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Nanosized Structures in High-Temperature Oxidation of Lubricating Oil Hydrocarbons

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Abstract—Peculiarities of high-temperature (150–170°C) oxidation of hexadecane as a model mineral lubricant are considered. Kinetic features of the oxidation process are presented, indicating a nonisothermal reaction mode, which can be caused by accumulation and decomposition of associated polyhydro-peroxides in the oxidizing system. The association of polyhydro-peroxides leads to formation of structures like reversed micelles, and evidence for their formation was obtained by the dye solubilization technique. The formation a microheterophase system at early stages of oxidation leads to reaction inhibition due to the formation of micellar aggregates in hydrocarbon oxidizing systems.

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INTRODUCTION

The quality of hydrocarbon lubricating materials is determined by their viscosity and low volatility in the "working" temperature range [1]. From the chemical viewpoint these properties are provided primarily by the moleculr weight and branching of the hydrocarbon chains. In the case of normal hydrocarbons, the length of the hydrocarbon radical should be no less than C_{16}, and for branched derivatives, no less than C_5. The molecular weight should be no less than 550, implying that the number of carbon atoms in the molecule should be about 40 and more.

One of the most important performance characteristics of hydrocarbon lubricating oils is their high resistance to oxidation. Oxidation gives rise to a number of oxygen-containing products, in particular, acids, which much deteriorates the quality of oils and form precipitates, cocks, and deposits on the metallic surfaces of engines and mechanisms. This problem is especially urgent at elevated temperatures (≥170°C), when oxidation processes are much accelerated.

At the initial oxidation stages a chain free-radical mechanism with degenerate branching is operative [2–6]. At deeper stages the oxidation mechanism is complicated, and most oxygen-containing products are formed and accumulated at these stages. It is just these stage when the physicochemical and performance properties of the system are also formed, for example, enhanced viscosity, corrosion activity, precipitate formation, etc.

The time when the maximum concentration of hydroperoxides is attained is considered a border between the initial and deep oxidation stages. The nature of the maximum is not quite clear, but from the practical standpoint we can focus on such characteristics as the maximum concentration of peroxides and its attainment time, the maximum rate of radical formation, and the minimum length of oxidative chains.

Research into the features of high-temperature hydrocarbon oxidation is directly related with the search for new ways to protection of hydrocarbon materials from oxidative destruction. As shown in previous studies on the kinetics and products of the oxidation of hexadecane at 120–180°C [7, 8], already a few minutes after initiation of the reaction not only mono-, but also bi- and trifunctional compounds, including di- and trihydroperoxides, are formed, as well as various functional derivatives, for example, ketohydroperoxides. It is essential to mention that mono-, bi-, and trifunctional oxygen-containing compounds are sparingly soluble in nonpolar hydrocarbons.

Thus, high-temperature oxidation of hydrocarbons is accompanied by fast accumulation of polar products that are sparingly soluble in the oxidized medium. At the same time, polar compounds should exhibit surfactant properties and ability for micelle formation [9, 10]. They are also able to take part in forming high-molecular oxidation products [11, 12]. It was previously suggested that the reaction mechanism involves association of polar oxidation products via hydrogen bonding with subsequent formation of reversed micelles, and it is their formation that should strongly affect further hydrocarbon oxidation pathway [9, 13–15].

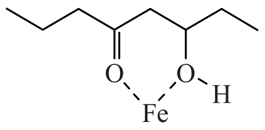
In the present work we summarized recent findings concerning the regularities and mechanism of high-temperature (170°C) hydrocarbon oxidation, and, in particular, formation of reversed micellar aggregates in systems being oxidized.

Kinetic Features of High-Temperature Hydrocarbon Oxidation

It was shown that the oxidation of hexadecane (HD) as a model mineral oil hydrocarbon at 150–170°C is much dependent on how efficient is heat removal, as well as removal or recycle of volatile products (condensate) from the reaction zone [16, 17].

Figure 1 shows the time dependence of the concentrations of hydroperoxides (HP) and carboxylix acids in the oxidation of hexadecane in various conditions. As follows from these data, the oxidation reaction proceeds with autoacceleration and involves almost no inductive period. The concentration of HP sharply increases already at the initial oxidation stage, however, if the condensate is not recycled, the concentration passes through a maximum and then stabilizes at a level of 0.05 M. The fraction of carboxylic acids in the oxidate in the process with no reflux is double that in the process with reflux.

