-88-9; n-$C_6H_{13}CH{=}NCH_3$, 6898-71-1; n-$C_6H_{13}N{=}C(CH_3)_2$, 32838-32-7; n-$C_6H_{13}C(CH_3){=}NCH_3$, 18641-72-0; c-$C_6H_{10}{=}NCH_3$, 6407-35-8; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; $CH_3(CH_2)_5C(CH)_3{=}NOH$, 7207-49-0; $CH_3(CH_2)_5C(CH_3)_2OH$, 628-44-4; MeMgBr, 74-83-9; 1-methylcyclohexanamine, 6526-78-9; cyclohexanone, 108-93-0; 4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane, 18715-80-5.

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[24] Full characterization of this material has been reported: Hoffman, R. V.; Kumar, A.; Buntain, G. A. *J. Am. Chem. Soc.*, submitted for publication.

Kinetics and Mechanism of the Reactions of *S*-Ethoxycarbonyl *O*-Ethyl Dithiocarbonate with *O*-Ethyl Xanthate and *O*-Ethyl Thiocarbonate Ions

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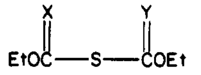
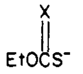
The forward and back reactions of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (**1**) with *O*-ethyl thiocarbonate (**4**) and *O*-ethyl xanthate (**5**) in 95% ethanol are studied kinetically. The back reaction products are bis(ethoxycarbonyl) sulfide (**3**) with **5** and bis(ethoxythiocarbonyl) sulfide (**2**) with **4**, respectively. Compound **1** reacts faster than **2** with **4**, which means that the carbonyl group is more reactive than the thiocarbonyl toward **4**. On the other hand, the reaction of **5** with **1** is faster than that with **3**, which indicates that **5** reacts more readily with the thiocarbonyl than the carbonyl group. Two mechanisms are proposed to account for the kinetics results: one through tetrahedral intermediates (two-step reactions) and the other concerted. The reactions of **4** exhibit $\Delta S^{\ddagger} > 0$, whereas those of **5** show $\Delta S^{\ddagger} < 0$. These ΔS values are explained by a larger solvation of **4** relative to **5** and similar degrees of solvation of transition states and substrates. The observed activation parameters do not allow discrimination between the two mechanisms.

In previous studies we have described the reactions of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (**1**) with primary and secondary amines in ethanol.[1] In addition to the carbamates and thiocarbamates formed by attack of the amines at the carbonyl and thiocarbonyl groups of **1**, the formation of bis(ethoxythiocarbonyl) sulfide **2** and bis(ethoxycarbonyl) sulfide **3** was observed. The latter compounds were produced by reactions of **1** with *O*-ethyl thiocarbonate **4** ion and *O*-ethyl xanthate **5** ion, which had been formed by in aminolysis of **1**.



$EtOC(=X)SC(=Y)OEt$

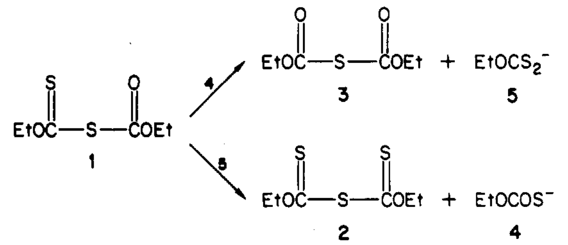
1, X=S, Y=O
2, X=Y=S
3, X=Y=O



$EtOC(=X)S^-$

4, X=O
5, X=S

In a study of the thiolyses of **1** with **4** and **5** (eq 1) in ethanol at 0 °C, we found that the disappearance of **1** in its reaction with **5** was faster than that with **4**, which suggested that the thiocarbonyl group of **1** was more reactive than the carbonyl toward these ions.[2] However, this comparison is uncertain because **1** was in excess over **4** and **5**, and the reactions were complicated by reverse attack on **1** by the product ions **5** and **4**, respectively.



(1)

In order to shed more light on the reactivities of carbonyl and thiocarbonyl groups toward thioanions, we report in this paper a kinetic study of the reactions of **1** with **4** and **5** in ethanol and also the corresponding reverse steps: the reactions of **3** with **5** and **2** with **4** in the same solvent, where **4** and **5** are in excess over the substrates.

