A. A. Volod 'kin,\* G. E. Zaikov, and N. M. Evteeva

N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 119991 Moscow, Russian Federation. Fax: +7 (499) 137 4101. E-mail: chembio@sky.chph.ras.ru

The transesterification of methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate with tetrakis(hydroxymethyl)methane depends on the equilibrium constants of the reversible reactions; for the final step, the equilibrium constant is K << 1. The molecular geometries and the enthalpies and entropies of the equilibrium reactions were calculated by the semiempirical PM6 quantum chemical method. The thermodynamic equilibrium constants of the reversible reactions were calculated by the Boltzmann equation from the Gibbs energies  $\Delta G_f^{\circ}$ . For tris-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl](hydroxymethyl)methane, the dipole moment is  $\mu = 0.97$  D and the energy of the O—H homolysis is  $D_{\text{OH}} = 347.3$  kJ mol<sup>-1</sup>. For tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane,  $\mu$  is 5.6 D and  $D_{\text{OH}}$  is 321 kJ mol<sup>-1</sup>. The geometry of the structure affects the H—O homolysis energy and the chain termination coefficient under the conditions of inhibited cumene oxidation.

**Key words:** methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate, tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane, transesterification, quantum chemical calculations, PM6 level, structure, equilibrium, NMR spectra, IR spectra.

The results of the transesterification of methyl 3-(3,5di-*tert*-butyl-4-hydroxyphenyl)propanoate with polyols are known and generalized in reviews.<sup>1,2</sup> However, information on the synthesis of tetrakis[3-(3,5-di-*tert*-butyl-4hydroxyphenyl)propanoyloxymethyl]methane is inconsistent, mainly referring to patent data.<sup>3–7</sup> A reaction with tetrakis(hydroxymethyl)methane is step transesterification leading to four compounds, the yields and ratio of which vary with time. Tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane (phenozan-23)<sup>1,7</sup> is an efficient antioxidant used to prepare polymeric products.

Interest in the transesterification reaction is due to the development of methods for the synthesis of phenozan-23. During the reaction, the increasing viscosity negatively affects the reaction outcome and necessitates a temperature raise above 120 °C. However, base-catalyzed transesterification at high temperatures is accompanied by oxidation and degradation processes, which complicates isolation and purification of the target product. The mechanism of the step transesterification remains unknown so far, nor are data available regarding the effect of intermediate products on the "consumer" properties of phenozan-23.

In the present work, we revealed the rules governing the transesterification, obtained bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]bis(hydroxymethyl)methane and tris[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl](hydroxymethyl)methane, and studied their antioxidant properties in inhibited oxidation of cumene as a model reaction. Quantum chemical calculations of the starting reagents, intermediates, and final products in the transesterification at the PM6 level were used to determine the thermodynamic equilibrium constants and the binding energies of the phenolic H—O bond ( $D_{OH}$ ). The structures of the compounds obtained were confirmed by <sup>1</sup>H NMR and IR spectroscopy.

The methodology of the preparation of tetra[3-(3,5di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane depends on the conditions of methanol separation in the final transesterification step, which has an abnormally low equilibrium constant. Under the transesterification conditions, the time-dependent partition of methanol in the liquid—gas system changes the reaction rates.

## **Results and Discussion**

A reaction of methyl 3-(3,5-di-tert-butyl-4-hydroxy-phenyl) propanoate (1) with tetrakis(hydroxymethyl)-methane at 140–200 °C was accompanied by liberation of methanol. Under these conditions, the final mixture contained the starting compound 1 and transesterification products 2-5 (Scheme 1).

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 1673-1677, September, 2012.

1066-5285/12/6109-1689 © 2012 Springer Science+Business Media, Inc.

