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

Phenomenology of Oxidation of a Cumene Feed Containing Hydroperoxide:

II.[1] Limiting Hydroperoxide Concentration: True Causes and Approaches for Overcoming Thereof[2]

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Abstract—It is demonstrated that, in the course of the cumene oxidation reaction promoted by dissolved oxygen (O_2^{liquid}), newly-formed retarders-inhibitors (In) reduce the values of relationships between radicals and inhibitors, in particular $R^•/In$ and $ROO^•/In$, thus leading to a decrease in cumene hydroperoxide formation rate, in the degree of cumene conversion, and in process selectivity. Clear evidence of the dominant role of dissolved oxygen in the increase in formation of retarders/inhibitors is provided, and it is also proven that pre-removal of retarders/inhibitors is effective in overcoming the hydroperoxide concentration limit, and in noticeably increasing the degree of cumene conversion, without major losses in selectivity.

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4. The impacts of radicals and inhibitors on hydroperoxide formation rate and on process selectivity in a bubbling-type process. One of the basic tenets of the peroxide theory is that "the only intermediate (labile) product of hydrocarbon oxidation is the peroxide radical" and, therefore, that "all molecular products result from transformations of the peroxide radical" [2]. It is further stated that "free radicals $R^•$ and $RO_2^•$, being rather reactive, rapidly disappear in the course of chain termination reactions. Correspondingly, during an oxidation process a stationary (kinetically equilibrium) concentration of these radicals is established, at which the rates of formation and of decay of the radicals are equal" [2]. In fact, the above-cited passage implies the existence, during hydrocarbon oxidation, of a concentration of the radicals in a kinetic equilibrium, which is predetermined by the major reactions,[3] in particular those of propagation of radical chains (1, 2), degenerate branching (11), and termination of chains (in the manner it is presented in [2]).

$$R^• + O_2 \rightarrow RO_2^•, \tag{1}$$

$$RO_2^• + RH \rightarrow ROOH + R^•, \tag{2}$$

$$ROOH \rightarrow RO^• + OH^•. \tag{11}$$

The precise description of the chain termination reactions is not provided here because they are great in number and well-known to those skilled in the art, whereas the detailed discussion of these reactions stands beyond the subject matter of this article.

The above perception is implicitly confirmed by the experimental data reported in [3, 4], as well as by the data obtained in the subject research. However, the same data clearly demonstrates that the existing schemes of radical reactions, in combination with termination reactions [2], fail to explain a variety of cases observed under different process conditions of bubble-type oxidation, unless the scheme of reactions (1), (2), and (11) is supplemented by reactions (4) and (12) describing a reaction between the radicals and the retarders/inhibitors (In), in relation to the

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[1] For Article I, see [1].
[2] The text was submitted by the author in English.
[3] Numbering of sections and chemical reactions is consistent with that used in Article I.

overall scheme of the formation of main and side products within various ranges of cumene conversion, O_2^{liquid} concentration, process temperature, and other relevant variables of an oxidation process:

$$RO_2^\bullet + In \rightarrow RO^\bullet + InO, \qquad (4)$$

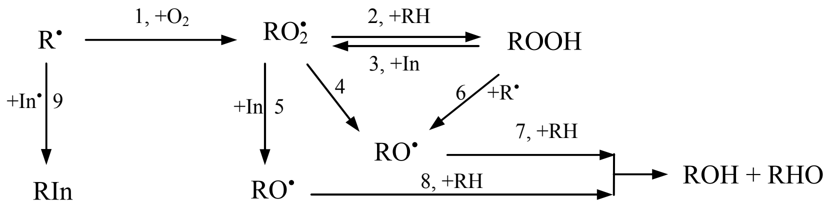
$$R^\bullet + In^\bullet \rightarrow RIn. \qquad (12)$$

Scheme 1 presents, in a simplified form, the general scheme of radical transformations involved in the process under question.

To the best knowledge of the author of this article, none of previous publically available references consider, in relation to the general simplified chemistry of radical transformations (Scheme 1), either the reactions (4) and (12) between radicals $R^\bullet$, $RO_2^\bullet$ and inhibitors, or the correlations of reactions involved with the achieved target values of a cumene oxidation process, specifically reaction rates and process selectivity. (It should be noted, though, that of all the previous public art, the reactivity of free radicals $R^\bullet$, and their quick disappearance in the course of chain termination reactions, as well as the existence of a kinetically equilibrium concentration of radicals, are mentioned in the fundamental work covering hydrocarbon chain reactions [2]).

The majority of radicals $R^\bullet$ are formed in the liquid phase, and particularly in propagation and degenerate branching reactions (although the mutually reversible reaction paths 2 and 3, as they are depicted in Scheme 1, are not truly reversible from the purely chemical point of view, but they rather demonstrate the mere existence of these mutually reversible reaction paths). Moreover, it should be noted that neither radical transformation reaction path 3 (see Scheme 1), nor even the entire combination of reaction paths 3 and 4 (Scheme 1) and chemical reactions (4) and (12), cannot be considered relevant as an explanation of the precipitous increase in the formation of by-products at a high degree of cumene conversion in a bubbling-type process. Nonetheless, whether or not reaction paths 3, 4, and 6 are included in the general reaction scheme, bubbling-type oxidation is characterized by a state of radicals in a kinetic equilibrium, which is likely to be disturbed not only by chain termination reactions, but also by formation of retarders/inhibitors and their subsequent reactions with radicals $RO_2^\bullet$ and $R^\bullet$ (Note: For the purpose of simplicity, the term “inhibitor(s)” may be used throughout this entire article, to refer to “retarder(s)/inhibitor(s)”, interchangeably with the conventional definition of “inhibitor”). Moreover, this disturbance of equilibrium (more specifically, a transition to another equilibrium state) suggests a change in the relationship between the concentrations of radicals and inhibitors: ($[R^\bullet]$ & $[RO_2^\bullet]$)/[In], which in turn slows down the ROOH formation rate, and affects the selectivity value. In view of the above discussion, the overall variety of radical transformations in a bubbling-type process can be described by Scheme 1.

Scheme 1.



Reaction paths: 4 and 5 – two independent paths of $RO_2^\bullet$ transformation; 7 and 8 – two independent paths of $RO^\bullet$ transformation into ROH and RHO, corresponding to dimethylbenzyl alcohol and acetophenone, respectively; In – various inhibitor types (including In, its radical $In^\bullet$, InH, “adhesions,” strong, weak, and synergism of two or more inhibitors and/or retarders). For the sake of simplicity, reaction paths for $R^\bullet$ formation are not indicated in Scheme 1.

The simplified Scheme 1 allows understanding of the roles played by the inhibitors at every step of bubble-type cumene oxidation (Figs. 1 and 2), beginning with an induction period (I), and ending with a period where cumene hydroperoxide (CHP) concentration in the reaction mixture apparently declines (IV).

The impact of inhibitors on the reaction during the induction period of cumene oxidation is considered in [4]. It is nevertheless worth mentioning that the changes in hydroperoxide formation rate, and in selectivity value observed when the cumene conversion rate and, correspondingly, the hydroperoxide concentration are very low, ultimately originate from the concentration of radicals $R^\bullet$ and $RO_2^\bullet$ at a kinetic equilibrium, that is only disturbed by transformations of these radicals according to the inhibitor-free reaction paths 1, 2 and 4, 7, as well as by the inhibitor-involving paths 5, 8, and 9, as indicated in the simplified Scheme 1, above.

At the second oxidation step (region II in Fig. 1), when the radical chain is well developed, the radical concentration is sufficiently high, and the concentration of inhibitors is small (i.e., when the condition of $([R^\bullet] \& [RO_2^\bullet]) \gg [In]$ is met), the bubbling-type cumene oxidation reaction proceeds with high selectivity (when estimated as a total value provided by both O_2^{gas} and O_2^{liquid} paths), despite the growing degree of cumene conversion. In this case, radical transformation in the liquid phase basically follows reaction paths 1 and 2, as well as, though to a less significant extent, paths 4 and 6 (as is denoted in Scheme 1), while the contribution of paths 5, 8, and 9 is almost negligible. The low concentration of inhibitors/retarders at this step of bubbling-type oxidation predetermines an unchanging and linear trend of the resultant (with the participation of both O_2^{gas} and O_2^{liquid} paths) hydroperoxide formation rate, and a sufficiently high selectivity. However, in commercial practice, the condition of $([R^\bullet] \& [RO_2^\bullet]) \gg [In]$ is only satisfied within a very narrow range of cumene conversion rate, corresponding to a hydroperoxide concentration range limited to between about 4–5 wt % and about 18–20 wt %, which is substantially narrower than that shown in Fig. 1. Moreover, as is noted in [5], this range becomes even more contracted with an elevation of process temperature and process pressure (and, correspondingly, of the concentration of dissolved oxygen), due to a faster accumulation of inhibitors, expressed by a transfer from the case of $([R^\bullet] \& [RO_2^\bullet]) \gg [In]$ to the condition of $([R^\bullet] \& [RO_2^\bullet]) \le [In]$.

