

Liquid-Phase Oxidation of Benzothiophene and Dibenzothiophene by Cumyl Hydroperoxide in the Presence of Catalysts Based on Supported Metal Oxides

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Abstract—The liquid-phase oxidation of benzothiophene and dibenzothiophene by cumyl hydroperoxide in the presence of supported metal oxide catalysts was carried out in octane in an N_2 atmosphere at 50–80°C. The cumyl hydroperoxide, benzothiophene, and dibenzothiophene conversions and the yield of sulfones were determined for catalysts of various natures. In the presence of MoO_3/SiO_2 , the most efficient and most readily regenerable catalyst, the benzothiophene conversion was ~60% and the dibenzothiophene conversion was as high as 100% upon almost complete consumption of cumyl hydroperoxide. The influence of unsaturated and aromatic compounds (oct-1-ene, toluene) on the catalytic effect was studied. The kinetics of substrate oxidation and cumyl hydroperoxide decomposition and an analysis of the cumyl hydroperoxide conversion products suggested a benzothiophene and dibenzothiophene oxidation mechanism including the formation of an intermediate complex of the hydroperoxide with the catalyst and the substrate and its transformation via heterolytic and homolytic routes.

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INTRODUCTION

Great attention is being given to motor fuel desulfurization because of the requirements imposed on sulfur level reduction. Petroleum fractions contain considerable amounts of benzothiophene (BT), dibenzothiophene (DBT), and their alkyl-substituted derivatives. These compounds (benzothiophenes) are low-reactive toward the hydrogenolysis of the C–S bond and, as a consequence, are difficult to remove by conventional hydrodesulfurization.

Novel ultradeep desulfurization technologies have originated from the development of the oxidation of thiophene derivatives into sulfones and the removal of the products by extraction or adsorption [1–3]. Catalytic systems using hydrogen peroxide or *tert*-butyl hydroperoxide as the oxidizer and capable of desulfurizing diesel fuel under mild conditions (50–90°C) are being tested [4]. However, commercialization of these processes will need optimization of the oxidizer, the catalyst, and the method for isolating the oxidation products of thiophene derivatives from the petroleum fraction. Research in this field is being advanced intensively.

In addition to being investigated in the presence of catalytic systems containing aqueous H_2O_2 and formic or acetic acid that are used in the oxidation of organic sulfides [1, 2], benzothiophenes oxidation by hydrogen peroxide was mainly studied on model mixtures in the

presence of catalysts based on water-soluble metal phthalocyanines [5], polyoxometalates [6, 7], supported $H_3PW_{12}O_{40}$ [8], WO_x/ZrO_2 [9, 10], titanium-containing molecular sieves [11], vanadium silicates [12], V_2O_5/TiO_2 , V_2O_5/Al_2O_3 [13–15], supported Pd, Cr_2O_3 , MnO_x , and Co–Mo/Al₂O₃ [16]. Acetic acid [6, 7], acetonitrile [5, 8, 9, 11, 12, 15, 16], or another polar solvent [9, 15] was additionally added to the reaction mixture to enhance the catalytic activity. For example, it was reported [9] that the diesel fuel was purified on WO_x/ZrO_2 to 90 ppm S (instead of 15 ppm S, required in 2006 by the United States Environmental Protection Agency [13]). The main drawback of hydrogen peroxide is the presence of the aqueous phase, resulting in unproductive H_2O_2 decomposition [13, 16], a nonfull sulfone selectivity of the benzothiophene conversion [15], and catalyst deactivation because of the leaching of the active component [12].

Systems with a phase mediator suggested for an Fe-containing catalyst with the tetraamido macrocyclic ligand [17] and for heteropolytungstates [18, 19] are better in this respect. In the latter case, the sulfur content of the diesel fuel was decreased using extraction of sulfones from 500 to 0.1 ppm S at a small ratio of the concentrations of hydrogen peroxide and sulfur ($O/S \leq 3$) [19]. The adsorption of the oxidation products by porous compounds, namely, SiO_2 , Al_2O_3 , and carbon, was used instead of extraction [17, 20].

The system for oxidative desulfurization can be facilitated by combining benzothiophenes oxidation and sulfones adsorption in the presence of supported catalysts that can easily be regenerated and by using an organic hydroperoxide as the oxidizer well soluble in petroleum fractions. However, these systems are understood much less well. There have been reports on the oxidation of DBT and its alkyl-substituted derivatives by *tert*-butyl hydroperoxide in the presence of a SiO_2 -supported rhenium(V) oxo complex [21], WO_3/ZrO_2 [10], and other supported metal oxides [22, 23]. Benzothiophene is much more difficult to oxidize [22]. The sulfur content was decreased to <5 ppm in the presence of the $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst when the light gas–oil fraction was treated with *tert*-butyl hydroperoxide followed by the adsorption of the oxidation products of organic sulfides on SiO_2 [23].

