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Abstract

Full Text

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ON THE INTERACTION OF INHIBITORS OF HYDRO-CARBON AUTOXIDATION WITH ALKYL AND PEROXIDE RADICALS

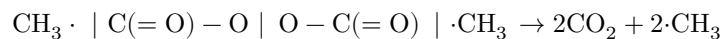
(Presented by Academician N. N. Semenov, 27 XII 1957)

Previously we showed experimentally that some inhibitors of the liquid-phase oxidation of petroleum hydrocarbons by molecular oxygen are capable of retarding the oxidative process only when they are added to the substance being oxidized (white oil) before the start of the reaction, whereas others do so also when introduced at various stages of development of the process. It was proposed that inhibitors of group I are capable of binding the active particles that initiate the chain reaction (mainly hydrocarbon radicals $R\cdot$); inhibitors of group II, however, interact with peroxide compounds formed at the initiation stage (hydroperoxides $ROOH$) and at the stage of reaction development ($ROOH$ and peroxide radicals $RO_2\cdot$), giving inactive products ⁽¹⁾. These assumptions were confirmed by the absence of interaction of group I inhibitors with hydrocarbon hydroperoxides ⁽²⁾ and by the absence of their influence on the thermal decomposition of hydroperoxides in solutions, whereas antioxidants of group II sharply accelerated it ⁽¹⁾.

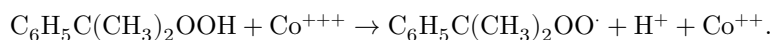
Later it was found that there exists a group III of inhibitors which, like representatives of groups I and II, delay the autoxidation of hydrocarbons when added to the system before the start of the reaction, but which, in contrast to group II inhibitors, are capable of stopping the developing (uninhibited) process only at its autocatalytic stage. A certain commonality in the chemical structure of the inhibitors of each group was noted, and a classification of antioxidants according to kinetic features was proposed ⁽³⁾.

In order to obtain more complete experimental confirmation of the stated ideas about the nature of the action of antioxidants of groups I and II and to explain the peculiarities of the action of inhibitors of group III, experiments were undertaken involving the direct introduction into oxidizing white oil of alkyl ($R\cdot$) and peroxide ($RO_2\cdot$) radicals and the study of their influence on the activity of antioxidants of groups I, II, and III at various stages of oil oxidation. The group I antioxidant used was *n*-oxydiphenylamine, that of group II was 4,4'-diaminodiphenyl disulfide, and that of group III was 2,6-di-*tert*-butyl-4-methylphenol (Ionol), the first two being added in an amount of 0.1 mmol and the third in an amount of 1 mmol per 100 g of oil. As a source of hydrocarbon radicals $R\cdot$ we used acetyl peroxide, which readily decomposes on heating of its solutions, as Karasch showed ⁽⁴⁾, with formation mainly of CO_2 and CH_3

radicals according to the equation



Peroxide radicals RO_2 were obtained by the interaction of cumene hydroperoxide with Co naphthenate, proceeding, according to Karasch (⁵), according to the scheme



Acetyl peroxide was added (in the form of its 2% solution in petroleum ether) in an amount of 0.03 wt.% peroxide relative to the oil; cumene hydroperoxide, 0.3%; Co naphthenate, 0.01%. The initial white oil (ρ_4^{20} 0.8814) was purified immediately before the experiment (^{1, 3}). Oxidation of the oil (30 g) was carried out at 117° by bubbling with oxygen in a glass apparatus described earlier (¹), in the absence of metals. When the radical sources were added before the start of the experiment, they were introduced into the oil before admitting O_2 , when it had reached the tempera-

of the experiment (in this case the antioxidants were dissolved in the oil beforehand).

