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Oxidation of Sulfides with Hydrogen Peroxide to Sulfoxides and Sulfones

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Abstract—Oxidation of sulfides with hydrogen peroxide to sulfoxides and then sulfones was studied. The conditions optimal for the formation of sulfoxides and sulfones were found.

Oxidation of sulfides with hydrogen peroxide is a widely used synthetic route to sulfoxides and sulfones [1]. Although sulfoxides are readily oxidized further to sulfones, under definite conditions the reaction can be stopped at the stage of sulfoxide formation. Oxidation of sulfides to sulfoxides occurs at relatively low temperatures and in short time. The second stage, oxidation of sulfoxides to sulfones, requires higher temperatures and longer time. Sulfones can be prepared both by direct oxidation of sulfides and by oxidation of sulfoxides. In some cases, the latter route is preferable, since each oxidation stage can be performed under optimal conditions; as a result, higher yield and purity of the target product can be attained [2].

In this work we studied oxidation of dimethyl sulfide (DMS), tetramethylene sulfide (TMS), and petroleum sulfide concentrate (PSC) with hydrogen peroxide to the corresponding sulfoxides and oxidation of these sulfoxides to sulfones.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC with a Tsvet 4-67 chromatograph [flame ionization detector; 2100 × 4-mm column; stationary phase 10% polyethylene glycol succinate on Chromaton N-AW-HMDS, 0.2–0.25 mm fraction, washed with water and treated with hexamethyldisilazane; carrier gas nitrogen, GOST (State Standard) 9293–74]. The stationary phase used retains water and allows determination of the nonaqueous oxidation products [3]. Analysis conditions: column temperature 140–180°C, vaporizer temperature 200–240°C, carrier gas flow rate 40–60 ml min^{-1}, sample volume 0.1–0.2 μl. The component contents were determined by internal normalization of the peak areas using benzene as reference. The absolute determination error was 0.4% at a confidence level of 98%.

The oxidation products of petroleum sulfides cannot be analyzed chromatographically because of the low thermal stability of petroleum sulfoxides and high boiling temperature of the sulfone concentrate obtained from them. Therefore, the content of sulfoxide sulfur in the oxidation products was determined by nonaqueous titration of the product with a solution of $HClO_4$ in dioxane [4], and the content of sulfones, by IR spectroscopy, from the intensity of the absorption band of the sulfone stretching vibrations at about 1320 cm^{-1} [5]. The concomitant compounds, mainly sulfoxides, do not absorb in this range. Also, the content of sulfonic and carboxylic acids was determined by potentiometric titration [6].

Oxidation was performed as follows. A flask was charged with a required amount of the starting compound and heated to a required temperature, after which H_2O_2 was added. The mixture was heated at the prescribed temperature with vigorous stirring. The instant of H_2O_2 addition was considered as the reaction start. After the reaction completion, the flask was cooled, and samples of the product were taken. The content of H_2O_2 in the oxidation products was determined by titration with a $KMnO_4$ solution [7]. To each sample we added MnO_2 to decompose the unchanged H_2O_2 and terminate oxidation. After that, the sample was filtered and analyzed.

Hydrogen peroxide was used as 27.5% (here and hereinafter, wt %) aqueous solution [GOST (State Standard) 177–88]. TMS and DMS were 98 and 99.5% pure, respectively. The sulfide concentrate was recovered from the 260–360°C fraction of Arlan crude oil

Table 1. Oxidation of DMS to DMSO (τ = 10 min)

T, °C	H_2O_2 : DMS molar ratio	Composition of dehydrated oxidation product, %				H_2O content in oxidation product, wt %
		DMS	DMSO	DMSF	H_2O_2	
0	0.75	4.5	92.6	0.4	0.8	44.5
	1.1	1.2	94.2	1.2	1.0	45.4
	1.2	0.8	91.5	2.4	2.2	46.2
5	0.8	4.0	93.7	0.9	1.1	43.8
	1.0	1.0	94.8	3.0	1.5	45.0
	1.2	0.6	92.1	3.5	1.8	46.7
10	0.7	3.1	92.2	0.8	0.9	44.3
	1.1	0.9	94.2	3.1	1.2	46.1
	1.3	0.8	92.0	3.8	1.8	47.2