Cumyl hydroperoxide (CHP) is a commercially available chemical. The purpose of the present work is to obtain new data on the efficiency of the catalytic systems based on CHP and SiO_2 -supported transition metal oxides in the oxidation of BT and DBT and to elucidate the oxidation mechanism of these substrates.

EXPERIMENTAL

Catalyst Preparation and Chemicals

Catalysts supported on SiO_2 and Al_2O_3 were prepared by the impregnation of the support with a solution of a metal salt (Table 1). Dilute solutions of ammonium paramolybdate and paratungstate were used to prepare samples 1–5; after the support was added, water was evaporated with stirring at 80°C. Samples 6–12 were prepared by incipient-wetness impregnation at room temperature. The amount of salt in the impregnating solution was adjusted so that, after the samples were dried in air (at 100°C for 2 h) and calcined at 500°C (for samples 1–10), the resulting metal compound contents of the catalysts were equal to those presented in Table 1. The catalysts obtained were stored in air. The supports were SiO_2 (280 m²/g) and Al_2O_3 (300 m²/g) calcined at 500°C, ZrO_2 (430 m²/g), and TiO_2 (anatase, 350 m²/g).

Benzothiophene, dibenzothiophene, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich), and commercial cumyl hydroperoxide (93.1%, OAO Omsk-Kauchuk, Russia) were used. The other chemicals were analytical grade.

Catalytic Experiments

Benzothiophene and dibenzothiophene were oxidized in an octane solution at 50–80°C for 2–5 h in a temperature-controlled reactor with a magnetic stirrer under a nitrogen atmosphere. In most experiments, the catalyst (50–12.5 mg) and octane (0.5 ml) containing cumyl hydroperoxide (0.5–0.025 mmol) were added to an octane solution (4.5 or 5.0 ml) containing BT or

Table 1. Composition of the supported catalysts and compounds (precursors) used in supporting

Sample no.	Composition	Precursor
1	15% $\text{MoO}_3/\text{SiO}_2$	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
2	18% $\text{MoO}_3/\text{SiO}_2$	"
3	15% $\text{MoO}_3/\text{Al}_2\text{O}_3$	"
4	12% WO_3/SiO_2	$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{42} \cdot 10\text{H}_2\text{O}$
5	21% WO_3/SiO_2	the same
6	10% $\text{V}_2\text{O}_5/\text{SiO}_2$	NH_4VO_3
7	7% $\text{Fe}_2\text{O}_3/\text{SiO}_2$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
8	7% $\text{Co}_3\text{O}_4/\text{SiO}_2$	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
9	6% CuO/SiO_2	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot 3\text{CuO}$ in 15 M HNO_3
10	27% $\text{Na}_7\text{PW}_{11}\text{O}_{39}/\text{SiO}_2$	$\text{Na}_7\text{PW}_{11}\text{O}_{39} \cdot 10\text{H}_2\text{O}$
11	10% $\text{AlCl}_3/\text{SiO}_2$	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$
12	10% $\text{ZnCl}_2/\text{SiO}_2$	ZnCl_2 in 5.3 M HCl

DBT (0.213–0.0107 mmol). Before the experiment, the reactor was purged with nitrogen, heated, and sealed.

Analysis of Solutions

The cumyl hydroperoxide concentration in the reaction solution was determined by titration with sodium thiosulfate. A 0.5-ml sample was added to a mixture of KI (0.5 g) and glacial acetic acid (5 ml). The resulting mixture was stored for 10 min and, before titration, was diluted with water to 50 ml.

Solutions were analyzed for BT or DBT and their oxidation products by gas chromatography on a Kristall 2000m chromatograph (photoionization detector, HP-5 capillary column 30 m × 25 mm × 0.25 μm (film thickness)) in a temperature-programmed mode: heating from 60 to 90°C at a rate of 3 K/min; from 90 to 200°C, 5 K/min; from 200 to 280°C, 20 K/min; at 280°C, 10 min. The concentrations of BT, DBT, benzothiophenesulfone (BTS), and dibenzothiophenesulfone (DBTS) were determined using calibration curves. The lower detection limit for BT and DBT in their solutions (on the sulfur basis) was ~0.3 ppmw S. The oxidation products, BTS, DBTS, and the products of CHP conversion were identified by gas chromatography coupled with mass spectrometry.

The preparation of solutions for analysis included the following procedures. After a catalytic run, the solution in the reactor was cooled to ~20°C and separated from the catalyst and the resulting sulfone. The sulfone was extracted by washing of the catalyst in the reactor with two 5-ml portions of benzene. The sulfone and BT and DBT admixtures were determined in a benzene solution. The material balance was calculated by the summation of the amounts of the compounds determined in these two solutions.