The results of the first series of experiments (Fig. 1) show that the introduction of $\cdot\text{CH}_3$ radicals at the stage of initiation of the reaction sharply accelerates the oxidation

Fig. 1. Effect of adding a source of formation of $\cdot\text{CH}_3$ radicals on the oxidizability (increase in acid number) of uninhibited and inhibited white oil at various stages of the oxidative process. **1** —uninhibited oil; **2** —uninhibited oil containing a source of radical formation added before the start of the experiment; **3** —oil with antioxidant added before the start of the experiment; **4** —oil containing antioxidant and a source of radicals added before the start of the experiment; **5** —inhibited oil after addition of a source of radicals during the experiment (the moment of addition is indicated by an arrow); **6** —uninhibited oil containing a source of radical formation after addition of antioxidant during the experiment.

of the uninhibited oil, practically eliminating the induction period of the process (curves 1 and 2, Fig. 1). Retarders of groups I and III inhibit the onset of oil oxidation in the presence of added $\cdot\text{CH}_3$ radicals, whereas the retarder of group II is unable to do this (curves 4, Fig. 1). The latter also loses its stabilizing action when alkyl radicals are introduced into the oil inhibited by it after the start of the experiment, whereas retarders of groups I and III completely protect the oil from oxidation under these conditions (curves 5, Fig. 1). When antioxidants are introduced into oil oxidizing under the influence of added $\cdot\text{CH}_3$ radicals (uninhibited oil), retarders of groups I and III again, unlike the representative of group II, completely stop the process (curves 6, Fig. 1).

The same results were obtained with the three tested antioxidants under the same conditions when the source of radicals was tetraethyllead, added (as an oil solution) in an amount of 0.03%.

In the second series of experiments, under analogous conditions, the interaction of the same antioxidants with peroxide radicals $C_6H_5C(CH_3)_2OO\cdot$ was studied. From the results obtained, shown in Fig. 2, it follows that the introduction of peroxide radicals at the stage of initiation of the reaction also accelerates the process of oil oxidation extraordinarily strongly (control experiments showed that Co naphthenate and cumene hydroperoxide separately give a smaller acceleration). Antioxidants of groups II and III retain their inhibiting action upon introduction of RO_2 radicals both before and after the onset of oxidation (in the first case, the Ionol merely eliminates the accelerating effect of the introduced radicals), and also when these inhibitors are added to oil oxidizing under the influence of the introduced radicals (Fig. 2, and). The antioxidant of group I does not stop the reaction when RO_2 radicals are introduced either before or after the start of the experiment. Its addition to oil oxidizing under the action of added RO_2 radicals likewise does not retard the reaction (Fig. 2).

Thus, the results of testing the influence of $R\cdot$ and RO_2 radicals on the oxidation of inhibited oil showed that, under the action of alkyl radicals, retarders of groups I and III retain their inhibiting influence, which confirms their ability to interact with these radica-

lams at the moment when they appear, i.e., in the initiation stage of the chain reaction (with formation of inactive radicals incapable of continuing the chain). Hence one can understand why the action of inhibitors of group I is limited to the initiation period of the reaction. They are not in a position

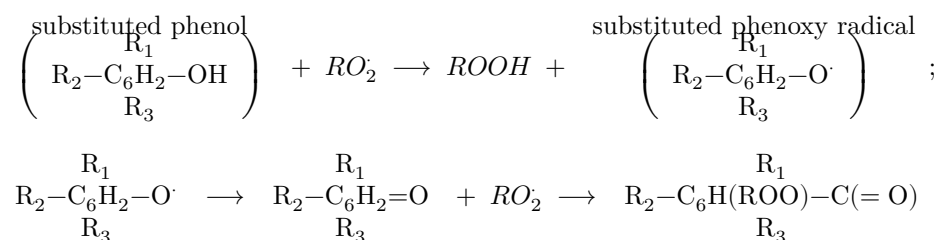
Fig. 2. Effect of adding a source of formation of RO_2 radicals on the oxidizability of uninhibited and inhibited white oil at different stages of the oxidative process.

Fig. 2. Effect of adding a source of formation of RO_2 radicals on the oxidizability of uninhibited and inhibited white oil at different stages of the oxidative process. The designations of the curves are the same as in Fig. 1.