Experimental Section

Materials. The syntheses of **1**,[3] **2**,[4] **3**,[4] the potassium salt of **4**,[5] and the sodium salt of **5**[6] have been described previously. Ethanol (95%) and the chemicals used in the analyses (benzene, hydrochloric acid, sodium carbonate, and methyl caproate) were analytical reagent grade. Ethanolic solutions of **4** and **5** were freshly prepared prior to use.

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Table I. Experimental Conditions and k_{obsd} in 95% Ethanol

reactn	temp, °C (±0.1 °C)	10^3[nucl], M[a]	$10^3 k_{obsd}$, s^{-1}	no. of runs	$10^2 k$, s^{-1} M^{-1}[b]
1 + **4**	20.7	2.0–7.9	0.24–1.05	4	13 ± 4
	24.6	2.0–7.9	0.49–1.67	4	21 ± 3
	25.0				24[c]
	30.2	3.0–5.9	1.18–2.31	4	38 ± 2
	35.4	2.0–7.9	1.65–6.08	3	75 ± 3
	39.4	2.0–7.9	1.78–8.25	4	110 ± 10
1 + **5**	15.4	100–200	0.83–1.65	3	0.83 ± 0.04
	20.3	50–200	0.58–2.41	4	1.22 ± 0.05
	25.0	25–200	0.46–3.21	12[d]	1.56 ± 0.05
	30.7	50–200	1.28–4.60	4	2.2 ± 0.01
	36.5	50–200	1.78–6.42	3	3.1 ± 0.2
2 + **4**	20.8	3.9–7.9	0.15–0.30	4	3.8 ± 0.4
	25.0				6.6[c]
	25.5	2.0–7.9	0.14–0.55	3	6.9 ± 0.3
	28.1	3.9–7.9	0.36–0.73	3	9.5 ± 0.5
	35.9	2.0–7.9	0.33–1.71	4	24 ± 2
3 + **5**	25.0	200–400	0.13–0.27	3	0.07 ± 0.004
	35.0	200–400	0.34–0.68	3	0.17 ± 0.01
	45.2	200–300	0.80–1.18	3	0.38 ± 0.02

[a] Molar concentration of nucleophile **4** or **5**. [b] Rate constants obtained as slopes from k_{obsd} vs. [nucl] plots. Errors shown are standard deviations. [c] Values obtained by interpolation of the corresponding Arrhenius plots at 25 °C. [d] Some of these runs were carried out at ionic strength 0.2 M (maintained with $NaClO_4$) and no significant differences (less than 3%) were observed.

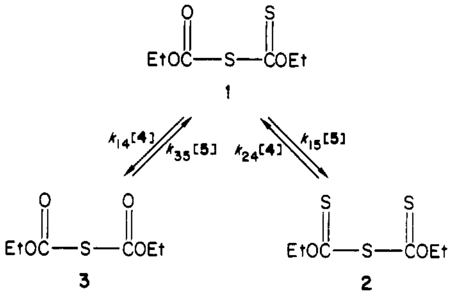
Kinetic and Product Studies. Reaction of 1 with 4. Solutions of **4** (2.5 mL) in ethanol at the reaction conditions (Table I) were introduced into 1-cm cells and placed in the thermostatted cell holder of a Pye Unicam SP 1800 spectrophotometer. After thermal equilibration, a stock solution (100 μL) of **1** in ethanol was injected into the solutions. By repetitive scanning, an isobestic point at 288 nm and an absorbance increase at 305 nm were observed. The reactions were followed by monitoring the increase of absorbance with time of product **5** at 305 nm. The initial concentration of **1** was 6.1 × 10^{-5} M in all runs. Pseudo-first-order rate constants (k_{obsd}, Table I) were obtained from "infinity" plots (at least 33-fold excess of **4** over **1** was employed).

The reactions were also followed by HPLC (with UV detector), after treatment of the samples with hydrochloric acid to decompose the ions **4** and **5** followed by neutralization with sodium carbonate. Only the disappearance of **1** was observed by this technique since product **3** shows a very weak UV signal at the wavelength used. Decomposition of **1** and formation of **3** during the reactions were detected by GLC analysis after treatment of the reaction samples with hydrochloric acid followed by neutralization. The reactions went to completion as shown by the absence of **1** and the presence of **3** at "infinity" time.