Scheme 1

$$\begin{array}{rcl} \operatorname{RCOOMe} + \operatorname{C}(\operatorname{CH}_2\operatorname{OH})_4 & \stackrel{K_1}{\longrightarrow} \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\$$

 $R = 3,5-Bu_2^t-4-HOC_6H_2CH_2CH_2$ 

The compositions of the reaction mixtures were examined by LC and NMR spectroscopy. Compounds 3–5 were isolated in the individual state; their structures were confirmed by <sup>1</sup>H NMR and IR spectra. The ratio of compounds 1–5 in the reaction mixtures was determined from the integral intensities of the signals for the methyl protons in COOMe ( $\delta$  3.70 (1)) and for the methylene protons in COOCH<sub>2</sub> ( $\delta$  4.04 (3), 4.01 (4), and 4.09 (5)).

The <sup>1</sup>H NMR spectra of compounds **3** and **4** show signals for the protons of the group CH<sub>2</sub>OH. When the ratio of **1**: tetrakis(hydroxymethyl)methane is 4:1, the yield of compound **2** under the transesterification conditions does not exceed 3–4%. Liquid chromatography data for the reaction mixtures agree with their <sup>1</sup>H NMR spectra. According to kinetic data, the liquid phase of the system liberating methanol at P = 1 atm and 190 °C reaches equilibrium 40–50 min after the start of the reaction. During the next hour, the concentration of compound **4** ( $C_4$ ) passes through a maximum, while the concentration of compound **5** ( $C_5$ ) increases (Fig. 1).

The ratio of compounds 4 and 5 remains the same even when methanol is removed *in vacuo*. This can be attributed to the effect of the equilibrium constants of the reversible reactions on the final outcome of the step transesterification. Quantum chemical calculations gave  $K_4 =$ = 1.6 · 10<sup>-4</sup> (298 K) for the thermodynamic equilibrium constant of reaction (4). It is wise to assume that the equilibrium in the system 5–4–MeOH is shifted toward to the formation of compound 4. Reverse transesterification in a reaction of compound 5 with methanol proceeded at room temperature to give the starting compound 1.



Fig. 1. Changes in the concentrations  $C_i$  of the reactants (i = 1, 3–5) during the transesterification of compound 1 with tetrakis(hydroxymethyl)methane at 190 °C; the initial molar ratio of the reactants is 4 : 1; aluminosilicate modified with NaOH (4.5 wt.%) as a catalyst.

The enthalpies  $H_{\rm f}^{\circ}$  and entropies  $S_{\rm f}^{\circ}$  of formation of the compounds involved in the transesterification were calculated at the PM6 level with the MOPAC 2009 program,<sup>8</sup> and the results obtained were used to calculate the Gibbs energy changes  $\Delta G_{\rm r}^{\circ}$  in reversible reactions (1)–(4) (Tables 1, 2).

The formation of compound **5** in reaction (4) involves the most considerable decrease in the entropy, which probably accounts for its high reactivity in inhibited oxidation reactions.

**Table 1.** PM6-calculated enthalpies  $H_{\rm f}^{\circ}$  and entropies  $S_{\rm f}^{\circ}$  of formation of the compounds at 298 K

Compound	$H_{ m f}^{\circ}$	$S_{ m f}^{\circ}$
	/kJ mol <sup>-1</sup>	$/J K^{-1} mol^{-1}$
PET*	33.0	437
1	67.9	713
2	89.7	869
3	147.1	1299
4	206.6	1773
5	261.9	2170
MeOH	11.5	240

\* PET is tetrakis(hydroxymethyl)methane.

**Table 2.** PM6-calculated changes in the enthalpy  $(\Delta H_r^{\circ})$ , entropy  $(\Delta S_r^{\circ})$ , and Gibbs energy  $(\Delta G_r^{\circ})$  for reactions (1)–(4) at 298 K

Reac-	$\Delta H_{\rm r}^{\circ}$	$\Delta G_{\rm r}^{\ \circ}$	$\Delta S_{\rm r}^{\circ}$	Equilibrium	
tion	kJ mol <sup>-1</sup>		$J K^{-1} mol^{-1}$	constant	
1	0.3	12.5	-41	$K_1 = 6.4 \cdot 10^{-3}$	
2	1.0	13.8	-43	$K_2 = 3.8 \cdot 10^{-3}$	
3	3.1	2.8	1	$\tilde{K_3} = 3.2 \cdot 10^{-1}$	
4	-1.1	21.6	-76	$K_4 = 1.6 \cdot 10^{-4}$	