Table 2. Oxidation of DMSO to DMSF

T, °C	H_2O_2 : DMSO molar ratio	τ, h	Composition of dehydrated oxidation product, %		Acidity, g KOH l^{-1}	Yield of DMSF, %
			DMSO	H_2O_2		
40	1.1	20	12	2.3	6.0	48
	1.2	25	10	1.6	6.4	55
	1.3	30	8	1.6	7.4	62
60	1.1	15	6	1.5	6.8	61
	1.2	20	2	1.5	8.0	68
	1.3	25	2	1.4	8.4	72
80	1.1	10	1	0.8	7.5	68
	1.2	15	–	0.8	8.4	70
	1.3	20	–	0.4	9.2	66

[8]; it contained 8.8% sulfide sulfur and 12.8% total sulfur and had the average composition $C_{14.5}H_{27.0}S$.

In experiments on oxidation of DMS to dimethyl sulfoxide (DMSO), we examined the influence of temperature and H_2O_2 : DMS ratio on the yield of reaction products (Table 1). Oxidation was performed at 0.5 and 10°C. The very low boiling point of DMS (37.2%) caused certain problems. Since the reaction is exothermic, even at 10°C it is necessary to take special measures to prevent evaporation of DMS in the initial oxidation stage. In the range 0–10°C, the temperature affects the product composition insignificantly; the yield of DMSO is fairly high. The major influence on the product composition is exerted by the H_2O_2 : DMS molar ratio. When this ratio is as low as 0.7–0.8, the products contain a large amount of unchanged DMS, and dimethyl sulfone (DMSF) is absent. At the H_2O_2 : DMS molar ratio increased to 1.1–1.2, DMS is fully consumed and DMSF appears. This fact suggests the consecutive mechanism of DMSF formation via DMSO. The product obtained by oxidation of DMS is a transparent aqueous solution. To isolate DMSO, the oxidation product was heated at reduced pressure (30–40 mm Hg) on a water bath (40–50°C) to remove water, after which DMSO was distilled in a vacuum (bath temperature 72–82°C, 10–15 mm Hg). The purity of the distilled DMSO was 99.6%, bp 189°C, n_D^{20} 1.4785, d_4^{20} 1.1000.

Found, %: C 30.82; H 7.62; S 41.01.

C_2H_6OS. Calculated, %: C 30.76; H 7.69; S 41.02.

Oxidation of DMSO to DMSF was studied at 40, 60, and 80°C (Table 2). The H_2O_2 : DMSO molar ratio was varied from 1.1 to 1.3, and the oxidation time, from 10 to 30 min. The oxidation product obtained under the above conditions was evaporated at 700 mm Hg to remove about 30–40% of water. Then the oxidation product was cooled to 5°C to crystallize dimethyl sulfone. The crystals were separated, recrystallized from water, and dried in a water-jet-pump vacuum. The resulting DMSF is a colorless crystalline substance readily soluble in organic solvents; purity 99.8%, mp 109°C, bp 238°C.

Found, %: C 25.59; H 6.36; S 34.02.

$C_2H_6O_2S$. Calculated, %: C 25.53; H 6.38; S 34.04.

Oxidation of TMS to tetramethylene sulfoxide (TMSO) was studied at 20, 40, and 60°C (Table 3). These data show that, after oxidation for 1 h at 20°C, the content of DMSO in the dehydrated oxidation products was 94%, and after oxidation for 3 h it reached 97%. The content of TMSO after oxidation for 1 h at 60°C was 98%. Thus, oxidation of TMS to TMSO occurs with a high rate. At all the examined temperatures, the formation of TMSO is virtually complete in 1–3 h. Oxidation occurs in a two-phase system and is accompanied by a large heat release in a short time. The reaction mixture undergoes autocatalytic self-heating, which results in intense decomposition of excess H_2O_2. Therefore, H_2O_2 was added gradually to maintain its optimal concentration in the mixture in the course of the process.