Reaction of 1 with 5. Pure liquid **1** (0.2–1.0 μL) was injected into thermostatted solutions of **5** in ethanol (2 mL) containing benzene (10 μL) as internal standard at the appropriate reaction conditions (Table I). Aliquots (150 μL) were removed at time intervals through a silicone rubber cap and added to ethanolic hydrochloric acid to decompose **5**. After neutralization with sodium carbonate the samples were analyzed by HPLC in a Series 2 Perkin-Elmer apparatus provided with a Perkin-Elmer silica column of 7200 theoretical plates under the following conditions: eluant, *n*-hexane–chloroform 95/5 (v/v) in the isocratic mode; flow rate, 2 mL/min; temperature, ambient; internal standard, benzene; UV detector, Perkin-Elmer LC-15. The initial concentration of **1** was 6.1–30.4 × 10^{-4} M, and the excess of **5** over **1** was at least 33-fold. The reactions were measured by following the height of the signal of **1** (h_1) relative to that of benzene (h_b) at different times. Plots of ln (h_1/h_b) vs. time were linear for at least four half-lives. The slopes of these plots are the pseudo-first-order rate constants (k_{obsd}). In some runs, the ionic strength was modified by $NaClO_4$ addition and no significant differences of k_{obsd} were seen. The experimental conditions and k_{obsd} are shown in Table I.

Immediately after the disappearance of **1** the only product observed by HPLC analysis was **2** (the other product **4** had been previously decomposed). At longer times a slow decomposition of **2** was observed and a stable compound was isolated and identified as *O*-ethyl *S*-ethyl xanthate (**6**) by its UV–vis spectrum. The same product was obtained in a direct (and slow) reaction of **2** with **5** in ethanol.

Scheme I



Reaction of 2 with 4. An ethanolic stock solution of **2** (0.25–0.5 mL) was added to thermostatted solutions of **4** in ethanol (25 mL) at the appropriate experimental conditions (Table I). Reaction samples (1 mL) removed at time intervals were quenched by addition to ethanolic hydrochloric acid, diluted to 5 mL with ethanol, and scanned in the region 250–320 nm with a Pye Unicam SP 1800 spectrophotometer (decompostion of **4** with acid was necessary because of absorbance interference with **2**). The initial concentration of **2** was 1.4–2.8 × 10^{-4} M, and at least a 15-fold excess of **4** over **2** was used. Pseudo-first-order rate constants (k_{obsd}) were obtained in duplicate by plotting ln *A* vs. time, where *A* is the absorbance of **2** at 302 nm. The experimental conditions and values of k_{obsd} are shown in Table I.

The reaction was also studied by HPLC (with UV detector), which showed a decrease in **2** and an initial increase in **1** followed by a decrease with time (Scheme I).

The reactions went to completion as indicated by the absence of **2** at "infinity" time. This was also shown by both HPLC and GLC analysis performed after decomposing the ions with ethanolic hydrochloric acid followed by neutralization with sodium carbonate. Compound **3** was the final product as indicated by GLC analysis.

Reaction of 3 with 5. Pure **3** (4 μL) was injected into thermostatted ethanolic solutions of **5** (10 mL) at the reactions conditions (Table I). Samples (1 mL) were quenched by addition to ethanolic hydrochloric acid. A solution of 4.73 × 10^{-3} M methyl caproate in dichloromethane (1 mL) was then added as internal standard for GLC analysis, and the solutions were diluted to 5 mL with dichloromethane. GLC analysis was carried out on a Perkin-Elmer 900 gas chromatograph equipped with flame ionization detector and a 10 ft × $^1/_8$ in. stainless steel column filled with 5% SE-30 on Chromosorb W. Peak integration was carried out with a Perkin-Elmer M-1 integrator.

The initial concentration of **3** was 1.6 × 10^{-3} M in all runs, and at least 12-fold excess of **5** over **3** was used. No good pseudo-first-order rate constants (k_{obsd}) were found from plots of ln S_3/S_{MC} vs. time, where S_3 and S_{MC} are GLC signal areas of **3** and methyl caproate, respectively. The plots were linear only for one half-life, and k_{obsd} was determined from the slope of the linear portion of the plot.