Step III, corresponding to region III in Fig. 1, features a noticeable slowdown of the resultant hydroperoxide formation reaction rate, and a significant increase in the amount of by-products formed. With an increase in cumene conversion, an oxidation process passes over the point when hydroperoxide concentration rise equals zero, i.e., $d[CHP]/dt = 0$. Oxidation finishes with step IV, where hydroperoxide concentration in the oxidized products substantially falls (Fig. 1). The oxidation pattern described above is widely known for reactions utilizing cumene as well as other hydrocarbons as a feed, as is noted in [2], but, to the best knowledge of the author of this article, neither the true reasons for the occurrence of limiting concentrations of various hydroperoxides and for the point of $d[\text{Hydroperoxide}]/dt = 0$ (in the particular case of cumene hydroperoxide, $d[CHP]/dt = 0$) with an increase in the degree of hydrocarbon conversion, nor the core essence of radical transformations at each of these steps, have ever been investigated. The causes of the anomalous increase in the quantities of by-products during step III (as opposed to step II, with its highly developed radical chain and small concentration of inhibitors in the reaction mixture), have also never been subject to in-depth research.

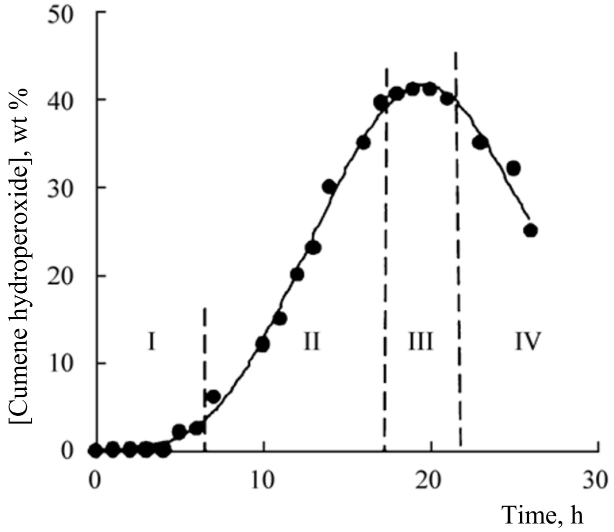


Fig. 1. Determination of cumene hydroperoxide concentration limit at $T = 110°C$, $P = 0.5$ MPa: (I) Induction period; (II) Developed chain; (III) Hydroperoxide concentration limit (plateau); (IV) Decay of reaction.

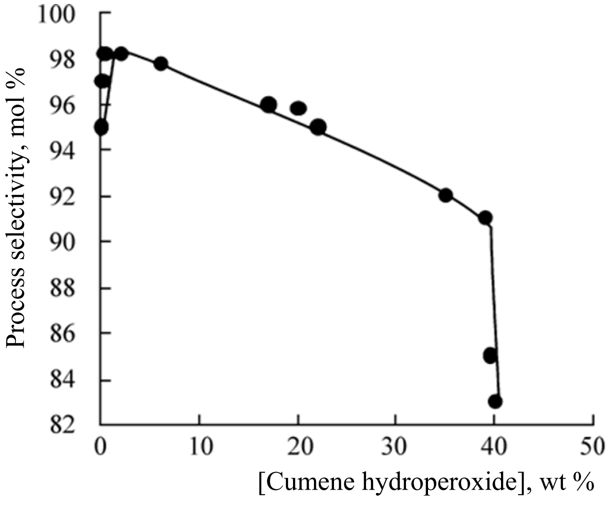


Fig. 2. Process selectivity vs. hydroperoxide concentration in the experiment without pre-removal of inhibitors.

The generally recognized scheme, simplistically expressed as: Cumene → Cumene hydroperoxide → Dimethylbenzyl alcohol, is obviously irrelevant as a model for explanation, or prediction, of reaching a maximum hydroperoxide concentration ($[\mathrm{CHP}]_{\mathrm{limit}}$), of attaining a point where $dW_{\mathrm{HP}}/dt = 0$, and of a complete "decay" of hydroperoxide formation (as can be seen in Fig. 1), for a developed chain of radicals. Moreover, all of these phenomena (i.e., $[\mathrm{CHP}]_{\mathrm{limit}}$, $dW_{\mathrm{HP}}/dt = 0$, and decay of hydroperoxide formation) are in total contradiction with the experimentally proven fact that the contribution of reaction paths 4 and 6 to the formation of by-products (indicated as "ROH" in Scheme 1), in the course of degenerate branched chain and hydroperoxide thermal decomposition reactions, is insufficient for the kinetically equilibrium concentration of newly-formed radicals $\mathrm{RO}_2^{\bullet}$ to completely shift towards ROH (see path 7 in Scheme 1).

The only possible rationale for the anomalous slowdown of ROOH formation at step III, is supported by an assumption of the existence of at least one more independent path of $\mathrm{RO}_2^{\bullet}$ expenditure (see reaction path 5 in Scheme 1), which to a significant extent disturbs and affects the kinetic equilibrium state of the radicals. This path comprises a reaction between radicals $\mathrm{RO}_2^{\bullet}$ and inhibitors formed in the course of oxidation reactions. With an increase in the degree of cumene conversion, in temperature, and in the concentration of dissolved oxygen, the concentration of inhibitors grows, thus suppressing the hydroperoxide formation rate. The above assumption is substantiated by the public revelation, in references [2, 6–12], of the occurrence of reactions between radicals and inhibitors with formation of molecular products $\mathrm{RO_2In}$, including the statement that a strong inhibitor "can even stop a chain reaction."

Based on the data presented in Figs. 1 and 2, a conclusion can be readily drawn that an increase in the degree of cumene conversion leads to two chemical reactions occurring in the opposite directions. On the one hand, a rise in cumene conversion rate and in hydroperoxide concentration promotes a simultaneous increase in $\mathrm{RO}_2^{\bullet}$ concentration in accordance with reaction path 3 (see Scheme 1). On the other hand, cumene oxidation yields phenol acting as inhibitor [2] and aldehydes that act as retarders, the concentration of which grows with an increase in the degree of cumene conversion, thereby reducing the $\mathrm{RO}_2^{\bullet}$ concentration along reaction path 5.

The significant retarding influence of benzaldehyde and butyraldehyde on the hydroperoxide formation reaction rate is demonstrated in [4]. The reported data is more of a qualitative, rather than of a quantitative nature, because, as the test runs progressed, the concentrations of aldehyded gradually decreased, as a result of their oxidation into corresponding acids. However, under the studied conditions, the degree of conversion of aldehydes was far from 100%, and their retarding effect on the hydroperoxide formation rate remained noticeable even at the end of test runs. The failure of formed aldehydes to be converted completely, and their retarding impact on oxidation rate, as well as the negative effect of aldehydes on process selectivity, were also conclusively proven by commercial practice of cumene oxidation processes (Not surpriseingly, pre-removal of aldehydes formed during the cumene oxidation stage, resulted in an appreciable acceleration of reaction rate, and in a considerable increase in selectivity value [5]). In particular, the incompleteness of aldehyde conversion into respective acids, including conversion of even very reactive aldehydes such as $\mathrm{CH_2O}$, was clearly evidenced by the necessity to utilize costly purification not only of cumene recycle streams, but also of desired end products of a phenol process, to remove aldehydes therefrom.

It appears, based on [2, 6–12], that inhibitors can play a similar role, reducing the concentration of radicals $\mathrm{R}^{\bullet}$ (reaction path 9), which in turn will lead to a decrease in the concentrations of $\mathrm{RO}_2^{\bullet}$ and, ultimately, in the content of ROOH. As a result, the rate of ROOH (i.e., hydroperoxide) formation at the end of step II, and during step III, slows down due to the parallel occurrence of the reactions between radicals $\mathrm{R}^{\bullet}$ and $\mathrm{RO}_2^{\bullet}$ and inhibitors by independent paths 5 and 9 (see Scheme 1).

Under the condition of ($[\mathrm{R}^{\bullet}]$ & $[\mathrm{RO}_2^{\bullet}]$) $\ll$ [In], the by-product formation rate accelerates primarily along reaction path 5, because, as is stated above, reaction paths 4 and 6 make a relatively minor contribution to the formation of radicals $\mathrm{RO}^{\bullet}$, responsible for appearance of by-products, judging from the insignificant concentration of by-products at step II (see Fig. 1). As a consequence, with an increase in the In concentration, a relatively small concentration of radicals $\mathrm{RO}_2^{\bullet}$ is established at kinetic equilibrium, at which the net hydroperoxide concentration rise is equal to zero ($d[\mathrm{CHP}]/dt = 0$) and, thus, hydroperoxide concentration reaches its limiting value ($[\mathrm{CHP}]_{\mathrm{limit}}$) during step III, when attempts to increase the cumene conversion value are made. In parallel to the decrease in concentration of $RO_2^•$, and their transformation into $RO^•$ (by reaction paths 4, 5, and 6), the concentrations of by-products (ROH) grow (due to reaction paths 7 and 8), with path 8 having a dominant influence, as compared to paths 4, 6, and 7. In the actuality, the two processes – namely, $RO_2^•$ formation and $RO_2^•$ expenditure (both with and without the participation of inhibitors) – occur in the opposite directions, resulting in the abovementioned change in the relationship ($([R^•] \& [RO_2^•])/[In]$) and, correspondingly, in the significant deceleration of hydroperoxide formation, in the attainment of the its concentration limit (see Fig. 1), and in the increase in the formation rates and the quantities of by-products. The latter, in turn, leads to the serious loss of process selectivity with an increase in the degree of cumene conversion (see Figs. 2 and 3).

