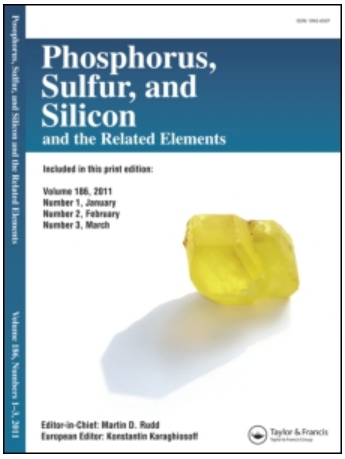

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PYROTHIOCARBONATES I. AMINOLYSIS OF S-(ETHOXYCARBONYL) O-ETHYL DITHIOCARBONATE

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The reaction of S-(ethoxycarbonyl) O-ethyl dithiocarbonate (**1**) with equimolar amounts of butylamine, benzylamine, diethylamine and piperidine in ethanol solution at 0°C is reported. The mole ratio of O-ethyl thiocarbamate (**2**) and O-ethyl carbamate (**3**) formed as main products is larger than unity during all the reaction. Bis(ethoxythiocarbonyl) sulfide (**4**) and bis(ethoxycarbonyl) sulfide (**5**) are also produced and their formation is explained in terms of the reaction of **1** with $EtOCS_2^-$ and $EtOCOS^-$, respectively, which are the leaving groups in the aminolysis of **1**. Reactions **4** → **2** and **5** → **3** also take place. When 50% of **1** has been consumed compound **4** is not detected and compound **5** is found at very low concentration, indicating that generation of **4** and **5** occurs mainly after aminolysis of **1**. The fact that the ratio of **2**:**3** is larger than unity in this aminolysis step, and that S-methyl O-ethyldithiocarbonate is aminolyzed more readily than S-methyl O-ethylmonothiocarbonate under the same conditions as the aminolysis of **1**, suggests that the thiocarbonyl group of **1** is more reactive than the carbonyl group.

INTRODUCTION

The S-(ethoxycarbonyl) O-ethyl dithiocarbonate (**1**) which is used as collector in copper sulfides ores by flotation, may be formally regarded as derived from the unstable $EtOCS_2H$ and unknown EtOCOSH acids.

Recently, we described the reactions of pyrothiocarbonate **1** with primary and secondary aliphatic amines in ethanol solution.[1] At 0°C, the corresponding thiocarbamate **2** and carbamate **3** are the main reaction products. It has been established by ^{1}H-NMR and VPC that product **2** predominates over product **3** in the reaction mixtures and based on this, the thiocarbonyl group of **1** apparently shows a higher reactivity than its carbonyl group. It must be mentioned here that this is in contrast with a recent publication on the aminolyses of some closely related thioacyl acyl sulfides, which reports that the amine preferentially attacks the carbonyl carbon.[2]

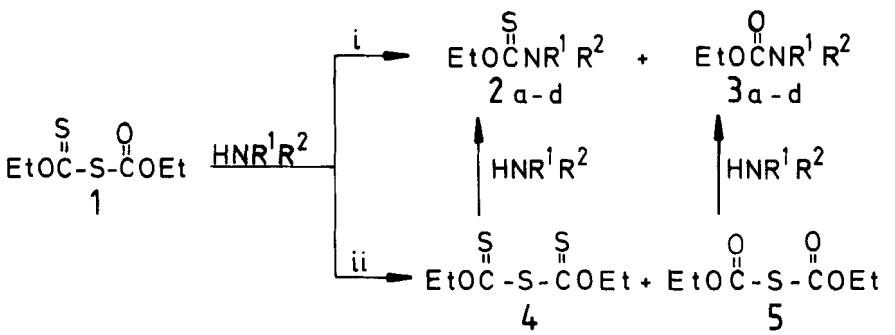
A study of the secondary products present in the mixtures using different mole ratios of **1** and amine showed the existence of the corresponding urea and thiourea derivatives and also the presence of bis(ethoxythiocarbonyl) sulfide (**4**) and bis(ethoxycarbonyl) sulfide (**5**).[1] In connection with the formation of ureas and thioureas, some experimental evidence indicates the existence of carbon disulfide and carbonyl sulfide, which are probably generated by decomposition of the leaving groups $EtOCS_2^-$ and $EtOCOS^-$ involved in the aminolysis of **1**.