Table 2. Oxidation of benzothiophene by cumyl hydroperoxide in the presence of various catalysts

No.	Catalyst	Pretreatment	Conversion, %		BTS, mmol	Selectivity of BTS formation on CHP, %
			CHP	BT		
1	7% $\text{Fe}_2\text{O}_3/\text{SiO}_2$	500°C, 2 h, for 1 day	27	5.5	0.009	13
2	6% CuO/SiO_2	"	24	*	0.0048	8.0
3	7% $\text{Co}_3\text{O}_4/\text{SiO}_2$	"	29	*	0.0049	6.7
4	10% $\text{V}_2\text{O}_5/\text{SiO}_2$	"	97.5	42.0	0.091	37
5	15% $\text{MoO}_3/\text{SiO}_2$	"	92	60	0.12	52
6	SiO_2	100°C, for 1 day	10	*	0	—
7	"	500°C, 2 h, immediately	26	*	0	—
8	Al_2O_3	"	18	*	0	—
9	10% $\text{AlCl}_3/\text{SiO}_2$	without additional drying	31	*	0	—
10	"	100°C, 2 h, immediately	31	*	0	—
11	10% $\text{ZnCl}_2/\text{SiO}_2$	100°C, 2 h, immediately	26	*	0	—
12	ZrO_2	100°C, 2 h, for 1 day	77	51.3	0.094	49
13	TiO_2	100°C, 2 h, for 1 day	46	30.7	0.060	52

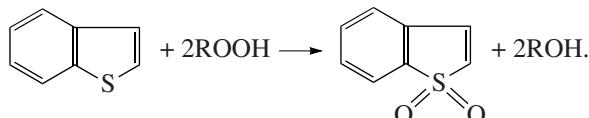
Note: Conditions: 50 mg of the catalyst, 5 ml of octane, 0.213 mmol of BT, 0.5 mmol of CHP, 50°C, N_2 atmosphere, 2 h.

* The change in the BT concentration does not exceed the measurement error.

RESULTS AND DISCUSSION

Influence of the Nature of Catalysts Containing Transition Metals on Benzothiophene Oxidation by Cumyl Hydroperoxide

Among the sulfur atoms of organic sulfides, the sulfur atom in the benzothiophene molecule has the lowest electron density, which is responsible for the low reactivity of BT toward oxidation to sulfone [1]. It is known that CHP decomposes in the presence of ions of variable-valence metals to form intermediate radicals [24]. The radical decomposition of CHP was also observed under the action of Lewis and Brønsted acids [25, 26]. The oxidation of BT to BTS by hydroperoxide could occur as a conjugated or parallel reaction. We tested three groups of compounds in benzothiophene oxidation: SiO_2 -supported oxides of variable-valence metals (Fe, Co, Cu) that decompose peroxides through radical formation, metal oxides (Mo(VI), Ti(IV), Zr(IV)) forming stable peroxide complexes, and other compounds possessing Lewis or Brønsted acidity. We determined the CHP conversion and the BTS yield in the presence of these compounds at nearly stoichiometric concentrations of CHP and BT (0.1 and 0.0427 mol/l, respectively), assuming that all BT is converted into BTS via the reaction



The BTS selectivity was calculated as the molar ratio of the amount of hydroperoxide consumed in sulfone formation to the total amount of consumed hydroperoxide: $(2\text{BTS}/\text{CHP}) \times 100\%$. Since the acid properties of the catalyst samples depend on the presence of water, different regimes of their treatment before experiments

were used. In most cases, the catalysts were tested immediately or one day after heating at a preset temperature. The results of the tests are given in Table 2. Note that the balance between the starting amount of BT and the amount of (BT + BTS) determined after the reaction was observed in all cases. This indicated that the oxidation of benzothiophene yielded only benzothiophene-sulfone.

In the presence of 7% $\text{Fe}_2\text{O}_3/\text{SiO}_2$, 6% CuO/SiO_2 , or 7% $\text{Co}_3\text{O}_4/\text{SiO}_2$, the CHP conversion was ~30% at a considerably lower BT conversion and, accordingly, a low selectivity (~10%) BTS formation with respect to CHP (Table 2, nos. 1–3). Thus, benzothiophene oxidation as a conjugated reaction in the free-radical decomposition of hydroperoxide typical of variable-valence ions (Fe, Cu, Co) proceeds to a low extent.

The CHP conversion on 10% $\text{V}_2\text{O}_5/\text{SiO}_2$ approaches 100% at a BT conversion of 42% and a BTS selectivity of 37% (Table 2, no. 4). A BT conversion lower than 60% and a higher BTS selectivity (52%) at a CHP conversion of ~90% were observed under the same conditions in the presence of 15% $\text{MoO}_3/\text{SiO}_2$ (Table 2, no. 5). The activity and selectivity remained unchanged after the catalyst was stored in air.

According to published data [27], DBT is readily oxidizable to sulfone by *tert*-butyl hydroperoxide in the presence of silica gel. We studied the influence of various supports on BT oxidation by cumyl hydroperoxide. In the presence of SiO_2 containing no supported metal compounds, CHP consumption was observed. Pretreatment of the sample affected the CHP conversion: silica gel heated at 100°C one day before the experiment exhibited a lower activity than silica gel calcined at 500°C immediately before the run (Table 2, nos. 6, 7). Alumina calcined at 500°C before the run also accelerated the conversion of CHP (Table 2, no. 8).