The oxidation product obtained by oxidation of TMS under the above conditions is a single-phase transparent colorless aqueous solution. To isolate TMSO, the oxidation product was treated with MnO_2 to remove residual H_2O_2, heated at reduced pressure (30–40 mm Hg) to remove water (bath temperature 40–50°C), and vacuum-distilled (bath temperature 140–160°C, vapor temperature 85–100°C, residual pressure 3–5 mm Hg).

Tetramethylene sulfoxide is thermally unstable. Its loss in the course of distillation was evaluated from the decrease in the content of sulfoxide sulfur. The average loss of sulfoxide sulfur is 3%, which corresponds to 10% loss of TMSO. Under the optimal conditions, the yield of TMSO is 89–91%. The purity of the distilled product is 99.6%, bp 45°C (3 mm Hg), n_D^{20} 1.5203, d_4^{20} 1.1816.

Found, %: C 45.72; H 7.83; S 30.5.

C_4H_8OS. Calculated, %: C 46.1; H 7.7; S 30.8.

Oxidation of TMSO to tetramethylene sulfone (TMSF) was performed at 60, 70, 80, 90, and 100°C (Table 4). The reaction occurs in the homogeneous system with a lower heat effect and at a lower rate than oxidation of TMS to TMSO. After oxidation for 8 h at 60°C, the content of TMSF in the dehydrated oxidation product was 60%, and after oxidation for 10 h, 88%. After oxidation for 5 h at 80°C, the content of TMSF was as high as 99%. The optimal oxidation temperature is 80–90°C. To attain a high yield of TMSF, H_2O_2 should be taken in a 35% excess. The product obtained by oxidation of TMSO under these conditions is an aqueous solution containing 35–40% TMSF, 60–50% water, and 4–7% impurities. Tetramethylene sulfone is infinitely miscible with water, forms no binary azeotrope with water, and strongly differs from water in the boiling point. However, TMSF cannot be isolated from the oxidation products by common distillation, since it is thermally unstable and starts to decompose at temperatures above 170°C, forming in the presence of oxygen acidic compounds and condensation products. According to analyses, the oxidation product always contaions residual H_2O_2, which promotes decomposition of TMSF in the course of distillation to acetic and sulfuric acids. Therefore, prior to distillation, the oxidation product was treated with 6% aqueous alkali to decompose H_2O_2, after which it was fractionated on a 2–3-TP batch distillation column; the temperature in the still was 100°C, and the residual pressure, 20 mm Hg. TMSF was isolated from the oxidation product in 96% yield and was 99.7% pure.

We also examined the possibility of recovering TMSF from the oxidation product by extraction with organic solvents. The extractant should selectively recover TMSF with minimal extraction of impurities; it should be sparingly soluble in water and should also meet such general requirements as availability, stability under regeneration conditions, and low cost [9]. The best suited are aromatic hydrocarbons, in particular, benzene. Study of the phase equilibria showed that, in extraction of TMSF from the oxidation product with benzene, the separation of TMSF from impurities is fairly efficient; the impurities mostly remain in the aqueous phase. Under the optimal extraction conditions (benzene : oxidation product weight ratio 2.4 : 1, 25°C, six extraction steps), the recovery of TMSF from the oxidation product is 94–96%. Distillation of benzene from the extract was performed at 200 mm Hg. The energy consumption for distillation of benzene from the extract is much less than that for distillation of water from the oxidation product (because of considerably higher heat capacity and heat of vaporization of water).