As already mentioned, high-temperature hydrocarbon oxidation characteristically involves fast accumulation of bi- and polyfunctional oxygen-containing products. The band at 360 nm, characteristic carbonyl absorption, appears in the UV spectrum of the oxidate already at the initial oxidation stages (20–30 min) [18]. After treatment of the oxidate with iron trichloride, the spectrum acquires an absorption band at 460 nm due to formation of colored iron complexes like:



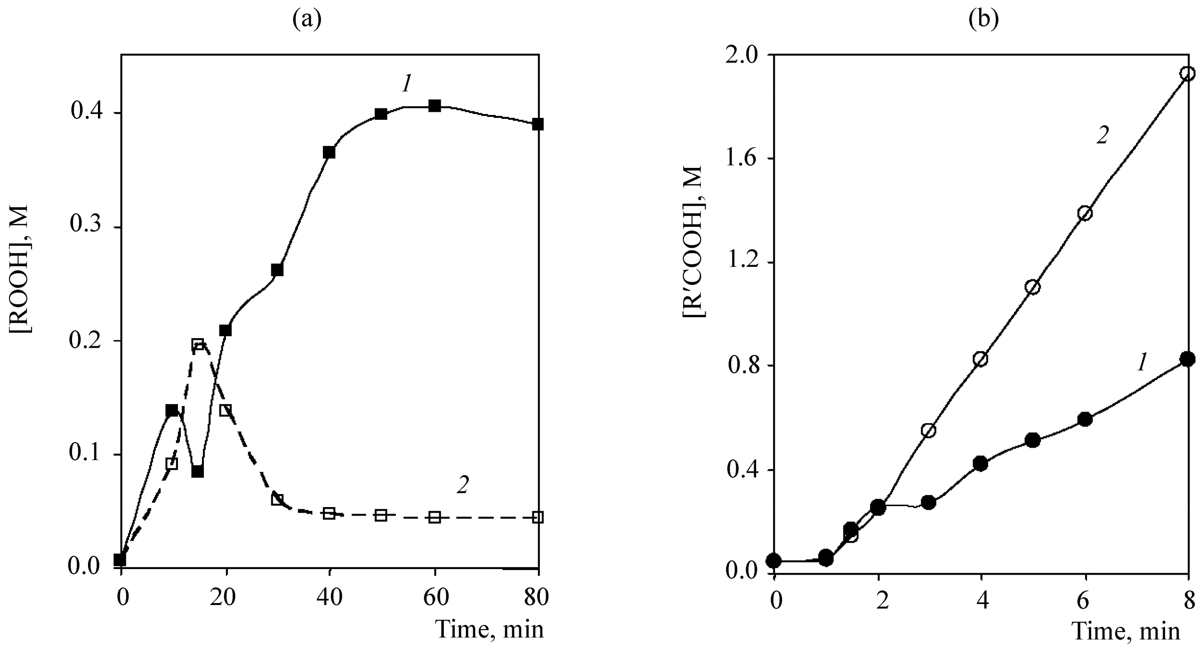


Fig. 1. Time dependences of the concentration of (a) hydroperoxides and (b) carboxylic acids on hexadecane oxidation: (*1*) with condensate return and (*2*) without condensate return. Temperature 170°C.

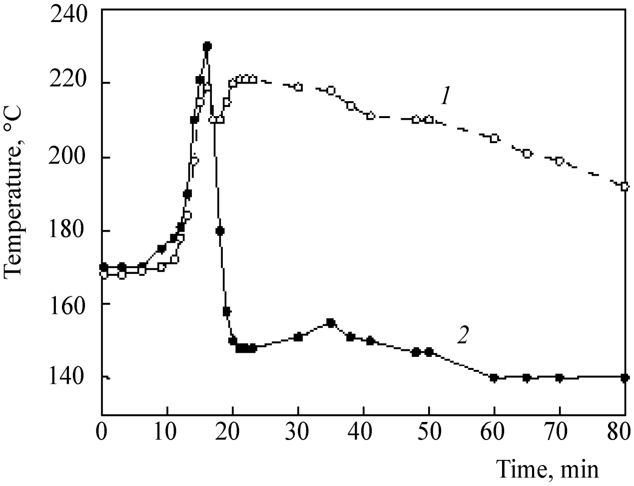


Fig. 2. Time dependence of the hexadecane temperature on nonisothermic oxidation: (*1*) with condensate return and (*2*) without condensate return.

The formation of volatile products at the initial stages of the process is associated with the occurrence of deep oxidation reactions with C–C bond cleavage. Visually, at a certain moment vigorous "boiling up" of the hydrocarbon in the reactor commences, an abundant condensate appears in the reflux condenser, and gas evolution enhances. This process under the chosen conditions is short-time and generally completes within 2–4 min. Kharitonov [15] observed similar phenomena, specifically periodic short-time pressure jumps in the reactor, in the course of liquid-phase hydrocarbon oxidation.