The reactions were also followed by HPLC analysis (with UV detector), which showed an initial increase of the **2** signal with time, followed by a decrease after longer periods. The decrease was attributed to reaction of **2** with excess **5** yielding **6**, as was also observed in the reaction of **1** with **5**. Compounds **1** and **3** were not detected, the former due to its low concentration, and the latter because of its lack of absorbance at the wavelength employed.

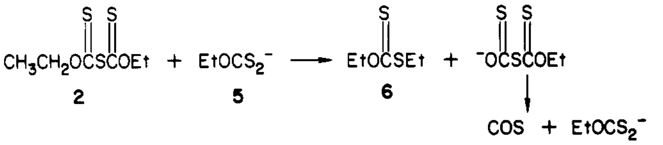
Results and Discussion

The reactions follow eq 2 under our conditions,

$$k_{obsd} = k[\text{nucl}] \qquad (2)$$

where *k* is the second-order rate constant for the reaction of the substrate with the nucleophile, and [nucl] is the molar concentration of the latter. The values of *k* (Table I) were obtained as the slopes of k_{obsd} against [nucl] plots

Scheme II



at several temperatures in 95% ethanol. The reactions are summarized in Scheme I.

The reactions of 4 with 1 and 2 did not give the products expected from attack by the anionic oxygen of 4. Sulfur was therefore the nucleophilic atom of 4 in these reactions.

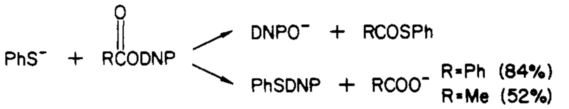
Comparison of the reactivities of the substrates at 25 °C can be made by interpolation of the Arrhenius plots for the reactions of 4 with 1 (Table I). These figures show that 1 is more reactive than 2 toward 4, and more reactive than 3 toward 5. The reactions of 1 with 4 and 5 involve attack of the anionic nucleophiles at the carbonyl and thiocarbonyl groups of 1, respectively, since the attack of 4 and 5 at the thiocarbonyl and carbonyl groups of 1, respectively, merely regenerates 1.

In the reaction of 2 with 4 at 25 °C, accumulation and decomposition of 1 were observed. This is consistent with Scheme I using the values of the second-order rate constants involved and the concentrations of 4 and 5. With these values $k_{14}[4] \gg k_{15}[5]$ (4 was at least in 15-fold excess over 2 and, therefore, had a larger excess over 5 during the reactions), and $k_{14}[4] = 4 \times k_{24}[4]$.

The reactions of 3 with 5 did not show good pseudo-first-order kinetics, and only the initial rate of decomposition of 3 was used to obtain k_{obsd}. The lack of first-order rates is understandable since $k_{15}[5] \approx k_{14}[4]$ (5 was in at least 12-fold excess over 4, but $k_{14} \approx 15 \times k_{15}$), so the rate of the reverse path $k_{14}[4]$ was not constant. Accumulation and decomposition of 1 were not found in this reaction in view of its high rate of breakdown ($k_{14}[4] + k_{15}[5]$) compared to its formation ($k_{35}[5]$), which suggests that 1 was in steady-state concentration.

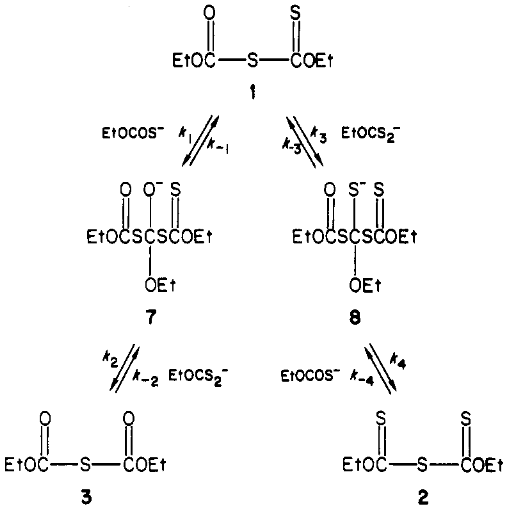
In the reactions of 1 and 3 with excess 5 a slow decomposition of product 2 was observed. This was attributed to the reaction of 5 with 2 yielding *O*-ethyl *S*-ethyl xanthate (6). The same product was obtained in the direct reaction of 2 with 5. Since attack of 5 at a thiocarbonyl group of 2 would only regenerate 2, production of 6 must arise from attack of 5 on an alkyl carbon attached to oxygen (Scheme II).