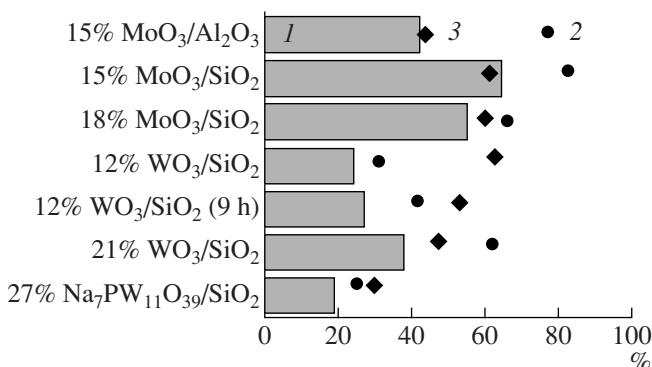


Fig. 1. Oxidation of benzothiophene by cumyl hydroperoxide in the presence of the supported Mo- and W-containing catalysts: (1) BT conversion (%), (2) CHP conversion (%), and (3) the selectivity of BT oxidation by CHP (%). Conditions: 0.427 mmol of BT, 1 mmol of CHP, 10 ml of octane, 100 mg of the catalyst, 50°C, N₂ atmosphere, 5 h.

The catalytic activity of the supports can be due to admixtures of iron or other metal ions or the presence of acid sites causing the homolytic decomposition of CHP. The second assumption is corroborated by the fact that the CHP conversion was higher after Lewis acids (AlCl₃ and, to a lower extent, ZnCl₂) were supported on SiO₂ (Table 2, nos. 9–11). However, in spite of CHP decomposition, BT was consumed in none of these experiments and no sulfone was formed.

The process changed to BT oxidation after ZrO₂ and TiO₂ were introduced into the system, and the BT conversion and BTS selectivity approached the corresponding parameters for the MoO₃/SiO₂-supported catalyst (Table 2, nos. 12, 13). Thus, BT was oxidized by cumyl hydroperoxide in the presence of vanadium(V), molybdenum(VI), zirconium(IV), and titanium(IV) oxides and WO₃, which can form intermediate peroxide complexes activating peroxide oxygen [24, 28].

The activities and selectivities of the supported MoO₃ and WO₃ catalysts are compared in Fig. 1. The BT oxidation activity (diagram 1) and CHP consumption (2) for the 15% MoO₃/SiO₂ sample are higher than those for the 15% MoO₃/Al₂O₃ catalyst at a higher BT oxidation selectivity on the consumed CHP basis (3). The activity of the 12% WO₃/SiO₂ sample was lower than the activity of its MoO₃ analogue, but the same high selectivity of CHP was achieved. An increase in the reaction time (from 5 to 9 h), WO₃ content, and reaction temperature (to 80°C) did not result in an increase in the BT conversion but increased the contribution from the CHP decomposition reactions. The supported heteropolytungstate Na₇PW₁₁O₃₉ manifested a lower activity and selectivity than the WO₃/SiO₂ samples.

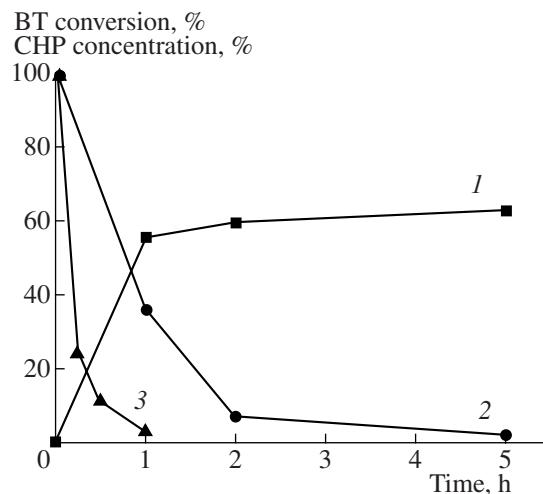


Fig. 2. Oxidation of benzothiophene and cumyl hydroperoxide consumption with time in the presence of the 15% MoO₃/SiO₂ catalyst: (1) BT conversion (%) and the CHP concentration in the (2) presence and (3) absence of BT (in % of the initial value). Conditions: 0.213 mmol of BT, 0.5 mmol of CHP, 5 ml of octane, 50 mg of the catalyst, N₂ atmosphere, 50°C.

