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Dedicated to the memory of the Russian Academician N. M. Emanuel

Phenomenology of Oxidation of a Cumene Feed Containing Hydroperoxide: I. Two Paths of Cumene Hydroperoxide Formation Reaction[1]

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Abstract—This article presents direct evidence of the occurrence of cumene oxidation resulting from the presence of gaseous oxygen (O_2^{gas}) at the gas–liquid interface, demonstrating a markedly higher magnitude of process selectivity, as compared to oxidation that is promoted by dissolved oxygen (O_2^{liquid}). The significant contribution of O_2^{gas} to the formation of cumene hydroperoxide under bubble-type process conditions is also discussed, emphasizing that the hydroperoxide formation rate is composed of two components: $W_{total} = W_1^{gas} + W_1^{liquid}$, where the first component, W_1^{gas}, is a function of k_1^{gas}, $[O_2^{gas}]$, and of the liquid–gas interface area, while the second component, W_1^{liquid}, is subject to equation: $W = k[R^\bullet][O_2^{liquid}]$.

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The classical notions of the core mechanism of oxidation reactions are based on the Bakh–Engler's peroxide theory [1, 2], and on the theory of radical-chain character of the oxidation process, that has been proposed and proven by the Russian academician N.N. Semenov [3]. These theories were later further developed to a great extent, and for a wide spectrum of hydrocarbons, by N.M. Emanuel and his co-researchers [4–8], as well as by many other scientists throughout the world [9–12]. Of course, it should be noted that the abovementioned references [1–12] by no means exhaustively represent the entirety of the vast number of various research work, and publications on the subject, that have been performed and issued to date.

The theory of hydrocarbon oxidation carried out by means of air bubbling (i.e., the so-called "bubbling-type oxidation"), is inherently connected with the previously held assumption that the oxidation reaction is completely promoted by oxygen (O_2^{liquid}) dissolved in the liquid phase (represented by the oxidized products), while gaseous oxygen (O_2^{gas}) at the liquid-gas interface does not affect oxidation at all. This assumption is based on prior studies of hydrocarbon oxidation reactions and related calculations, which ostensibly demonstrated that oxidation through O_2^{gas} at the liquid-gas interface could possibly occur "only if the [air bubble] surface area is 1 000 to 10 000 m^2 per 1 cm^3 of the liquid phase. This specific area can only be attained under the condition that the gas bubbles and the liquid film reach 1 to 10 millimicrons, which actually never takes place during liquid-phase oxidation." [6] (Note: All of the quoted text in this article has been translated from Russian). Thus, the supporters of the abovementioned assumption contemplate oxidation as a purely homogeneous process [4–6], in which the necessity of mixing of the phases is dictated by the requirement of quick delivery of oxygen into the liquid phase, "because otherwise oxygen diffusion deep into the liquid would not be sufficient for oxygen expenditure into the reaction." [6].

The same assumptions, within the context of the aforementioned oxidation theory, have led to the formula-

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[1] The text was submitted by the author in English.

tion of the requirement that the process occur in a kinetic regime, in which the rate of oxygen transfer from the gas phase into the liquid phase is significantly higher than the rate of expenditure of dissolved oxygen in oxidation reactions. Observance of the kinetic regime would allow stabilization of the limiting (in terms of solubility) O_2^{liquid} concentration in the liquid phase, that would ensure a constant rate of the reaction promoted by O_2^{liquid} molecules [4–6]. In the opposite case of the process occurring in a diffusion regime, the lack of understanding thereof has resulted in incorrect estimations of reaction rate and of a decrease in process selectivity. Furthermore, with an increase in pressure, and with a proportional growth in O_2^{liquid} concentration as a linear function of pressure, the deviation from linear dependence of the reaction rate (W) on O_2^{liquid} concentration is explained, within the framework of the kinetic regime, by a shift in rate-limiting stage from reaction (1) (see below), in which $W \approx [O_2] \approx P_{O_2}$, to reaction (2) [4–6], in which the W value is independent of P_{O_2}, where W is reaction rate and P_{O_2} stands for partial pressure of oxygen:

$$R^{\bullet} + O_2^{liquid} \rightarrow RO_2^{\bullet}, \quad (1)$$

$$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}. \quad (2)$$

The above-described assumption has been folowed, as an undeniable postulate, over the course of more than 40 years by many researchers, including those working in fields dealing with cumene oxidation. However, to the best knowledge of the author of this article, for the vast majority of hydrocarbons, including cumene, no direct tests that indisputably prove the occurrence of oxidation solely due to dissolved oxygen have ever been conducted. Likewise, there has been no solid evidence obtained in the course of direct tests, to confirm or deny the fact that oxidation occurs due to presence and action of O_2^{gas} at the liquid-gas interface.

The study reported below, has been conducted with the goal of obtaining direct experimental evidence that confirms or denies that cumene oxidation takes place at the liquid-gas interface with the participation of O_2^{gas} molecules (as is discussed in this Article I). Another objective was investigating, through direct testing, into the true causes of limiting concentrations of cumene hydroperoxide (CHP), seeking an approach for overcoming this "barrier," and revealing the root causes of a decrease in the magnitude of process selectivity with a growth in the degree of cumene conversion (see details in the following Article II, published in the Russian Journal of General Chemistry, 2011, vol. 81, no. 5, p. 865).

During the abovementioned recent experiments, cumene oxidation, specially promoted by O_2^{gas}, was carried out without air bubbling through an oxidized product, with O_2^{liquid} concentration in the liquid phase being kept at its minimum possible level. Oxidizer reactors of two types were used: (a) Atmospheric oxygen only entered into the reactor from the environment, i.e., without supplying forced air into the liquid phase. Thus, the oxidation process (conventionally called "unforced" or "static") occurred through contact between an oxidation feed, which had been placed in the reactor, and air solely at the liquid-gas interface. In other words, the oxidation reaction was carried out under the conditions of natural diffusion of atmospheric oxygen coming into contact with the oxidized products; (b) A hard surface of a predetermined area was set in a reactor, onto which an oxidation reaction mixture was continuously delivered, thereby generating a thin liquid film on the hard surface. An air stream was continuously passed along this liquid film. All oxidate was collected in a separately located vessel, so that the oxidate from the vessel was pumped back to the reactor top to reflux the hard surface with the liquid phase, thus creating and maintaining thereon a consistent film of oxidized products. This type of oxidation process may conventionally be referred to as "forced" or "dynamic", due to forced (though without intermixing) contact between the countermoving flows of the gaseous phase (air) and the liquid phase (oxidized products) at the liquid-gas interface.

The oxidation promoted by O_2^{gas} was carried out within a temperature range of 23 to 65°C. The oxidizer feed temperature was maintained at a constant level by means of thermostatic temperature control over the continuous oxidate draw-off from the reactor to the collector vessel. For the purpose of comparison with the experimental results obtained for oxidation process types (a) and (b) above, a cumene oxidation test was performed in the traditional (bubbling-type) mode, using a hollow bubble type reactor with air being injected through a liquid phase formed by the oxidized products. The experiments were mostly conducted under atmospheric pressure. To avoid an induction period, about 5 wt % to about 35 wt % of hydroperoxide was introduced into the 99.92 wt % pure cumene feed prior to the test, where the introduced hydroperoxide was 99.4 wt % pure, with minimum possible contents of typical by-products of oxidation, such as dimethylbenzyl alcohol, acetophenone, dicumyl peroxide, organic acids, and phenol. The oxidate was sampled at certain time intervals, and was tested in accordance with standard analytical methods, specifically: the chemical method for analyzing hydroperoxide; GC for dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide; the chemical method for organic acids; and the chemical method for phenol.

1. Static (diffusion) oxidation promoted by O_2^{gas}. *A. Fixed interface area.* References [13, 14] describe the research efforts that provided, for the first time, firm evidence of the fact that the cumene oxidation reaction conducted with air bubbling through the liquid phase does not only follow a single reaction path promoted by dissolved oxygen (O_2^{liquid}), but rather proceeds by two independent paths – cumene oxidation by an oxygen molecule at the gas-liquid interface (O_2^{gas}), as well as by an oxygen molecule in the liquid phase (O_2^{liquid}), and that the contribution of the reaction through O_2^{gas} to hydroperoxide formation cannot be neglected. This discovery, to a great extent, shattered the previous notion of the single-path reaction mechanism, which had seemed inviolable for many years. Therefore, obtaining direct and undisputable evidence of the reaction occurrence by both paths, and especially through participation of oxygen at the gas-liquid interface, became an urgent goal.

Verification of the participation of O_2^{gas} molecules in cumene oxidation at the gas-liquid interface was performed, in a direct experiment, in the “static oxidation” regime, involving natural (not restricted by any means) diffusion, without any intermixing of the gas phase and the liquid phase, and without air bubbling through the liquid phase. During the test, contact between air and the oxidized products at their interface was arranged, and a constant oxygen concentration in the air above the phase interface was maintained. The test results are graphically illustrated in Fig. 1. The test was conducted under atmospheric pressure, in order to minimize the O_2^{liquid} content, so that the resultant validation (or invalidation) of the oxidation reaction occurrence at the liquid-gas interface under influence of gaseous oxygen (O_2^{gas}) molecules would not be distorted in any manner. The test was performed under low temperatures (e.g., as low as 23°C). This choice was primarily intended to minimize the formation of process inhibitors, such as aldehydes, phenol, etc., which to a great extent slow down the reaction rate, and thereby distort the overall pattern of the oxidation process, in particular with regard to the desired hydroperoxide product. Conducting the process at a low temperature also allows determination of the limit of process selectivity when cumene oxidation proceeds at the liquid-gas interface and is promoted by O_2^{gas} molecules, within the studied range of the degree of cumene conversion and, especially, at high hydroperoxide concentrations. The third reason behind the selected process conditions was that they allowed discovering whether the energy barrier of the oxidation process promoted by O_2^{gas} at the liquid-gas interface is overcome (i.e., whether radicals $R^\bullet$ and $ROO^\bullet$ that ensue formation of hydroperoxide and by-products are formed), at such a low temperature. Finally, this temperature choice was relevant for revealing the effect of cumene oxidation promoted by O_2^{gas} under low temperature conditions, both on hydroperoxide formation rate and on process selectivity, over an extended period of time (two years).