Thioanions are known to attack aromatic or aliphatic carbon centers located near a carbonyl group. Benzenethiolate, for instance, reacts with 2,4-dinitrophenyl benzoate and acetate in ethanol to give 84% and 52%, respectively, of aromatic carbon–oxygen scission (eq 3, DNP = 2,4-dinitrophenyl).[7] Thus, the more electron withdrawing the R group of the ester the larger the proportion of aromatic C–O scission. Although the reaction of 5 with 2 is not very similar to that shown in eq 3, the R group of 2 has greater electron-withdrawing power than phenyl, and it seems reasonable that at least at slow attack of 5 at the aliphatic carbon of 2 may take place. In the reaction of 1 with 5, product 6 was not detected, which shows that thioanion attack at the thiocarbonyl group of 1 is much faster than that at the alkyl carbon of the same substrate, supporting the above conclusion. Since sulfur compounds are considered as "soft" bases in terms of the principle of "hard and soft acids and bases,"[8] they can easily react with "soft" acidic centers such as thiocarbonyl, aryl, and alkyl carbons.



(3)

Scheme III



Although the existence of tetrahedral intermediates in reactions of sulfur and oxygen nucleophiles with carbonyl and thiocarbonyl compounds is well documented,[9-13] there is no information on the stabilities of the possible tetrahedral intermediates (7 and 8, Scheme III) in the reactions of the present study. Nevertheless, if they exist,[10,14] the mechanism of the reactions under study would be that shown in Scheme III. Application of the steady-state treatment to tetrahedral intermediates 7 and 8 gives eq 4 for the four reactions under study (the macroscopic rate constants are defined in Scheme I).

$$k_{14} = \frac{k_1 k_2}{k_{-1} + k_2} \qquad k_{35} = \frac{k_{-1} k_{-2}}{k_{-1} + k_2}$$
$$k_{15} = \frac{k_3 k_4}{k_{-3} + k_4} \qquad k_{24} = \frac{k_{-3} k_{-4}}{k_{-3} + k_4} \tag{4}$$

Any rate-limiting steps in Scheme III would be determined by the leaving abilities of 4 and 5 from the tetrahedral intermediates. It is known that the leaving abilities of similar substituted sulfide groups are inversely related to their basicities.[10] The basicity of *O*-ethyl xanthate ion 5 (as measured by the pK_a of its conjugate acid in water) is p$K_a \approx 1.6$ at 25 °C,[15,16] and that of *O*-ethyl monothiocarbonate ion 4 is p$K_a \leqslant 2.2$ at the same temperature.[15] These values are not significantly different and therefore

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(14) The[illegible]s attached to the central carbon of intermediates 7 and 8 will have [illegible]abilizing effect less than that reflected in the acidities of their conju[illegible]e acids because those acidities involve a resonance contribution not involved in the tetrahedral intermediates. We thank one of the reviewers for this comment.

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Table II. Activation Parameters in 95% Ethanol[a]

reactn	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$, kcal mol^{-1}
1 + 4	21 ± 1	20 ± 1	6 ± 8	18 ± 3
1 + 5	11.0 ± 0.6	10.4 ± 0.6	−32 ± 6	20 ± 2
2 + 4	22 ± 1	21 [illegible] 1	7 ± 1	19 ± 1
3 + 5	16 ± 1	15 ± 1	−22 ± 3	22 ± 2

[a] Errors shown are standard deviations.

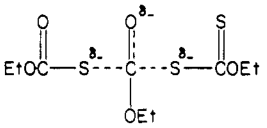
no difference in the leaving abilities of **4** and **5** from the tetrahedral intermediates can be assessed. Accordingly, any rate-limiting steps of Scheme III cannot be determined with certainty.