Possible Mechanism of BT and DBT Oxidation by Cumyl Hydroperoxide on the MoO₃/SiO₂ Catalyst

The dependence of BT conversion at almost complete CHP conversion (5 h) on the reactant concentration was studied in the presence of the 15% MoO₃/SiO₂ catalyst. At a high BT concentration and a small CHP excess, the BT conversion was 64% and remained almost unchanged with an increase in the CHP concentration (Table 3, nos. 1, 2). A decrease in the BT concentration by one order of magnitude at the same CHP concentration exerted no effect on the BT conversion (Table 3, nos. 1, 3, 4). The BT conversion decreased insignificantly (Table 3, no. 5) with a simultaneous tenfold decrease in the CHP and BT concentrations (to 0.00427 mol/l or 200 ppm S). The study of the vari-

Table 3. Benzothiophene and cumyl hydroperoxide conversions at different initial reactant concentrations in the presence of the 15% MoO₃/SiO₂ catalyst

No.	[BT] _{init} , mol/l	[CHP] _{init} , mol/l	Conversion, %	
			BT	CHP
1	0.0427	0.1	64	88
2	0.0427	0.2	67	89
3	0.0213	0.1	61	96
4	0.00427	0.1	63	96
5	0.00427	0.01	54	84

Note: Conditions: 100 mg of the catalyst, 10 ml of octane, 50°C, N₂ atmosphere, 5 h.

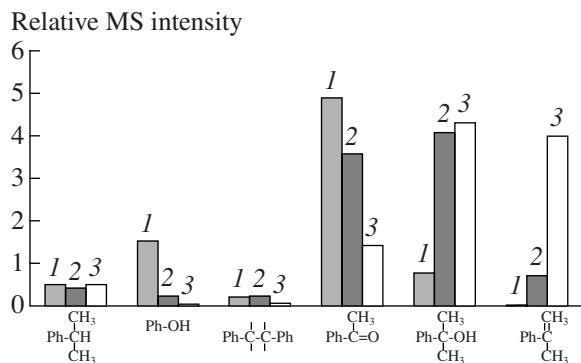
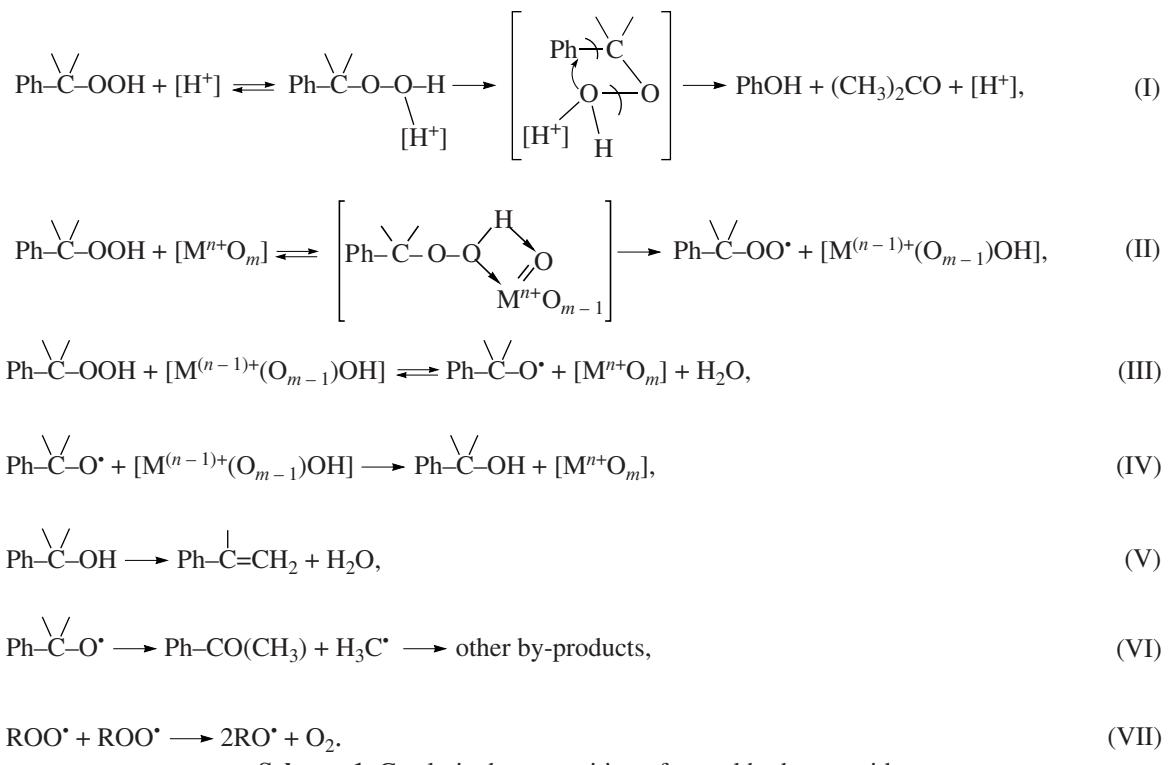


Fig. 3. Composition of the products of CHP conversion and the relative areas of their mass spectrometric peaks: (1) CHP decomposition in the absence of the substrate, (2) BT oxidation, and (3) DBT oxidation. Conditions: (2) 0.213 mmol of BT or (3) 0.0534 mmol of DBT, (1, 2) 0.5 or (3) 0.125 mmol of CHP, (1, 2) 5 or (3) 5.5 ml of octane, 50 mg of the catalyst, N_2 atmosphere, 50°C, (1) 2 or (2, 3) 5 h.