The data presented in Fig. 1, demonstrates that hydroperoxide formation rate was constant over the period of two years, and that a hydroperoxide concentration of 36.3 wt % was ultimately achieved, without any tendencies for either reaction rate or process selectivity to decrease. Moreover, the magnitude of selectivity remained anomalously high and substantially invariable, reaching more than 99 mol %, over the

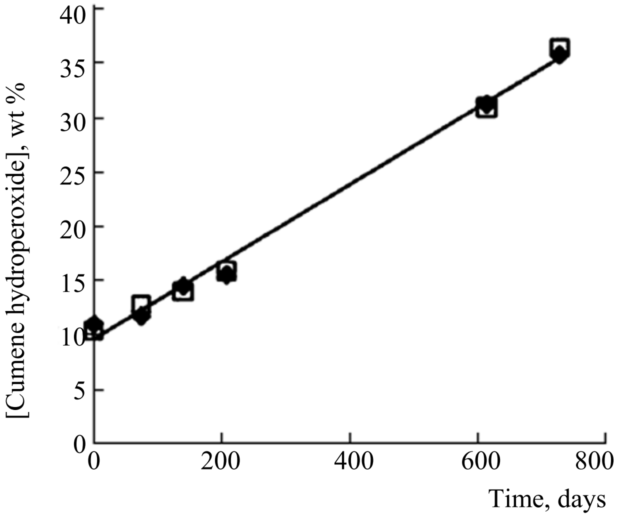

Fig. 1. Cumene hydroperoxide concentration as a function of time: $T = 23°C$, $P = 0.1$ MPa, $[CHP]_0 = 10$ wt %, interface area is 12 cm^2; (□) and (♦) refer to two independent test runs.

entire length of the test performance (Table 1), as opposed to the results that would have been obtained for cumene oxidation conducted in the bubbling mode.

The obtained results provided clear evidence that, under the conditions imposed in the test, oxygen diffusing from the gas phase into the liquid phase does not limit the hydroperoxide formation rate: $W_{HP} = f(\text{time})$. It was found that the lack of liquid phase mixing does not prevent oxygen from diffusion deep into the liquid and, therefore, from being sufficient for enabling oxygen expenditure into the reaction, even presuming that hydroperoxide is formed solely due to oxygen dissolved in the liquid phase. Moreover, despite a very low concentration of dissolved oxygen (about 0.04 wt % under pressure of 0.1 MPa [15, 16]), the amount of oxygen contained in the reaction mixture was sufficient for hydroperoxide formation. In fact, the oxygen concentration in the liquid phase ($[O_2^{liquid}]$) remained constant over the entire course of the test run, in spite of its expenditure into hydroperoxide – even theoretically presuming that the O_2^{gas} dissolution rate is very low (at least markedly slower than the rate of its expenditure into hydroperoxide formation), the principal fact is the presence of about 106×10^{-5} moles of O_2^{liquid} in liquid phase, as compared to about 1.5×10^{-5} moles (which is equivalent to only about 1.5% relative to the former value) of oxygen expended into formation of hydroperoxide. This predetermines that the constancy of the concentration of dissolved oxygen during the test run may be formulated as: $[O_2^{liquid}]_i = [O_2^{liquid}]_0 = \text{const}$.

Taking into account the reported values of the total amounts of cumene expended into formation of dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide (about 0.08 wt %, about 0.006 wt %, and about 0.017 wt %, respectively), of the increase in hydroperoxide content (about 26 wt %), and of the amount of oxygen dissolved in the liquid phase (about 0.05 wt % under pressure of 0.1 MPa [15, 16], which is very small), it may be concluded that, under temperature of 23°C, the portion of hydroperoxide formed with participation of dissolved oxygen (about 2 relative percent) is negligible, as compared to 98% formed in the reaction of cumene with O_2^{gas}. This proves that the abovementioned 26 wt % increase in hydroperoxide content, as was observed from the beginning to the end of the experiment, was substantially provided by the O_2^{gas}-aided reaction at the liquid–gas interface, rather than by participation of O_2^{liquid} molecules in the liquid phase. The obtained results also serve as conclusive evidence that, irrespective of the particular path of hydroperoxide formation (i.e., through participation of O_2^{liquid} or of O_2^{gas}), oxygen expenditure into chemical reactions does not change the value of $[O_2^{liquid}]_i$ in the oxidized products: $[O_2^{liquid}]_i = [O_2^{liquid}]_0 = \text{const}$. Moreover, irrespective of the particular method of oxygen delivery, namely contact with O_2^{gas} (superficial static oxidation through the liquid-gas interface) or air bubbling through the reaction mixture [17], the formation of radicals $R^{\bullet}$ and $ROO^{\bullet}$, which give rise to hydroperoxide, takes place even at the very low temperature (23°C) under which the test was conducted. When the diffusion method of air delivery was used, the equation $W = k_1[R^{\bullet}][O_2^{liquid}]$ (see the description below) remained linear (see the discussion of Figs. 2 and 3, below), even at a high hydroperoxide concentration ($[CHP]_{final} = 36.3$ wt %), as opposed to the cases of introduction of inhibitors and of bubbling-type cumene oxidation (see the discussion of Fig. 9 in Section 3, Bubbling-type vs. Static Oxidation of Cumene, below). Finally, it should be noted that the magnitude of oxidation selectivity, under the conditions of diffusion regime of oxygen delivery, is anomalously high, ranging from about 99.5 to 99.7 mol %.

Table 1. Effect of cumene hydroperoxide concentration on selectivity of oxidation promoted by O_2^{gas}: $T = 23$°C, $P = 0.1$ MPa

Test Run #	$[CHP]_0$, wt %	$[CHP]_{final}$, wt %	$[Phenol]_{final}\times10^4$, wt %	Cumene conversion[a] deg , %	Process selectivity,[a] mol %
1	0.23	0.38	Zero	0.13	99.93
2	4.90	19.53	2	11.62	99.43
3[b]	10.00	36.30	2	20.51	99.55
4	35.20	44.35	8	7.32	98.70
5[c]	35.20	37.68	2616	2.02	97.10

[a] Based on the total of hydroperoxide and by-products formed. [b] Data relevant to Fig. 1. [c] With addition of 0.1 wt% HCOOH.

Verifications of the effect of hydroperoxide content on the rate of O_2^{gas}-aided cumene oxidation, and of the impact of inhibitor (newly formed phenol) on reaction rate and process selectivity, under very mild conditions of “unforced” cumene oxidation at the liquid-gas interface, are summarized in Figs. 2, 3 and in Table 1.

Analysis of the obtained results (test runs *2*, *3*, and *4* in Table 1) confirmed that oxidation in the diffusion regime of O_2^{gas} delivery takes place within the full range of hydroperoxide concentrations, specifically from about 5 wt % to about 45 wt %, and, moreover, that the oxidation process does not cease, with no limiting point of hydroperoxide concentration being observed, as opposed to the case of bubbling-type oxidation, in which the achievement of an upper hydroperoxide concentration limit (at about 40 wt %) is followed by a consistent declining trend, despite continuing air injection into the reactor [4, 14, 17]. The following patterns were further observed in the case of O_2^{gas}-aided oxidation at the liquid-gas interface: (a) hydroperoxide formation rate is described by a linear function within a hydroperoxide concentration range of 5–45 wt % (see Fig. 2); (b) The magnitude of oxidation selectivity is exceptionally great (more than 99 mol %), and remains as high as about 98.7 mol % even at about 45 wt % of hydroperoxide (run *4* in Table 1); (c) The contribution of chain termination and cross-coupling termination reactions, leading to formation of radicals $RO^•$ and, correspondingly, of by-products ROH, is negligible; (d) The initiation of chains of radicals proceeds at a constant rate: $W_i = \text{const}$ (see Fig. 2); and (e) Despite the very low temperature of 23°C, about $(2–8)\times10^{-4}$ wt % of a phenol inhibitor is still formed (see Table 1).

Introduction of formic acid into the oxidized products (line *2* in Fig. 2) revealed that, at the most initial step of the test run, where formation of by-products (dimethylbenzyl alcohol, acetophenone, and inhibitors) affecting the reaction rate was negligible, a substantial (about 6-fold) decrease in reaction rate was observed, although as little as about 0.1 wt % of HCOOH was added to the oxidized products.

Figure 3 graphically illustrates the effect of phenol concentration on the selectivity of oxidation occurring in the diffusion regime of O_2^{gas} delivery to the gas–liquid interface, based on the data obtained in the course of experiments that were conducted over an extended period of time (924 h) involving addition of $(19–933)\times10^{-4}$ wt % of phenol into the cumene feed. This data confirmed the above-noted conclusions with regard to the significant negative impact of this inhibittor on process selectivity and, in addition, revealed the quantitative characteristics of this impact.

The differences between reaction rates and magnitudes of selectivity in the compared experiments (see lines *2* and *3* in Fig. 2), in which inhibitor concentration was the only time-varying factor, conclusively prove that, even under exceptionally mild oxidation process conditions, the phenol inhibitor [4] is directly involved in the reaction with radicals $ROO^•$, leading to their recombination and transformation into radicals $RO^•$ (i.e., leading to formation of the by-products) (see details in Article II). In view of the substantial avoidance (or, at

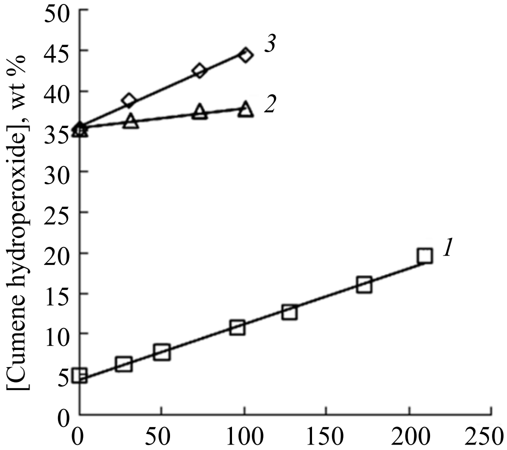

Fig. 2. Formation of cumene hydroperoxide at a varying CHP content in the cumene feed: $T = 23°C$, $P = 0.1$ MPa. $[CHP]_0$, wt %: (*1*) 10.2; (*2*) 35 + 0.1 wt % HCOOH; (*3*) 35.