Recycling the condensate to the reaction mixture determines the actual temperature of hydrocarbon oxidation. Actual temperature monitoring during hexadecane oxidation at 170°C revealed a sharp increase in the temperature of the reaction mixture (up to 230°C) at the "boil up" moment after ~15-min oxidation (Fig. 2). Thus, the oxidation process occurs nonisothermally, and the overheat at the initial stages can attain 60°C with respect to the preset temperature. As the condensate is recycled after the exothermic process has been complete, the hydrocarbon temperature gets even lower of the initial level. Analogous overheat inside the reactor was reported by Lindsay Smith et al. [20]: As the time of hexadiene oxidation was prolonged from 210 to 347 min, the temperature inside the reactor increased from 180 to 187.5°C.

A different picture was observed when all volatile products were removed from the reaction zone and collected in a trap (Fig. 2). The removal of volatile products did not exclude sharp overheats at the inital stage of the process, but under the reflux mode this overheat was short, and then the temperature fell down and the reaction slowed down.

The hexadiene oxidation process can be arbitrarily into several stages depending on whether the condensate is present or absent (Fig. 3). Stages *A* and *B* correspond to radical initiation. Therewith, stage *A* involves accumulation of hydroperoxides, and stage *B* an exothermic process develops. The subsequent stage *C* involves heat absorption and decrease of the oxidate temperature. In the case when a cold condensate is returned to the reactor, the temperature fall is explained specifically by the large volume of the

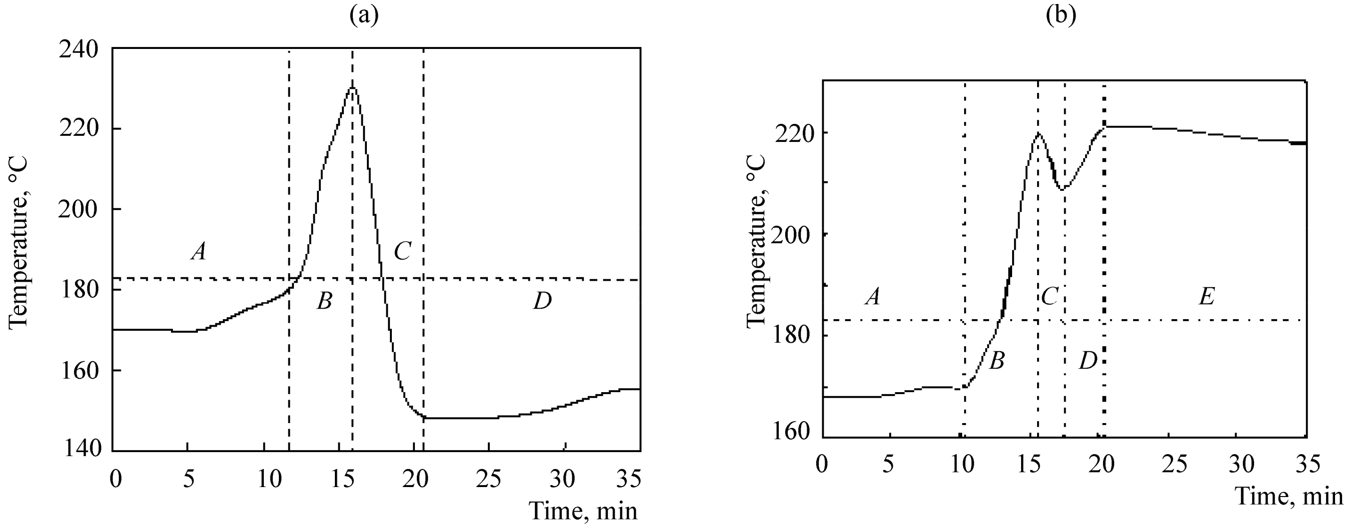


Fig. 3. Stages of liquid-phase hexadecane oxidation: (a) with cold condensate return and (b) without condensate return.