The O—H homolysis energy  $D_{OH}$  is an indicator of the antioxidant efficiency of phenol derivatives. The  $D_{OH}$  values can be calculated from the energies of formation of phenol ( $E_{f^{\circ}InH}$ ) and the corresponding phenoxyl radical ( $E_{f^{\circ}In}$ ) from the atoms and the energy of formation of the H atom by dissociation of molecular hydrogen ( $E^{\circ}_{H} = 218.0 \text{ kJ mol}^{-1}$ ). The calculated energies of formation of compounds **1**—**5** and their phenoxyl radicals from the atoms and the O—H homolysis energies are given in Table 3.

The calculated  $D_{OH}$  value of structure 5 differs from the experimental energy<sup>11</sup> by 20 kJ mol<sup>-1</sup>. Apparently, this difference results from inaccurate procedures for determination of experimental values as well as from the semiempirical PM6 approximation. At least, the calculated and experimental O—H homolysis energies for 2,4,6tri-*tert*-butylphenol<sup>11,12</sup> differ by 10 kJ mol<sup>-1</sup>. It is also known<sup>13</sup> that quantum chemical calculations provide results varying with the procedure used.

The O—H homolysis energy in structure **4** is substantially higher than those of the other compounds of the series studied, which should affect its antioxidant properties. Compound **5** is the best antioxidant against heat aging of polymers, while compound **4** fails under these conditions. The dipole moment, which is a symmetry indicator, suggests that structure **4** is more symmetrical ( $\mu = 0.97$  D) than structure **5** ( $\mu = 5.6$  D).

Structure **5** is asymmetric because its substituents are nonequivalent compared to compound **4**; this nonequivalence changes the O—H homolysis energy. An X-ray diffraction study<sup>14</sup> of tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane has revealed the nonequivalence of its substituents, which agrees with our calculated data. The distances between the phenolic O atoms, as well as the angles between the O—H bonds and the ring C atoms, are different in structures **4** and **5** (Table 4).

The inhibition period  $\tau$  of cumene oxidation and the chain termination coefficient *f* in reactions of the peroxyl radical with antioxidants **3**–**5** at a constant initiation rate  $(W_i = 1.5 \cdot 10^{-8} \text{ mol } \text{L}^{-1} \text{ s}^{-1})$  were determined by the gasometric method<sup>15</sup> (Fig. 2).

Table 3. PM6-calculated energies of formation of compounds 1-5, their phenoxyl radicals, and the O-H homolysis energies

$-E_{\rm f}^{\circ}_{\rm InH}$	$-E_{\rm f}^{\circ}{}_{\rm In}$ .	D <sub>OH</sub>
	kJ mol <sup>-1</sup>	
667.4	569.4	316.0
1287.5	1186.4	319.1
1741.3	1641.0	318.3
2208.3	2079.0	347.3
2682.0	2579.0	321.0*
	$\frac{-E_{\rm f}\circ_{\rm InH}}{667.4}$ $\frac{667.4}{1287.5}$ $1741.3$ $2208.3$ $2682.0$	$\begin{array}{c c} -E_{\rm f}^{\circ}{}_{\rm InH} & -E_{\rm f}^{\circ}{}_{\rm In}. \\ \hline & {\rm kJ\ mol^{-1}} \\ \hline \\ 667.4 & 569.4 \\ 1287.5 & 1186.4 \\ 1741.3 & 1641.0 \\ 2208.3 & 2079.0 \\ 2682.0 & 2579.0 \\ \hline \end{array}$

\* For compound **5**,  $D_{OH} = 341 \text{ kJ mol}^{-1.9,10}$ 

**Table 4.** PM6-calculated distances between thephenolic O atoms in structures 4 and 5

Distance $d/A$	d∕Å		
4	5		
O(1)-O(2) 14.442	14.151		
O(1)-O(3) 13.394	12.782		
O(2)-O(3) 13.357	9.613		
O(2)-O(4) -	11.332		
O(3)-O(4) -	6.829		

The above parameters are interrelated by the formula

$$f = \tau W [\text{InH}]^{-1}$$
,

where InH are compounds 3-5. The chain termination coefficient (inhibitive capacity of the antioxidant) characterizes the number of chains that are terminated by its single molecule. According to the data obtained, the coefficient *f* approximates to 8, 2, and 4 for compounds 5, 4, and 3, respectively. Therefore, compound 5 as an antioxidant is superior to compound 4. With consideration of the number of hydroxy groups in structures 3-5, the coefficient *f* converted to one OH group is 2 for 3 and 5 and smaller than unity for 4.

