Catalysed Decomposition of Bis(ethoxythiocarbonyl) Sulphide with Tributylphosphine. A Kinetic Study in Dimethyl Sulphoxide, Acetonitrile, and their Mixtures with Toluene

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The reaction of bis(ethoxythiocarbonyl) sulphide (**1**) with tributylphosphine in acetonitrile, dimethyl sulphoxide, and in their mixtures with toluene was subjected to kinetic study. The effect of water content in acetonitrile was also investigated. Activation parameters were measured and related to charge development in the formation of the first transition state, in accord with the proposed mechanism.

Bis(ethoxythiocarbonyl) sulphide (**1**) reacts with tertiary amines leading to xanthates as leaving groups.[1] In the aminolysis[2] and thiolysis[3] of *S*-(ethoxycarbonyl) *O*-ethyl dithiocarbonate in ethanol the formation of xanthates was also observed. It seemed interesting to investigate the solvent effect on the title reaction in order to clarify the mechanism and the polarity of the transition state involved. The solvents were selected according to their effect on the reaction rates and on the stabilization of the products.

Experimental

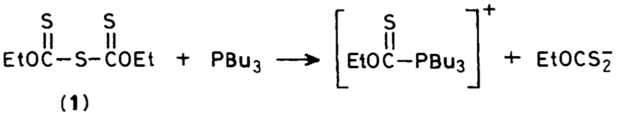
Materials.—Bis(ethoxythiocarbonyl) sulphide,[4] potassium *O*-ethyl xanthate,[5] and *S*-methyl *O*-ethyl xanthate[6] were obtained as described. Tributylphosphine (Merck) was redistilled under nitrogen, b.p. 240—242 °C. Acetonitrile and dimethyl sulphoxide for liquid chromatography (Burdick and Jackson) were used as purchased. Toluene (p.a., Merck) was dried by refluxing with sodium and distilled from a fractionating column. Solvent mixtures were prepared and stored under nitrogen. Stock solutions of (**1**) and tributylphosphine were also prepared under nitrogen and used immediately. Karl Fisher reagent (Merck), kindly supplied by Professor C. Reichardt, was used to determine the water content of all solvents used.

Kinetic Measurements.—Quartz cells (1 cm; Hellma 110QS) containing a solution of (**1**) (3.01×10^{-5}M) in the appropriate solvent were placed in the thermostatted cell holder of a Pye–Unicam SP-1800 spectrophotometer. After thermal equilibration a stock solution (10—65 μl) of tributylphosphine in toluene (or acetonitrile in the water–acetonitrile study) was injected into the reaction solution. The reaction was followed by monitoring the absorbance increase with time at 320 nm.

The observed rate constants (k_{obs}) were determined by the Guggenheim method and the second-order rate constant k as slopes of plots of k_{obs} *versus* $[PBu_3]$.

Results and Discussion

The spectrophotometric study shows the increase of an absorption band at 310 nm for reactions of (**1**) with PBu_3. By adding a methyl iodide solution to the mixture this band disappears and two new ones appear at 250 and 278 nm. This behaviour was also observed for a solution of potassium *O*-ethyl xanthate, suggesting that the xanthate is one of the products of the reaction [equation (1)]. This fact was confirmed by h.p.l.c. using *S*-methyl *O*-ethyl xanthate as standard.



$$\mathrm{EtO}\overset{\overset{S}{\|}}{\mathrm{C}}-\mathrm{S}-\overset{\overset{S}{\|}}{\mathrm{C}}\mathrm{OEt} + PBu_3 \longrightarrow \left[\mathrm{EtO}\overset{\overset{S}{\|}}{\mathrm{C}}-PBu_3\right]^+ + EtOCS_2^- \quad (1)$$

(**1**)

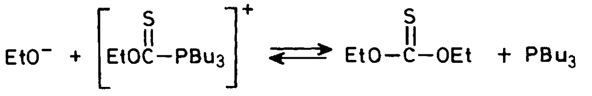
Conductivity experiments show an increase of conductivity up to an equilibrium value, similar to the behaviour shown by the absorbance. A slow decrease of both absorbance and conductivity can be observed afterwards, showing that the xanthate decomposes to other products.

