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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Study of the Inhibiting Activity of 4-(4'-Hydroxyphenyl)and 4-(2'-Hydroxy-5'-methylphenyl)methyl Cyclohexane Carboxylic Acid Ethyl Esters in Photooxidation of Petroleum Phosphors

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Abstract—4-(4'-hydroxyphenyl)- and 4-(2'-Hydroxy-5'-methylphenyl)methyl cyclohexane carboxylic acid ethyl esters were synthesized from phenol and *para*-cresol. The structure of the esters synthesized was studied, and their inhibiting activity in photooxidation of a petroleum phosphor produced from the heavy pyrolysis tar fraction was examined.

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An interesting and promising research area is photochemical oxidation of petroleum and petroleum products. In contrast to thermal treatment, light exposure enables selective delivery of energy to a component of the reaction mixture, which is important for such multicomponent systems as oil.

Petroleum phosphors (PPs) are labile oil products and, when exposed to solar light and atmospheric oxygen, they are subject to photooxidative processes making shorter their service life. Therefore, it is necessary to find inhibitors that stabilize PPs without interfering with the components responsible for luminescence.

It is known [1, 2] that compounds containing OH, NH, and SH functional groups, capable of homolytic dissociation under the action of free radicals, and aromatic rings are oxidation inhibitors.

There are numerous alkyl phenol compounds [3-7] serving as additives to oils, fuels, and polymeric materials, emulsifiers, inhibitors, and thermal and light stabilizers [1, 8-10].

In this communication, we present results obtained in

cycloalkylation of phenol and *para*-cresol with 1-methylcyclohexenecarboxylic acid ethyl ester (MCHAEE) in the presence of a KU-23 catalyst in the H-form and in analysis of synthesized 4-(4'-hydroxyphenyl)- (ester 1) and 4-(2'-hydroxy-5'-methylphenyl)methyl cyclohexane carboxylic acids ethyl esters (ester 2) as PP photooxidation inhibitors.

EXPERIMENTAL

As starting products served phenol [GOST (State Standard) 6417–74], *para*-cresol [TU (Technical Specification) 6-09-244–77] and MCHAEE produced by reacting isoprene with acrylic acid ethyl ester in a 1-1 autoclave. The reaction was performed in the atmosphere of argon at a temperature of 200°C in the course of 2 h at a 1 : 1 isoprene : ester molar ratio. After the experiment was complete, the reaction products were subjected to rectification; MCHAEE: bp 211°C, n_{D}^{20} 1.4610, ρ_{4}^{20} 0.9701, M 168.

We used KU-23 cation exchanger (GOST 20298– 74) as a catalyst. The KU-23 catalyst was prepared by removing water at temperatures not exceeding 110°C (KU-23 of the 10/60 modification contains 55–70 wt % water and is thermally stable at 150–170°C). In the course of operation, KU-23 was gradually deactivated because of the thermally induced abstraction of sulfo groups and pore clogging by tarry substances. Owing to the microporous structure and improved kinetic properties of the KU-23 cation exchanger, its efficiency exceeds that of KU-2. KU-23 was regenerated with 2–4% hydrochloric acid (4.0–4.5 volumes of water per volume of the catalyst).

Phenols were cycloalkylated with MCHAEE in a batch-type laboratory installation. Reaction products were separated from the catalyst by filtration in the hot state (40–45°C) and then subjected to rectification. The unreacted starting ester was evaporated under atmospheric pressure, and then unreacted phenol (or *para*-cresol) and the target reaction product were in a vacuum (at a residual pressure of 1.3 kPa).

As object of study served heavy pyrolysis tar (HPT) fraction of straight-run gasoline produced from oil at Ethylene–Polyethylene oil refinery in Sumgait.

In turn, a fraction boiling-out at above 400°C was isolated by vacuum distillation of HPT. Oil phosphors were produced by deasphalting and detarring of this fraction by the method described in [11] and stored at room temperature without exposure to light.

The inhibiting activity of the synthesized esters 1 and 2 was examined in aerobic photooxidation of PPs. Formulations were prepared with addition of 2 wt %

ester **1** or ester **2** to PPs. As a reference inhibitor was taken 2,6-di-*tert*-butyl-4-methylphenol (ionol).