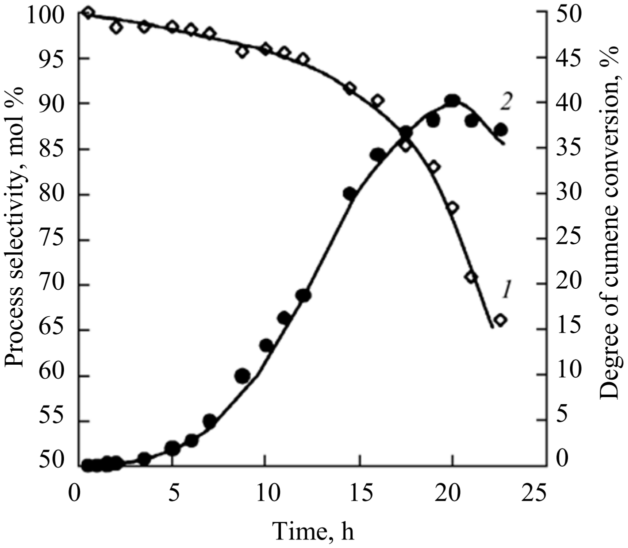


Fig. 3. Magnitude of (*1*) process selectivity and (*2*) degree of cumene conversion into cumene hydroperoxide over oxidation steps I through IV.

At step IV (as illustrated in Fig. 1), during which analytically tractable hydroperoxide concentration apparently declines, while inhibitors continue to grow in quantity, the only distinction of the pattern of radical transformations, as compared to step III, is that the hydroperoxide formed in the course of steps II and III is mainly expended along reaction path 3, with subsequent transformation of radicals $RO_2^•$ by paths 4 trough 8 (see Scheme 1). However, it should be pointed out that, although analytically tractable hydroperoxide concentration in the oxidized products consistently declines, the formed inhibitors are not meant to have completely stopped the radical chain reaction, and the cumene oxidation process as a whole. This presumption is supported by the data depicted in Fig. 3, which also serves to refute the existing notion that a chain reaction would be completely stopped by the presence of inhibitors/retarders, such as phenol or aldehydes, or by large quantities of inhibitors. If, during the step of decline in hydroperoxide concentration, by-products had only been formed from hydroperoxide, then the degree of cumene conversion would have had to be a constant value, and its differential would have had to equal zero when cumene expenditure into any chemical reactions stops, while, in actuality, judging from curve *2*, it never reaches zero, despite the complete "decay" of hydroperoxide formation.

In addition, the material balance reveals that, within the hydroperoxide concentration decline region (region IV in Fig. 1), the total actual expenditure of cumene into formation of the reaction products is 1.5×10^{-2} mol l^{-1}, whereas the cumene equivalent of hydroperoxide expenditure into formation of the same reaction products, evaluated by deduction: $[CHP]_{limit} - [CHP]_i$, equals 0.39×10^{-2} mol l^{-1}, i.e., about 3.8-fold less, as compared to the actual quantity of the products formed. It should be noted that both the actual cumene expenditure and the cumene equivalent of hydroperoxide expenditure were measured with the same level of accuracy, and the difference between these two components of the material balance extends far beyond the margin of a methodological error in estimation of the concentrations of hydroperoxide and of the by-products (including dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide). In view of the above considerations, it becomes clear that such a considerable difference (i.e., 3.8 times) would never be possible, unless formation, along with expenditure, of hydroperoxide occurred simultaneously. This discovery serves as convincing evidence of the fact that radical formation, leading to formation of hydroperoxide, takes place during all of the considered cumene oxidation steps, as are indicated in Fig. 1, including step III ($d[CHP]/dt = 0$) and step IV ($d[CHP]/dt \ll 0$), and not only during step II, where the condition of $d[CHP]/dt \gg 0$ is met. Consequently, the value of W_{HP}, which is derived from the variation in hydroperoxide concentration in the oxidation mixture, actually represents the difference between hydroperoxide formation rate and hydroperoxide expenditure rate for all of the cases under discussion.

Even more convincing proof of the fact that an oxidation process does not cease after hydroperoxide

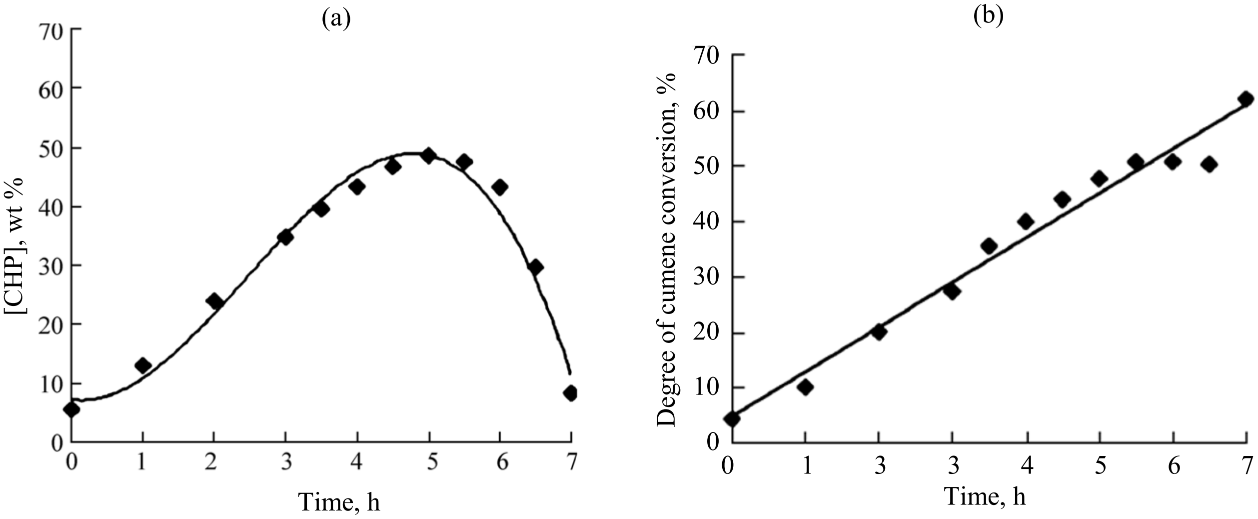


Fig. 4. (a) Formation and expenditure of hydroperoxide and (b) degree of cumene conversion as a function of time: $T = 125°C$, $P = 0.4$ MPa.

concentration reached its limiting value ($[CHP]_{limit}$) and then, during step IV, dramatically declined, is illustrated by the graphs provided in Fig. 4.

It can be clearly seen that, despite the hydroperoxide concentration reaching its limiting value of about 52 wt %, and then drastically declining from about 48.5 to about 8.3 wt % (Fig. 4a), the degree of cumene conversion continues growing (Fig. 4b). At this point in the process, the major contribution to the formation of by-products (dimethylbenzyl alcohol, acetophenone, and dicumyl peroxide) is made by inhibitors, such as phenol, the concentration of which rises over this period by a factor of 29.2, while the contribution of the reactions of hydroperoxide thermal decomposition and its conversion into the by-products is no higher than about 15% relative to the overall amount of the resultant by-products. The latter figure has been specifically verified in an individual test that was performed in the absence of oxygen, at $[CHP]_0 = 48$ wt %. The above facts are relevant in that they confirm that the most profound impact on the deceleration of hydroperoxide formation rate, on the decline in the cumene conversion rate, and on the formation of by-products, is exerted not so much by the hydroperoxide thermal decomposition reactions, but more by the simultaneous reactions between radicals $R^\bullet$ and $RO_2^\bullet$ and inhibitors, by two independent reaction paths 5 and 9 (see Scheme 1). During the cumene conversion steps I through IV (as indicated in Fig. 1), these simultaneous reactions change the ratio between the concentrations of radicals and inhibitors, starting from the condition of $[R^\bullet]$ & $[RO_2^\bullet]) \gg [In]$ at step I, and finishing with the condition of $([R^\bullet]$ & $[RO_2^\bullet]) \leq [In]$ at step IV.