Assuming that the initiation stage of the oxidative process includes, in addition to dissociation of the molecule of the initial hydrocarbon RH into free radicals (i.e., a reaction not requiring oxygen), also its direct reaction with molecular O_2 (^{6a,9}), with the formation of the same free radicals either directly or (most probably) with intermediate formation of a peroxide compound ($RH\cdot O_2$ or $ROOH$, according to Bach), it may be supposed that inhibitors of group II retard the process in the initiation stage by interacting with these peroxides (²) with the appearance of stable products, and stop a reaction that has already begun and has been strongly accelerated owing to their demonstrated above ability to react with peroxide radicals RO_2 , as well as with the hydroperoxides $ROOH$ formed in this phase (secondarily), with the appearance of stable products.

The mechanism of retardation by inhibitors of group III of the oxidation process

in the initiation stage is the same as for group I-binding, as was shown above, the alkyl radicals that start the chain. They retard the autocatalytic stage of the process that has begun by reacting with the peroxide radical RO_2 . The chemical mechanism of this interaction, now elucidated for the example of ionol (^{7,8}), confirms the ability of one molecule of this inhibitor to bind two peroxide radicals according to the scheme:



The loss of the retarding action by antioxidants of group III when they are introduced into the system at a later stage of the reaction (³) is due to their inability (in contrast to retarders of group II) to react actively with hydroperoxides, which at this stage of the reaction accumulate and, decomposing partly by a chain pathway, cause branching of the reaction chain (⁶). Confirmation that retarders of group III react in the course of the oxidative process not with hydroperoxides but with peroxide radicals is provided by the results of the following experiments, carried out in our laboratory by V. K. Savinova and V. P. Zhakhovskaya. Cumene hydroperoxide (5 g) in an ethylbenzene solution (60 ml) was heated in an oil bath (170°): 1) in pure form, 2) in the presence of yanol (10 g), 3) in the presence of yanol (7 g) and cobalt naphthenate (0.2 g). In the first experiment the hydroperoxide was destroyed by 86% in 10.5 hours; in the second, over the same time, by 70%, and 7.5 g of yanol was found in the residue (m.p. 67°, identified by the m.p. of a mixed sample); in the third, in 3 hours the hydroperoxide decomposed by 95%, no yanol was found in the residue, and only 4 g of dimethylphenylcarbinol was found (m.p. 29°, identified by the m.p. of a mixed sample), together with an unknown crystalline product with m.p. 180° (a control experiment carried out under the same conditions showed that yanol with cobalt naphthenate does not react in the absence of hydroperoxide).

The experimental material presented makes it possible to suppose that the initial stages of the process of oxidation of hydrocarbons inhibited by retarders acting in different ways develop according to the following scheme:

Uninhibited autooxidation of hydrocarbons (RH) in the liquid phase	Changes introduced by retarders (AH) of groups I, II, and III
Initiation	

Uninhibited autooxidation of hydrocarbons (RH) in the liquid phase	Changes introduced by retarders (AH) of groups I, II, and III
$RH \rightarrow R\cdot + H\cdot$	$R\cdot + A_I H \rightarrow RH + A_I\cdot$ –inactive radical
$RH \xrightarrow{+O_2} ROOH \rightarrow R\cdot$ and other active radicals	$R\cdot + A_{III} H \rightarrow RH + A_{III}\cdot$ –inactive radical
Chain propagation	$ROOH + A_{II} H \rightarrow$ stable products
$R\cdot + O_2 \rightarrow RO_2\cdot$	$RO_2\cdot + A_{II} H \rightarrow ROOH + A_{II}\cdot$ –inactive radical
$RO_2\cdot + HR \rightarrow ROOH + R\cdot$	$ROOH + A_{II} H \rightarrow$ stable products
...	$RO_2\cdot + A_{III} H \rightarrow ROOH + A_{III}\cdot$
	$A_{III}\cdot + RO_2\cdot \rightarrow ROOA_{III}$ –stable product

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Note: Figure translations are in progress. See original paper for figures.

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