Thiyl radicals in gas-phase thermolysis of xanthic acid esters

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Gas-phase thermolysis of xanthic acid esters and their reaction with acetylene at 250– 600 °C have been studied for the first time. The direction of the thermolysis is determined by the nature of the substituents at the oxygen and sulfur atoms. The main products of the thermolysis are gaseous hydrocarbons, carbon monoxide and hydrogen sulfide. The yields of liquid products of the thermolysis and of the reactions with acetylene are 4-46 %. The role of thiyl radicals in thiophene molecule formation and reaction routes to carbon disulfide, dithiocarbonates, and stilbene are discussed.

Key words: xanthic acid esters, acetylene, gas-phase reactions; thiyl radicals, isomerization; dithiocarbonates.

Liquid-phase thermolysis of xanthic acid esters (~200 °C) is a convenient method for the transformation of alcohols to olefins *via* xanthates. In preparative organic chemistry this reaction is known as the Chugaev reaction.¹ It occurs *via* formation of the intermediate cyclic product,^{2,3} probably through a prior rearrangement of *O*-alkyl- and some functional substituted *O*-organyl-*S*-methylxanthates to appropriate dithiocarbonates.⁴ Gas-phase reactions of xanthic acid esters have not been reported up to now.

We studied gas-phase thermolysis of xanthic acid esters RSC(S)OR' (1) (Table 1) at 250-600 °C. In all cases substantial resin formation and gas evolution are observed. As a result the yield of liquid products of the thermolysis was insignificant even with a moderate duration (20-60 s) of the reactants' contact.

The gaseous products of the pyrolysis of compounds 1a-c are methane, ethane, propane, butane, ethylene, propylene, butenes, hydrogen sulfide, carbon monoxide, and C_5-C_6 hydrocarbons. The appropriate thiols RSH, carbon disulfide, thiophene, as well as the products of the rearrangement of the starting xanthates, 2a-c, were identified in the condensates.

$$\begin{array}{ccc} \text{RSCOR'} & \stackrel{\Delta}{\longrightarrow} & \text{RSCSR'} & (1) \\ \begin{array}{c} \text{II} & \text{II} \\ \text{S} & \text{O} \end{array} \\ \textbf{1a-c} & \textbf{2a-c} \\ \textbf{a: } \text{R} = \text{R'} = \text{Et} \\ \textbf{b: } \text{R} = \text{Pr}, \ \text{R'} = \text{Et} \\ \textbf{c: } \text{R} = \text{Bu}, \ \text{R'} = \text{Et} \end{array}$$

The rearrangement according to Eq. (1) occurs at temperatures >300 °C and is supposedly determined by the higher thermal stability of dithiocarbonates. Since symmetric dithiocarbonates (RS)₂CO or (R'S)₂CO do

not form during this process, it may be suggested that the isomerization provides an intramolecular mechanism and proceeds without R'(R') or RS'(R'S') radicals.

The formation of thiophene on the thermolysis of xanthates 1a-c attests that generation from indicated compounds of vinylthiyl or butenylthiyl radicals which are precursors of thiophene in gas-phase processes takes place.⁵ It should be noted that vinylthiyl radicals undergo intermolecular condensation to thiophene, while butenylthiyl radicals are subjected to intramolecular condensation with the considerably higher rate⁶ (Eq. (2)).

$$C_2H_5S-C(S)OR' \xrightarrow{\Delta} CH_2=CHSH \xrightarrow{-H} CH_2=CHSH$$

 $\longrightarrow CH_2=CHS'$
 $C_4H_9S-C(S)OR' \xrightarrow{\Delta} CH_3CH_2CH=CHSH \xrightarrow{-H} (2)$

CH₂CH₂CH=CHS¹

O-Ethyl-*S*-benzylxanthate (1d) is the most thermal stable. Its thermolysis is not accompanied with gas evolution and isomerization according to Eq. (1). Benzylmercaptan and toluene are mainly formed at 350 °C. When the temperature of the thermolysis of xanthate 1d increases the content of the products changes: benzylmercaptan disappears from the products, while carbon disulfide and stilbene arise. Probably toluene and stilbene are the products of the transformation of radicals and carbenes, which are generated on the thermolysis of xanthate 1d (Eqs. (3) and (5)).