The course of the above reaction, based on product criteria, suggests that formation of carbamate **2** and **3** may occur by attack on substrate **1** (pathway *i*, Scheme 1) and/or on the symmetrical sulfides **4** and **5**. These could be generated by

amine-catalyzed disproportionation of **1** (pathway *ii*) in an analogous way to that described by Yoshida.[3] An alternative route to the transesterification products **4** and **5** involves the attack of the leaving groups $EtOCS_2^-$ and $EtOCOS^-$ at the thiocarbonyl and carbonyl groups of the mixed sulfide **1**.[4]

$$\mathbf{4} \xleftarrow{EtOCS_2^-} \mathbf{1} \xrightarrow{EtOCOS^-} \mathbf{5}$$

In the present work we study the variation of concentration with time of the products and of some intermediates observed during the reaction of **1** with butylamine, benzylamine, diethylamine and piperidine in ethanolic solution. Through this study we attempt to establish the sequence of the steps involved in the reaction of **1** with the different amines, and also to shed light on the reactivity of the carbonyl and the thiocarbonyl groups of **1**.



HNR^1R^2, a = butylamine ; b = benzylamine ; c = diethylamine ; d = piperidine

SCHEME 1

RESULTS AND DISCUSSION

The quantitative analysis of compounds **1**, **2**, **3**, **4** and **5** was carried out in the mixture reactions at several times by VPC, after quenching with acid. This renders the thioanions $EtOCS_2^-$ and $EtOCOS^-$ into the corresponding unstable acids, and also the reactive free-base form of the amine is converted into its unreactive conjugate acid. The ionic species $EtOCS_2^-$ and $EtOCOS^-$ were quantitatively analysed by VPC as their S-methyl esters $EtOCS_2Me$ (**6**) and EtOCOSMe (**7**), following quenching of the reactions by addition of methyl iodide.

$$EtOCXS^- \begin{cases} \xrightarrow{H^+} EtOH + CXS \\ \xrightarrow{MeI} EtOCXSMe \end{cases} \qquad X = O, S$$

It is noteworthy that no difference in the concentrations of **1**, **3**, **4** and **5** was found when either the acid or the methyl iodide treatment of the samples was used. Only a small difference (less than 10%) was observed in the analysis of **2a**, which was attributed to the reaction EtOCSNHBu + MeI → MeSCONHBu + EtI. The S-methyl thiocarbamate was evaluated by VPC by comparison with an authentic sample.[5]

During the reactions, the thiocarbamate **2**, carbamate **3**, bis(ethoxythiocarbonyl) sulfide (**4**) and the ammonium thiocarbonates were found in different proportions depending on both the reaction time and the amine, but the bis(ethoxycarbonyl) sulfide (**5**) was only detected at low concentration after the first minute of the reaction (0.002M and 0.0012M for butylamine and benzylamine respectively). Table I shows the concentrations at several times of the species involved in the representative reaction of **1** with butylamine in ethanol solution at 0°C. The results indicate that there are two consecutive steps in the reaction pathway. The substrate reacted more than 50% after one minute suggesting that the aminolysis reaction rate is very fast.

The mass balance for butylamine is good; in fact adding the concentrations of **2**, **3**, **6** and **7** we can conclude that part of the amine was used up as counterion of the thiocarbonates formed during the reaction. Taking into account that the aminolysis stoichiometry is 1 : 2 (substrate : amine) and that only equimolar proportions were used, the second step must be slow because it would be controlled by the amine regeneration through the decomposition of the ammonium thiocarbonates.

$$EtOCX\bar{S}H_2\overset{+}{N}R^1R^2 \rightarrow HNR^1R^2 + CXS + EtOH \qquad X = O,S$$

It is noteworthy that after one minute of reaction, the molar amounts of **2** and **7** and also the ones of **3** and **6** are similar. These results allow us to disregard the disproportionation reaction prior to the aminolysis, since this would imply that the molar amounts of **2** and **6** and also the ones of **3** and **7** were similar, in contrast to the experimental results.

TABLE I

Reaction of **1** with butylamine in ethanol solution at 0°C[a]

Time (min)	Concentration, 10^2 M					
	1	**2a**	**3a**	**4**	**6**	**7**
1	13.7	11.5	4.6		5.8	12.9
3	12.8	12.3	4.7		5.9	10.2
5	11.6	12.9	4.9	0.2	6.2	9.4
15	9.7	14.1	5.4	0.4	6.2	7.7
30	6.6	15.8	5.9	0.8	6.5	6.0
60	4.9	16.9	6.2	1.8	—[b]	
90	3.0	17.2	6.4	2.3	9.1	
120	1.8	17.7	6.5	2.7	7.5	
300		18.1	6.5	3.3	6.5	
1200		19.6	6.5	1.1	5.2	

[a] $[\mathbf{1}]_0 = 33.4 \times 10^{-2}$ M; $[BuNH_2]_0 = 35.0 \times 10^{-2}$ M.
[b] No value determined.