We prepared films with a thickness of about 30 μ m from a benzene solution of the formulations and irradiated the films with a PRK-2 quartz mercury lamp for 6 h. The distance between the lamp and a sample was 20 cm. A BS-4 light filter was used to imitate the solar light. ¹H NMR spectra were measured with a Varian T-60 instrument. IR spectra of the samples before and after irradiation were recorded with a UR-20 spectrophotometer in the spectral range 700–4000 cm⁻¹.

The stabilizing efficiency of the inhibitors on the process of PP photooxidation was studied by analyzing the n/n_{inh} ratio, where n and n_{inh} are coefficients characterizing the amount of oxidation products formed without the inhibitors being tested and in their presence. The coefficients were calculated from the D_v^1/D_v^0 ratio, where D_v^0 and D_v^1 are the optical densities of the C=O group at 1730 cm⁻¹ before and after the irradiation, respectively.

The degree of PP photooxidation in the absence and in the presence of the inhibitors was determined by IR spectroscopy from the change in the optical density of the absorption band at 1730 cm⁻¹ in relation to the irradiation duration.

The electronic absorption spectra of PPs and esters **1** and **2** were recorded with a Specord UV-VIS spectrophotometer in the range 200–700 nm.

The reaction of phenol and *para*-cresol cycloalkylation by cyclic esters proceeds by the scheme.



The interaction of phenol with MCHAEE mostly gives *para*-alkylphenol with a minor amount of *ortho*-

and disubstituted phenols (2,4- and 2,6-isomers). The reaction of *para*-cresol with MCHAEE mostly gives

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ortho-alkylphenol with a minor amount of disubstituted compounds.

We studied the effect of temperature in the range 80-140°C, phenol (para-cresol) : MCHAEE ratios of 0.5 : 1 to 3 : 1 mol : mol, catalyst amount of 5 to 25 wt % relative to the raw material, and experiment duration in the range from 3 to 6 h on the yield and composition of the reaction products. Experimental data demonstrated that the yield of the target product grows with increasing temperature, but the selectivity with respect to the alkyl-substituted phenol falls under the same conditions because of the reaction of dealkylation and realkylation. As the amount of the catalyst is raised from 5 to 25 wt %, the overall yield of esters 1 and 2 becomes higher, but the selectivity with respect to monocyclo alkyl phenol decreases. The yield of esters 1 and 2 is strongly affected by the phenol (*para*-cresol) : MCHAEE molar ratio. A 1 : 1 molar ratio of the starting components provides a high yield of the esters and high selectivity with respect to monocyclo alkyl phenol. We found that reactions catalyzed by cation exchangers are slow; their optimal duration is 5-5.5 h, whereas deviation from this time leads to a decrease in the yield of esters 1 and 2.

An analysis of the data obtained enabled us to find the optimal experimental conditions: temperature 120– 125° C, 1 : 1 molar ratio of the starting components, catalyst amount 10–12 wt % relative to the raw material at a reaction duration of 5–5.5 h. Under these conditions, the yields of esters (1) and (2) reach a value of 63.5–68.6%, and the selectivity, 89.7–93.2%. The physicochemical characteristics of esters 1 and 2 are listed in the table.

The IR spectrum of ester **1** shows absorption bands at 700, 780, 820, and 880 cm⁻¹, associated with nonplanar deformation vibrations of a substituted benzene ring. The absorption bands peaked at 1510 and 1580 cm⁻¹ are related to deformation vibrations of the benzene ring, and that at 1610 cm⁻¹, to the C=C bond of the aromatic ring. A pendulum vibration peaked at 725 cm⁻¹, characteristic of the CH₂ group, appears in

Physicochemical characteristics of esters ${\bf 1}$ and ${\bf 2}$

Ester	bp, °C/P, Pa	mp, °C	$n_D^{\ 20}$	$ ho_4^{20}$	М
1	183-187/666.5	-	1.5030	1.0426	260
2	215-217/666.5	81-82	_	-	276

the spectrum. Also, bands of deformation and stretching vibrations characteristic of the methyl group are observed at, respectively, 1380 and 2860 cm⁻¹, and bands characteristic of the methylene group, at 1470, 2920, and 2940 cm⁻¹. In addition to the absorption bands mentioned above, the spectrum contains a band at 1200 cm⁻¹, which corresponds to stretching vibrations of the O–H group of phenol. Also, a band of stretching vibrations, responsible for the C=O group of the ester, is observed at 1750 cm⁻¹. The absorption band at 950 cm⁻¹ is responsible for CH₂ groups in the ring.