The reaction rate constant  $(k_7)$  was determined from the equation

$$\Delta[O_2]/[RH] = -k_2/k_7 \ln(1 - t\tau^{-1}),$$

where  $k_2 = 1.75 \text{ L mol}^{-1} \text{ s}^{-1}$  (see Refs 16, 17) is the rate constant of the ROO<sup>•</sup> initiation from cumene, [RH] =  $= 7.18 \text{ mol } \text{L}^{-1}$  is the concentration of cumene, and  $\Delta[O_2]$  is the amount of consumed oxygen.



**Fig. 2.** Oxygen consumption kinetics in the initiated oxidation of cumene at 50 °C in the presence of compounds **3–5** and AIBN;  $W_i = 1.5 \cdot 10^{-8} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ ; **[3]**<sub>o</sub> =  $1.34 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ , **[4]**<sub>o</sub> =  $2.55 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ , **[5]**<sub>o</sub> =  $9.1 \cdot 10^{-7} \text{ mol } \text{L}^{-1}$ .

For antioxidants **3**, **4**, and **5**,  $k_7$  is  $2.5\pm0.2\cdot10^4$ ,  $1.8\pm0.2\cdot10^4$ , and  $3.1\pm0.2\cdot10^4$  L mol<sup>-1</sup> s<sup>-1</sup>, respectively. According to the literature data,  $k_7$  is  $2.3\cdot10^4$  (see Ref. 18) and  $1.5\cdot10^4$  L mol<sup>-1</sup> s<sup>-1</sup> (see Ref. 19) for compounds **1** and **5**, respectively. It should be noted that Tsepalov *et al.*<sup>19</sup> seem to have used the commercial stabilizer Irganox 1010 without analyzing its composition.

To sum up, we found that the methodology of the preparation of tetrakis[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propanoyloxymethyl]methane depends on the conditions of methanol separation in the final step. Under the transesterification conditions, the time-dependent partition of methanol in the liquid—gas system is crucial for the reaction rates and the composition of the reaction mixtures. The presence of compound **4** in the transesterification product should be detrimental to the "consumer" properties of the antioxidant (*e.g.*, phenozan-23).

## **Experimental**

<sup>1</sup>H NMR spectra were recorded on a Bruker WM-400 instrument (400 MHz) with reference to the signals of the residual protons of deuterated solvent (CDCl<sub>3</sub>). IR spectra were recorded for crystals on a Perkin-Elmer 1725-X spectrometer using the diffuse reflection method. Liquid chromatography was carried out on a Bruker LC-31 chromatograph (IBM Cyano column, hexane—propan-2-ol (9 : 1) as an eluent). The chain termination coefficients *f* of compounds **1**—**5** were determined according to a known method<sup>15</sup> for inhibited oxidation of cumene at 50 °C in the presence of AIBN as an oxidation initiator. Semiempirical PM6 quantum chemical calculations were carried out with the MOPAC 2009 program package. The structures of phenoxyl radicals were calculated by the restricted Hartree—Fock method.

Methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate (1). Method *A*. Methyl acrylate (2.5 mL, 0.03 mol) was added at 115 °C to a solution of potassium 2,6-di-*tert*-butylphenoxide (4.88 g, 0.01 mol) in DMSO (4 mL). The reaction mixture was cooled, kept for 3 h, and neutralized with 10% HCl. The product was crystallized from hexane. The yield of compound 1 was 5.16 g (88%), m.p. 66 °C (*cf.* Ref. 20: 66 °C).