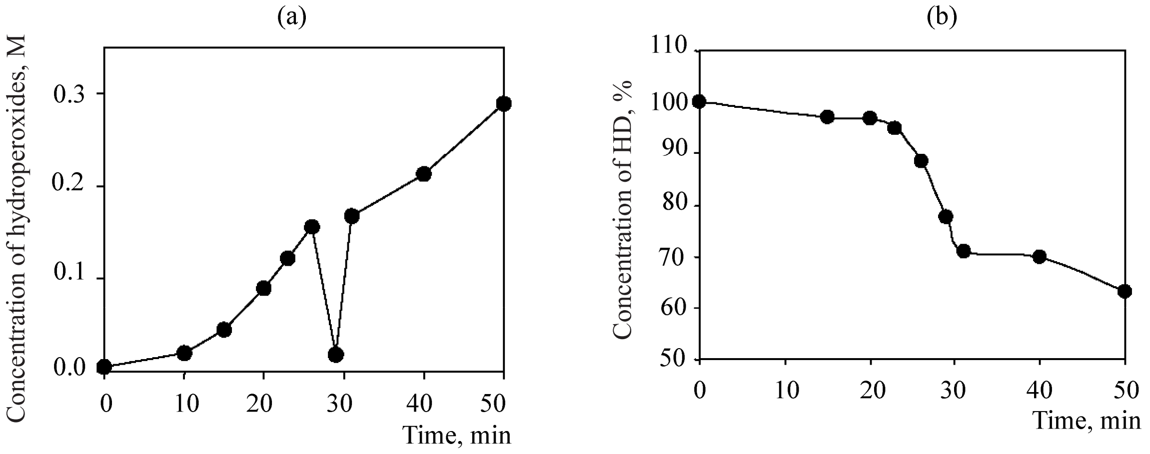


Fig. 4. Dynamics in the oxidate composition: (a) concentration of hydroperoxides and (b) concentration of hexadecane.

condensate. However, the observation of the temperature fall in the process involving no condensate recycle suggests that this phenomenon is general in nature and explained by mechanistic reasons.

It is reasonable to suggest that the overheat is produced by autocatalytic decomposition of hydroperoxides. Evidence for this suggestion is provided by the unusual trend in HP concentration: The HP concentration fell down by virtually an order of magnitude (from 0.156 to 0.018 M) over a very narrow temperature range (Fig. 4a, Table 1).

Experimentally, the minimum HP concentration corresponds to the initiation of enhanced condensation of volatile oxidation products on “colder” reaction walls. It is noteworthy that from this point on the HP concentration is very fast restored. The overheat zone is characterized by fast oxidation of the starting hydrocarbon, the fraction of carboxylic acids in the oxidate increases and that of HD sharply decreases (Fig. 4b, Table 1).

Thus, the overheat is associated with deep thermooxidative destruction of HD. A probable reason for such a high exothermicity lies in aggregation of polar ROOH molecules, and, therewitn, the decomposition of one peroxy group give rise to induced decomposition of the whole aggregate (nanoreactor).

Table 1. Composition dynamics on hexadecane oxidation in the “boil up” mode

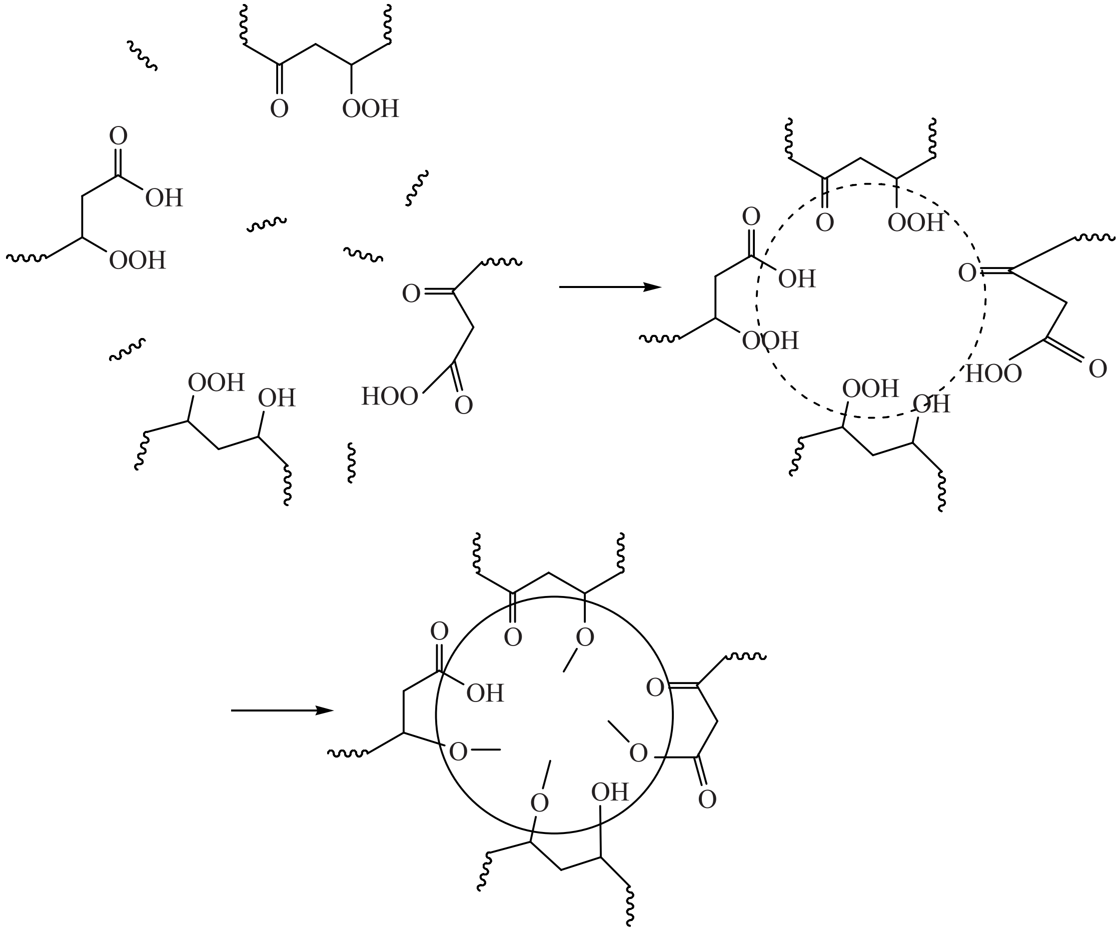
Oxidation time, min	Hydroperoxide, M	Carboxylic acids, M
26	0.156±0.002	0.117±0.005
29	0.018±0.002	0.181±0.005
31	0.168±0.002	0.213±0.005