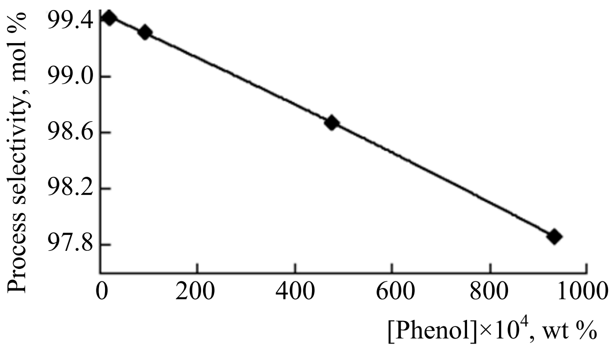

Fig. 3. Process selectivity as a function of phenol concentration in cumene oxidation promoted by O_2^{gas} in a static regime: $T = 25°C$, $P = 0.1$ MPa, $[CHP]_0 = 10$ wt %, test run length = 924 h.

least, minimization) of other common negative impacts on the oxidation process, under the process conditions imposed in the experiment, the noticeable decline in process selectivity upon addition of phenol (see Fig. 3), or of very small quantities of HCOOH, into the oxidized products can only be explained, for these specific cases, by the presence of reaction retarders (which are hereinafter referred to, purely for simplification purposes, as inhibitors and denoted as In or InH) and of actual inhibitors (which are hereinafter also denoted as In or InH) in the reaction medium. In fact, the observed difference in the magnitudes of selectivity (about 99 mol % in run *4* vs. about 97 mol % in run *5*, as can be seen from Table 1; or about 99.4 mol % vs. about 97.8 mol %, as indicated in Fig. 3), between the runs with low and high concentrations of phenol, can only be attributed to the essentially different amounts of radicals $R^•$ and $ROO^•$ formed in the course of oxidation reactions, as well as to different relationships between the concentrations of radicals and inhibitors $[R^•]/[InH]$ and $[ROO^•]/[In]$ in the cases of low and high concentrations of phenol. As a result, when any reaction retarder or inhibitor (such as HCOOH, aldehydes [14, 17], or phenol) is present in the reaction mixture, the above-noted cases feature small concentrations of radicals $R^•$ and $ROO^•$, while these concentrations slightly exceed the concentrations of In and InH. As long as this slight excess is maintained, cumene hydroperoxide formation in the reaction taking place in the diffusion regime of oxygen (O_2^{gas}) delivery to the liquid-gas interface, proceeds at a lower rate. Moreover, the formed radicals $R^•$ and $ROO^•$ are expended, for instance, in accordance with reaction (3):

$$R^• + InH \rightarrow RH + In^•. \qquad (3)$$

The resultant rate of hydroperoxide formation noticeably slows down (line *2* in Fig. 2), because the reactions $R^• + O_2^{gas} \rightarrow RO_2^•$ and $RO_2^• + RH \rightarrow RO_2H + R^•$ are substantially avoided, or, even though they may occur, $ROO^•$ is expended into formation of by-products in accordance with reactions (4) and (5):

$$ROO^• + In \rightarrow ROOIn^• \rightarrow RO^• + InO, \qquad (4)$$

$$RO^• + RH \rightarrow ROH + R^•. \qquad (5)$$

Under the abovementioned conditions, the values of $[R^•]/[InH]$ and $[ROO^•]/[In]$ relationships decrease due to the occurrence of reaction (3), while formation of by-products in the liquid phase continues at a progresssively accelerating rate due to the occurrence of reactions (4) and (5) as a result of the gradually increasing concentration of phenol. Therefore, the above-discussed factors lead to deterioration in process selectivity in the presence of HCOOH and phenol, despite the very mild process conditions of cumene oxidation.

In the case of a sufficiently high concentration of hydroperoxide, and correspondingly of $ROO^•$, in the cumene feed, and a small concentration of retarders/inhibitors (as described by the graph in Fig. 1, by lines *1* and *3* in Fig. 2, and by run *4* line in Table 1), the condition of $[R^•] \gg [InH]$ and $[ROO^•] \gg [In]$ is met. As a result, hydroperoxide is formed in appreciably larger quantities in reactions (1) and (2), while reactions (4) and (5), that lead to the formation of by-products, continue to proceed in the same manner as in the experiments described above (see Figs. 1 and 2 and Table 1).

The results of the test runs conducted in the diffusion regime of oxygen delivery, both with and without the addition of HCOOH and phenol, substantiate a conclusion that molecules of phenol and HCOOH act as inhibitors in the reaction between $R^•$ and oxygen present at the gas–liquid interface, thereby slowing down hydroperoxide formation rate, while at the same time these molecules promote an acceleration of transformation of $ROO^•$ into $RO^•$, the latter being a source of by-products formation and, thus, of a loss in selectivity value. Therefore, like in oxidation under influence of O_2^{liquid} [17], reducing the concentration of retarders/inhibitors in the liquid phase is a prerequisite for enhancing process selectivity and for accelerating the hydroperoxide formation reaction rate in the course of oxidation promoted by oxygen at the gas–liquid interface.

Comparison of test runs *1* through *4* (Table 1), at different initial concentrations of hydroperoxide and low concentrations of phenol formed in the reaction $[(2–8)\times10^{-4}$ wt %], with respect to the oxidized products, revealed that, despite the extremely mild oxidation conditions (including the low O_2^{liquid} concentration, the low process temperature, and the low concentration of retarders/inhibitors in the liquid phase), an increase in hydroperoxide concentration resulted in a certain decline in selectivity. Specifically, the selectivity value equaled 99.43 mol % at $[CHP]_{final} = 19.5$ wt %, and fell to 98.7 mol % at $[CHP]_{final} \approx 45$ wt %. This minor decline in selectivity value, however, extends beyond the margin of a methodological error in estimation of the contents of by-products, such as dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide. This decline, even corresponding to the very high final hydroperoxide concentration of about 45 wt %, was significantly lower than that in the presence of 0.1 wt % of HCOOH. The anomalously high magnitude of selectivity (98.7 mol %) at a final hydroperoxide concentration of about 45 wt % is clearly explained by an appreciably greater selectivity of cumene oxidation promoted by oxygen at the gas–liquid interface, as opposed to O_2^{liquid} [13, 14, 17], as well as by the mild oxidation conditions imposed in the experiments discussed, and in particular by the low retarder/inhibitor concentration in the reaction mixture. During the experiments, the relative contributions of each of the abovementioned factors to achievement of the anomalously high selectivity were not investigated. Nonetheless, the collected experimental data, as well as the information disclosed in references [13, 14, 17], lead to a conclusion that none of the selectivity-affecting factors (including process temperature, hydroperoxide formation rate in oxidation through oxygen at the gas–liquid interface vs. oxygen dissolved in the liquid phase, and the amount of retarders/inhibitors formed during the reactions) can be neglected in attempts to optimize the oxidation process design. However, for purely theoretical considerations, the following revelations, which are opposed to the previously existing notions [4, 6], are of greater importance: (a) Even under the mildest possible process conditions, decomposition of hydroperoxide present in the liquid phase occurs with formation of $ROO^\bullet$ radicals, and the chain propagation reactions lead to formation of $R^\bullet$ radicals, which in turn form hydroperoxide, when oxygen at the liquid–gas interface participates in the reaction; (b) Cumene oxidation promoted by oxygen present at the liquid–gas interface, proceeds with an anomalously high magnitude of selectivity; (c) The reactions of propagation and degenerate branching of the $ROO^\bullet$ radical chains in the liquid phase, lead to formation of $RO^\bullet$ radicals and, ultimately, to formation of by-products, though in limited quantities; and (d) In the course of O_2^{gas}-aided oxidation at the liquid–gas interface, an increase in hydroperoxide concentration does not lead to an acceleration of hydroperoxide formation (lines *1* and *3* in Fig. 2), as opposed to oxidation by O_2^{liquid}. This is yet another independent difference between oxidation promoted by O_2^{gas} and oxidation by O_2^{liquid}.

Of significant scientific interest are the established facts that a phenol molecule behaves in an essentially different manner with respect to the radicals formed in the course of oxidation reactions – specifically that a markedly higher phenol concentration is required for phenol to act as a prominent inhibitor of hydroperoxide formation in the reaction between $R^\bullet$ and oxygen at the liquid–gas interface, while its inhibiting impact in the reaction between O_2^{liquid} and $R^\bullet$ in the liquid phase manifests itself to a much greater extent (indeed, as is discussed in Article II, even a relatively low content of phenol leads to a noticeable slowdown of hydroperoxide formation). Moreover, phenol plays a considerable role in transformation of $ROO^\bullet$ into $RO^\bullet$, which is a source of by-products formation and, therefore, results in a decline in process selectivity.

The newly established, and previously unknown, facts of the limited extent of inhibition of the oxidation reaction occurring at the gas–liquid interface with participation of O_2^{gas}, and of the inhibitor-affected decline in process selectivity under conditions of the low temperature range, deserve further detailed research to be undertaken to reach a better understanding of the root causes of the significant distinctions between the oxidation processes promoted by oxygen present at the gas–liquid interface and by O_2^{liquid}.

B. Variable interface area. The dominance of O_2^{gas} at the liquid–gas interface in the overall hydroperoxide formation was demonstrated through a series of experiments that were performed at a varying interface surface area (Fig. 4), under process conditions similar to those described above ($T = 23°C$, $P = 0.1$ MPa, no air bubbling through the liquid phase). In addition, these experiments were characterized by consistently constant values of the rate of initiation ($W_i = \text{const}$) and the length of chain ($\nu = \text{const}$), as well as by proven constancy of peroxide radicals concentration ($[ROO^\bullet] = \text{const}$), which implies that constant relation-

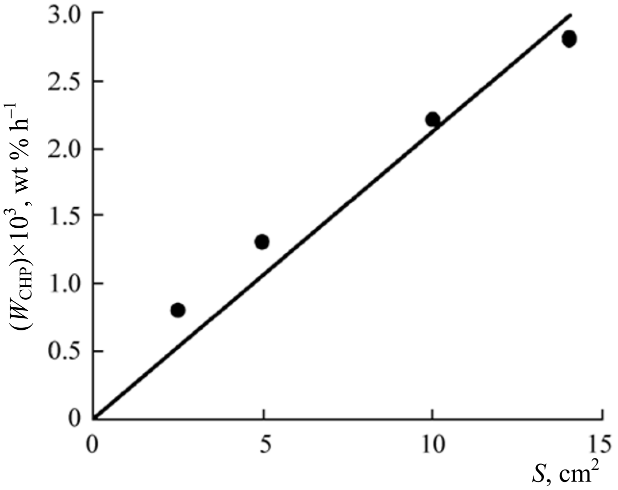

Fig. 4. CHP formation rate as a function of liquid–gas interface area: $T = 23°C$, $P = 0.1$ MPa.

ships between the rate constants of the reactions of termination and propagation of radical chains (k_2, $k_6^{1/2}$, $k_i^{1/2}$, in accordance with the common definitions adopted in [4, 6]) are sustained.