Tetramethylene sulfone obtained by this procedure is a colorless hygroscopic solid (at room temperature) with pleasant odor, soluble in water, ethanol, benzene, acetone, and other organic solvents; the product purity

Table 3. Oxidation of TMS to TMSO (H_2O_2 consumption 1.05 mol per mole of TMS)

T, °C	τ, h	Composition of dehydrated oxidation product, %				Acidity, mg KOH per gram oxidation product
		TMS	TMSO	TMSF	unidentified component	
20	1	3.49	94.69	–	1.82	0.24
	3	0.86	97.64	–	1.50	0.36
	6	0.20	97.97	–	1.83	0.44
40	1	1.31	06.84	–	1.85	0.33
	3	–	98.48	–	1.52	0.42
	6	–	97.82	–	2.18	0.51
60	1	0.11	98.09	0.15	1.65	0.41
	3	–	98.66	0.39	0.95	0.48
	4	–	98.69	0.41	0.90	0.61
65	3	–	97.80	1.35	0.75	0.58

Table 4. Oxidation of TMSO to TMSF (H_2O_2 consumption 1.35 mol per mole of TMSO)

T, °C	τ, h	Composition of dehydrated oxidation product, %				Acidity, mg KOH per gram oxidation product
		TMSO	TMSF	unidentified components		
				light*	heavy**	
60	8	39.30	60.42	0.11	0.17	2.1
	10	11.41	88.23	0.15	0.21	3.7
70	6	2.30	98.10	0.37	0.91	5.2
	8	1.21	99.11	0.30	0.39	4.58
80	5	0.49	97.38	0.19	0.21	5.2
	6	0.107	99.22	0.38	0.29	5.94
90	5	0.04	97.38	1.02	1.56	9.8
	6	0.08	99.22	0.55	0.15	10.2
100	4	0.07	97.74	0.18	1.21	10.3
	5	0.03	98.20	0.65	1.12	12.4

* Retention time in chromatographic column shorter than that of TMSF.
** Retention time in chromatographic column longer than that of TMSF.

is 99.8%, bp 283°C, n_D^{30} 1.4812, d_4^{30} 1.2644.

Found, %: C 39.92; H 6.64; S 27.21.
$C_4H_8O_2S$. Calculated, %: C 39.98; H 6.70; S 27.16.

Oxidation of PSC to sulfoxides was performed at 80, 90, and 100°C (Table 5). With increasing temperature, products with SO_3H and COOH groups are actively formed, and the PSC oxidation rate grows. For example, as the temperature is increased from 80 to 100°C, the acidity of the aqueous phase obtained after oxidation for 15 min grows from 0.9 to 2.6 g KOH l^{-1} and the content of sulfoxide sulfur in the oxidation product increases by a factor of 2. The sulfonic and carboxylic acids that are formed effectively catalyze oxidation of sulfides to sulfoxides, as demonstrated by the example of PSC oxidation in the presence of butane-, hexane, and *p*-toluenesulfonic acids and CH_3COOH. Oxidation of PSC in the presence of sulfonic and acetic acids occurs with a higher yield of sulfoxides than oxidation on the presence of only one of these acids [10]. Sulfones appear in the oxidation product only after conversion of the major fraction of sulfides to sulfoxides, whereas acids are formed already in the very first minutes of oxidation simultaneously with sulfoxides. After oxidation, the aqueous and hydrocarbon layers were separated. The hydrocarbon layer (sulfoxide concentrate) was neutralized with an Na_2CO_3 solution, washed with an Na_2SO_4 solution, and kept under reduced pressure (80–100 mm Hg) to remove emulsified and dissolved water.

Table 5. Oxidaiton of PSC into sulfoxides (H_2O_2 consumption 1.2 mol per mole of sulfide sulfur)

T, °C	τ, min	Sulfoxide sulfur in oxidation product, %	Acidity, g KOH l^{-1}				Oxidation of sulfides to sulfoxides, %
			hydrocarbon phase		aqueous phase		
			SO_3H	CO_2H	SO_3H	CO_2H	
80	5	0.9	0.11	0.30	0.45	0.25	10.2
80	15	3.4	0.15	0.35	0.62	0.30	38.6
90	5	4.7	0.23	0.50	0.45	0.35	53.4
90	15	6.3	0.25	0.62	0.81	0.40	71.5
100	15*	6.6	0.20	0.61	2.02	0.63	75.0
100	30**	7.4	0.25	0.80	3.95	0.75	84.0

* 0.8% sulfones.
** 11% sulfones.