The previously (and mistakenly) accepted erroneous notion that an oxidation process would be completely stopped upon reaching the point of $[CHP]_{limit}$, $dW_{HP}/dt = 0$, and $d[CHP]/dt < 0$, may evidently be explained by the failure of the researchers to take into account the total variety of the products formed, as well as by their inability to make a complete material balance due to the lack, at that time, of precision methods for measuring by-products. The same explicable and excusable failures led to an erroneous classical assumption that "hydroperoxide destruction does not begin before the maximum [hydroperoxide concentration limit] is reached" and that this "[destruction] leads to formation of products of deeper oxidation" [13]. The obtained experimental data of cumene oxidation, has clearly demonstrated that the "destruction" of cumene hydroperoxide (or, more specifically, transformation of $RO_2^\bullet$), proceeds during all of the four oxidation steps. Additionally, analytical tests of the yielded by-products revealed that the "destruction" of cumene hydroperoxide in fact results in formation of products of less deep oxidation, primarily dimethylbenzyl alcohol, dicumyl peroxide, and acetophenone. Formation of these products occurs in accordance with the hydroperoxide conversion reaction paths 3 and 6, as well as by the radical transformation reaction paths 4, 7 and 5, 8 (see Scheme 1, above). On the contrary, no products of deep oxidation have been detected by the author of this article, even in the so-called "heavies" that remain in a very small percentage after completion of the downstream process stage of concentrating the hydroperoxide (more specifically after stripping of cumene and a significant portion of hydroperoxide).

The distinction of the radical chain reactions at step IV, is that the net effect of the two simultaneous processes occurring in the opposite directions – hydroperoxide formation and hydroperoxide expenditure, or formation and expenditure of $RO_2^\bullet$ – shifts towards formation of radicals $RO^\bullet$ and molecules of ROH and RHO (corresponding to dimethylbenzyl alcohol and acetophenone, respectively), rather than towards appearance of ROOH. Moreover, the only parameter that varies to a significant extent in the course of step I through step IV, and simultaneously, though in opposite directions, affects both hydroperoxide formation reaction rate and process selectivity, is the concentration of newly-formed retarders/inhibitors, which consistently grows with the progress of an oxidation process. This observation naturally suggests that the declines both in hydroperoxide formation rate and in process selectivity are primarily caused by the presence of inhibitors and retarders and, more specifically, are explained by their power, efficiency, and quantitative relationships $[R^\bullet]/[In]$ and $[RO_2^\bullet]/[In]$ under the conditions of $([R^\bullet]\ \&\ [RO_2^\bullet]) \ll [In]$.

Conclusive and hardly disputable evidence of the crucial impact of retarders/inhibitors (as opposed to the common presumption of the hydroperoxide concentration and chain termination reactions having the key effects) over the entire course of the four oxidation steps, as well as of the critical importance of the relationship $([R^\bullet]\ \&\ [RO_2^\bullet])/[In]$ for hydroperoxide formation rate and for selectivity value, was obtained through a series of tests, in which retarders/inhibitors accumulated during steps I, II, and III, were removed from the reaction mixture after cumene hydroperoxide concentration had reached its limiting value ($[CHP]_{limit} \approx 40$ wt %) and hydroperoxide formation had "decayed".

The data presented in Fig. 5 (line *2*), clearly demonstrates that, despite the achievement of a hydroperoxide concentration limit (about 40 wt %), hydroperoxide formation rate recovers, after removal of inhibittors, until it reaches its maximum point, i.e., the same value as was attained for a lower hydroperoxide concentration (4–20 wt %) during step II (see Fig. 1 and Fig. 5, curve *1*), which featured a small concentration of inhibitors and a developed chain of radicals. Moreover, when inhibitors were removed, hydroperoxide concentration grew to about 64 wt %, without any apparent declining trend, and the dW_{CHP}/dt relationship was linear within the entire studied range of hydroperoxide concentration (i.e., about 40 to about 64 wt %), as opposed to the occurrence of steps III and IV in the case of an increasing concentration of retarders/inhibitors. If the reactions of termination of the radical chain ($RO_2^\bullet + R^\bullet$ and $RO_2^\bullet + RO_2^\bullet$, with formation of ROOR), 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 $2RO^\bullet$) were responsible for the crucial impact, then, in view of the substantial growth in hydroperoxide concentration from about 40 to about 64 wt %, the pre-removal of retarders/inhibitors would lead to a significant increase in the amounts of the chain termination products, and in particular of ROOR and ROH (i.e., by-products of cumene oxidation, such as dicumyl peroxide, dimethylbenzyl alcohol, and acetophenone). However, the experimental results have demonstrated that, in the actuality, the relative quantity of the by-products in the equivalent of newly-formed hydroperoxide was appreciably lower when hydroperoxide concentration reached 64 wt %, than it was at hydroperoxide concentration of 40 wt % (the value corresponding to the point of "cessation" of the oxidation reaction in the presence of inhibitors/retarders and of reaching $[CHP]_{limit}$, as is expected by the supporters of the classical assumptions).

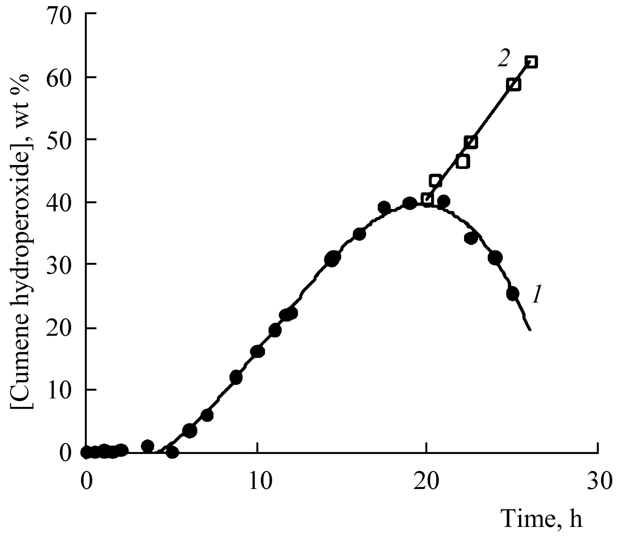


Fig. 5. Cumene Oxidation at $T = 110$ °C; $P = 0.5$ MPa: (*1*) Cumene, without pre-removal of inhibitors, (*2*) Inhibitor-free oxidate.

The dominant influence of retarders/inhibitors is further confirmed by the fact that, with retarders/inhibitors removed, substantially no declining trend of cumene oxidation selectivity was observed within the specified studied range of hydroperoxide concentration: about 83 mol % was reached for 40 wt % of hydroperoxide, while an unusually high value of about 84 mol % was demonstrated for a surprisingly large hydroperoxide concentration of 64 wt %. Furthermore, the lack of a major decline in process selectivity at a large hydroperoxide concentration (upon preremoval of retarders/inhibitors) proves the fallacy of the common notion that, with an increase in the degree of cumene conversion, both the existence of a limiting hydroperoxide concentration and the low selectivity value are explained by the effects of hydroperoxide as a reaction intermediate. As is demonstrated by the experimental results above, preremoval of retarders/inhibitors was relevant, resulting in elimination of the crucial negative impact, and thus allowed the hydroperoxide concentration limit to be overcome, i.e., increasing the degree of cumene conversion and simultaneously raising hydroperoxide concentration by as much as about 1.5 times, without a substantial loss in process selectivity, as compared to step III.

In terms of the radical transformations defined by Scheme 1, the aforementioned discovery can be interpreted as follows. When retarders/inhibitors, including phenol, aldehydes, and acids, are removed, any radical transformations by reaction paths 5, 8, and 9 substantially cease (or, at least, are minimized), so that the hydroperoxide formation reaction proceeds unimpeded by paths 1 and 2. The latter leads to a recovery of hydroperoxide formation rate from its lowest level (dW_{CHP}/dt = min), which was observed at step III with a high inhibitor concentration, to its utmost level (dW_{CHP}/dt = max), equal to the rates occurring at step II with a small content of inhibitors. Therefore, the experimental data graphically illustrated in Figs. 1–5, as well as the conclusions drawn thereupon, are fully consistent with, and thus completely confirm the correctness of, the general scheme of transformations of radicals developed above, for any (low, medium, and high) concentration of inhibitors in the cumene feed.

It is worth mentioning that the low content of retarders/inhibitors is the only case where discarding the contribution of reaction paths 4, 6, and 7 (see Scheme 1) to the selectivity loss would be unacceptable. On the contrary, at a relatively high concentration of inhibitors, the growth in by-product quantities is mostly attributable to reaction paths 5 and 8, as well as to path 9, which leads to a slowdown of hydroperoxide formation rate along reaction paths 1 and 2. As a result, minimization, by pre-removing retarders/inhibitors, of radical transformation paths 5 and 8 predictably reduces the amounts of by-products in relation to the quantity of hydroperoxide (which increases due to reaction paths 1 and 2). This triggers an enhancement of process selectivity, as compared to steps III and IV, where the selectivity value dramatically falls with a rise in retarder/inhibitor concentration, as is shown in Figs. 2 and 3.