The graph in Fig. 4 clearly demonstrates that hydroperoxide formation rate varies as a linear function of the O_2^{gas}-liquid contact area. If the reaction occurred with the participation of O_2^{liquid} only, as it was assumed by the authors of [4, 6], the amount of newly-formed hydroperoxide would remain constant despite the variations in liquid–gas interface area, for the following reasons: (a) The rate of oxidation reaction promoted by O_2^{liquid} is determined by the concentration of dissolved oxygen in the liquid phase; (b) O_2^{liquid} concentration in the liquid phase was constant during the test runs, because: (i) The portion of oxygen expended into hydroperoxide formation equals no more than about 1–2% relative to the overall quantity of O_2^{liquid} in the reaction mixture, even if hydroperoxide were solely formed under influence of O_2^{liquid}. This portion is negligible, considering the extreme slowness of the hydroperoxide formation reaction under the conditions imposed in the test; and (ii) The $(O_2^{liquid})_i$ to $(O_2^{liquid})_{HP}$ mole ratio equals 102, which is an atypically high value for an oxidation process promoted solely by O_2^{liquid}; (c) The rate of oxygen expenditure into hydroperoxide formation is negligible and does not limit the formation of hydroperoxide, judging from the linearity of $W_{CHP} = f(t)$ (This suggestion is also supported by the reasoning set forth in item (b) above, as well as by the fact that the rate of oxygen dissolution in the reaction mixture is not crucial for determination of hydroperoxide formation rate under these particular operating conditions; and (d) The reaction mechanism and its limiting stage – including the relationships between the rate constants of the reactions of termination and propagation of radical chains (k_2, $k_6^{1/2}$, $k_i^{1/2}$), the reactions of cross-coupling termination of the chain ($R^\bullet + RO_2^\bullet$, ending in formation of $RO^\bullet$ and ROH), and the reactions of induced decomposition of hydroperoxide ($R^\bullet$ + ROOH, ending in formation of 2 $RO^\bullet$), as well as the value of W_i – remained strictly constant during the test run, due to the complete similarity of the conditions imposed in the comparative tests, and, in particular, of process temperature, air flow rate, oxygen dissolution rate, composition of reaction mixture, process pressure, concentration of dissolved oxygen, content of inhibitors, and degree of cumene conversion.

However, the data presented in Fig. 4 reveals a totally different pattern of hydroperoxide formation, which accelerates corresponding to growth in the interface area, despite the fulfillment of all of the conditions (a) through (d) listed above. This conclusively proves that the rise of hydroperoxide formation rate was ensured by the reaction involving O_2^{gas}, and not O_2^{liquid}, especially in view of the very small concentration of O_2^{liquid} in the liquid phase under pressure of 0.1 MPa. The experimentally established fact of the acceleration of hydroperoxide formation rate with a growth in interface area, can hardly be interpreted in any other manner, because the liquid–gas interface area was the only variable in the experiments discussed, with all other parameters kept unchanged.

Therefore, direct experimental evidence of the occurrence of cumene oxidation under the influence of O_2^{gas} at the liquid–gas interface, has been provided. In particular, it has been demonstrated that oxidation rate is affected by interface area as a linear function (Fig. 4): $W_{HP} = f(S)$. Moreover, the selectivity of cumene oxidation promoted by O_2^{gas} has been determined, under the experiment conditions presented in Fig. 4, to equal more than 99 mol %, which is an extremely high value, being independent of the gas–liquid interface area.

The theoretical importance of the verification, through direct experiments, of the occurrence of oxidation under the influence of O_2^{gas}, as well as of the extremely high magnitude of process selectivity, becomes even more evident when compared against the publically available reports [6], according to which, “hydroperoxide does not decompose at a temperature of 30–65°C, which substantially prevents oxidation even when hydroperoxide is specially fed as an initiator,” and it is not until the temperature reaches above 70–80°C that hydroperoxide begins decomposing with formation of radicals and oxidation proceeds through the mechanism of degenerate branched chain reactions, where process selectivity declines with a rise of hydroperoxide concentration.

The abovementioned assumptions [6] have been completely refuted by the obtained data, which is illustrated in Figs. 1–4, and which is further summarized as follows:

1) Cumene oxidation by O_2^{gas} took place at about 20°C, i.e., at markedly lower temperatures as opposed to oxidation by O_2^{liquid} [4, 6].

2) Under low temperatures, oxidation proceeded through the mechanism of degenerate branched chain reactions, in a similar manner as it does at higher temperatures, judging from the formation of dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide (see Tables 2 and 3, below).

3) The reactions of propagation, degenerate branching, and termination of radical chains, leading to formation of by-products, occurred to a very limited extent, despite the high hydroperoxide concentration (about 36 wt % to about 45 wt %) in the cumene feed. As a result, cumene oxidation occurring at the liquid–gas interface with participation of O_2^{gas}, becomes similar to a process that proceeds by the mechanism of low-branched chain reactions.

4) During the oxidation under study, an exceptionally high magnitude of selectivity (more than 99 mol %) was achieved within the entire range of hydroperoxide concentration, up to about 45 wt %.

To discover which specific radicals participate in oxidation through oxygen present at the phase interface, and to reveal the true reasons behind the anomalously high selectivity achieved, a series of test runs of oxidation promoted by O_2^{gas} were performed, with a hydroperoxide-containing reaction mixture in some of the runs, and with an almost hydroperoxide-free reaction mixture in the others. Comparison of the data obtained during the unforced (diffusion) oxidation under the influence of O_2^{gas} with a cumene feed that was almost free of hydroperoxide (0.12 wt %), versus the same with a cumene feed containing about 5 wt % hydroperoxide, as presented in Tables 2 and 3, respectively, led to the discovery that hydroperoxide formation rate at $[CHP]_0 = 0.12$ wt % was more than two orders of magnitude (precisely, 256-fold) lower than that at $[CHP]_0 = 4.9$ wt %. In particular, at an initial hydroperoxide concentration of 0.12 wt %, the extreme slowness of hydroperoxide formation rate is illustrated by the fact that hydroperoxide concentration increased by as little as 0.03 wt % over the period of 50 days (see Table 2), and by 0.156 wt % over 196 days (not indicated in Table 2). Therefore, O_2^{gas}-aided oxidation did not occur for practical purposes, as compared to the runs with an initial hydroperoxide concentration exceeding 5 wt % (as presented in Table 3 and Figs. 1 and 2), and the reaction $RH + O_2^{gas} \rightarrow R^{\bullet} + HO_2^{\bullet}$ was avoided.

The presentation of the direct experimental proof of an extremely low (i.e., close to zero) rate of hydroperoxide formation at a very small initial hydroperoxide concentration (0.12 wt %, Table 2) in the cumene feed, during the O_2^{gas}-aided oxidation test, supports the above conclusion that a direct contact between molecules of cumene and O_2^{gas} at the liquid–gas interface in the absence of hydroperoxide, which otherwise serves as a source of radicals in the oxidized products, fails to form radicals $R^{\bullet}$ and, therefore, does not bring any considerable contribution to formation of radicals $ROO^{\bullet}$ and, as a consequence, to formation of hydroperoxide. This conclusion fully corresponds to the assumption postulated in reference [17]. Therefore, the particular type of oxidizing agent, whether O_2^{gas} or O_2^{liquid}, does not affect

Table 2. Unforced static cumene oxidation: $T = 23°C$, $P = 0.1$ MPa, $S = 10.7$ cm^2, $[CHP]_0 = 0.12$ wt %

Days	[Acetophenone], wt %	[Dimethylbenzyl alcohol], wt %	[CHP], wt %	[Dicumyl peroxide], wt %	Δ(cumene conversion), %	Δ(process selectivity),[a] mol %
0	0	0.001	0.12	0		
27	0	0.001	0.15	0	0.03	100
50	0	0.002	0.15	0	0.03	96.91

[a] Δ(cumene conversion) and Δ(process selectivity) values are hereinafter estimated w/o consideration for hydroperoxide, dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide at the initial point of the run.

Table 3. Unforced cumene oxidation: $T = 23°C$, $P = 0.1$ MPa, $[CHP]_0 = 4.9$ wt %, $S = 10.7$ cm^2

Days	[Acetophenone], wt %	[Dimethylbenzyl alcohol], wt %	[CHP], wt %	[Dicumyl peroxide], wt %	Δ(cumene conversion), %	Δ(process selectivity), mol %
0	0.002	0.02	4.9	0		
27	0.002	0.022	6.28	0.0014	1.09	99.72
50	0.0035	0.031	7.7	0.0017	2.22	99.43

the character of the occurring chain reactions – both cases are characterized by an induction period, with an extremely low reaction rate in the substantial absence of hydroperoxide (less than 5 wt %).

The opposite scenario was observed when hydroperoxide was present in the liquid phase in an amount of about 5 wt %, as is presented in Table 3. The review of the data presented in Table 3, together with the oxidation results obtained at an initial hydroperoxide content of about 10 wt % and about 35.2 wt % (Figs. 1 and 2, Tables 1 and 2), reveals that the oxidation reaction promoted by O_2^{gas} occurs at a noticeable speed only when a sufficient amount of hydroperoxide is contained in the liquid phase. In the experiments discussed, hydroperoxide formation rate varied as a linear function, with cumene oxidation selectivity being extremely high (i.e., more than 99 mol %).

Comparison of Table 3 with lines *1* and *2* in Fig. 2, leads to a predictable conclusion that, to ensure the occurrence of oxidation promoted by O_2^{gas}, as in the case of oxidation by O_2^{liquid}, a sufficient concentration (i.e., concentration at a kinetic equilibrium) of hydroperoxide in the reaction mixture is required, because hydroperoxide is a source of radicals $R^•$, the amount of which needs to be sufficient. When this requirement is met (i.e., when $[CHP]_0 > 5$ wt %), hydroperoxide is formed at the phase interface at a sufficient rate (see lines *1–3* in Fig. 2, and Table 3), due to a contact between radicals $R^•$ and oxygen O_2^{gas} present at the liquid–gas interface.

In view of the above consideration, it can be stated that oxidation under the influence of O_2^{gas} only takes place when the reactions of degenerate branching, with participation of $ROO^•$, give rise to the presence of radicals $R^•$ in the liquid phase (it should also be noted that the radicals $R^•$ are formed from hydroperoxide, rather than in a reaction between RH and O_2^{gas}). This is the reason why the oxidation reaction substantially does not develop in the absence of hydroperoxide in the liquid phase, and occurs extremely slowly if hydroperoxide is present in low concentrations, such as about 0.12 wt %. In fact, the action of O_2^{gas} as a reactant, does not differ from that of O_2^{liquid}, with respect to hydroperoxide formation with participation of radicals $R^•$. Provided that a sufficient amount of radicals $R^•$ are present or formed in the liquid phase, the oxidation process takes place regardless of the oxidizing agent type; otherwise, oxidation promoted by O_2^{gas} fails to develop. Consequently, hydroperoxide formation at the liquid–gas interface involves contact of molecules of O_2^{gas} with radicals $R^•$ that have been formed in the liquid phase, and that are present at the phase interface. The dependence of the oxidation and hydroperoxide formation rate on the concentration of radicals $R^•$, provides further evidence that the reaction between $R^•$ and O_2^{gas} is the rate-limiting stage of the oxidation process proceeding at the liquid–gas interface.

In the light of the abovementioned discussion, the radical chain development scheme for the cumene oxidation reactions aided by O_2^{gas} at the liquid–gas interface, with the liquid phase containing hydroperoxide giving rise to $R^•$, must have the appearance as described by reactions (6) and (2):

$$R^• + O_2^{gas} \xrightarrow{\text{slow}} ROO^•, \quad (6)$$

$$ROO^• + RH \rightarrow ROOH + R^•, \quad (2)$$

where $R^•$ is a radical of the liquid phase; and O_2^{gas} is an oxygen molecule of the gas phase.