A more probable suggestion is that the formation of polyhydroperoxide aggregates (poly-HP) is the basic characteristic of high-temperature hydrocarbon oxidation. Obviously, poly-HP are generally similar to mono-HP associates in that they feature a high local concentration of HOO groups. Moreover, the high hydrophilicity of poly-HP and polyfunctional derivatives favor their association. Such intra- and/or intermolecular associates can be considered as nanosized reactors with a high concentration of thermally extremely labile hydroperoxy groups. Their induced decomposition is quite an exothermic process that causes an increase in the local concentration of free radicals of all types and formation of C–C, C–O–C, and other bonds, both inside the molecule to form a ring and between neighboring molecules.

As a result, a great number of various oxygen-containing functional groups form, which has repeatedly been shown experimentally [11, 12], even though the mechanism of their formation still remains unknown [20–22]. In terms of colloid chemistry, such highly functionalized associates are similar to “cross-linked” reversed micelles [23] which are probably stabilized in the hydrocarbon by layers of less polar monofunctional derivatives that function here as co-surfactants (Scheme 1).

As a result, high-temperature liquid-phase hydrocarbon oxidation at the initial stages occurs as a microheterogeneous process controlled by diffusion [17].

Scheme 1.



Evidence for the Formation of Heterophase Nanostructures on Hydrocarbon Oxidation

Evidence for the presence of a microheterophase was obtained by means of a technique of colloid chemistry—dye solubilization. This technique is widely used in colloid chemistry, for example, for testing the ability of washing additives possessing surfactant properties to solubilize products insoluble in hydrocarbons [24–26]. Methyl Orange, like other water-soluble dyes, is widely used to indicate solubilization with reversed micelles in nonpolar hydrocarbon media in the presence of a series of surfactants [27–29]. In this case, the concentration of methyl orange is readily determined by UV spectroscopy.

Figure 5 shows the dynamics of the concentration of methyl orange solubilized with samples of hexadecane oxidized at 170°C. At the first minutes of the oxidation reaction the dye virtually does not dissolve. Beginning with 15th min, the dye concentration in the oxidized product increases step-wise and stabilizes at the oxidation time 20–30 min. Consequently, the concentration of products capable of forming micelles increases with oxidation progress.

In colloid chemistry micelle formation is frequently proved by determining the critical micelle concentration (CMC) via correlation of a certain physicochemical parameter of a mixture (or a solution) with the concentration of a compound in focus [24]. Hydrocarbon oxidation gives various oxygen-containing products (hydroperoxides, alcohols, carboxylic acids, polyfunctional compounds, etc.), and their relative fractions changes with time. In this connection it seems reasonable to suggest that the degree of hexadecane oxidation can sufficiently objectively be estimated by such an integral parameter as the refractive index of the oxidate n_D^{20} which reflects changes that have accumulated in the system and relates, to a certain extent, to the total quantity of oxidation products.

Figure 6 presents the dependence of the log concentration of solubilized dye on refractive index for a

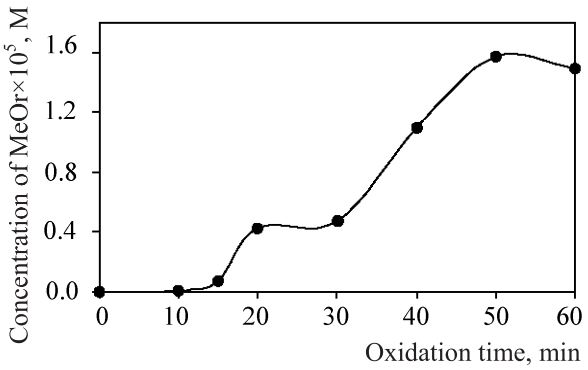


Fig. 5. Dynamics in the concentration of solubilized Methyl Orange on hexadecane oxidation.