However, a growth in the degree of cumene conversion, with hydroperoxide content held within a range of about 40 to about 64 wt %, which implies an increase in $\mathrm{RO}_2^{\bullet}$ concentration, predictably intensifies reaction paths 4, 6, and 7, which comprise $\mathrm{RO}_2^{\bullet}$ transformation into $\mathrm{RO}^{\bullet}$ and subsequent conversion of the latter into ROH and RHO, which represent the major oxidation by-products. Nonetheless, reaction paths 4, 6, and 7 bring a markedly lesser contribution to the loss of selectivity, than reaction paths 5 and 8. This fact is convincingly substantiated by experimental data obtained during step II, which is characterized by a relatively low yield of by-products, as well as by data for steps III and IV, where the yield of by-products reaches anomalously high values due to the occurrence of reaction paths 5 and 8, that are emphatically affected by retarders/inhibitors.

An oxidation pattern similar to that illustrated in Fig. 1, including the trend of hydroperoxide concentration rate variation with an increase in [In], the existence of a hydroperoxide concentration limit (corresponding to the case of $dW_{\mathrm{CHP}}/dt = 0$), and overcoming of the $[\mathrm{CHP}]_{\mathrm{limit}}$ hurdle upon pre-removal of retarders/inhibitors from the cumene feed, was also obtained for process temperatures of 120°C and 125°C, and for a wide range of process pressure values (in particular, under 0.1 MPa, 0.3 MPa, 0.5 MPa, and 0.8 MPa) [4, 5]. The latter serves as additional evidence supporting the theory that a change in the relationship $([\mathrm{R}^{\bullet}]\ \&\ [\mathrm{RO}_2^{\bullet}]\ \&\ [\mathrm{RO}^{\bullet}])/[\mathrm{In}]$, as well as the influence of this relationship on dW_{CHP}/dt, and on the values of cumene conversion and process selectivity, are regular and predictable, and not incidental, at least within the studied range of process conditions.

A similar picture of dominant impact of retarders/inhibitors, in comparison with other paths of radical transformations in the oxidation medium, was established in a series of experiments in which different pressure values were selected (and, correspondingly, the concentration of dissolved oxygen varied), while the degree of cumene conversion was held constant (see Fig. 6). An about 10-fold increase in the concentration of dissolved oxygen in the cumene feed, led to a growth in the contents of dimethylbenzyl alcohol and acetophenone by about 300% and about 200% (relative), respectively, and to a consequent loss in selectivity value. A similar picture was also observed with respect to inhibitors formed, such as phenol and aldehydes: their concentration rose with an increase of oxygen concentration in the oxidized products, thereby causing a decline in the magnitude of selectivity [5]. Therefore, at a high concentration of dissolved oxygen, the condition of $([R^\bullet]\ \&\ [RO_2^\bullet]) \ll [In]$ is satisfied, and by-products are formed by two independent paths of radical transformation, one of which is reaction path 5, and the other comprises reaction paths 4 and 7 (as defined by Scheme 1), thus naturally resulting in a decline of selectivity at the same degree of cumene conversion (about 20%) (Fig. 6). On the contrary, when the condition of $([R^\bullet]\ \&\ [RO_2^\bullet]) >> [In]$ is met, by-products are basically formed by the only radical transformation path represented by reaction paths 4 and 7, allowing the cumene oxidation reaction to occur with a higher selectivity, as can be seen for the low O_2^{liquid} concentration region in Fig. 6.

In the actuality, dissolved oxygen (O_2^{liquid}) has a more complex effect than is described above. On the one hand, it serves as a kinetic factor because an increase in O_2^{liquid} concentration speeds up hydroperoxide formation by reaction paths 1 and 2 covering reactions between radicals and oxygen. However, this acceleration only takes place until the concentration of dissolved oxygen reaches about 0.25 wt % (corresponding to pressure of 0.5 MPa). A further increase in O_2^{liquid} concentration (and, consequently, further pressurization) causes the hydroperoxide formation rate to reach its maximum value, as reported in [4], the reasons for which are explained in this article, as well as in [5]. On the other hand, an increase in O_2^{liquid} concentration leads to a dramatic growth in the concentration of retarders/inhibitors [5]. In this context, it should be kept in mind that the rate of inhibitor formation is not limited to any specific value, as opposed to the hydroperoxide formation rate, so that In concentration consistently grows with an increase in $[O_2^{liquid}]$, thus leading to a dominant role of reaction paths 5 and 8 (see Scheme 1), and therefore to accumulation of by-products and significant losses (by about 2.5 mol %) in process selectivity (Fig. 6).

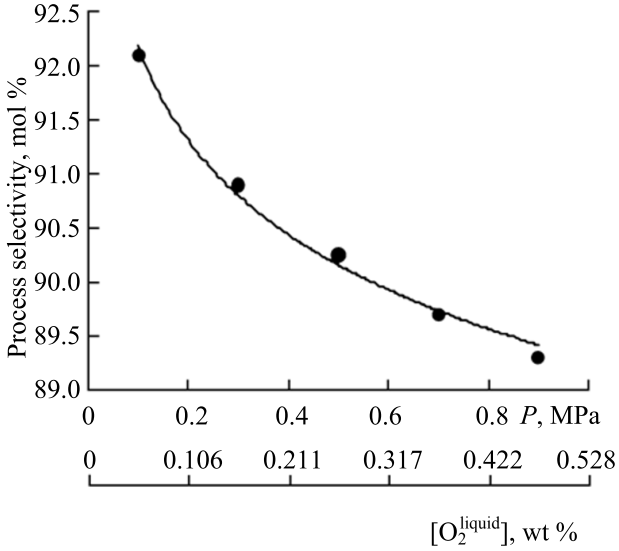


Fig. 6. Effect of pressure on the selectivity of bubbling-type oxidation at a constant degree of cumene conversion: $T = 110°C$.

The abovementioned dual impact of O_2^{liquid} is clearly demonstrated by the data presented in Figs. 7 and 8. In particular, Fig. 7 illustrates the trend of formation and expenditure of hydroperoxide in a closed system, when cumene is oxidized solely by dissolved oxygen, while Fig. 8 depicts the temporal variation in selectivity value at a relatively high oxygen concentration in the oxidized products, specifically under pressure of 0.5 MPa and temperature of 110°C. It becomes evident that process selectivity remains rather low (less than 90 mol %, see Fig. 8), both in the portion of hydroperoxide concentration growth (region *a* in Fig. 7) and, especially, in the portion of hydroperoxide concentration decline (region *b* in Fig. 7), despite the imposed temperature conditions that were atypically mild as compared to commercial practice of an oxidation process. The main reason behind this poor selectivity is the high O_2^{liquid} concentration in the oxidized products and, as a consequence, the vigorous formation of inhibitors, leading to intensification of reaction path 9, as well as of reaction paths 5 and 8.

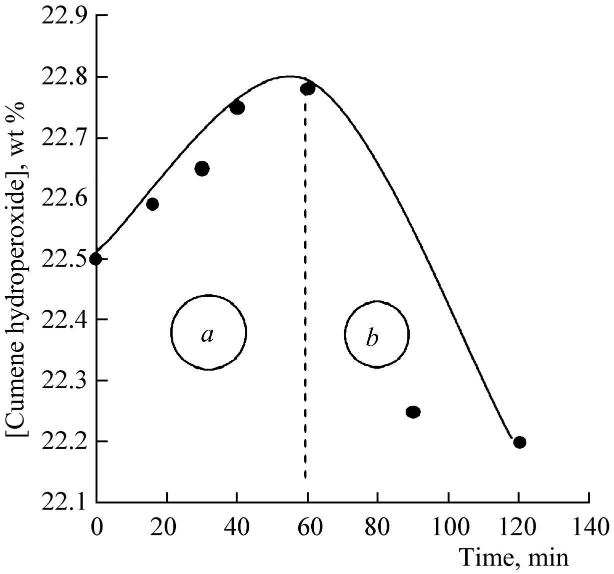


Fig. 7. Formation and expenditure of hydroperoxide in oxidation reactions promoted solely by O_2^{liquid}: at $T = 110°C$: (*a*) hydroperoxide concentration growth region; (*b*) hydroperoxide concentration decline region.

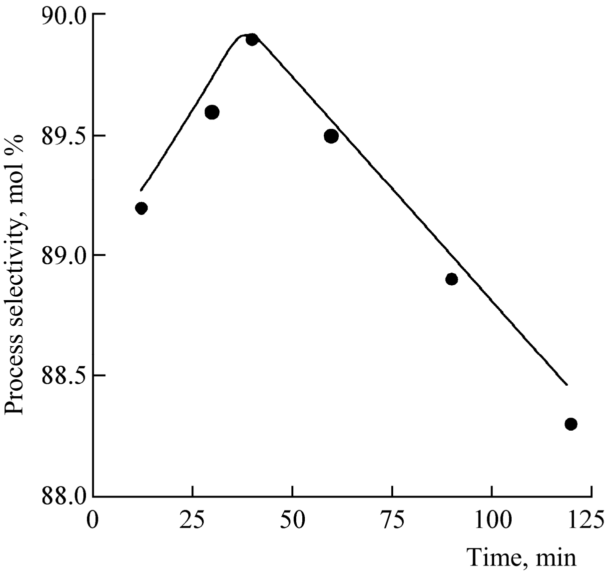


Fig. 8. Variation in selectivity value in the course of formation and expenditure of hydroperoxide, with oxidation reactions promoted solely by O_2^{liquid}: $T = 110°C$.