A review of reactions (6) and (2) reveals that they are only distinct from the commonly recognized scheme of cumene oxidation into hydroperoxide, described by reactions (1) and (2) in accordance with the assumptions disclosed in reference [4], in that formation of radicals $ROO^•$ involves the participation of O_2^{gas} molecules at the phase interface, and not of O_2^{liquid} molecules in the liquid phase by reaction (1). On the other hand, whether O_2^{gas} or O_2^{liquid} leads the oxidation reaction, the limiting stage in both cases is in fact the reaction between radicals $R^•$ and oxygen molecules (O_2^{gas} or O_2^{liquid}, respectively), i.e., reaction (6) or reaction (1), rather than reaction (2), which is the same in both compared schemes. Of course, this distinction is only relevant for the particular conditions (low temperature and pressure of 0.1 MPa) under which the experiments were conducted. Reference [17] clearly explains that, with an increase in temperature and pressure, reaction (1) makes a more significant contribution to the overall rate of hydroperoxide formation, with the reaction between $R^•$ and oxygen (O_2^{gas} and O_2^{liquid}) proceeding by both paths.

Despite the low temperature of 23°C, further development of the radical chain in the liquid phase, leading to transformation of radicals into by-products following the degenerate branched chain mechanism, still occurs, though to a very small extent (see Tables 1 and 2). Therefore, while oxidation promoted by O_2^{liquid}, with a small concentration thereof in the reaction mixture, follows the branched chain mechanism, the mild process conditions (low temperature and a correspondingly low concentration of retarders/inhibitors) bring it into proximity with the non-branched chain reaction pattern. This is one, but not the only, cause of the high selectivity of O_2^{gas}-aided oxidation.

When comparing O_2^{gas} and O_2^{liquid} as oxidizing agents, and specifically with respect to their reaction with the $R^{\bullet}$ radical, it should be noted that, at a hydroperoxide concentration of 5 wt % or greater, when the induction period is over, formation of $R^{\bullet}$ and $ROO^{\bullet}$, as well as their subsequent conversion into the desired hydroperoxide product, under the influence of O_2^{gas} are characterized by the following distinctions: (a) a sufficiently high reaction rate (see Figs. 1 and 2); (b) occurrence under very low temperature (23°C); and (c) an anomalously high selectivity value (see Table 1), as opposed to radical transformations in the course of cumene oxidation promoted by O_2^{liquid} (which are further discussed in Section 3, Bubbling-type vs. Static Oxidation of Cumene, below).

Apart from the above-listed distinctions, two additional important features of O_2^{gas} are noteworthy. Formation of $R^{\bullet}$, $RO^{\bullet}$, and $ROO^{\bullet}$ takes place despite the discouraging effects of: (1) the lack of thermal decomposition of hydroperoxide at very low temperatures (e.g., at 23°C); and (2) deep association of hydroperoxide molecules at a high concentration of hydroperoxide.

The aforementioned results provide additional evidence supporting the conclusion that is drawn above, in the discussion of cumene oxidation occurring with, and without, addition of phenol and formic acid as retarders/inhibitors, as well as the conclusion that was made in references [14, 17], with regard to cumene oxidation carried out at notably higher temperature values (110–120°C) and hydroperoxide concentration values (40–64 wt %). Specifically, it is clear that the magnitude of process selectivity is affected not so much by the concentration of hydroperoxide, which is the source of appearance and transformation of radicals, but by the presence of retarders/inhibitors in the reaction mixture, because a variation in the content of inhibitors has a very significant impact on the relationships $[R^{\bullet}]/[InH]$ and $[ROO^{\bullet}]/[In]$, and therefore on the quantities of resulting hydroperoxide and by-products.

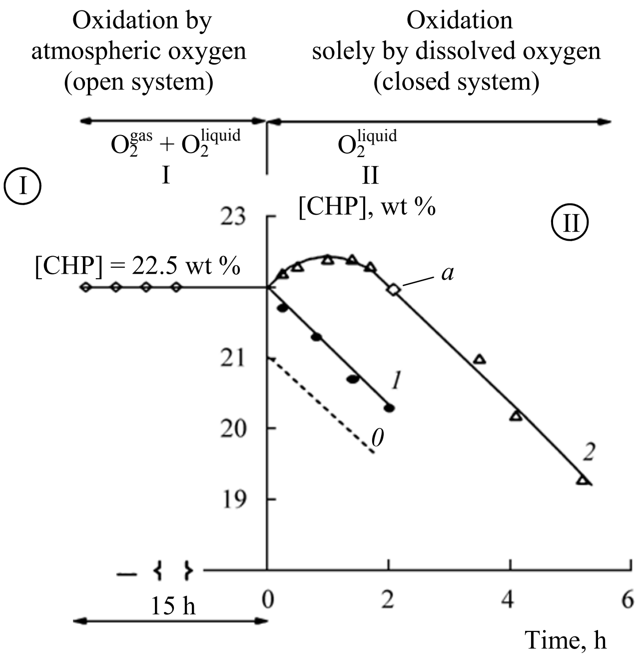

Fig. 5. Formation and conversion of CHP in an open system and a closed system, at $T = 110$°C: (I) air bubbling (oxidation aided by O_2^{liquid} and O_2^{gas}); (II) oxidation aided by O_2^{liquid}; (*0*) thermal decomposition of CHP in the absence of O_2^{liquid}, at $P = 0.1$ MPa; (*1*) CHP decomposition in the absence of O_2^{liquid}, at $P = 0.1$ MPa; (*2*) CHP conversion in the presence (at "3 h" point) and in the absence of O_2^{liquid} (over the period of 3 h to 5 h), at $P = 0.5$ MPa; "15 h" indicates the period of time during which the process was brought to a stable concentration of the reaction mixture.

Figure 5 presents the data of cumene oxidation tests that were performed successively in an open system and in a closed system, under pressures of 0.1 MPa and 0.5 MPa, all under the same temperature of 110°C. The tests were intended for: (1) determining the portion of hydroperoxide formed in the reaction of cumene with O_2^{gas} at the liquid–gas interface under the conditions of an open system with air bubbling; and (2) studying the phenomenology of oxidation promoted by O_2^{liquid}, the concentration of which, in the reaction mixture contained in the closed system, was about ten times higher than that in the open system (about 0.43 wt % and about 0.05 wt %, respectively).

In the open system, oxidation was influenced by both O_2^{liquid} and O_2^{gas}, while the closed system only involved oxygen dissolved in the oxidized products, O_2^{liquid} (as a result of the lack of air input from the outside). Moreover, oxidation in the closed system continued until the complete exhaustion of O_2^{liquid}, so as to determine *in situ* the concentration of dissolved oxygen based on the complete composition of the products formed.

The utility of the abovementioned developed method is not only explained by its substantially higher accuracy, as compared to all other relevant alternate methods, but, most importantly, this method is the most appropriate for measuring the effect of the presence of hydroperoxide and of other oxygen-containing compounds in the reaction mixture on the solubility of O_2^{liquid} therein, as opposed to the case of pure cumene [16].

The obtained results (illustrated by line *1* and curve *2* in Fig. 5) suggest that, despite the same hydroperoxide concentration (22.5 wt %), transitioning the oxidation process from the open system into the closed system (the "0 h" point), made the amount of newly-formed hydroperoxide fundamentally different. Indeed, at $[O_2^{liquid}]_0 \approx 0.43$ wt % (under pressure of 0.5 MPa), hydroperoxide formation proceeded, and its concentration reached its maximum point, with its subsequent drop to a point (2.3 h during step II) where it equaled the hydroperoxide concentration of step I (during which the residence time in the reactor was also 2.3 h). Then, at $[O_2^{liquid}] = 0$, hydroperoxide was expended into by-products solely in the course of a thermal decomposition reaction. At $[O_2^{liquid}]_0 \approx 0.05$ wt % (under pressure of 0.1 MPa), an increase in hydroperoxide concentration during step II was almost zero (not indicated in Fig. 5), so that the hydroperoxide entering along with the reaction mixture from the open system (step I) was only expended, with the expenditure rate equal to the rate of thermal decomposition of hydroperoxide in the absence of oxygen in the reaction medium (illustrated by line *0* in Fig. 5).

During step I, at $[O_2^{liquid}]_0 \approx 0.05$ wt % (under pressure of 0.1 MPa), the hydroperoxide formation rate was about 0.75 wt % h^{-1}, due to air injection, while it dropped almost to zero in the following step II. This unambiguously suggests that hydroperoxide formation under atmospheric pressure and temperature of 110°C, with air bubbling through the reaction mixture, occurs almost solely by action of O_2^{gas} at the liquid–gas interface, i.e., at the boundary between the surface of air bubbles and the liquid phase.

When bubbling-type oxidation was carried out under a higher pressure (e.g., 0.5 MPa), with a relatively high concentration of O_2^{liquid}, both formation and expenditure of hydroperoxide took place during step II, as is illustrated by curve *2* in Fig. 5. This serves as evidence that hydroperoxide formation in step I proceeded by both O_2^{gas} and O_2^{liquid} paths. The yield of hydroperoxide from step I is determined by the residence time of the oxidation mixture in the reactor; accordingly, as compared to hydroperoxide yield under atmospheric conditions, this value under higher pressure may be either higher (the usual case), or equal (see dot "*a*" on curve *2* in Fig. 5), or even lower. In fact, the final result depends on the adequate selection, by the designer, of appropriate values of reactor size, residence time, temperature value, degree of cumene conversion into hydroperoxide, and of the quality of initial cumene feed as well as of cumene recycle streams, which contain various amounts of reaction inhibitors/retarders that strongly affect the rates of formation of hydroperoxide and by-products. The quantitative ratios between the amounts of hydroperoxide formed under influence of O_2^{gas} and O_2^{liquid} for a specific reactor and for the process conditions described above, are provided in [17]. In the particular context of cumene oxidation conducted in the static and dynamic regimes, this data obtained from the test performed under temperature of 110°C, is relevant as clear evidence that, at atmospheric pressure and under exceptionally mild process conditions, oxidation occurring at the liquid–gas interface primarily involves O_2^{gas} in the hydroperoxide formation reaction.

2. Dynamic oxidation promoted by O_2^{gas}. The oxidation reaction is known not to be limited by oxygen diffusion from the gas phase into the liquid phase, as is noted in [4, 6]. Nonetheless, in order to verify whether cumene oxidation rate is affected by the rate of air flow above the gas–liquid interface, another series of experiments were carried out, in which cumene was oxidized by atmospheric oxygen in the dynamic regime of interphase contact, rather than in the static regime, as was performed in the test reported in Figs. 1–4 and in Tables 1–3. For this purpose, air was continuously passed along a moving surface that was represented by a film of the liquid phase (oxidized products) created by means of continuous refluxing of the hard reactor surface with the reaction mixture, the latter being drawn off from the reactor and then continuously returned into the reactor for refluxing. In a number of runs, air was fed in significant excess quantities, as compared to the quantities required by the stoichiometry of cumene conversion, while in other runs the amount of excess air was relatively small (5–10%). The rate of hydroperoxide formation was found to be substantially constant despite a variable air inflow rate. The supporting experimental data is graphically illustrated in Fig. 6 and Fig. 7.