The rate of formation of xanthate cannot be measured at molar fractions of toluene greater than 0.42 and 0.61 in mixtures with acetonitrile and dimethyl sulphoxide, respectively, due to the fact that decomposition of xanthate occurs faster in the less polar solvent mixtures probably due to destabilization of the products of the initial reaction.

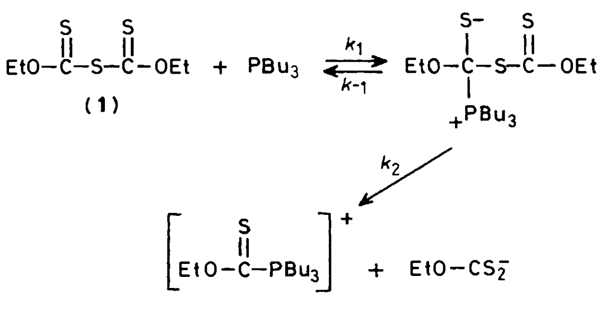
Decomposition of xanthate produces CS_2 which with the excess of phosphine of the medium form an addition compound [equation (2)]. This was checked by visible spectrophotometry.

$$CS_2 + PBu_3 \rightleftharpoons \overset{+}{P}Bu_3-CS_2^- \quad (2)$$

Although we were concerned with the kinetics of the initial reaction, by taking into account the described decomposition, attempts were made to identify the phosphonium species. In fact, ^{31}P n.m.r. (excess of substrate) shows only a signal corresponding to free phosphine, suggesting that the decomposition of initial products leads to phosphine. On the other hand the formation of *OO*-Diethyl thiocarbonate through equation (3) was disregarded upon consideration of its u.v. spectrum.[7]



$$EtO^- + \left[\mathrm{EtO}\overset{\overset{S}{\|}}{\mathrm{C}}-PBu_3\right]^+ \rightleftharpoons \mathrm{EtO}-\overset{\overset{S}{\|}}{\mathrm{C}}-\mathrm{OEt} + PBu_3 \quad (3)$$



Scheme.

A possible reaction mechanism is shown in the Scheme. The steady-state condition leads to $k_{obs} = k_1k_2(k_{-1} + k_2)^{-1}[PBu_3]$. Assuming that the leaving abilities of *O*-ethyl xanthate and tributylphosphine from the intermediate are in inverse order

Table 1. Experimental conditions, k_{obs}, and k values in acetonitrile–toluene mixtures

X_{AN}	T/°C (±0.1 °C)	10^3 [PBu_3]/mol dm^{-3}	10^2k_{obs}/s^{-1}	No. of runs	k*/mol^{-1} s^{-1} dm^3
1.00	35	0.648—4.21	2.48—15.96	5	37 ± 2
	30	0.648—3.24	2.19—10.84	5	34 ± 2
	25	0.648—4.21	2.14—12.27	6	29 ± 1
	15	0.648—4.21	1.49—9.27	5	21.6 ± 0.6
0.93	35	0.648—4.21	1.94—13.23	5	32 ± 2
	30	0.648—4.21	1.76—11.65	4	28.0 ± 0.7
	25	0.648—4.21	1.69—10.00	5	23 ± 1
	15	0.648—4.21	1.34—7.59	5	17.5 ± 0.2
0.89	35	0.648—4.21	1.59—10.33	5	26 ± 2
	30	0.648—3.24	1.35—6.76	3	20.8 ± 0.2
	25	0.648—4.21	1.26—7.53	5	17.6 ± 0.6
	15	0.648—4.21	0.96—5.61	5	13.1 ± 0.6
0.83	35	0.648—3.24	1.41—6.27	4	18.7 ± 0.3
	30	0.648—4.21	1.35—7.37	5	16.9 ± 0.4
	25	0.648—4.21	0.97—6.29	5	14.7 ± 0.5
	15	0.648—4.21	0.86—4.75	5	10.3 ± 0.9
0.75	35	0.648—2.59	1.24—4.12	4	14.8 ± 0.9
	30	0.648—4.21	1.04—5.25	5	11.9 ± 0.4
	25	0.648—4.21	0.89—4.70	5	10.8 ± 0.6
	15	1.62—4.21	1.52—3.60	4	7.8 ± 0.5
0.67	35	0.648—4.21	0.97—5.90	5	13.5 ± 0.5
	30	0.648—4.21	0.83—4.94	5	11.3 ± 0.5
	25	1.62—4.21	1.85—4.33	4	9.4 ± 0.7
	15	0.648—4.21	0.46—2.85	5	6.8 ± 0.2
0.58	35	1.62—4.21	1.76—4.93	4	11.8 ± 0.8
	30	0.648—3.24	0.67—3.25	4	10.1 ± 0.4
	25	2.27—4.21	1.99—3.68	3	8.7 ± 0.1
	15	0.648—4.21	0.35—2.38	5	5.6 ± 0.2

* The errors are standard errors.