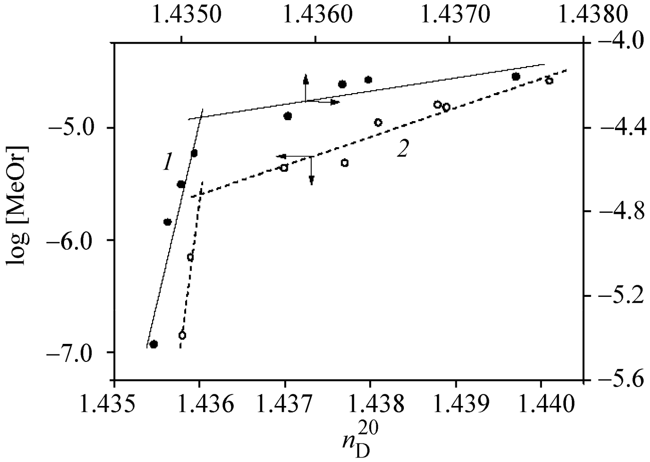


Fig. 6. Dependence of the log concentration of solubilized dye on refractive index: (*1*) hexadecane solution of AOT (0.001–0.2 M) and (*2*) oxidized hexadecane.

solution of a typical surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), in the starting (curve *1*) and oxidized hexadecane (curve *2*). The concentration of AOT was varied in the range 0.01–0.2 M.

In both cases the n_D^{20}–log [MeOr] dependences can, to a first approximation, be fitted by two straight lines which intersect in a point corresponding to the concentration 0.05 M. This value is nicely consistent with the reported CMC value for hydrocarbon solutions of AOT [30, 31]. As follows from the resulting data, the ability to solubilize Methyl Orange and form reversed micelles is strongly dependent on the degree of HD oxidation.

It was found that a sample of oxidized HD, modeled by mixing corresponding quantities of carboxylic acids (short- or long-chain), as well as alcohols and diols, slightly solubilized Methyl Orange. Consequently, the required solubilization effect is provided not only by the complex composition of the reaction products. Probably, a necessary factor here is the presence of self-organized structures like reversed micelles formed by deep hydrocarbon oxidation products. It should be noted that similar results were obtained using for the water-soluble reagent of a cationic dye R6G, as well as iodine.

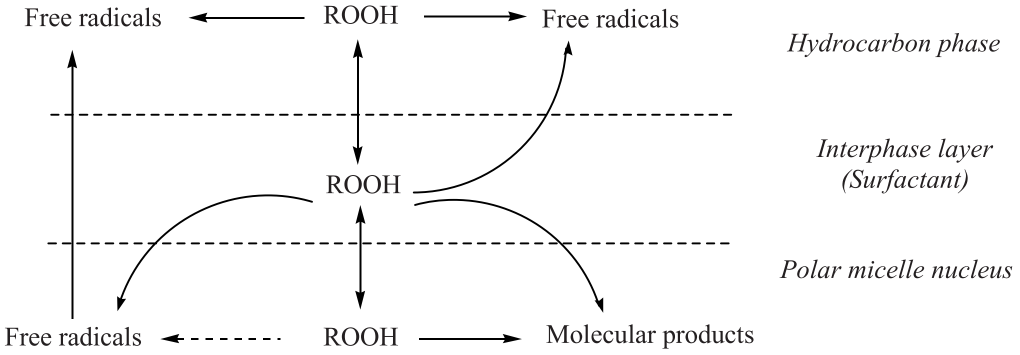
Effect of Micellar Structures on the Mechanism of Hydrocarbon Oxidation

The action of various additives to liquid hydrocarbons is traditionally considered in terms of the effect of their functional groups on various chemical processes, primarily on oxidative destruction [32, 33]. Actually, the reactivity of functional groups in antioxidants in free-radical reactions is of primary importance in choosing the antioxidant. The requirements to antioxidants include, along with a high reactivity, low volatility, solubility in nonpolar hydrocarbons, and other properties not directly related to reactivity. Therefore, antioxidants contain, along with functional groups, alkyl substituents which act to improve the solubility in hydrocarbons and to reduce volatility at high temperatures. Empirical choice of alkyl substituents most frequently leads to those containing 8–18 carbon atoms; the frequently used alkylating agents are commercially available fractions of ethylene oligomers containing up to 40 carbon atoms [33]. Due to the presence of nonpolar alkyl fragments in compounds with polar functional groups, most oil additives are, to a greater or lesser extent, oil-soluble surfactants.