Table I shows that **7** is not observed after 30 minutes of reaction whereas **6** is still detected after 20 hours. On the other hand a total balance of the thiocarbonyl groups (**1** + **2** + 2 × **4** + **6**) indicate that this is constant with time, but the total balance of the carbonyl groups (**1** + **3** + **7**) indicate that the concentration of these groups is decreasing as time progresses. These results indicate a greater stability of the dithiocarbonate ions than the monothiocarbonate ones and this lack of stability is responsible for the decrease of the concentration of the carbonyl groups during the reaction.

The presence of the symmetrical pyrothiocarbonates **4** and **5** is due to the attack of the ionic leaving groups of the aminolyses reactions on the pyrothiocarbonate **1**. To check these reactions, in separate experiments the potassium thiocarbonates were added to an ethanolic solution of **1**; in fact, when **1** was in excess over either potassium monothiocarbonate or dithiocarbonate, **5** or **4** were formed, respectively.

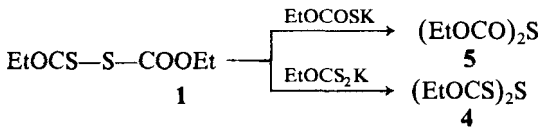


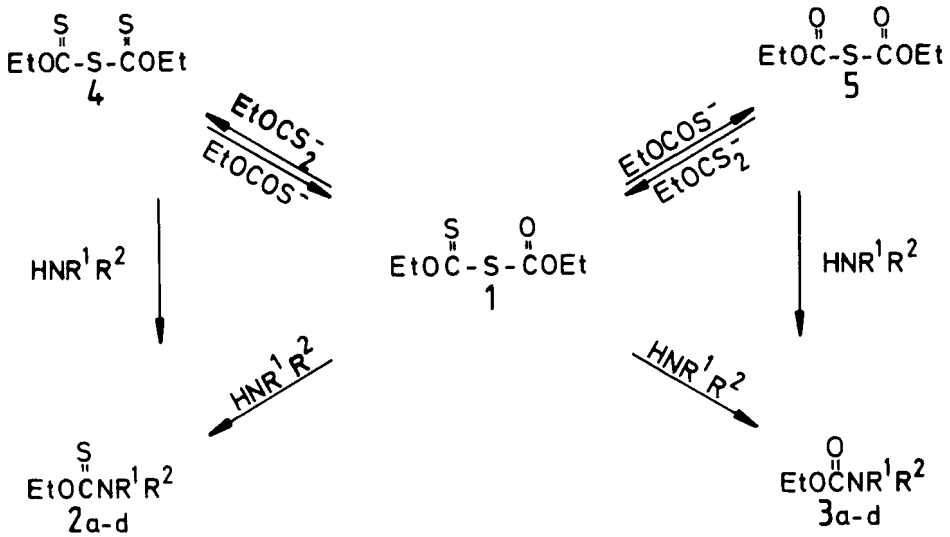
Table I also shows that the concentration of **4** increases to a maximum and then decreases. From the above discussion the increase of concentration can be attributed to the transesterification reaction of **1** (due to the attack of $EtOCS_2^-$ to the thiocarbonyl group of **1**) and the decrease can be attributed to the aminolysis reaction of **4**,[1] yielding **2** and $EtOCS_2^-$.

It is important to notice that at 300 min **1** disappears completely while **4** is still present in the reaction medium. This result suggests that either **1** has a greater reactivity than **4** towards amine, or that in the reaction of **1** with $EtOCS_2^-$, **4** and $EtOCOS^-$ were formed, the latter decomposing in the reaction medium.

All the reactions discussed are summarized in Scheme 2. Observations during the first minute would indicate that the step **1** → **2** is faster than **1** → **3**. During the second step (after 1 min) the full scheme is operating. As the reaction progresses pathway **1** → **4** becomes more important than **1** → **5** probably due to the relative lower stability of $EtOCOS^-$ than $EtOCS_2^-$ towards decomposition.

Table II shows the ratio **2** : **3** for the reaction of **1** with different amines. It can be observed that after one minute of reaction the above ratio is greater than unity, which suggests a greater reactivity of the thiocarbonyl group than the carbonyl one of **1**. In all cases, the ratio increases as time progresses, which can be accounted for in terms of the greater importance of the aminolysis of **4** compared to the one of **5** as the reaction proceeds, in view of the increasing concentration of **4** relative to that of **5** (the formation of **4** from **1** is favored over that of **5** due to the greater stability towards decomposition of $EtOCS_2^-$ compared to $EtOCOS^-$, as discussed earlier). It is worth pointing out that there is no apparent relationship between the nature of the amine and the concentration ratio **2** : **3**. This suggests that the mechanism of paths **1** → **2** and **1** → **3** are not simple ones.