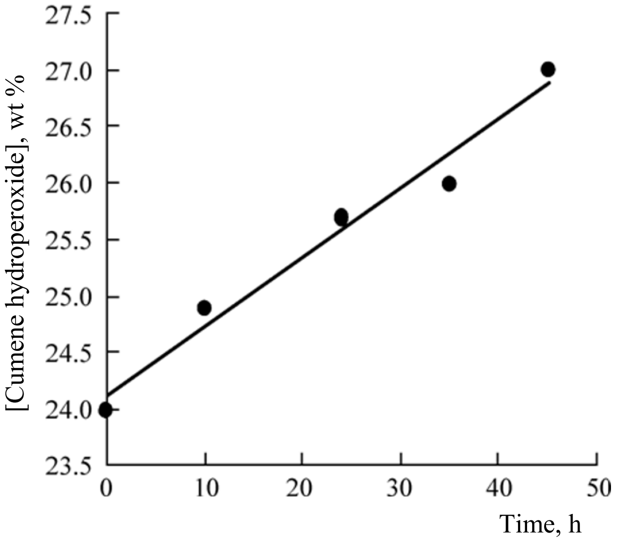

Fig. 6. Hydroperoxide accumulation under dynamic oxidation conditions: $T = 40°C$, $P = 0.1$ MPa, S = const, $[CHP]_0 = 24$ wt %.

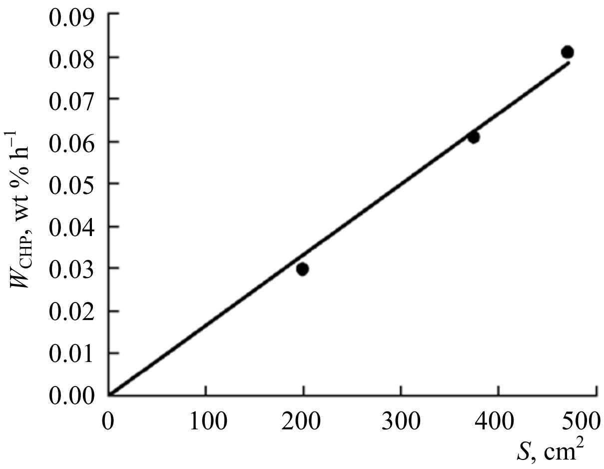

Fig. 7. Hydroperoxide formation rate as a function of liquid–gas interface area under dynamic oxidation conditions: $T = 40°C$, $P = 0.1$ MPa, $[CHP]_0 = 24$ wt %.

As in the static oxidation tests, in the course of the experiments performed in the dynamic regime with a varying liquid–gas interface area, special care was taken to strictly observe the similarity of process conditions (in particular, the constancy of process temperature/pressure/concentration of dissolved oxygen, etc.), critical for the steadiness of the relationship between the rate constants of O_2^{liquid}-aided reactions of propagation and termination of radical chains in the liquid phase. The only variable parameter was liquid–gas contact area. Moreover, the oxygen excess, as compared to the quantities required for chemical reactions, as well as oxygen concentration in the spent air from the reactor, were strictly maintained to be stable and constant.

The results obtained for different areas (200 cm^2, 376 cm^2, and 471 cm^2) of contact between the countermoving flows of the liquid phase and the gaseous phase, convincingly proved both that oxidation under the influence of O_2^{gas} at the liquid–gas interface actually occurs in the dynamic regime, and that the rate of oxygen diffusion from the gas phase into the liquid phase is independent of the air flow rate when oxygen is fed in excess, as compared to the stoichiometry of cumene conversion.

The study further established that hydroperoxide formation occurring in the dynamic regime is described by a linear function (Fig. 6) until hydroperoxide concentration reaches 27 wt %, without a declining trend of reaction rate, in the same manner as it was observed for static oxidation (cf. Figs. 1–4). Additionally, the oxygen diffusion rate was found to be independent of the rate and quantity of air inflow, while, on the contrary, the reaction rate was discovered to depend on interface area in a linear relationship, within the interface area range of 0 to 471 cm^2 (Fig. 7): $W_{HP} = f(S)$. An increase in interface area from zero to 471 cm^2 leads to a proportional acceleration of hydroperoxide formation rate, as it was also observed in the static oxidation case (Fig. 4).

Moreover, at hydroperoxide concentration of about 27 wt %, the selectivity of O_2^{gas}-aided oxidation in the dynamic regime, in the same manner as under the static conditions, was revealed to be about 98 mol %, which is an appreciably higher value, as compared to the bubbling-type cumene oxidation with the same hydroperoxide content (see details in Section 3, Bubbling-type vs. Static Oxidation of Cumene, below).

Both the conditions imposed in the tests and the experimental results lead to a conclusion that the rate of oxygen transfer from the gas phase into the liquid phase does not limit the process, with the vast majority of hydroperoxide being formed with participation of O_2^{gas} at the liquid–gas interface, while the contribution of reactions occurring in the liquid phase under influence of O_2^{liquid} molecules to formation of hydroperoxide and by-products, is negligible in view of the very low concentration of dissolved oxygen. The same conclusion was additionally supported by results of the series of experiments performed under atmospheric pressure and temperature of 110°C, where successive oxidation steps in an open system and in a closed system were arranged (in the open system, air was injected through the liquid phase and oxidation was influenced by both O_2^{gas} and O_2^{liquid}; the closed system involved oxidation solely promoted by O_2^{liquid}). This arrangement of two successive steps ensured that the O_2^{liquid} concentration in the open system was exactly equal to the O_2^{liquid} concentration at the initial time of oxidation in the closed system. It was also revealed [13] that in the open system a constant hydroperoxide concentration, being equal to 22.2 wt %, was readily maintained both inside and at the outlet of the reactor, thus proving that continuous formation of hydroperoxide does in fact take place. On the contrary, in the closed system, the expenditure of hydroperoxide, that had been accumulated during the first step of the test, and lack of formation of hydroperoxide, was observed. The rate of this expenditure was found to be exactly equal to the rate of thermal decomposition of hydroperoxide in the absence of oxygen dissolved in the reaction mixture, as was demonstrated in an experiment conducted in a nitrogen environment with dissolved oxygen preremoved by nitrogen. These revelations supply additional evidence that, in an open system in the presence of both O_2^{gas} and O_2^{liquid}, hydroperoxide formation is only affected by O_2^{gas}, while the contribution of O_2^{liquid} is negligible under pressure of 0.1 MPa.

Similar experiments, in which a higher O_2^{liquid} concentration was used, and correspondingly a higher pressure was imposed [13], also supported the abovementioned conclusions and, furthermore, additionally demonstrated that an increase in the concentration of dissolved oxygen predictably increases the amount of hydroperoxide formed with participation of O_2^{liquid} molecules.

Regarding the temperature impact on the dynamic oxidation promoted by O_2^{gas}, an about two-fold temperature elevation (from about 30°C to about 60°C) resulted in about a 10-fold acceleration of hydroperoxide formation rate (Fig. 8).

Based on the experimental data, the activation energy (E_a) of the hydroperoxide formation under the influence of O_2^{gas} carried out in the dynamic regime, was estimated to be about 16 kcal mol^{-1} (with the correlation coefficient r being equal to 0.9996), and this estimation is markedly different from the value of $E_a = 26.3$ kcal mol^{-1}, that was previously obtained for cumene oxidation promoted by O_2^{liquid} [17]. It appears that the variation in E_a values (about 16 kcal mol^{-1} vs. about 26 kcal mol^{-1}) stems from a noticeable difference in the reactivity of O_2^{gas} and O_2^{liquid} molecules, which in turn originates from a different state of O_2^{gas} and O_2^{liquid} molecules in the gas phase, as opposed to the liquid phase. This explanation is also supported by the discovery, in the study discussed, of the significant distinction in selectivity values between oxidation processes promoted by O_2^{gas} and by O_2^{liquid}, as well as of the fact that, when O_2^{gas} participates in the oxidation reaction, as opposed to O_2^{liquid}-aided oxidation, hydroperoxide concentration within the range of about 5–45 wt% has no effect on hydroperoxide formation rate (see lines *1* and *3* in Fig. 2).

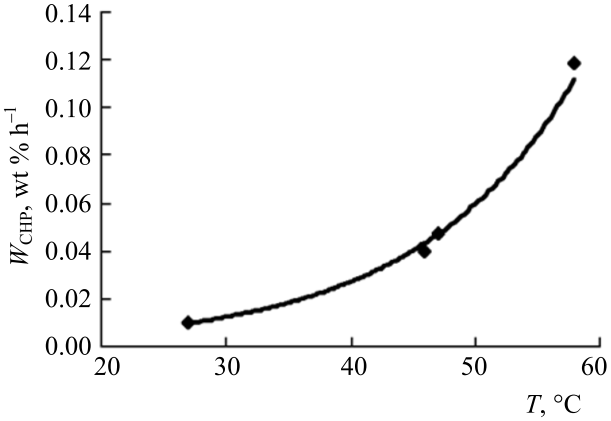

Fig. 8. Cumene hydroperoxide formation rate as a function of temperature in a film-type reactor: P = 0.1 MPa, $[CHP]_0$ = 11 wt %, S = const.

The experimental results obtained with the static and dynamic process types did not reveal any fundamental contrast – at least, within the studied ranges of process conditions – between the compared regimes of oxidation promoted by O_2^{gas}. Therefore, both regimes belong to the category of processes in which: (a) cumene oxidation occurs with the participation of O_2^{gas} at the liquid–gas interface; (b) oxidation rate is a linear function of interface area; and (c) selectivity of oxidation under the influence of O_2^{gas} is anomalously high, as opposed to oxidation occurring under the influence of the O_2^{liquid}.

3. Bubbling-type vs. static oxidation of cumene. The distinctions between the conventional bubbling-type oxidation and the static oxidation are clearly demonstrated by the data obtained in comparative experiments that were conducted under the same conditions, including temperature of 23°C, pressure of 0.1 MPa, the same flow rates of air delivery and cumene feed, an interface area of 7.1 cm^2, and the same continuous run period of 137 days (Fig. 9). In the bubbling-type oxidation run, air was injected through a special sparger that was effective in fracturing the air flow into 1–2 mm bubbles, while in the static oxidation run air was delivered above the surface of the reaction mixture.