The problem of the antioxidant activity of oil-soluble surfactants containing no active groups has been considered in one of the first work in this field [34] on an example of neutral calcium alkyl salicylates. A series of works on the effect of various surfactants on the rate and mechanism of accumulation and consumption of hydroperoxides in model oxidation reaction should be mentioned [35–39].

At present lubricating materials are considered as complex colloid systems [33, 40]. This relates not only to the structure of principal oil hydrocarbons, but also to solutions of additives in nonpolar hydrocarbons [41, 42]. The concepts of a complex colloid structure of

Scheme 2.



nanosized compositions were developed using the example of superbasic washing additives including reversed micelles of alkaline-earth metal sulfonates [43–46].

Liquid lubricating materials can be presented as two-phase microheterogeneous systems comprising a hydrocarbon nonpolar phase for which, in particular, all classical concepts of the mechanism of hydrocarbon oxidation are valid, and a micellar microphase (or nanophase) with fairly high polarity and high concentration of polar functional groups. The surfactant resides between these two phases and ensures stability of the whole system and component transfer from one phase to the other (Scheme 2).

In the hydrocarbon phase, hydroperoxides decompose predominantly by a radical mechanism, provided inhibitors capable of decomposing HP into molecular products are lacking.

It is known that reversed micelles are formed due to mutual attraction of polar groups in a nonpolar phase. Obviously, the appearance of a polar –OOH group in a hydrocarbon results in that HP localizes mostly in a more polar environment, i.e. in the interphase layer or in the polar nucleus of a reversed micelle.

The localization of HP in the interphase layer forces hydroperoxide molecules to pass into the structured and much more viscous surfactant layer. As a result, the readily polarizable hydroperoxide fragments turn out to reside in a much more polar environment, which may affect their lifetime and further decomposition mechanism. Therewith, the decomposition products can further diffuse either into micelle nuclei or into the hydrocarbon phase. Probably, free radicals will prefer to diffuse to hydrocarbon.

If HP will diffuse to the polar nucleus of a reversed micelle, the polarizable HOO group will reside in a strongly polar environment (the polarity of nuclei in reversed microemulsions is close to that of water). Various surfactant nuclei can much vary in composition and in chemical nature. It is quite probable that in the case in hand HP will primarily decompose by an ionic or a molecular mechanism and form the same products as the chain termination reaction in the recombination of peroxide radicals, specifically carbonyl compounds, unsaturated alcohols, ethers, and molecular oxygen.

The effect of reversed micelles in hydrocarbons on the rate and mechanism of HP decomposition was demonstrated in experiments on the accumulation and consumption of HP in hexadecane in the presence of a micelle-forming surfactant AOT [47]. The resulting data are shown in Table 2.

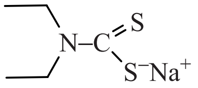
As seen from these data, the AOT concentration has a strong impact on the accumulation rate, maximum position, and absolute HP concentration. Constructing semilogarithmic anamorphoses for the initial HP accumulation regions allowed calculation of the coefficient A in the equation $\log [\mathrm{ROOH}] = A\tau + B$, which relates to the rate of HP accumulation. The dependence of A on AOT concentration passes through a maximum which corresponds to the AOT concentration close to the CMC of the given surfactant in hydrocarbons.

The effect of surfactants on hydrocarbon oxidation is much dependent on the length of their hydrocarbon substituents. Figure 7 shows the results of hexadecane oxidation in the presence of AOT, as well as various dialkyl dithiocarbamic acid (DTC) derivatives.

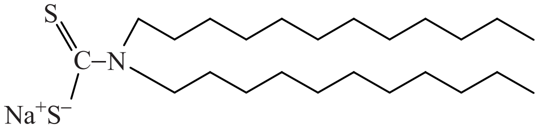
It should be noted that sodium diethyl dithiocarbamate (DTCNa-C_2) is a polar compound insoluble

Table 2. Kinetics of hydroperoxide accumulation on hexadecane oxidation at 170°C in the presence of AOT

Oxidation time, min	Concentration of ROOH at the concentration of AOT, M					
	0	0.01	0.03	0.06	0.13	0.20
0	0.002	0.001	0.002	0.003	0.002	0.005
10	0.008	0.005	0.007	0.006	0.006	0.013
15	0.022	0.012	0.029	0.033	0.024	0.044
20	0.047	0.029	0.059	0.117	0.055	0.137
30	0.22	0.170	0.043	0.056	0.06	0.071
40	0.199	0.124	0.109	0.085	0.044	0.075



DTCNa-C_2



DTCNa-C_{12}

in hydrocarbons. It can be introduced in HD only due to solubilization in an AOT micelle. This composition of additives exhibits a well-defined inhibiting effect, and the inductive period of HP formation increases from ~10 min (HD + AOT) to ~30 min. By contrast, addition of sodium didodecyl dithiocarbamate to the HD + AOT composition shortens the inductive period, even though the maximum concentration of HP decreases.