ation of the BT and CHP concentrations during the reaction (Fig. 2) revealed that cumyl hydroperoxide

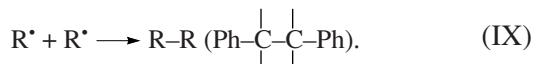
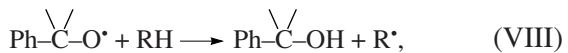
was consumed in two processes: BT oxidation and intrinsic decomposition. The BT conversion (curve 1) reached its limit (~60%), and then the reaction ceased due to the consumption of CHP (curve 2). The decomposition of CHP without BT under the same conditions was much faster (curve 3) than that in the presence of benzothiophene. The data presented here show that the oxidation of BT to BTS by cumyl hydroperoxide on MoO_3/SiO_2 proceeds through the formation of a CHP–BT–catalyst complex.

An analysis of the products of CHP decomposition and the products of CHP conversion during BT and DBT oxidation under the same conditions on MoO_3/SiO_2 suggested a mechanism for the oxidation of these substrates in the system. It is known from the literature [29–31] that cumyl hydroperoxide under the action of Brønsted acids undergoes a molecular rearrangement to form phenol and acetone (Scheme 1, reaction (I)), whereas the major products of free-radical decomposition are acetophenone and 2-phenyl-2-propanol along with α -methylstyrene (Scheme 1, reactions (II)–(VI)).



Scheme 1. Catalytic decomposition of cumyl hydroperoxide.

For CHP decomposition without BT on MoO_3/SiO_2 (Fig. 3, distribution 1), we found all products presented in Scheme 1 (reactions (I), (IV)–(VI)). Since the initial solution of CHP contained an isopropylbenzene admixture, the product of its free-radical transformation, namely, 2,3-diphenyl-2,3-dimethylbutane, was also found in the reaction mixture:

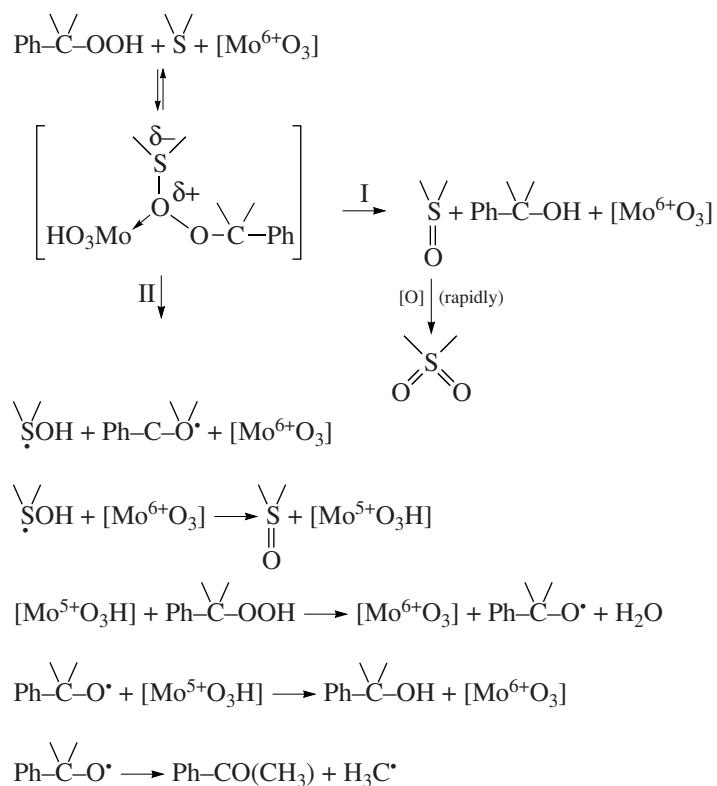


In the presence of BT, we observed a different distribution of the CHP transformation products (Fig. 3,

distribution 2). The fraction of 2-methyl-2-propanol (a product of BT oxidation by the hydroperoxide) was larger, and α -methylstyrene (the dehydration product of this alcohol) appeared. The changes in the amounts of the products of the acid-catalyzed and free-radical conversion of CHP were not proportional. The acetophenone yield decreased by a factor of 1.4, whereas the phenol yield decreased by a factor of 7. Unlike BT oxidation, the conversion of DBT under the same conditions (Fig. 3, distribution 3) did not yield phenol at all and yielded a smaller proportion of acetophenone. This decrease in the fraction of the CHP decomposition products along with the increase in the yield of 2-phenyl-2-propanol and α -methylstyrene is likely due to the higher conversion of DBT compared to that in the conversion of BT. The conversion of DBT to DBTS and the conversion of CHP in these experiments were close to 100% (Table 4).