Table 2. Experimental conditions, k_{obs}, and k values in dimethyl sulphoxide–toluene mixtures

X_{DMSO}	T/°C (±0.1 °C)	10^3 [PBu_3]/mol dm^{-3}	10^2k_{obs}/s^{-1}	No. of runs	k*/mol^{-1} s^{-1} dm^3
1.00	35	0.648—1.94	4.41—11.16	5	53 ± 2
	30	0.648—1.94	3.88—9.67	5	45 ± 2
	25	0.648—2.27	3.68—9.58	3	37 ± 5
	20	0.648—4.21	2.91—14.95	5	33 ± 2
0.93	35	0.648—2.59	3.35—11.56	5	42 ± 1
	30	0.648—2.59	2.69—9.41	4	35 ± 5
	25	0.648—4.21	2.89—14.00	5	30.7 ± 0.9
	20	0.648—2.59	2.22—6.86	4	25 ± 2
0.86	35	0.648—4.21	2.49—14.55	5	33 ± 2
	25	0.648—4.21	2.19—10.71	5	24.5 ± 0.9
	20	0.648—2.59	1.60—5.50	5	20.1 ± 0.3
0.78	35	0.648—2.59	1.93—6.44	4	23 ± 1
	30	0.648—3.24	1.45—6.62	4	19.7 ± 0.8
	25	0.648—4.21	1.36—7.06	5	16.1 ± 0.9
	20	0.648—3.24	1.24—4.99	3	14.4 ± 0.6
0.69	35	0.648—3.24	1.43—5.94	4	17.5 ± 0.5
	30	0.648—4.21	1.33—7.61	5	16 ± 1
	25	0.648—3.24	0.96—4.43	4	13.4 ± 0.1
	20	0.648—2.27	0.99—2.79	3	11.0 ± 0.2
0.61	35	0.648—4.21	1.01—6.03	5	14.0 ± 0.7
	30	0.648—4.21	0.93—5.08	5	11.4 ± 0.5
	25	0.648—4.21	0.74—4.25	5	9.8 ± 0.1
	20	0.648—2.27	0.68—2.04	3	8.4 ± 0.1
0.50	35	0.648—4.21	0.73—4.39	3	10.3 ± 0.1
	30	0.648—3.24	0.71—3.09	4	9.1 ± 0.1
	25	0.648—4.21	0.59—3.19	5	7.3 ± 0.1
	20	0.648—4.21	0.52—2.79	5	6.3 ± 0.2
0.39	35	0.648—4.21	0.67—3.43	3	7.7 ± 0.2
	30	0.648—3.24	0.64—2.44	4	6.8 ± 0.6
	25	0.648—3.24	0.58—2.09	4	5.8 ± 0.1
	20	0.648—4.21	0.41—2.10	5	4.6 ± 0.3

* The errors are standard errors.

Table 3. Activation parameters for the reaction of (**1**) with PBu_3 in acetonitrile–toluene mixtures*

X_{AN}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1.00	18.0 ± 0.8	−156 ± 3
0.93	20 ± 1	−152 ± 5
0.89	22 ± 2	−147 ± 5
0.83	20 ± 2	−155 ± 5
0.75	20 ± 2	−156 ± 6
0.67	22.7 ± 0.9	−149 ± 3
0.58	25 ± 2	−142 ± 5

* The errors are standard errors.

Table 4. Activation parameters for the reaction of (**1**) with PBu_3 in dimethyl sulphoxide–toluene mixtures*

X_{DMSO}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1.00	21 ± 2	−142 ± 8
0.93	23 ± 1	−140 ± 4
0.86	22 ± 1	−142 ± 4
0.78	22 ± 2	−148 ± 6
0.69	21 ± 2	−152 ± 8
0.61	23 ± 2	−149 ± 5
0.50	23 ± 2	−150 ± 6
0.39	23 ± 2	−152 ± 8

* The errors are standard errors.