**Method B.** A mixture of compound **5** (11.78 g, 0.01 mol) and 5% MeONa in MeOH (4 mL) was kept at 20 °C for 4 h. Then hexane (20 mL) was added for crystallization. The yield of compound **1** was 11.1 g (95%), m.p. 66 °C.

Bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]bis(hydroxymethyl)methane (3). A mixture of compound 1 (14.6 g, 0.05 mol), tetrakis(hydroxymethyl)methane (6.8 g, 0.05 mol), and 6% KOH/aluminosilicate (3 g) as a catalyst was kept under argon at 190 °C for 40 min. Then hexane (35 mL) was added. The lower layer containing 85% of compound **3** was separated and concentrated. The residue was chromatographed on silica gel. Yield 8.4 g, m.p. 105–106 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), &: 1.43 (s, 36 H, Bu<sup>1</sup>); 2.67 (t, 4 H, Ar<u>CH<sub>2</sub>CH<sub>2</sub></u>, J = 8.21 Hz); 2.86 (t, 4 H, ArCH<sub>2</sub><u>CH<sub>2</sub></u>, J = 8.13 Hz); 3.28 (s, 4 H, CH<sub>2</sub>OH); 4.04 (s, 4 H, COO<u>CH<sub>2</sub></u>); 5.01 (s, 2 H, OH); 6.98 (s, 4 H, Ar). IR, v/cm<sup>-1</sup>: 3637 (OH), 3270 br (OH), 2951 (CH), 1744 (C=O). Tris[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl](hydroxymethyl)methane (4). A mixture of compound 1 (29.2 g, 0.1 mol), tetrakis(hydroxymethyl)methane (4.53 g, 0.033 mol), and NaOH (0.2 g, ~0.005 mol) was kept *in vacuo* (1.3  $\cdot$  10<sup>4</sup> Pa). The content of compound 4 in the reaction mixture was 82% (LC data). The yield of compound 4 was 22 g, m.p. 64—65 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.43 (s, 54 H, Bu<sup>t</sup>); 2.62 (t, 6 H, Ar<u>CH<sub>2</sub>CH<sub>2</sub>, J = 8.63 Hz</u>); 2.85 (t, 6 H, ArCH<sub>2</sub><u>CH<sub>2</sub>, J = 8.68 Hz</u>); 3.18 (s, 2 H, C<u>H<sub>2</sub>OH</u>); 4.01 (s, 6 H, COO<u>CH<sub>2</sub></u>); 5.09 (s, 3 H, OH); 6.98 (s, 6 H, Ar). IR, v/cm<sup>-1</sup>: 3645 (OH), 3517 br (OH), 2912 (CH), 1742 (C=O).

Tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyloxymethyl]methane (5). A mixture of compound 1 (116.9 g, 0.4 mol), tetrakis(hydroxymethyl)methane (13.6 g, 0.1 mol),  $K_2CO_3$  (1.5 g, ~0.01 mol),  $Na_2CO_3$  (4 g, ~0.04 mol), and phenol (4.7 g, 0.05 mol) was heated to 140–145 °C and kept *in vacuo* (1.3 · 10<sup>4</sup> Pa) for 2 h. Then the pressure was lowered to 2.6 · 10<sup>3</sup> Pa and the reaction mixture was kept for 8 h, dissolved in cyclohexane (300 mL), and cooled to 4–5 °C. The precipitate that formed was separated. The yield of compound **5** was 61.24 g (52%), m.p. 116–117 °C (*cf.* Ref. 7: 116–117 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), 8: 1.43 (s, 72 H, Bu<sup>1</sup>); 2.61 (t, 8 H, Ar<u>CH<sub>2</sub>CH<sub>2</sub></u>, *J* = 8.99 Hz); 2.86 (t, 8 H, ArCH<sub>2</sub><u>CH<sub>2</sub></u>, *J* = 7.72 Hz); 4.04 (s, 8 H, COO<u>CH<sub>2</sub>)</u>; 5.01 (s, 4 H, OH); 6.98 (s, 8 H, Ar). IR, v/cm<sup>-1</sup>: 3646 (OH), 2958 (CH), 1744 (C=O).