Table 6. Oxidation of sulfoxide concentrate to sulfones (H_2O_2 consumption 1.4 mol per mole of total sulfur, 100°C)

τ, h	Catalyst, mol mol^{-1} total sulfur		Content of sulfones, %	Acidity, g KOH l^{-1}	Viscosity at 20°C, $mm^2 s^{-1}$
	H_2SO_4	CH_3CO_2H			
6.0	–	–	36.0	6.2	957.6
9.0	–	–	44.2	8.2	964.5
5.0	–	0.15	82.7	12.0	1424.5
6.5	–	0.15	83.8	12.2	1490.0
5.5	0.1	–	86.3	14.6	1502.28
6.5	0.15	–	88.2	16.4	1610.0
5.0	0.08	0.1	94.0	11.2	1354.3
5.5	0.08	0.1	95.4	11.0	1360.1
6.5	0.08	0.1	97.0	11.0	1414.0
10.0	0.08	0.1	97.6	11.2	1489.2

The composition of the dehydrated sulfoxide concentrate was determined with a Finnigan Type 4021 gas chromatograph–mass spectrometer (the United States). Because of the low thermal stability of sulfoxides, it was impossible to analyze the sulfoxide concentrate directly. Therefore, the sulfoxides were preliminarily reduced to sulfides with HI [11]. The chromatograms and total mass spectra of the initial sulfides used to prepare sulfoxides and of sulfides obtained by back reduction of sulfoxides proved to be identical. Hence, oxidation of sulfides is not accompanied by structural changes. The sulfoxide concentrate from the 260–360°C fraction of Arlan crude oil mainly consists of heterocyclic sulfoxides, in particular, 15–18% monothiacycloalkanes, 38–40% dithiacycloalkanes, 23–25% trithiacycloalkanes, and 18–20% tetrathiacycloalkanes.

The sulfoxide concentrate also contains unoxidized sulfides, substituted thiophenes, and hydrocarbons.

The sulfoxide concentrate is a viscous oily liquid of light yellow color with a weak characteristic odor; it is soluble in the majority of organic solvents, and the solubility in water is 7.8 g l^{-1}. The glass transition point is –67°C. The product starts to decompose at 120–140°C. The sulfoxide sulfur content is 7.4%, and the total sulfur content, 11%; n_D^{20} 1.5092, d_4^{20} 1.0195, *M* 267; $C_{12.8}H_{24.7}SO_{1.3}$.

The dependence of the content of sulfones in the oxidation product as influenced by the amount of acid catalysts and time of oxidation of sulfoxides to sulfones was studied at 100°C (Table 6). It was found that, in the absence of catalysts, the oxidation is slow. The presence of acids in the reaction medium also leads to increased yield of sulfones. As in oxidation of PSC, in the presence of a mixture of acids the reaction rate and the yield of the target product increase. For example, when oxidation of the sulfoxide concentrate to sulfones is performed for 5–7 h in the presence of CH_3COOH and H_2SO_4, the yield of sulfones increases to 95–97%. After oxidation in this mode, the aqueous acid layer was separated after settling for 30 min. The oxidation product was washed with water to remove traces of acids, dried in a water-jet-pump vacuum, and vacuum-distilled (1 mm Hg, bath temperature 110–165°C).

The composition of the resulting sulfone concentrate was studied by mass spectrometry. The sulfone concentrate is a mixture of various thiacycloalkane 1,1-dioxides, aromatic sulfides, and alkylthiophenes; it is a brown viscous liquid with a specific petroleum odor, readily soluble in organic solvents and virtually insoluble in water; n_D^{20} 1.4814, d_4^{20} 1.0312, total sulfur content 12.4%, sulfoxide sulfur absent, M 298, average composition $C_{12.0}H_{22.6}SO_{2.4}$.

CONCLUSION

The yield of sulfoxides and sulfones in oxidation of sulfides and sulfoxides, respectively, with hydrogen peroxide was studied in relation to the reaction temperature, time, and substrate : H_2O_2 ratio. Formation of sulfoxides occurs under milder conditions and at considerably higher rates than formation of sulfones.

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