Table 5. Experimental conditions, k_{obs} and k values for the reaction of (**1**) with PBu_3 in acetonitrile–water mixtures at 25 °C

$[H_2O]$ (p.p.m.)	$10^3[Bu_3P]$/mol dm^{-3}	$10^2k_{obs}/s^{-1}$	No. of runs	k*/s^{-1} mol^{-1} dm^3
110	0.65—3.24	2.36—9.78	5	29 ± 1
180	0.65—3.24	2.17—8.91	4	25 ± 2
280	0.65—2.59	1.75—6.40	4	23.9 ± 0.1
330	0.65—3.24	1.93—8.08	5	23.4 ± 0.5
690	0.65—3.24	1.72—7.82	5	23 ± 1
890	0.65—3.24	2.09—8.16	4	23.4 ± 0.1
1550	0.65—3.24	1.85—8.00	5	23.4 ± 0.4

* The errors are standard errors.

to their basicities (pK_a 1.6 and 8.43 in water at 25 °C, respectively),[8,9] $k_2 \gg k_{-1}$ should hold and $k_{obs} = k_1[PBu_3]$. Thus nucleophilic attack of the phosphine on the thiocarbonyl group of (**1**) is the rate-determining step.

Tables 1 and 2 show k_{obs} and $[PBu_3]$ at several temperatures and compositions for acetonitrile–toluene and dimethyl sulphoxide–toluene mixtures. The second-order rate constants show a slight decrease with increasing toluene concentration at all temperatures. This result suggests that the transition state is more polar than the reactants.

Tables 3 and 4 show the activation parameters obtained. In the toluene–acetonitrile mixtures a slight dependence of $\Delta H^{\ddagger}$ with the composition can be observed whereas in the toluene–dimethyl sulphoxide mixtures practically no dependence is observed. These results can be understood in terms of lower stabilization of the transition state relative to the reactants in acetonitrile mixtures. The strong solvating ability of dimethyl sulphoxide probably leads to preferential solvation over the whole composition range observed. The negative $\Delta S^{\ddagger}$ values in all solvent mixtures are consistent with greater polarity of the transition state compared with the reactants which leads to a greater ordering of solvent molecules around the former.

On the other hand, a kinetic study of the title reaction in water–acetonitrile mixtures (Table 5) shows a strong dependence of k on the composition only for water content <300 p.p.m. This corresponds to *ca.* 6—20 water molecules for each phosphine molecule, enough for the formation of a first solvation shell, and we can infer selective water solvation of the phosphine. In other words, solvation of the phosphine by water is expected to be essentially constant for water content >300 p.p.m. and no influence on its concentration can then be detected in this range. It is possible that the dependence of k on the composition of the acetonitrile–toluene and dimethyl sulphoxide–toluene mixtures involve, to some extent, a contribution by traces of water which cannot be removed at all.

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References

1 H. Yoshida, *Nippon Kagaku Zasshi*, 1969, **90**, 1036.

2 M. A. Palominos, J. G. Santos, J. A. Valderrama, and J. C. Vega, *Phosphorus Sulfur*, 1983, **15**, 245.

3 M. A. Palominos, J. G. Santos, J. A. Valderrama, and J. C. Vega, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2641.

4 S. Juliá, G. Tagle, and J. C. Vega, *Synth. Commun.*, 1982, **12**, 897.

5 A. I. Vogel, 'Practical Organic Chemistry,' Longman Green, London, 1961, p. 499

6 Houben-Weyl, 'Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1955, vol. 9, p. 773.

7 P. Raizman and Q. E. Thompson, 'The Analytical Chemistry of Sulphur and its Compounds,' ed. J. H. Karchmar, Wiley, New York, 1972, Part II, p. 574.

8 R. J. Millikan and C. K. Sauers, *J. Org. Chem.*, 1979, **44**, 1664.

9 G. M. Kosolapoff, 'Organic Phosphorus Compounds,' Wiley, New York, 1972, vol. 1, p. 128.

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