The amount of air delivered to the reaction was the same in both runs, and the oxidation conditions were such, that the rate of air expenditure into chemical reactions was significantly slower than the rate of oxygen transfer from the gas phase into the liquid phase. These conditions ensured the constancy of the concentration of the oxygen dissolved in the liquid phase, as well as the constancy of the concentration of oxygen in the gas phase in the static O_2^{gas}-aided oxidation regime. The low temperature was deliberately selected for the test to minimize the formation of retarders/inhibitors which markedly decrease both hydroperoxide formation rate and process selectivity.

The graph in Fig. 9 demonstrates that, despite the low temperature and the small degree of cumene conversion, the obtained curves of hydroperoxide formation have fundamentally different patterns. Indeed, curve *2* depicts a linear relationship in oxidation under the influence of O_2^{gas} at the phase interface (see also the graph in Fig. 1, relating to a notably greater degree of cumene conversion), while curve *1* refers to a nonlinear relationship in bubbling-type oxidation, where reaction rate declines with an increase in cumene conversion rate. The comparative data is also summarized in Table 4, below.

In accordance with the classical theory [4], reaction rate for bubbling-type oxidation is determined by the following simplified equation: $W = k_1[R^\bullet][O_2^{liquid}]$, where "$W$ stands for the rate of oxygen absorption" [4], which is equivalent to the rate of O_2^{liquid} expenditure into chemical reactions. The above equation requires that: (a) The reaction rate should be equal to the rate of oxygen transfer from the gas phase into the liquid phase; (b) To ensure the linearity of equation (I), the concentration of dissolved oxygen must be constant: $[O_2^{liquid}] = \text{const}$, which implies that the rate of oxygen expenditure into chemical reactions must be slower than the rate of oxygen dissolution in the liquid phase; (c) Phase intermixing must be maintained, so that oxygen diffusion deep into the liquid would be sufficient for oxygen expenditure into the reaction, and oxygen concentrations in different layers of the liquid would be the same and equal to the limiting (in terms of solubility) value; and (d) Air should be fed in an excess quantity, so that oxygen would be present in a certain excess, as compared to the stoichiometry of required oxygen expenditure into the chemical reactions.

The same four requirements are also critical – necessary and sufficient – for the reaction to occur in a kinetic regime. All of them are only relevant to an equilibrium state of radicals, in which the radical chain in the liquid phase is well developed.

In view of the above consideration, all of the requirements mandatory for providing the linear nature of reaction rate in the equation formulated above, were met during the bubbling-type atmospheric oxidation runs (see curve *1* in Fig. 9) performed for the research discussed in this Section. In particular: (a) The rate of oxygen dissolution in the liquid phase equaled about $8.8´10^{-4}$ mol min^{-1} [16], whereas the rate of oxygen expenditure into chemical reactions, based on the quantity of hydroperoxide formed, was about 0.32×10^{-5} mol min^{-1}, which was almost two orders of magnitude slower than the oxygen dissolution rate; (b) $[O_2^{liquid}] = \text{const}$, i.e., the requirements of an adequate degree of phase intermixing, and of rapid oxygen transfer from the surface layer deep into the liquid phase, were satisfied; (c) Oxygen excess, as compared to the stoichiometry of oxygen expenditure into the chemical reactions, was maintained; and (d) The low process temperature, and the low degree of cumene conversion, minimized the formation of by-products.

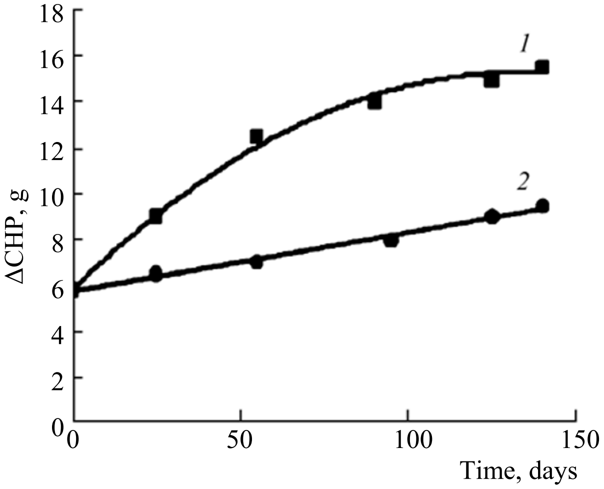

Fig. 9. Cumene hydroperoxide formation in bubbling vs. static regimes of cumene oxidation: $T = 23°C$, $P = 0.1$ MPa, $[CHP]_0 = 10.2$ wt %; (*1*) bubbling-type oxidation; (*2*) static oxidation.

Table 4. Bubbling-type vs. static (O_2^{gas}-aided) cumene oxidation runs: $T = 23°C$, $P = 0.1$ MPa, $S = 7.1$ cm^2

Days	Δ[CHP], wt %		Δ(cumene conversion), %		Δ(process selectivity),[a] mol %	
	Bubbling	O_2^{gas}	Bubbling	O_2^{gas}	Bubbling	O_2^{gas}
27	4.12	2.04	3.46	1.64		
54	8.14	3.31	6.72	2.65	95.62	
90	10.24	5.06	8.38	4.04		
123	10.52	6.75	9.4	5.38		
137	11.87	7.43	9.67	5.92	96.91	99.07

[a] The estimated Δ[CHP], Δ(cumene conversion), and Δ(process selectivity) are net of hydroperoxide and total by-products contained in the initial oxidation mixture.

However, a deviation from the linearity of hydroperoxide formation rate was observed during bubbling-type oxidation (curve *1* in Fig. 9). Therefore, this nonlinearity could not be caused by a failure to meet the above-listed requirements predetermined by the equation: $W = k_1[R^{\cdot}][O_2^{liquid}]$. In fact, the only influence that varied in the course of the test run, and could potentially cause this equation to deviate from a linear relationship, at $[O_2^{liquid}] = const$, was the concentration of radicals $R^{\bullet}$ responsible for formation first of radicals $ROO^{\bullet}$, and then of hydroperoxide. This concentration declined with time under the effect of retarders/inhibitors. In turn, transformation of $ROO^{\bullet}$ into $RO^{\bullet}$, the source of by-product formation in the comparative tests, is supposed to have caused different selectivity values. Thus, under the very mild conditions of the bubbling-type test run, the relationships $[R^{\bullet}]/[InH]$ and $[ROO^{\bullet}]/[In]$ were the only time-varying factors having an influence on the rates of hydroperoxide and of by-products formation, that ultimately led to a deterioration in process selectivity.

Analysis of the data presented in Table 4 and in Fig. 9, reveals that the average hydroperoxide formation rate equals 0.06 wt % h^{-1} for O_2^{gas}-promoted oxidation at the liquid–gas interface, and 0.15 wt % h^{-1} for bubbling-type oxidation (as evaluated for the linear portion of the hydroperoxide formation curve). These two values can be considered comparable as they only differ from one another by a factor of 2.5. This comparability, as well as the experimental results of oxidation accomplished at the boundary of the liquid film in the dynamic regime (see Figs. 6–8), lead to the only possible conclusion that the value of relationship between reaction rates: $W_{liquid}/W_{interf} \approx 10^6/S$, where W_{liquid} is the rate of reaction occurring in the liquid phase, W_{interf} is the rate of reaction taking place at the phase interface, and S is the interface area, requires an additional verification and complete revision. This relationship was estimated within the framework of the kinetic-molecular theory of gases, and in particular based on the number of collisions between radicals $R^{\bullet}$ and O_2 molecules present in the liquid phase and at the liquid–gas interface [6]. The same necessity for complete revision is also applicable to a number of assumptions which were originally derived from the above-noted estimation: (a) that oxidation at the liquid–gas interface under influence of O_2^{gas}, is only possible when the interface area equals about 10^7 to 10^8 cm^2 per each cubic centimeter of volume (but this condition is never feasible in real-world liquid-phase oxidation practice); (b) that the constancy of the relationship W_{liquid}/W_{interf} can never be achieved; and (c) that the occurrence of an oxidation reaction promoted by O_2^{gas} at the liquid–gas interface is impossible.

The above-noted assumptions (a) through (c) are in evident contradiction with the experimental data that has been reported in Tables 1–4, and graphically illustrated in Figs. 1–8, above, and which actually serves as direct evidence of approximate comparability of hydroperoxide formation rates in the two phases under discussion. Moreover, these estimations/assumptions directly contradict the results of the cumene oxidation test runs that were performed successively – first in an open system, and then in a closed system, under the same temperature, pressure, and time values [14], which demonstrated, in particular: (a) a noticeable difference between the amount (by weight) of hydroperoxide formed in an open system functioning in the air bubbling regime, i.e., under influence of O_2^{liquid} together with O_2^{gas}, and the amount of hydroperoxide formed in a closed system when being only influenced by O_2^{liquid} (in the absence of O_2^{gas}); and (b) a substantial difference between the magnitudes of cumene oxidation selectivity for the process occurring under combined action of O_2^{liquid} and O_2^{gas} in the air bubbling regime, and for the oxidation reaction solely promoted by O_2^{liquid} (in the absence of O_2^{gas}) in a closed system, these magnitudes being more than 90 mol % and about 50 mol %, respectively.

Furthermore, the data presented in Table 4 demonstrates that, with the same degree of cumene conversion, the selectivity value in bubbling-type oxidation was considerably lower than that in oxidation through O_2^{gas} at the phase interface (see Table 3). For example, at comparable cumene conversion values (5.92% for bubbling conditions and 6.72% for static oxidation through O_2^{gas}), the selectivity value in the former case was 95.6 mol %, as opposed to 99.07 mol % in the latter case. This verified difference in selectivity values, as well as in activation parameters, for the hydroperoxide formation reaction occurring in the liquid phase, as opposed to the reaction proceeding at the phase interface (see discussion in Section 2, Dynamic Oxidation Promoted by O_2^{gas}, above), places in question the presumption adopted in reference [6], according to which, "the state of O_2 molecules dissolved in a non-polar liquid is unlikely to be notably different from the state of O_2 molecules in a gas phase."

It is appropriate to recall, at this point, that the direct experimental evidence supplied in the study under discussion, as well as the research results reported in references [13, 14], have conclusively proven that bubbling-type oxidation occurs under the actions of both dissolved oxygen (O_2^{liquid}) and of oxygen present at the liquid–gas interface (O_2^{gas}). It has also been known that hydroperoxide formation rate in the liquid phase is described as $W_{\text{HP}} = f([O_2^{\text{liquid}}])$, and that the same at the liquid–gas interface is a function of interface area: $W_{\text{HP}} = f(S)$, provided that $[O_2^{\text{gas}}]$ = const. Therefore, in view of equality between O_2^{liquid} concentrations in both compared test runs (see Fig. 9 and Table 4), the difference in hydroperoxide formation rates in these runs is only determined by the gas–liquid interface area:

$$S_{\text{total}} = S_{\text{liquid}} + S_{\text{bubble}}.$$

In the bubbling-type oxidation run, the contribution of air bubble surface (S_{bubble}) makes the total interface area (S_{total}) about two times larger than in the static oxidation run occurring at the liquid–gas interface under influence of O_2^{gas}, in which $S_{\text{bubble}} = 0$ due to the absence of air injection through the liquid phase. This suggestion explains the about two times lower value of hydroperoxide formation rate (line *2* in Fig. 9), as compared to bubbling-type oxidation (curve *1* in Fig. 9). The higher hydroperoxide formation rate in bubbling-type cumene oxidation is a result of the greater interface area created by air bubbles in the liquid phase.