The above data allow us to formulate a mechanism of BT and DBT oxidation (Scheme 2). The key intermediate is the complex of molybdenum oxide with

cumyl hydroperoxide stabilized by the addition of a BT or DBT molecule. When the substrate and the oxidizer are in excess, the entire catalyst (more exactly, all surface Mo^{6+} ions) is bound into this ternary complex. The formation of the stable ternary complex prevents the conversion of CHP into phenol and acetone and the free-radical decomposition of CHP initiated by Mo^{6+} (M^{n+} in Scheme 1, reaction (II)). The redox decomposition of the intermediate complex yielding sulfoxide, which is known [32] to transform rapidly into sulfone, can proceed via two routes (Scheme 2): route I is electrophilic oxygen atom transfer with CHP conversion into 2-phenyl-2-propanol, and route II is the free-radical oxidation of benzothiophene-yielding products of free-radical CHP decomposition as well. The occurrence of the reaction via route II results in the nonproductive consumption of some CHP, as was observed for BT oxidation. As is evident from the composition of the products of CHP conversion, route I is dominant in the oxidation of the more reactive substrate DBT.



Scheme 2. Oxidation of benzothiophene and dibenzothiophene by cumyl hydroperoxide in the presence of the $\text{MoO}_3/\text{SiO}_2$ catalyst.

Regularities of Dibenzothiophene Oxidation by Cumyl Hydroperoxide in the Presence of the $\text{MoO}_3/\text{SiO}_2$ Catalyst

Effect of the ratio of the reactant and catalyst concentrations. The conditions ensuring the highest

extent of the reaction on $\text{MoO}_3/\text{SiO}_2$ were studied using DBT oxidation as an example. When the reaction occurs in octane at 50°C, DBTS is formed. The found amount of sulfone was equivalent to the amount of

Table 4. Oxidation of dibenzothiophene by cumyl hydroperoxide at different DBT contents

No.	DBT, mmol	CHP, mmol	Conversion, %		DBTS, mmol
			CHP	DBT	
1	0.213	0.5	96	99	0.183
2	0.107	0.25	97	99	0.092
3	0.0503	0.125	100	100	0.049
4	0.0213	0.05	100	100	0.0131
5	0.0107	0.025	100	100	0.006

Note: Conditions: 15% MoO₃/SiO₂ catalyst (50 mg), 5.5 ml of octane, N₂ atmosphere, 50°C, 5 h.

Table 5. Dependences of the dibenzothiophene and cumyl hydroperoxide conversions on the amount of the catalyst and on the oxidation time

No.	Catalyst weight, g	Reaction time, h	Conversion, %		DBTS, mmol
			CHP	DBT	
1	0.05	1	80	88	0.179
2	0.05	2	88	95	0.220
3	0.05	5	96	99	0.183
4*	0.05	5	86	100	0.216
5	0.025	2	71	86	0.156
6	0.0125	2	56	71	0.139
7**	0.05	2	94	96	0.205

Note: Conditions: 15% MoO₃/SiO₂ catalyst, 5.5 ml of octane, 0.213 mmol of DBT, 0.5 mmol of CHP, N₂ atmosphere, 50°C.

* 0.75 mmol CHP taken.

** The fourth cycle of repeated tests of the catalyst.

reacted DBT (Table 4, nos. 1–3), and only at low concentrations was a smaller amount of DBTS with respect to oxidized DBT detected (Table 4, nos. 4, 5), apparently because a portion of the product remained on the catalyst. The reaction occurred to the extent of ≥99% in a wide range of DBT concentrations (1760–90 ppmw S) and at a near-stoichiometric CHP concentration. In this case, the residual DBT content (in terms of sulfur) ranged from 20 to 1 ppm and an almost 100% conversion of CHP was achieved. The major products of CHP conversion were 2-phenyl-2-propanol and α -methylstyrene, acetophenone was formed in small amounts, and no phenol was detected.

The conversion of DBT and CHP was about 100% in 5 h, although the main fraction of the reactants was consumed already in 1–2 h (Table 5, nos. 1–3). With an increase in the CHP excess, a larger amount of unreacted hydroperoxide remained in the solution (Table 5, no. 4). A decrease in the amount of the catalyst decreased the DBT and CHP conversion and the DBTS yield (Table 5, nos. 2, 5, 6).

The reusability of the catalyst was demonstrated for a 2-h-long reaction followed by washing the products off the catalyst with benzene and subsequent DBT oxidation under the same conditions. The conversion of CHP and DBT and the DBTS yield did not decrease throughout four testing cycles (Table 5, compare nos. 2 and 7).

The influence of olefins and aromatic compounds on DBT oxidation. Fuel fractions are known to contain large amounts of readily oxidizable hydrocarbons, which can be involved in reactions with hydroperoxide and can reduce the efficiency of the oxidation of benzothiophenes. This is particularly true for olefins, whose content in cracking gasoline reaches 20–30%. For this reason, the influence of admixtures of unsaturated and aromatic compounds on DBT oxidation was studied. When up to 30 wt % oct-1-ene was introduced into the reaction mixture (Table 6, nos. 1–6), the conversion of DBT and CHP decreased gradually and slightly. However, no olefin oxidation products were detected by chromatography and the DBTS yield was equivalent, within the analysis accuracy, to the amount of the reacted DBT. In the presence of the olefin, the conversion of DBT and CHP can be enhanced by extending the reaction time (Table 6, compare nos. 6 and 7). In the presence of 20% toluene, the conversion of DBT and CHP and the DBTS yield remained as high as those in the absence of toluene (Table 6, no. 8).