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Startir	ng R	R'	Reaction temper- ature /°C	Yield of the liquid products (wt. %)	Content of the liquid products (%)							
com- pound					RSH	CS ₂	2	1	Benzene	Thiophene	Toluene	Phenol
la	Et	Et	350	8.6	23.0	0.7	9.0	67.0				
			400	7.1	54.0	1.5	32.0	11.2				
			450	5.0	51.0	3.5	43.0	2.0		Traces		_
			500	4.8	11.0	13.5	63.0	Traces		11.2	_	_
			550	3.5	Traces	42.0	38.0		Traces	18.0	Traces	
1b	Pr	Et	350	10.6	32.0	_	3.0	64.0	_	_		
			400	9.2	50.0	1.2	28.0	20.2		-		
			450	8.5	37.9	4.0	53.0	8.0	Traces	Traces		_
			500	7.8	2.9	12.0	75.0	3.0	Traces	3.5	_	
			550	6.6	1.5	53.0	25.0	Traces	3.5	16.0	Traces	—
1c	Bu ⁿ	Et	350	17.4	24.0	_		76.0				_
			400	16.6	29.0	1.0	15.0	53.0		1.5		
			450	14.3	57.0	2.0	32.0	6.0	Traces	3.0		
			500	10.2	8.0	5.2	72.5	2.5	Traces	11.0		
			550	9.4	6.0	32.0	42.5	1.5	1.5	16.0		_
1d]	$PhCH_2$	Et	250	46.4	0.5	—	_	93.0		_	6.5	_
	-		300	41.2	6.0	-		91.0			3.0	
			350	36.5	33.0	—	_	43.0			23.0*	
			450	25.6	—	2.5		8.0			89.0*	_
			500	23.4		22.0		3.0	Traces		75.0*	
			550	22.2		25.0		_	2.0		72.0*	
			600	20.1		28.0	—	_	5.0	_	70.0*	
1e	Bu	Ph	300	18.8	3.5	0.5		95.0	_	_	_	_
			375	15.0	16.0	10.0		71.0	Traces	Traces	_	2.0
			450	11.5	40.0	21.0		30.0	2.5	2.5	_	3.0
			500	5.3	38.0	42.0		3.0	3.4	8.4		5.0
			550	4.3	5.0	70.5		1.5	5.0	12.5		6.5

Table 1. Characteristics of the liquid products of the pyrolysis of xanthic acid esters RSC(S)OR'

* Including stilbene (2-17 %).

$$PhCH_2 - SC(S)OEt - PhCH_2S' + C(S)OEt$$
 (4)

2 PhCH:
$$\longrightarrow$$
 PhCH=CHPh (5)

During thermolysis O-phenyl-S-butylxanthate (1e) transforms to butanethiol, carbon disulfide, thiophene, benzene, and phenol according to the schemes presented above, but it does not isomerize to dithiocarbonate according to Eq. (1).

Co-thermolysis of esters 1a-c with acetylene leads to formation of the same products as the thermolysis of 1a-c alone (Table 2). In this case acetylene inhibits thermal destruction of xanthates (some part of xanthate (7-17 %) does not react even at 600 °C) and does not effect on their isomerization, supporting the intramolecular mechanism of this process. Yield increases on the co-thermolysis of acetylene with xanthates **1a,b** (R = Et, Pr; R' = Et). It is the xanthates that generate vinylthiyl radicals through the cleavage of the RS-C bonds which react effectively with acetylene to form thiophene^{7,8} (Eq. (6)). It should be noted that the greater amount of vinylthiyl radicals is formed when R = Et.

$$CH_2=CHS^{\cdot} + CH \equiv CH \longrightarrow$$

 $\longrightarrow CH_2=CHSCH=CH \xrightarrow{-H^{\cdot}}$ (6)
 $\longrightarrow \boxed{]}$

It seems likely that in the case of xanthate 1c (R = Bu, R' = Et) only butenylthiyl radicals are generated and subsequently they quickly undergo intramolecular

Table 2. Reaction of xanthates 1a-c with acetylene

Starting com-	Reaction temper-	Yield of the liquid	Content of t liquid produ	he cts (%)	
pound	ature ∕°C	products (wt. %)	Thiophene	2	
1a	450	4.8	4.1	21.6	
	500	4.2	24.2	24.5	
	550	3.6	55.2	26.4	
	600	3.0	62.0	22.7	
1b	450	4.4		4.0	
	500	3.8	6.5	30.0	
	550	3.2	24.0	30.4	
	600	2.7	28.1	21.1	
1c	450	8.5	4.6	33.0	
	500	7.7	14.2	69.5	
	550	6.9	16.3	72.8	
	600	5.8	24.0	67.3	

cyclization into thiophene according to Eq (2).⁵ As a result acetylene does not effect on the yield of thiophene on the co-thermolysis with xanthate **1c**.