Although the ratio **2** : **3** could be a good criterion to assess the greater reactivity of the thiocarbonyl than the carbonyl group of **1**, this ratio cannot be considered a



SCHEME 2

TABLE II

Molar concentration ratios between thiocarbamate (**2**) and carbamate (**3**)

Time (min)	Amines			
	Butylamine	Benzylamine	Diethylamine	Piperidine
1	2.5	2.8	2.3	2.1
3	2.6	2.9	2.3	2.1
5	2.6	3.0	2.3	2.1
15	2.6	3.1	2.3	2.1
30	2.7	3.2	2.3	2.1
60	2.7	3.3	2.3	2.1
90	2.7	3.3	2.3	2.2
120	2.7	3.3	2.4	2.2
300	2.8	3.4	2.4	2.2
1200	3.0	3.4	2.5	2.3

quantitative measurement of the relative reactivities, since **2** and **3** exhibit more than one formation pathway, and furthermore different leaving groups are involved in the amine attack on the carbonyl or the thiocarbonyl groups of **1**.

In order to study the relative reactivity of the thiocarbonyl and carbonyl groups towards amines, without the interference of both transesterification reactions and the nature of the leaving group, the simultaneous aminolysis of the S-methyl esters, $EtOCS_2Me$, **6**, and EtOCOSMe, **7**, was carried out. These compounds were selected as models of the ethoxythiocarbonyl and the ethoxycarbonyl moieties of **1**. An equimolar mixture of **6** and **7**, of the same total molar concentration as that utilized

in the aminolysis of **1**, was treated with the appropriate amount of butylamine in ethanol solution at 0°C.

$$\mathbf{6}+\mathbf{7} \xrightarrow[-CH_3SH]{BuNH_2} \mathbf{2a}+\mathbf{3a}$$

The dithiocarbonate **6** reacted completely after 24 h while the product derived from the reaction of **7** could be detected only after 100 h. This fact supports the higher reactivity of the thiocarbonyl group of **1** in comparison to its carbonyl group. Further studies are currently in progress in order to have a more detailed view of these transesterification reactions.

EXPERIMENTAL

Materials. Preparations of **1**,[1] **2a–d**,[1] **3a–d**,[1] **6**,[6] **7**,[6] $EtOCS_2K$,[7] EtOCOSK[8] have been previously described. **4** and **5** were made by acylations of sodium sulfide with O-ethyl chlorothiocarbonate and ethyl chlorocarbonate respectively, using a phase-transfer catalyst.[9] Ethanol (95%) was analytical reagent grade and all the amines were purified by standard methods prior to use.

Procedure. A solution of 20 mmol of S-(ethoxycarbonyl) O-ethyl dithiocarbonate in 30 ml of 95% ethanol at 0°C was added to a solution containing 20 mmol of the appropriate amine in 30 ml of 95% ethanol at 0°C with stirring which was stopped after 30 sec. Samples of 5 ml were taken from the reaction solution at different times. The aliquots were quickly quenched by pouring into an excess of an aqueous cold solution of 10% HCl and extracted with chloroform (2 × 20 ml). The organic layer was washed with sodium bicarbonate solution, water and then dried over $MgSO_4$ prior to removal of the solvent in vacuo. The residue was diluted to 10 ml with toluene and analyzed by VPC.

The procedure for the detection of O-ethyl thiocarbonate ions was as above, except that the residue was diluted with benzene and that before pouring the aliquots into the HCl solution, 1 ml of methyl iodide was added and then shaken.

A solution of 20 mmol of **1** in 10 ml of 95% ethanol was mixed with 2 mmol of $EtOCS_2K$ or EtOCOSK in 50 ml 95% ethanol at 0°C. After 1 h, 5 ml of an aliquot was added to a cold 10% HCl solution. The procedure continued as mentioned above for the reaction of **1** with amines.

Analytical Method. VPC analyses were performed on a Perkin Elmer Model 900 gas chromatography equipped with a flame-ionization detector and a 10 ft × $\frac{1}{8}$-in stainless-steel column filled with 3% SE-30 on Chromosorb W. A flow rate of 60 ml/min of N_2 and an oven programmed temperature of 140–240° were used. Peak integration was carried out by a Perkin Elmer Model M-1 integrator. The concentrations are reported as the average of at least two measurements interpolated from calibration curves determined by injection of samples of known concentrations of different compounds.

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