The IR spectra of esters 1 and 2 are nearly the same. However, the spectrum of ester 1 contains absorption bands of a *para*-substituted benzene ring (840 cm⁻¹), and the spectrum of ester 2, those of *ortho*- (760 cm⁻¹) and *para*-substituted (840 cm⁻¹) benzene rings.

¹H NMR spectrum of ester **1** (CCl₄, δ , ppm): 1.12 and 2.8 (CH₃); 1.2–1.8 (multiplet of protons of the cyclohexane ring); 5.4 (OH); 6.4–7.2 (multiplet of protons of the benzene ring). The ¹H NMR spectra of esters **1** and **2** are nearly the same.

A broad band at 250–280 nm is observed in the electronic absorption spectrum of esters 1 and 2. This band indicates that the ester contains a phenolic group and an ester group (COOR) not bonded directly to the benzene ring, which indirectly confirms the structure of esters 1 and 2.

The electronic absorption spectrum of PPs covers a spectral range from 200 to 500 nm. The esters we synthesized absorb in the short-wavelength UV range (200–280 nm); the molar extinction coefficient of PPs is $\varepsilon_{max} = 8105$, and that of the esters, $\varepsilon_{max} = 4105$. Because the absorbing capacity of PPs substantially exceeds that of esters **1** and **2** and the concentration of the esters does not exceed 2 wt %, they cannot serve as UV absorbers for PPs. In addition, the triplet state energy of PPs (~1.12 eV) is lower than that of the esters synthesized (3.53 eV). It is known [12, 13] that the triplet state energy of the quenching acceptor must be lower than that of a donor. Therefore, it can be suggested that the esters cannot be used as quenching agents for excited states of PPs.

The photooxidation of PPs yields active species, such as singlet oxygen and alkyl and peroxide radicals ($^{1}O_{2}$, R[•], RO₂) [14]. Phenols having comparatively weak O–H bonds, compared with the C–H bond of a hydrocarbon, interact with these active species, as shown in [12]. The differences between the reactivities of these bonds are due to the difference in activation energies. The activation barrier of the reaction of a peroxide radical with the O-H bond of phenol is 28 kJ mol⁻¹ lower than the activation energy of the reaction of a peroxide radical with the C-H bond of hydrocarbons, This difference in the reactivities of O-H and C-H bonds can be attributed to the fact that the transition state O...H...OOR has a bipolar structure in which a hydrogen atom is between two negatively charged oxygen atoms. Such a bipolar structure is characterized by an energy gain associated with the interaction of two dipoles with a positively charged hydrogen atom. It is this Coulomb attraction that is responsible for the decrease in the activation energy of the reaction of RO_2^{\cdot} with phenol. At the same time, the rate of this reaction is affected by the formation of a hydrogen bond. Being a polar species, the peroxide radical tends to form a hydrogen bond with the O-H group. The stronger the O-H bond in phenol, the slower its reaction with RO₂.

Taking into account the aforesaid, we tested esters **1** and **2** as PP oxidation inhibitors. To study photoxidative processes occurring in PPs in the presence and absence of inhibitors, the variation of the optical density of carbonyl-containing groups, $D_{1730(C=O)}$, with the irradiation duration was examined (see the figure). The intensity of this band is an objective criterion characterizing the depth of PP oxidation. The nature of the absorption bands of carbonyl groups in the IR spectrum of PPs is complex; their peak intensity at 1730 cm⁻¹ is a qualitative characteristic for all the overlapping bands and, consequently, reflects the total content of carbonyl-



Optical density *D* of carbonyl groups vs. the irradiation duration τ . (*I*) PPHPT; PPHPT + additive: (*2*) ionol, (*3*) ester **1**, and (*4*) ester **2**.

containing compounds. It follows from the figure that introduction of 2 wt % ester 1 or 2 into PPs diminishes the accumulation of oxidation products. The stabilization efficiencies for esters 1 and 2 are 5.3 and 5.7. These values are comparable, which is presumably due to the position of the substituent in the structure of the esters. Substituents in *ortho-* and *para-* positions to the phenolic group affect the strength of the O–H bond and its inhibiting capacity. In the presence of alkyl electron-donor substituents in the structure of the esters, the –O–H bond is weakened and detachment of a hydrogen atom is facilitated, which facilitates formation of low-activity radicals.