The pattern of O_2^{liquid} influence on the process is fully confirmed by commercial practice of various oxidation technologies under different pressure values, as is disclosed in [5]. On the one hand, an increase in process pressure, and correspondingly in O_2^{liquid} concentration, to certain values, raises the hydroperoxide output rate per unit volume of the reactor [5], which implies an acceleration of the reactions by paths 1 and 2. On the other hand, the growth of O_2^{liquid} concentration, over the entire range of O_2^{liquid} concentrations shown in Fig. 6, simultaneously, and to a significant extent, boosts the concentrations of both aldehydes and phenol, which are process inhibitors causing great losses in selectivity due to reaction paths 5 and 8 (see Scheme 1). Thus, the dual, i.e., both positive and negative, impact of dissolved oxygen is a challenge that encourages researchers to seek optimum process conditions for cumene oxidation. Without such process optimization, the positive role of O_2^{liquid} may be offset, as it takes place within region *b* in Fig. 7; indeed, with the prolongation of the reaction, hydroperoxide concentration drastically declines, while by-products are rapidly accumulated to great quantities, as is evidenced by the fall in selectivity in the graph of Fig. 8. Under different combinations of pressure and temperature, the core essence of the dependencies illustrated in Figs. 6–8 remains invariable, as is discussed in [5], thus proving the universal nature of radical transformations presented in Scheme 1, above.

The ultimate temperature impact on radical transformations and, therefore, on formation of hydroperoxide and by-products (Fig. 9) is to a great extent similar to the negative effect of dissolved oxygen, the concentration of which is in strong correlation with the resulting values of hydroperoxide formation rate and process selectivity. Under low temperatures, where retarders/inhibitors have not yet accumulated to appreciable amounts, the process mostly follows reaction paths 1 and 2 (see Scheme 1), yielding the desired hydroperoxide product, while paths 4, 6, and 7, giving rise to by-products, constitute a very limited part. This explains the high selectivity value thereof.

Under high temperatures, while reaction paths 1 and 2 are dramatically intensified and the hydroperoxide formation rate rises, retarders/inhibitors are also formed very rapidly. As a consequence, reaction path 5 (see Scheme 1), covering $RO_2^{\bullet}$ transformation into $RO^{\bullet}$ (or into ROIn), becomes more active, resulting in a predictable growth in by-product concentrations, and in selectivity losses.

Additionally, temperature elevation predictably leads to a more marked impact of reaction paths 3, 4, 6, and 7 (see Scheme 1), due to different effects of activation parameters (E_a, log A) on the rates of both the main and the side reactions [5]. However, in view of the fact that In concentration and temperature affect the process in the same negative direction (from the

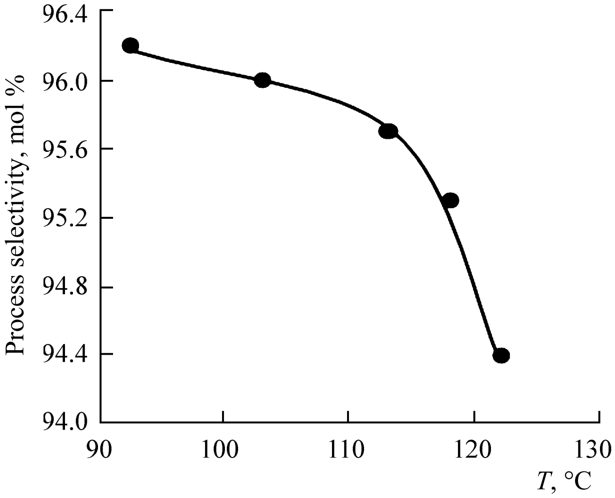


Fig. 9. Process selectivity as a function of temperature at constant degree of cumene conversion: $P = 0.5$ MPa.

viewpoint of by-product formation), the combined impact of these two factors on $RO_2^•$ transformations leads to a significant decrease in the selectivity of cumene oxidation in the case of $[RO_2^•] \gg [In]$, not to mention the condition of $[RO_2^•] \ll [In]$, thus even faster pushing the "decay" of the oxidation process, decreasing the value of $[CHP]_{limit}$, lowering the hydroperoxide output rate per unit volume of the reactor [5], and significantly deteriorating process selectivity. A comparison of a low-temperature option with a high-temperature option of cumene oxidation processes implemented in commercial reactors, as is reported in [5], fully supports the above discussion.

In particular, high temperature oxidation features a greater hydroperoxide output rate per unit volume of the reactor (i.e., a faster hydroperoxide formation rate and, correspondingly, a greater productivity), while also noticeably reducing the magnitude of selectivity through boosting the yield of by-products. Low temperature oxidation features a lower CHP output rate per unit volume of the reactor, while also reducing the yield of by-products. Extension of the residence time of the oxidized products in the reactors under low temperature, intended for increasing the hydroperoxide output rate, in fact leads to a growth in the amount of formed In, and to the condition of $[RO_2^•] \ll [In]$, thereby causing a decline of selectivity.

Therefore, the concentration of dissolved oxygen, process temperature, and the period of time during which the process occurs, are the factors that affect the amount of inhibitors formed in the course of the process, and that predetermine the variations in kinetic equilibrium states of radicals, which result in the observed occurrences, such as retardation of the hydroperoxide formation reaction, limitation of hydroperoxide concentration, and deterioration of process selectivity. The developed general scheme of radical transformations under the effect of In allows a qualitative, if not quantitative, understanding of the whole structure of oxidation reactions occurring during all of the four oxidation steps (as are depicted in Fig. 1), including the case in which retarders are subjected to removal from the oxidate at step III (see line *2* in Fig. 5). This scheme is also relevant as an explanation of the decline in process selectivity when temperature is elevated (Fig. 9), or when the concentration of dissolved oxygen (and process pressure) is increased (Fig. 6).

Taking into consideration the high reactivity of radicals $R^•$, as is noted in [2], and the well-known sequence of transformation of newly-formed radicals $ROO^•$ into by-products (ROH) in accordance with the simplified sequence of radical transformations (13), it may appear that the reaction between cumyl radicals and hydroperoxide molecules, rather than retarders/inhibitors, is the key factor that ultimately leads to the significant deceleration of hydroperoxide formation (ending with the case of $d[CHP]/dt = 0$ at step III, as indicated in Fig. 1), to the achievement of a hydroperoxide concentration limit ($[CHP]_{limit} \approx 40$ wt %), and to the serious loss in selectivity values (see Fig. 3), which is accompanied by the high concentration of $ROO^•$, and the consequent significant (precipitous) increase in the formation of by-products at a high degree of cumene conversion.

$$R^• + ROOH \rightarrow RH + ROO^• \rightarrow RO^• \rightarrow ROH. \quad (13)$$

However, this assumption has been refuted by the results of the test described above, which comprised pre-removing inhibitors during step III (by special treatment and washing of the oxidate), and subsequently subjecting the cumene feed, containing as high as about 40 wt % of hydroperoxide, to oxidation, so that the pure effects of cumyl radicals, in their theoretically possible reaction with hydroperoxide molecules, would be revealed. It was demonstrated (see Fig. 1) that the presence of retarders/inhibitors at step III led to the case of $d[CHP]/dt = 0$, while their removal provided the condition of $d[CHP]/dt \gg 0$. Moreover, the following advantages were observed in the absence of inhibitors, despite the increase in the concentrations of $R^•$ and ROOH: (a)

The oxidation reaction rate reached its utmost level ($dW_{HP}/dt = \max$), equal to the rates occurring at step II; (b) The oxidation reaction overcame the hydroperoxide concentration limit (as clearly demonstrated in Fig. 5), which could never be defeated in the presence of retarders/inhibitors (see Fig. 1); and (c) Hydroperoxide concentration grew from 40 to 64 wt % (see Fig. 5), while only a very minor decline in process selectivity was observed.

In the opposite case, i.e., if the reaction between $R^•$ and ROOH had been the only cause responsible for the reaction deceleration and the selectivity losses, then, in accordance with equation sequence (13), the removal of In at step III would have failed to accelerate hydroperoxide formation rate or to overcome the hydroperoxide concentration limit (whereas these effects were actually produced in the course of the test, as illustrated by line *2* in Fig. 5), and both hydroperoxide concentration and selectivity value would have continued to drastically decline, as it was observed during step IV (Fig. 1), and as it took place in other similar experiments that were carried out under different temperatures and different pressure values (and, correspondingly, different O_2^{liquid} concentrations) [4, 5].