Thus, the direction of gas-phase thermolysis of xanthic acid esters depends on the nature of the substituents at S and O atoms. Dialkylxanthates are the least stable and undergo the deep decomposition with essentially formation of gaseous reaction products. The yield of the condensate is only 4–17 % with a predominance in it of the appropriate alkanethiol at 400–500 °C, and dithiocarbonate — at 500 °C, while carbon disulfide and thiophene arise in the condensate in noticeable amounts only at 550 °C. This attests that the initial steps of the gas-phase thermolysis of dialkylxanthates are the cleav-

age of the C—S bonds and elimination of CS_2 , which are favorable for formation of alkanethiols, carbon disulfide and gaseous hydrocarbons. At high temperatures (>500 °C) alkanethiols are decomposed to hydrogen sulfide and alkenes as well as partly generate vinylthiyl radicals, involving in formation of the thiophene molecule (see Eqs. (2) and (6)). The rearrangement into dithiocarbonates taking partly place on gas-phase thermolysis is typical only for dialkylxanthates (mainly at 500 °C).

The initial step of the thermolysis of 1d ($R = PhCH_2$, R' = Et) is a cleavage of a PhCH₂-SC(S)OEt bond with formation of benzyl radical as demonstrated by considerable amount of toluene in the liquid products of the thermolysis. The gaseous products of the thermolysis arise from the extrusion of carbon disulfide and thermal destruction of O-alkyl residue as well. The inability of xanthate 1d to isomerization into dithiocarbonate according to Eq. (1) is likely determined by the competitive reaction occurring with the higher rate and attending with generation of stable benzyl radicals according to Eq. (3). Benzylmercaptan is formed as an intermediate product owing to cleavage of the PhCH₂S-C bond at temperatures \geq 450 °C, and thereafter it is completely decomposed, probably according to Eq. (4) to provide the generation of carbene and formation of stilbene and hydrogen sulfide (see Eqs. (4) and (5)).

Contrary to liquid phase thermolysis, gas-phase thermolysis of O-phenyl-S-ethylxanthate does not lead to its isomerization to the corresponding dithiocarbonate. The extrusion of carbon disulfide and the cleavage of a BuS—C bond become predominant at 500—550 °C. As this take place, butylmercaptan and butenylthiyl radicals are generated. The latter undergo the intramolecular

Table 3. Spectral parameters of compounds 1b and 2b

Com- pound	IR, v/cm ⁻¹	MS, m/z (I_{rel} (%))	¹ H NMR, δ
1b	2950 s, 2920 s, 2860 m (vCH); 1440 m, 1430 (vCH ₂); 1370 w, 1350 w, 1290 m, 1230 s, 1200 v.s (vC=S) ¹⁰ ; 1140 m, 1100 v.s, 1035 v.s, 1000 m	166 $[M+2]^+$ (1), 164 $[M]^+$ (6), 149 $[M-CH_3]^+$ (1), 119 (2), 118 (2), 117 $[M-CH_3-S]^+$ (65), 91 (5), 89 $[M-C_3H_7-S]^+$ (100), 75 (46), 74 (8), 73 (10), 61 (2), 59 (25), 58 (3), 49 (15), 48 (2) 47 (10), 46 (3), 45 (15), 43 (4), 41 (30), 39 (15)	1.05 (t, 3 H, MeCH ₂ C); 1.39 (t, 3 H, MeCH ₂ O); 1.63 (m, 2 H, CCH ₂ C); 3.08 (t, 2 H, CH ₂ S); 4.63 (q, 2 H, CH ₂ O)
2b	2960 s, 2915 s, 2865 m (vCH); 1635 s (vC=S) ¹⁰ ; 1455 m, 1440 m (vCH ₂); 1405 w, 1375 w, 1280 w, 1255 w, 1235 w, 1200 w, 1100 v.w, 1060 m, 1040 w, 1000 m, 860 v.s	166 $[M+2]^+$ (4), 164 $[M]^+$ (35), 151 (2), 140 (5), 138 (6), 137 (6) 136 $[M-CO]^+$ (75), 135 (15), 122 (2), 103 $[M-C_2H_5-S]^+$ (15), 95 (17), 89 $[M-C_3H_7-S]^+$ (50), 75 (12), 62 (17), 61 (20), 59 (10) 58 (16), 57 (15), 47 (30), 46 (22), 45 (40), 44 (45), 43 $[C_3H_7]^+$ (100), 42 (10), 41 (60), 39 (25)	0.96 (t, 3 H, <u>MeCH₂C</u>); 1.28 (t, 3 H, <u>MeCH₂S</u>); 1.63 (m, 2 H, CCH ₂ C); 2.99 (q, 2 H, MeC <u>H₂S</u>); 3.08 (t, 2 H, EtC <u>H₂S</u>)

cyclization resulting in the formation of the thiophene molecule.⁵

Acetylene, being an efficient trapping agent for vinylthiyl radicals in gas phase, has supposedly not managed to interact with butenylthiyl radicals, which undergo heterocyclization at a higher rate.