For a better understanding of the distinctions between the dependencies revealed for the rate of hydroperoxide formation (as are illustrated in Fig. 9), as well as for process selectivity, the simplified schemes of the reactions in question are provided below. Reactions (7), relating to bubbling-type oxidation, are fundamentally different from reaction (8), which describes static oxidation at the phase interface:

$$\text{Cumene} \xrightarrow{+O_2^{\text{liquid}}} \text{Cumene hydroperoxide} \rightarrow \text{Dimethylbenzyl alcohol,} \qquad (7)$$

$$\text{Cumene} \xrightarrow{+O_2^{\text{gas}}} \text{Cumene hydroperoxide.} \qquad (8)$$

Formations of acetophenone and dicumyl peroxide are omitted in reactions (7) and (8) because these reactions are the same in both types of oxidation and, consequently, irrelevant to the present study.

In view of the fact that dimethylbenzyl alcohol, in reactions (7), is produced in the course of the slow conversion of hydroperoxide in the liquid phase (as a result of $ROO^{\bullet}$ transformation, as is noted in [4]), direct formation of dimethylbenzyl alcohol at the interface in reaction (8) would be unlikely, partly due to the lack of hydroperoxide in the gas phase, and also for the reason of the insufficient time of contact between O_2^{gas} and the hydroperoxide-containing cumene feed (liquid phase) at the liquid–gas interface. Therefore, without formation of dimethylbenzyl alcohol in reaction (8), and taking into account that dimethylbenzyl alcohol is a major by-product affecting process selectivity, the selectivity of reactions promoted by O_2^{gas} at the liquid–gas interface is expected to appreciably exceed the selectivity of oxidation under the action of O_2^{liquid} in the liquid phase. This expectation has been confirmed by experimental evidence – a very high selectivity (99.4–99.6 mol %) was achieved when reactions proceeded according to reaction (8), while the selectivity value for reactions (7) of O_2^{liquid}-aided bubbling-type oxidation under temperature of

23°C only reached as high as about 97 mol %. Moreover, the abovementioned distinction in formation of by-products between reactions (7) and (8) is supported not only by the revealed difference in selectivity values, but also by the comparison of the rates of formation of acetophenone and dimethylbenzyl alcohol with the participation of O_2^{liquid} vs. O_2^{gas} for a bubbling-type oxidation process, which is disclosed in reference [17], and summarized in Table 5. The estimation presented in Table 5, demonstrates that the relative quantities of acetophenone and dimethylbenzyl alcohol formed with the participation of O_2^{liquid} are about 1.6-fold and about 29-fold, respectively, greater than those in the case of O_2^{gas}:

Table 5. Comparison of acetophenone and dimethylbenzyl alcohol formation rates under the influence of O_2^{liquid} vs. O_2^{gas} during bubbling-type oxidation: $T = 110$°C, $P = 0.3$ MPa

Reaction rate relationship	O_2^{liquid}	O_2^{gas}	O_2^{liquid}/O_2^{gas}
Acetophenone/ hydroperoxide	0.08	0.05	1.6
Dimethylbenzyl alcohol/ hydroperoxide	0.87	0.03	29.0

It should also be noted that direct experimental evidence of the very low selectivity (about 50 mol %) of cumene oxidation promoted by O_2^{liquid} in the liquid phase, was supplied by a test run in the absence of O_2^{gas}, under temperature of 110°C and pressure of 0.3 MPa [14, 17].

Another reason behind the nonlinear nature of hydroperoxide formation rate and of the slowdown of reaction rate with an increase in the degree of cumene conversion in the bubbling-type oxidation test (as is illustrated by curve *1* in Fig. 9), is the presence, in the liquid phase, of inhibitors and by-products (which also act as retarders of the hydroperoxide formation reaction, as is described in [14]), which are unlikely to exist in the gas phase. References [13, 14] explain that inhibitors have a double negative impact. On the one hand, they decrease the content of cumyl radicals $R^\bullet$, which are required for formation of $ROO^\bullet$ and, correspondingly, of hydroperoxide. On the other hand, due to the reaction between $ROO^\bullet$ and inhibitors (In) in the liquid phase, they cause formation of by-products (ROH), even under extremely mild oxidation conditions, in accordance with reactions (4) and (5), above.

In fact, the difference in the values of hydroperoxide formation rate and process selectivity between the compared oxidation regimes arises from two key factors: gas–liquid interface area and concentration relationships $[R^\bullet]/[In]$ and $[ROO^\bullet]/[In]$. The impact of the latter factor was convincingly proven by adding HCOOH and phenol into the reaction mixture, as well as by studying the “decay” step of the hydroperoxide formation reaction that caused the so-called “limiting” concentration of hydroperoxide, as is noted in [14], and additionally discussed in Article II.

The above-described comparative experiments have also proven that the reaction path promoted by O_2^{gas} makes a significant contribution to the overall formation of hydroperoxide, that this contribution is determined by the liquid–gas interface area, and that oxidation under the action of O_2^{gas} proceeds with a greater selectivity, as compared with the dissolved oxygen reaction path.

Thus, the above considerations lead to a conclusion that the rate of a chain process occurring in accordance with reactions (1) and (2), corresponding to bubble-type cumene oxidation, cannot be described by the simplified equation (9) assumed by the classical oxidation theory [4–9], but this rate is instead defined by equation (10), where W_1^{gas} is a function of k_1^{gas}, $[O_2^{gas}]$, and of the liquid–gas interface area, while W_1^{liquid} is subject to relationship (9).

$$W_{total} = k[R^\bullet][O_2^{liquid}], \qquad (9)$$

$$W_{total} = W_1^{gas} + W_1^{liquid} = W_1^{gas} + k_1^{liquid}[R^\bullet][O_2^{liquid}]. \qquad (10)$$

It should be pointed out that, although the parameters contained in equation (9) describe the relationship between oxygen concentrations in the gas phase and in the liquid phase, which actually adhere to the Henry’s linear function $[O_2^{liquid}] \approx K_H P_{O_2}$, this fact fails to provide neither direct nor presumptive evidence that the oxygen dissolved in the liquid phase exclusively leads the oxidation reaction. On the other hand, this point equally fails to prove that oxygen present in the gas phase takes no part in the reaction or, on the contrary, that the gaseous oxygen is solely responsible for the occurrence of the oxidation reaction and for its rate. It would be even less correct to interpret equation (9) as evidence of the reaction simultaneously proceeding along both paths.

Therefore, equation (9) is essentially unable to determine the contribution of either O_2^{gas} or O_2^{liquid} to the overall reaction rate, because, in fact, the reaction simultaneously occurs by both independent reaction paths, as is defined by equation (10), with different rate constants, k_1^{gas} and k_1^{liquid}, rather than by a single reaction path through O_2^{liquid}, as is presumed by equation (9). The relationship between oxygen concentrations in the gas phase and in the liquid phase, described as $[O_2^{\mathrm{liquid}}] \approx K_H P_{O2}$, is simply useless as a means of determining the contribution of each path to the overall hydroperoxide formation rate, because the existence of two paths of the hydroperoxide formation reaction converts equation (9) into equation (10) with two unknown rate constants, k_1^{gas} and k_1^{liquid}. Moreover, when using equation (9) for the bubbling-type oxidation test run, these reaction rate constants are fundamentally indeterminable in terms of either the hydrocarbon feed or the reaction products, as both the feed and the products are the same, demonstrating no difference from one another in the kinetic aspect. Instead, constants k_1^{gas} and k_1^{liquid} should be evaluated separately – the first under a static (or dynamic) oxidation regime, and the second in oxidation through dissolved oxygen in the absence of the gas phase.

The test data disclosed above leads to a conclusion that the previous theoretical notions assuming that the oxidation reaction only proceeds through the action of O_2^{liquid} [4], are not supported by experimental results, at least with respect to oxidation of cumene.

Finally, it is worth noting that the classical assumption of the necessity to study a bubbling-type oxidation process in the kinetic regime alone, was postulated for an oxidation process in which oxidation reactions only proceed in the liquid phase, and solely at the expense of oxygen dissolved in the liquid phase [4]. However, the above discussion, proven by corresponding disclosed experimental data, clearly demonstrates that cumene oxidation occurs by two independent reaction paths, i.e., through O_2^{liquid} and O_2^{gas}; as such, in hollow reactors operating without mechanical mixing of phases, the amount of hydroperoxide formed by a respective path depends upon the concentration of O_2^{liquid} in the reaction mixture and upon the magnitude of process pressure (which markedly affects the size and the rise rate of air bubbles, the gas content, and the area of the gas–liquid surface [17]) – for the first reaction path, and upon the area of the gas–liquid surface – for the second, as is noted in [13, 14, 17]. This, in combination with the aforementioned facts, implies that equation (9), as is assumed in [4], can never reflect either the essence or the reaction rate of bubbling-type cumene oxidation, even though the process develops in a kinetic regime – a regime that assumes that, under almost any process conditions, and in particular under high or low temperatures, reaction rate is significantly slower both than the rate of oxygen dissolution in the liquid phase and than the rate of oxygen expenditure into chemical reactions. Thus, it should be stated that the multiple contradictions arising when one uses equation (9) in trying to describe bubbling-type cumene oxidation, as are revealed in [17], are explained by the hydroperoxide formation reaction taking place by two independent paths, and not by a particular regime – kinetic or diffusion – in which it proceeds. Consequently, being aware of involvement of both reaction paths in cumene oxidation, one can never neglect either the impact of O_2^{liquid} concentration (homogeneous path -of reaction), or the mass transfer effects (heterophase path of reaction promoted by O_2^{gas}) in describing a bubbling-type cumene oxidation process.

In the light of the direct experimental proof of the two simultaneous paths (O_2^{gas} and O_2^{liquid}) of the oxidation reaction, and in view of a range of experimental data clearly demonstrating the contradictions of the earlier practiced assumption of exclusive contribution of dissolved oxygen to an oxidation process [13, 14, 17], it must be stated that any mathematical models (such as, by way of example, those disclosed in [12, 18–23]), as well as any kinetic models, which only consider one or the other single reaction path, rather than both paths together, appear to be erroneous from the chemical standpoint.

The conclusions relevant to the findings disclosed in this article, are provided in the overall Conclusions Section in Article II.

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