Some conclusions can be drawn from the macroscopic rate constants obtained for the four reactions at 25 °C (Table I): (1) Since the basicities of **4** and **5** are similar it seems reasonable to assume that k_{-1} and k_{-3} are not very different from k_2 and k_4, respectively. Therefore, eq 4 yields $k_{14}/k_{24} \approx k_1/k_{-4} \approx 4$ at 25 °C. Since k_1 measures the attack of **4** at the carbonyl carbon of **1**, and **2** has two thiocarbonyl groups, this means (after statistical correction) that the carbonyl group is about eight times as reactive as the thiocarbonyl group toward **4**. (2) Equation 4 yields $k_{15}/k_{35} \approx k_3/k_{-2} \approx 22$ at 25 °C. After statistical correction, the thiocarbonyl group of **1** would be about 44 times as reactive toward **5** as either of the carbonyl groups of **3**. This is in accord with Pearson's views,[8] since **5** is a "soft" base, and therefore, the rate constant for its attack on a "soft" acid such as the thiocarbonyl group of **1** will be larger than that for its binding to a "hard" acid such as the carbonyl group of **3**. (3) The macroscopic equilibrium constant for $\mathbf{1} \rightleftarrows \mathbf{3}$ is $k_{14}/k_{35} \approx 343$. This value explains why the reactions of **3** with **5** did not show good first-order kinetics, since the k_{14} step was important and the concentration of **4** was increasing significantly during the kinetics measurement.

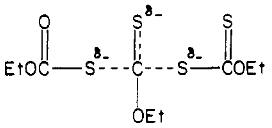
It is well-known that the push provided by an oxygen compound attached to a tetrahedral intermediate is greater than that exerted by an anlogous sulfur compound.[10,11,13] If this behavior can be extended to include oxyanions and thioanions, the push provided by the oxyanion in **7** should be greater than that exerted by the sulfur analogue in **8**. This suggests that expulsion of either leaving group from **7** is faster than the corresponding one from **8**, i.e., $k_{-1} > k_4$ (expulsion of **4**) and $k_2 > k_{-3}$ (expulsion of **5**).

Activation parameters for the four reactions under study are shown in Table II. Two sets of reactions can be grouped according to the $\Delta S^{\ddagger}$ values: those of **5** with **1** and **3**, with large negative $\Delta S^{\ddagger}$ values, and those of **4** with **1** and **2**, which show positive $\Delta S^{\ddagger}$ values. These are consistent with both Scheme III and a concerted mechanism without tetrahedral intermediates.

In the reactions of **5** with **3** and **1**, the transition states for a concerted process are **9** and **10**, respectively. The $\Delta S^{\ddagger} < 0$ values for these reactions can be explained by similar degrees of solvation of transition states and reactants. The loss of translational degrees of freedom of these bimolecular reactions would be responsible for the entropy loss in going from reactants to the transition states. Structure **9** should be slightly more solvated than **10**, since sulfur can delocalize a negative charge better than oxygen, but this should be compensated by a larger solvation of **3** compared to **1**. The errors for $\Delta S^{\ddagger}$ shown in Table II are too large to permit a clear distinction between $\Delta S^{\ddagger}$ values for these reactions, but the fact that $\Delta H^{\ddagger}$ is higher for the reaction of **5** with **3** suggests that stabilization by solvation of **3** relative to **9** is greater than that of **1** relative to **10**.



9



10

The $\Delta S^{\ddagger} > 0$ values for the reactions of **4** with **1** and **2** can be explained by considering reactants and transition states (**9** and **10**, respectively) for a concerted mechanism. The $\Delta S^{\ddagger}$ values intrinsic to bimolecular reactions must be more than compensated by different degrees of solvation of the transition and ground states. Since **4** is the common reactant for these reactions it must be well solvated relative to **5** in order to account for the great $\Delta S^{\ddagger}$ differences between the reactions of these two nucleophiles (the transition states are the same for both types of reactions). If there are similar degrees of solvation of **9** compared to **1** and of **10** relative to **2**, the monothiocarbonate ion much be much more solvated than **9** and **10**. The fact that **4** must desolvate before reaching the transition states will result in entropy gain and also in large $\Delta H^{\ddagger}$ values. Oxyanions are known to be more solvated by polar solvents than their sulfur analogues.[12] Since **4** has some oxyanion character, it is reasonable to assume that it will be more solvated than **5**. On the other hand, although **9** should be slightly more solvated than **10** this should be compensated by a little larger solvation of **1** relative to **2**.

One can arrive at the same conclusions by assuming the mechanism of Scheme III. Since the transition states in this mechanism should be similar to **9** and **10**, the values of the activation parameters for all four reactions can be explained as discussed for the concerted mechanism.

Although there is some consistency between the available data and the mechanism shown in Scheme III, the same is true for the concerted process, and the two mechanisms cannot be distinguished with our data.

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