The assumption of the responsibility of the reaction between cumyl radicals and hydroperoxide molecules for the deceleration of hydroperoxide formation and the selectivity losses, is additionally disproven by the results of the test which involved oxidation by O_2^{gas} under a very low temperature (23°C). These results demonstrated that, despite a growth in hydroperoxide concentration to about 45 wt % and, consequently, an increase in the concentrations of $R^•$ and ROOH, accompanied by a substantial absence of other retarders/inhibitors, the reaction rate did not decrease (see Fig. 2 in Article I). There was also no decrease in process selectivity, which instead remained almost constant (about 99 mol %) during the entire period of cumene oxidation (see run 4 in Table 4 of Article I). Moreover, the condition of $d[CHP]/dt = 0$, as well as a point of $[CHP]_{limit}$, which are typical of the increased retarder/inhibitor content case, were not attained during the abovementioned test.

The evidence discussed above, led to a conclusion that the contribution of the $[R^• + ROOH]$ reaction path to the slowdown of hydroperoxide formation rate, and to the decline in process selectivity, is negligible, as compared to that of the retarders/inhibitors. As a result, the reaction between ROOH and cumyl radicals $R^•$ has been excluded from the general reaction scheme, despite the assumption of the high reactivity of cumyl radicals [2, 13]. It is worth noting that the aforementioned discovery by no means disproves the notion postulated in [2, 13], with regard to high reactivity of $R^•$, in itself, but it serves as evidence that cumyl radicals are not capable of prevailing over the low reactivity of ROOH molecules, so as to form radicals $ROO^•$ and, ultimately, to decelerate hydroperoxide formation, to reach the points of $d[CHP]/dt = 0$ and $[CHP]_{limit}$, and to dramatically reduce the magnitudes of selectivity at step III and step IV (see Figs. 1 and 2), in contrast to the case that takes place in the presence of inhibitors accumulated in the oxidation mixture with an increase in the degree of cumene conversion.

The above-discussed experimental results have demonstrated that, adjustment of only one variable, such as raising the concentration of inhibitors in the cumene feed, changes the relationships $([R^•] \& [RO_2^•])/([In] \& [InH])$, and ultimately results in a significant reduction in the degree of cumene conversion and in hydroperoxide formation rate, in reaching of a $[CHP]_{limit}$ point, and in substantial losses of process selectivity (as illustrated by curve *1* in Fig. 5). On the contrary, pre-removal of inhibitors was found to develop the opposite set of results: acceleration of hydroperoxide formation rate, overcoming of the $[CHP]_{limit}$ point, and a very small decrease in selectivity value (see line *2* in Fig. 5). Therefore, the reactions between inhibitors and cumene hydroperoxide molecules, and the reactions between inhibitors and radicals $R^•$ and $ROO^•$, presented by reactions (3), (4), (14), and (15), below, should be added to Scheme 1. Of course, the reactions between radicals and inhibitors are more diverse than the complementary list presented below. However, this list provides a clear indication of the manner, as well as of the causes, of the above-described occurrences when the degree of cumene conversion increases.

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

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

$$InH + ROOH \rightarrow ROH + InOH, \qquad (14)$$

$$InH + ROO^• \rightarrow InO^• + ROH. \qquad (15)$$

A similar crucial effect of the relationships $([R^•] \& [RO_2^•])/([In] \& [InH])$, relevant to the liquid phase, was also observed in the case of cumene oxidation by O_2^{gas} under very mild process conditions ($T = 23°C$), accompanied by a substantial absence of inhibitors, which corresponds to a very small impact of reactions (3), (4), (14), and (15). Such conditions were favorable for reaching an unchanged hydroperoxide formation rate, a significantly higher hydroperoxide concentration, and an anomalously high selectivity of 99.7 mol % at hydroperoxide concentration of 45 wt %, as is discussed in [1], as well as for avoiding the challenge of $[\mathrm{CHP}]_{\mathrm{limit}}$ point which exists in the presence of inhibitors/retarders (see Figs. 1 and 3).

A review of the reactions between radicals $R^{\bullet}$ and molecules of O_2^{liquid} and O_2^{gas}, as well as of transformation of peroxide radicals with, or without, the participation of inhibitors/retarders in the liquid phase, provides a clear understanding of the substantial distinctions between the character of each reaction corresponding to each cumene oxidation step, of the difference in reactivity between O_2^{liquid} and O_2^{gas}, and of the key factors determining activation parameters and process selectivity. In particular, with "free radicals $R^{\bullet}$ being rather reactive," as is noted in [2, 13], these free radicals, coming into contact with O_2^{gas} at the liquid–gas interface, promote a successive formation of peroxide radicals and hydroperoxide, where hydroperoxide formation rate accelerates with an increase in interface area [1]. However, the short lifetime of formed radicals $RO_2^{\bullet}$, and the small value of their concentration at a kinetic equilibrium at the phase interface, greatly impede, and minimize, the reactions of $RO_2^{\bullet}$ transformation into $RO^{\bullet}$, and subsequent conversion of the latter into by-products (ROH and RHO). The lack of influence of the reaction medium (for example, in the form of solvating or inhibiting effect) on O_2^{gas} molecules, considerably lowers the energy barrier of the hydroperoxide formation reaction ($E_a \approx 16$ kcal mol^{-1} [1]). On the contrary, the high concentration of O_2^{liquid} molecules in the oxidized products, while accelerating the hydroperoxide formation rate, at the same time leads to a significant increase in the amount of newly-formed radicals $RO_2^{\bullet}$ that come in contact with inhibitors/retarders in the liquid phase, which results in predictable transformation of a major portion of $RO_2^{\bullet}$ into $RO^{\bullet}$, and then into ROH and RHO, thus reducing the selectivity value. It should be reminded, at this point, that the high concentration of inhibitors/retarders in the liquid phase, caused by the high concentration of O_2^{liquid}, noticeably boosts the formation of by-products, and thus has a significant impact on the selectivity of cumene oxidation. In addition, various effects of the reaction medium on O_2^{liquid} reactivity (including, but not limited to, solvation or a theoretically possible donor-acceptor interaction between, for example, hydroperoxide and O_2^{liquid} molecules), to a great extent elevates the energy barrier of the hydroperoxide formation reaction ($E_a \approx 26$ kcal mol^{-1} [1]). The elevation of energy barrier suggests a slowdown in the rates of formation of radicals $RO_2^{\bullet}$ and of hydroperoxide. All of the abovementioned factors affecting the reactions of cumene oxidation promoted by O_2^{gas} as opposed to O_2^{liquid}, result in variations in activation parameters and selectivity values, despite the generality of formation and transformation of the same radicals (in particular, of $R^{\bullet}$, $RO_2^{\bullet}$, and $RO^{\bullet}$).

In Scheme 1, reaction path 9, which involves transformations of radicals $R^{\bullet}$, is deliberately presented in a very simplified form, so as to focus on transformations of $RO_2^{\bullet}$ and $RO^{\bullet}$, responsible for formation of hydroperoxide and by-products. Reactions of radicals $R^{\bullet}$ were discussed in detail by many researchers, as is noted in [2, 6–13]. In accordance with the above references, radicals $R^{\bullet}$ can enter into reactions both with radicals formed in the course of degenerate branched chain reactions and with inhibitors:

$$R^{\bullet} + R^{\bullet} \rightarrow R\text{–}R, \quad (16)$$

$$RO_2^{\bullet} + R^{\bullet} \rightarrow ROOR, \quad (17)$$

$$R^{\bullet} + OH^{\bullet} \rightarrow ROH, \quad (18)$$

$$InH + RO_2^{\bullet} \rightarrow In^{\bullet} + ROOR, \quad (19)$$

$$In^{\bullet} + R^{\bullet} \rightarrow InR, \quad (20)$$

$$InH + R^{\bullet} \rightarrow In^{\bullet} + RH. \quad (21)$$

The occurrence of reactions (1), (3), (12), (13), and of (16) through (21), as well as of any similar reactions, results in a decrease in $R^{\bullet}$ concentration (see Scheme 1), thus reducing the amount of newly-formed radicals $RO_2^{\bullet}$, and consequently decelerating hydroperoxide formation.

The study discussed in this article, was intended neither for describing all possible reactions between radicals and inhibitors, nor for categorizing the specified reactions (or any other relevant reactions) into those of prevailing versus secondary impact, nor for uncovering any reactions that cannot occur under the considered process conditions. An exception was only given to the reactions of radicals: [$R^{\bullet}$ + ROOH] and [$ROO^{\bullet}$ + $ROO^{\bullet}$], with formation of by-products ROH, RHO, and ROOR, the extremely small contribution of which, to the formation of by-products, was conclusively demonstrated both within the proximity of the limiting hydroperoxide concentration (about 40 wt %, see Figs. 1 and 3) and at an anomalously high hydroperoxide concentration of about 64 wt % (see line *2* in Fig. 5). This conclusion is further supported by the fact that the abovementioned reactions provide far less contribution during oxidation step II (see Fig. 1), when the degree of cumene conversion is smaller and hydroperoxide concentration ranges from about 5 to about 20 wt %. This is the reason why the inclusion of reaction (13) in Scheme 1 (as reaction path 6) is merely nominal, while the ROOR formation from radicals $RO_2^\bullet$ is excluded completely, with very insignificant amount of ROOR formed in a commercially practiced bubbling-type oxidation process.