The inhibiting action of esters in the course of PP photooxidation involving RO_2^{-} occurs by the scheme



In the case of ${}^{1}O_{2}$, we have





 RO_2^{*} and ${}^{1}O_2$ interact with the phenolic group of esters 1 and 2 to give low-activity radicals involved in chain termination reactions. In the photooxidation of PPs, not only the OH group, but also the carbonyl group of an ester exhibits the inhibiting activity. Having absorbed a photon, this group forms a biradical, which, interacting with R^{*}, leads to chain termination:



CONCLUSIONS

(1) The optimal conditions of synthesis of 4-(4'-hydroxyphenyl)- and 4-(2'-hydroxy-5'-methyl-phenyl)methyl cyclohexane carboxylic acid ethyl esters from phenol and *para*-cresol were found and the physicochemical characteristics of the esters were determined.

(2) It was found that the esters synthesized exhibit a high inhibiting activity in photooxidation of petroleum phosphors via scavenging of alkyl and peroxide radicals.

REFERENCES

- Rasulov, Ch.K., Azizov, A.G., Salmanova, Ch.K., et al., *Neftekhimiya*, 2006, vol. 46, no. 4, pp. 306–309.
- 2. Uglev, V.V. and Kam'yanov, V.F., *Neftekhimiya*, 2000, vol. 40, no. 2, pp. 140–144.
- Dyubchenko, O.I., Nikulina, V.V., Terakh, E.I., et al., *Neftekhimiya*, 2005, vol. 45, no. 1, pp. 1–5.
- Markov, A.F., Prosenko, A.E., Shvarts, Ya.Sh., et al., *Khim.-Farm. Zh.*, 2006, vol. 40, no. 4, pp. 117–121.
- 5. RF Patent 2233262.
- 6. Rasulov, Ch.K., Zeinalova, L.B., Babaeva, R.K., et al.,

Protsess. Neftekhim. Neftepererab., 2007, no. 2, pp. 11–15.

- 7. Korenev, D.K., Zavorotnyi, V.A., and Kelarev, V.I., *Khim. Tekhnnol. Topl. Masel*, 2003, no. 1, pp. 61–63.
- Kuliev, B.V., Azizov, A.G., Ibragimova, M.D., et al., Protsess. Neftekhim. Neftepererab., 2006, no. 1, pp. 71– 77.
- 9. Mamedova, P.Sh., Farzaliev, V.M., and Babaev, E.R., *Neftekhimiya*, 2007, vol. 47, no. 1, pp. 58–62.
- 10. Rasulov, Ch.K., Zeinalova, L.B., Azimova, R.K., et al., *Neftekhimiya*, 2007, vol. 47, no. 6, pp. 442–444.
- 11. Akhmedbekova, S.F., Antioxidative Activity of Photooxidized Heavy Petroleum Residues, Cand. Sci. Dissertation, Baku, 2007.
- Krichevskii, G.E., Fotokhimicheskie prevrashcheniya krasitelei i svetostabilizatsiya okrashennykh materialov (Photochemical Transformations of Dyes and Light-Stabilization of Pigmented Materials), Moscow: Khimiya, 1986.
- Shlyapintokh, V.Ya., Fotokhimicheskie prevrashcheniya i stabilizatsiya polimerov (Photochemical Transformations and Stabilization of Polymers), Moscow: Khimiya, 1979.
- Nadzhafova, M.A., Mamedov, A.P., Rustamov, M.I., and Salmanova, Ch.K., *Neftekhimiya*, 2003, vol. 43, no. 4, pp. 273–281.