This result is most probably explained by the ability of metal carbamates to form reversed micelles in hydrocarbons [48]. Therewith, dithiocarbamate micelles have a more viscous and less permeable shell, at least for HP and peroxyl radicals.

A mixture of C_2 and C_{12} carbamates in the presence of AOT has no effect on the length of the inductive period of HP formation but much decreases the HP accumulation maximum. Thus, the antioxidant properties of reversed micellar aggregates are controlled not only by the nature, but also by the length of the hydrocarbon substituents in surfactants and/or antioxidants.

Liquid-phase oxidation is strongly associated with the appearance of a micellar nanophase. Chemically active oxygen-containing intermediates of the process almost all are polar or readily polarizable compounds, and their solubilization with the polar nucleus of a reversed micelle is a favorable process. Therewith, the reversed micelle plays the role of a kind of cage capable of retarding the free-radical oxidation process (Scheme 3).

If a system contains synthetic surfactants of various chemical nature, the properties of the whole system are determined by reaction at the phase interface, namely, the lipophilic–hydrophilic characteristics of antioxidant molecules.

Thus, considering the mechanism of high-temperature hydrocarbon oxidation in terms of the concept of nanosized structures allows purposeful creation of new and effective oxidation inhibitors for lubricating materials. Such systems should comprise

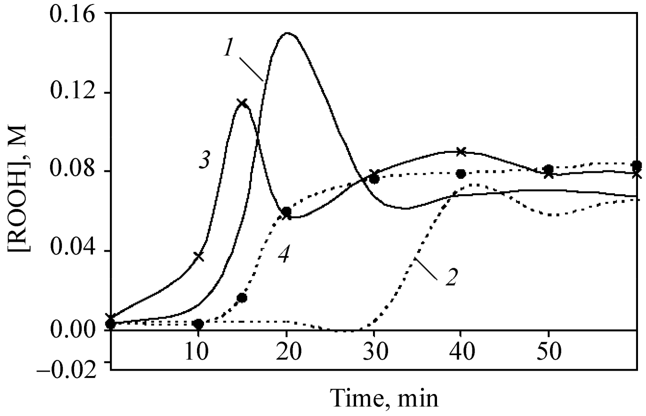
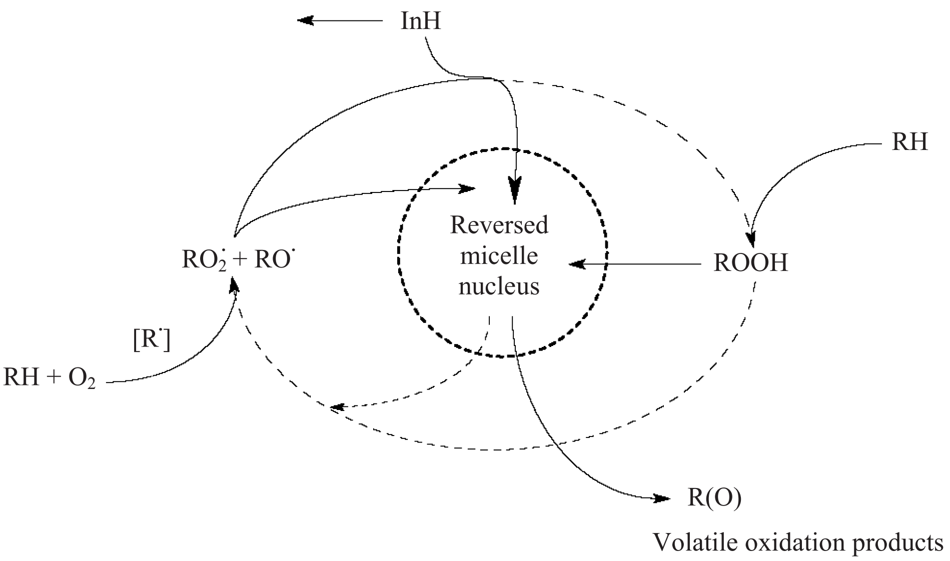


Fig. 7. Kinetics of hydroperoxide formation on hexadecane oxidation in the presence of a combination of AOT and sodium dialkyl dithiocarbamates: (*1*) AOT; (*2*) AOT + DTCNa-C_2; (*3*) AOT + DTCNa-C_{12}; and (*4*) AOT + DTCNa-C_2 + DTCNa-C_{16}. Temperature 170°C.

Scheme 3.



both traditional antioxidants that act in the hydrocarbon phase and micellar inhibiting systems that work in the polar nucleus of reversed micelles.

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