## References

- G. E. Zaikov, A. A. Volod'kin, Neokrashivayushchiesya stabilizatory polimerov na osnove metil-3-(3,5-di-tret-butil-4gidroksifenil)propanata, Konstruktsii iz kompozitnykh materialov [Undyeable Polymer Stabilizers Based on Methyl 3-(3,5-Ditert-Butyl-4-Hydroxyphenyl)Propanoate. Structures Made from Composite Materials], VIMI, Moscow, 2003, p. 11 (in Russian).
- L. V. Glushkova, A. A. Nazarov, Sintez i issledovaniya effektivnosti khimikatov dlya polimernykh materialov [Chemicals for Polymer Materials: Synthesis and Study of Efficiency], NIIKhIMpolimer, Tambov, 1986 (in Russian).
- 3. Ger. Pat. 2364126; Chem. Abstr., 1974, 81, 120260.
- 4. Eur. Pat. 148729; Chem. Abstr., 1986, 104, 148524.
- 5. Jpn Pat. 84-27853; Chem. Abstr., 1984, 101, 72439.
- 6. US Pat. 3282939; Chem. Abstr., 1967, 66, 18609.
- 7. SSSR Inventor's Certificate 1685920; Byull. Izobret., 1991, 29.
- 8. J. J. P. Stewart, J. Mol. Model., 2007, 13, 1173.
- S. L. Khursan, Sbornik lektsii na VIII Mezhdunarodnoi konferentsii "Bioantioksidant" [A Collection of Lectures Delivered at VIII Int. Conf. "Bioantioxidant"], Moscow, 2010, p. 195 (in Russian).
- 10. E. T. Denisov, Zh. Fiz. Khim., 1995, 69, 623 [Russ. J. Phys. Chem. (Engl. Transl.), 1995, 69].
- E. T. Denisov, T. G. Denisova, *Handbook of Antioxidants*, CRC Press, London-New York, 2000, p. 88.
- A. M. Vasserman, A. L. Buchachenko, G. A. Nikiforov, V. V. Ershov, M. B. Neiman, *Zh. Fiz. Khim.*, 1967, **41**, 705 [*Russ. J. Phys. Chem. (Engl. Transl.*), 1967, **41**].
- E. T. Denisov, Sbornik lektsii na VIII Mezhdunarodnoi konferentsii "Bioantioksidant" [A Collection of Lectures Delivered at VIII Int. Conf. "Bioantioxidant"], Moscow, 2010, p. 50 (in Russian).

14. Jpn Pat. 84-104348; Chem. Abstr., 1984, 101, 191363.

- N. M. Emanuel, E. T. Denisov, Z. K. Maizus, *Tsepnye* reaktsii okisleniya uglevodorodov v zhidkoi faze [Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase], Nauka, Moscow, 1965, p. 54 (in Russian).
- 16. V. F. Tsepalov, Issledovanie sinteticheskikh i prirodnykh antioksidantov in vivo i in vitro [In vivo and in vitro Study of Synthetic and Natural Antioxidants], Nauka, Moscow, 1992, p. 16 (in Russian).
- O. I. Dyubchenko, V. V. Nikulina, E. I. Terakh, A. E. Prosenko, I. A. Grigor'ev, *Russ. Chem. Bull. (Int. Ed.)*, 2007, 56, 1149 [*Izv. Akad. Nauk, Ser. Khim.*, 2007, 1107].
- N. M. Storozhok, M. G. Perevozkina, G. A. Nikiforov, *Russ. Chem. Bull. (Int. Ed.)*, 2005, 54, 328 [*Izv. Akad. Nauk, Ser. Khim.*, 2005, 323].
- V. F. Tsepalov, A. A. Kharitonova, G. P. Gladyshev, N. M. Emanuel, *Kinet. Katal.*, 1977, 18, 1261 [*Kinet. Catal.* (*Engl. Transl.*), 1977, 18].
- 20. A. A. Volod'kin, V. I. Paramonov, F. M. Egidis, L. K. Popov, *Khim. Prom-st.* [*Chemical Industry*], 1988, **12**, 7 (in Russian).

Received April 4, 2011; in revised form January 23, 2012