Thus, in the presence of both the olefin and the aromatic compound, DBT is selectively oxidized by cumyl hydroperoxide on the MoO₃/SiO₂ catalyst. The inhibition of the reaction observed upon the addition of large amounts of the olefin can be due to the competitive formation of an olefin complex on the catalyst. However, if the hydroperoxide concentration is increased slightly,

Table 6. Oxidation of dibenzothiophene by cumyl hydroperoxide in the presence of oct-1-ene or toluene

No.	Octene, wt %	Conversion, %		DBTS, mmol
		CHP	DBT	
1	0	88	95	0.220
2	3.0	81	94	0.190
3	4.5	91	89	0.214
4	9.7	77	91	0.193
5	20	59	75	0.175
6	30	57	73	0.144
7*	30	77	82	0.172
8	0**	83	97	0.185

Note: Conditions: 15% $\text{MoO}_3/\text{SiO}_2$ catalyst (0.05 g), 5.5 ml (octane + oct-1-ene), 0.213 mmol of DBT, 0.5 mmol of CHP, N_2 atmosphere, 50°C, 2 h.

* Reaction time 5 h.

** 20% toluene.

the same high DBT conversion can be achieved in the presence of 30% oct-1-ene as in the absence of the olefin (Table 7). The results presented in Table 7 also show that most of the excess hydroperoxide remains undecomposed after the oxidation of DBT is complete, which can be explained by the inhibiting effect of the olefin on the free-radical decomposition due to the competitive formation of a complex between the olefin and the catalyst.

CONCLUSIONS

This study showed that cumyl hydroperoxide, in combination with the $\text{MoO}_3/\text{SiO}_2$ or ZrO_2 and TiO_2 metal oxide catalysts, can be used efficiently in the selective liquid-phase oxidation of benzothiophene and dibenzothiophene to sulfones. In this system, almost stoichiometric quantities of the reactant are used and the reaction products are easily separable by adsorption

on a highly porous support. The possibility of the isolation of the resulting sulfone and of reuse of the catalyst is demonstrated.

A comparison between the oxidative removal of sulfur and the commercial hydrodesulfurization process shows that more severe conditions are required to adapt hydrodesulfurization to DBT and its derivatives, especially 4,6-dimethylbenzothiophene, in order to achieve ultrahigh purity of diesel fuels (<15 ppm S). These are high temperature, high hydrogen pressure, and a longer time of contact with the catalyst. As a consequence, the lifetime of the catalyst decreases, the hydrogen consumption increases, and, finally, the losses of the product and its cost increase. Therefore, the use of the oxidative catalytic system in benzothiophenes removal is appropriate for the ultradeep refining of petroleum fractions that were subjected to conventional hydrodesulfurization treatment and contain a residual amount of sulfur of ~250 ppm.

In the model system studied using cumyl hydroperoxide as the oxidizer in the presence of $\text{MoO}_3/\text{SiO}_2$ at $\text{ROOH/S} = 2.3$ (mol/mol) in octane at 50°C, the DBT conversion ranged from 99% to ~100% in a wide interval of sulfur concentrations (1800–90 ppm). These data are in agreement with the level of sulfur refining obtained by treating a light fuel fraction with *tert*-butyl hydroperoxide [23]. According to our data, the presence of a large amount (up to 20–30%) of an olefin or an aromatic compound exerts no effect on the selectivity of DBT oxidation by cumyl hydroperoxide and changes the reaction rate only slightly. This property of the catalytic system makes it possible to consume CHP very economically in the oxidation of DBT.

Due to the specific features of the reaction mechanism, the BT conversion under similar conditions is lower (~60%) with an almost complete conversion of the hydroperoxide. In this case, to achieve a higher BT conversion, we recommend multiple addition of cumyl hydroperoxide.

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Table 7. Oxidation of dibenzothiophene in the presence of oct-1-ene at different concentrations of cumyl hydroperoxide

No.	CHP, mmol	CHP conversion, %	DBT, mmol	DBT conversion, %	DBTS, mmol
1	0.5	77	0.213	82	0.172
2	1.0	59	0.213	97	0.234
3	0.375	54	0.107	95	0.100
4	0.5	57	0.107	99	0.102

Note: Conditions: 15% $\text{MoO}_3/\text{SiO}_2$ catalyst (0.05 g), 5.5 ml (octane + oct-1-ene), 30 wt % oct-1-ene, N_2 atmosphere, 50°C, 5 h.

emy of Sciences) for the GC-MS analyses of the reaction products.

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