Experimental

IR spectra of compounds **1b** and **2b** (as microlayers) were recorded on a Specord-75 IR spectrometer. ¹H NMR spectra in CDCl₃ were recorded on a Tesla BS-567A spectrometer (100 MHz) with HMDS as internal standard. Mass spectra were obtained on a GC-MS-5972AHP chromato-mass-spectrometer (capillary column 50 m \times 0.2 mm \times 0.5 µm, PONA, carrier gas — helium, temperature gradient mode, heating rate — 12 °C per min).

Gas analysis was carried out on a LKhM-8MD-5 chromatograph (column l = 6000 mm, with 25 % poly(triethyleneglycol butyrate) on an INZ-600 brick).

Analysis of the condensates and control of the purity of the resulting products was carried out on a LKhM-8MD-5 chromatograph (column 2000 \times 3 mm, with 5 % XE-60 silicone on Chromaton N-AW-HMDS, carrier gas — helium, temperature gradient mode 30 \rightarrow 230 °C, heating rate — 12 °C per min).

The starting xanthate acid esters were synthesized by interaction of potassium ethyl (or benzyl) xanthate with corresponding organyl halide according to the method⁹ described previously.

Thermolysis of xanthates (1a-d) was carried out in a quartz tube heated to the required temperature (see Table 1) (heated zone 650×30 mm) and purged with nitrogen. Xanthic acid esters were introduced into the reaction zone by an automatic loader at a rate of 15 mL h⁻¹ in the flow of nitrogen or acetylene (2 L h⁻¹).

Thermolysis of O-phenyl-S-butylxanthate (1e) was carried out in a tubular quartz reactor $(250 \times 15 \text{ mm})$ in the circular clearance (3 mm) between the walls of the reaction tube and the case of the thermocouple. Compound **1e** was introduced into the reaction zone by the automatic loader at a rate of 3.2 mL h⁻¹ in the flow of nitrogen (0.8 L h⁻¹).

Thiols, thiophene, carbon disulfide, benzene, toluene, and stilbene were identified in the products of thermolysis by means of chromato-mass spectrometry and by correlation with references. Dithiocarbonates 2a and 2c were identified by chromato-mass spectrometry. Dithiocarbonate 2b was isolated as individual compound by vacuum distillation from the condensates obtained on the thermolysis of 1b, b.p. = $78 \, ^{\circ}C$ (4 Torr) (cf. Ref. 10). The spectral parameters of 2b in comparison with the parameters of 1b are present in Table 3.

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References

- K. V. Vatsuro and G. L. Mishchenko, *The Name of Reac*tions in Organic Chemistry, Khimia, Moscow, 1976, 598 p. (in Russian)
- 2. N. A. Awadi and D. B. Bigley, J. Chem. Soc., Perkin Trans. 2, 1982, 773.
- 3. R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1983, 296.
- T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata, and K. Harono, *Tetrahedron Lett.*, 1965, 2717.
- 5. M. G. Voronkov and E. N. Deryagina, Usp. Khim., 1990, 52, 1339 [Russ. Chem. Rev., 1990, 52 (Engl. Transl.)].
- E. N. Sukhomazova, L. P. Turchaninova, N. A. Korchevin,
 E. N. Deryagina, and M. G. Voronkov, *Zh. Org. Khim.*,
 1990, 26, 1525 [J. Org. Chem. USSR, 1990, 26 (Engl. Transl.)].
- M. G. Voronkov, E. N. Deryagina, L. A. Ostroukhova, N. A. Korchevin, E. N. Sukhomazova, A. R. Zhnikin, and L. P. Turchaninova, *Zh. Org. Khim.*, 1989, 25, 2588 [J. Org. Chem. USSR, 1989, 25 (Engl. Transl.)].
- N. A. Korchevin, E. N. Sukhomazova, L. P. Turchaninova, G. G. Efremova, N. A. Kalinina, E. N. Deryagina, and M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 1988, 1041 [*Chem. Heterocycl. Compd.*, 1988 (Engl. Transl.)].
- 9. K. Weygand and G. Hilgetag, Organisch-Chemische Experimentierkunst, Leipzig, 1964.
- 10. L. J. Bellamy, Advances in Infrared Group Frequencies, Halster, 1968.

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