It is also worth mentioning that the paramount goal of the reported study was to investigate the phenomenology of cumene oxidation, carried out at various degrees of cumene conversion and under effects of various parameters, rather than to establish the kinetic regularities or to measure the specific rate constants of individual chemical reactions. In connection with the above-stated goal, an example of the revelation of the phenomenology of the simultaneous but opposite impacts of inhibitors on radicals $R^\bullet$ and $RO_2^\bullet$, is clearly demonstrated by recently obtained quantitative data on the effect of phenol addition on hydroperoxide formation rate (Fig. 10) in the absence of other retarders/inhibitors, the formation of which was almost prevented due to a very low temperature, the substantial avoidance of thermal decomposition reactions, and a low degree of cumene conversion. Under these conditions, the hydroperoxide-containing 99.7 wt % pure cumene feed was subjected to oxidation at the gas–liquid interface, by atmospheric oxygen delivered above the surface of the reaction mixture, without mechanical mixing of the phases. Therefore, oxidation occurred under the action of a high selectivity oxidizing agent (specifically O_2^{gas}), while O_2^{liquid} concentration in the liquid phase was at its lower limit, under pressure of 0.1 MPa.

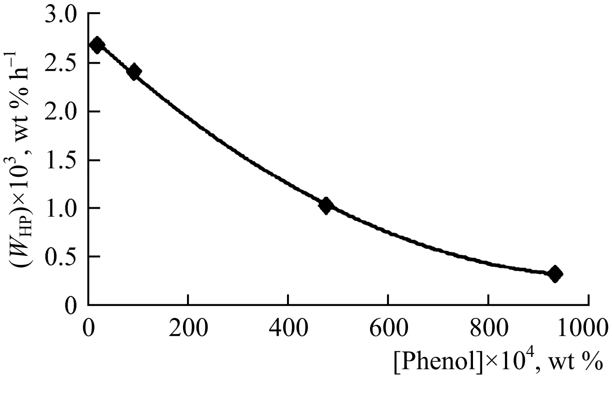


Fig. 10. Cumene hydroperoxide formation rate as a function of phenol concentration in cumene oxidation promoted by O_2^{gas} in a static regime: $T = 25°C$, $P = 0.1$ MPa, $[CHP]_0 = 10$ wt %, test run length = 924 h.

The obtained results, with regard to the slowdown of hydroperoxide formation rate, suggest that the decrease in the concentrations of $R^\bullet$ and $RO_2^\bullet$ was only caused by addition of phenol. The about 9-fold slowdown of reaction rate (W_{HP}), as was observed when phenol addition was increased (Fig. 10), is only explained by the reaction between phenol and radicals $R^\bullet$, while the sole cause of the acceleration in the formation of by-products and of the selectivity losses (see Fig. 3 [1]) is the interaction between radicals $RO_2^\bullet$ and phenol acting as inhibitor, as described by reaction (22).

$$RO_2^\bullet + In \rightarrow RO^\bullet + InO. \qquad (22)$$

As was illustrated in the previous discussion, under the exceptionally mild conditions ($T = 25°C$), when all of inhibitors other than phenol are substantially absent, the phenol impact manifests itself in decelerating the hydroperoxide formation rate (immediately caused by a reduction in $RO_2^\bullet$ concentration); and in accelerating the by-product formation rate (as is readily explained by an increase in $RO^\bullet$ concentration, and correspondingly deteriorating the process selectivity). This discovery clearly demonstrates the crucial role of the relationship between the concentrations of radicals and inhibitors: $([R^\bullet]\ \&\ [RO_2^\bullet])/([In]\ \&\ [InH])$, during the considered steps of cumene oxidation.

The different effects of various inhibitors on the rates of both the main and the side reactions, which are determined by varying relationships $([R^\bullet]\ \&\ [RO_2^\bullet])/([In]\ \&\ [InH])$ during the considered cumene oxidation steps, are relevant as a clarification of the true causes of a number of scenarios observed, such as:

(a) the low degree of cumene conversion;

(b) the decrease in selectivity value with an increase in the degree of cumene conversion;

(c) the existence of a limiting (maximum) hydroperoxide concentration; and

(d) the very dramatic deceleration of hydroperoxide formation rate and the abrupt decrease in process selectivity after the limiting hydroperoxide concentration is reached.

The clarification of these causes is certainly both of theoretical interest and of practical importance, especially with regard to implementation, in a commercial cumene oxidation process, of various corresponding novel techniques and approaches discussed in this article.

5. The dual impact of inhibitors and retarders in the cumene oxidation reaction. The veracity of the above-stated conclusions, and particularly of the fact that inhibitors are a crucial factor responsible for the limiting value of cumene conversion, for the decrease in selectivity value with an increase in the degree of cumene conversion, and for the existence of a limiting hydroperoxide concentration, is supported by the discovery, in earlier research efforts [14–18], of the predominant role of inhibitors as effective antioxidants for a broad range of hydrocarbons, consisting of jet engine oils, diesel oils, gas oil, and synthetic oils. Bearing in mind the substantial difference between cumene, as an individual hydrocarbon, and the abovementioned broad range of hydrocarbons, and taking into account the apparent difference between the oxidation mechanisms relevant to the respective hydrocarbons, it should nonetheless be noted that the roles of inhibitors in the compared processes are identical in the purely chemical aspect: they interact with radicals $R^{\bullet}$ and $RO_2^{\bullet}$ formed in the course of the process. For this particular reason, with regard to a cumene oxidation process, a decrease in the amount of newly-formed inhibitors (by means of their removal and the shift of the hydroperoxide formation reaction towards O_2^{gas}) results in an acceleration of hydroperoxide formation, in the overcoming of hydroperoxide concentration limit, and in an enhancement of cumene oxidation process selectivity. On the contrary, an increase in the concentration of inhibitors (by means of their purposeful introduction from outside the process, as is reported in [14–18] for the case of oxidation of hydrocarbons) becomes effective in decreasing the concentrations of radicals $R^{\bullet}$ and $RO_2^{\bullet}$, which are undesired for the particular applications under consideration, through the reactions between these radicals and the inhibitors, that eventually suppresses the oxidizability and the formation of undesired products having a negative effect on the stability of fuels and oils. Thus, along with their commonly known function as modifiers of oxidation rate, inhibitors are also responsible for the increase in the by-product formation rates.

Based on the discussion above, it is evident that inhibitors actually play a dual role in the course of hydrocarbon oxidation: by their nature, they decelerate the process, while at the same time they perform an opposite function of accelerating the conversion of radicals $RO_2^{\bullet}$ into undesired by-products. Moreover, a stronger slowing effect of an inhibitor on the oxidation reaction is accompanied by its more significant accelerating action on the reactions of formation of by-products. This dual impact is clearly demonstrated in the discussion of the tests performed under very mild conditions of cumene oxidation with addition of phenol (see Fig. 3 [1] and Fig. 10).

Conducting the process under mild conditions (including the lowest possible concentration of O_2^{liquid}, in compliance with the lowest pressure of 0.1 MPa, and temperature of about 25°C), which substantially prevent formation of other inhibitors/retarders of the hydroperoxide formation reaction, has revealed the dual impact of phenol as an inhibitor in a pure form. Specifically, a 49-fold growth in phenol concentration triggered a 9-fold slowdown of hydroperoxide formation rate and, simultaneously, a 8.4-fold acceleration of the rate of formation of other cumene oxidation products (by-products), thereby decreasing the process selectivity of cumene oxidation by about 1.6 mol % (from about 99.4 to 97.8 mol %). All of these values extend far beyond a possible margin of a methodological error in measurements. The impact of phenol as an inhibitor of hydroperoxide formation, comprises reducing the concentration of radicals $R^{\bullet}$, due to the occurrence of reactions (3), (12), (13), and (16) through (18), that ultimately affects the rate-limiting stage of the hydroperoxide formation reaction. The impact of phenol as an accelerator of by-product formation is expected to comprise speeding up the conversion of $RO_2^{\bullet}$ into $RO^{\bullet}$, for example by reaction (22), further giving rise to formation of by-products ROH and RHO. In actuality, reactions other than those specified above may also be relevant to the impacts discussed. Likewise, any particular reactions may provide quite different, or even insignificant, individual contribution to the observed gross effects of the interaction between radicals $R^{\bullet}$ and $RO_2^{\bullet}$ and inhibitors/retarders. However, this does not change the core essence of the dual roles of phenol, as well as of any other inhibittors/retarders, with respect to radicals $R^{\bullet}$ and $RO_2^{\bullet}$.

In fact, a similar dual impact on cumene oxidation (i.e., deceleration of the main reaction and acceleration of the side reactions), is also produced by the so-called “retarders” of the reactions, such as aldehydes and respective organic acids. The quantity of these impurities in the cumene feed entering a commercial hydroperoxide production process is not so significant (typically amounting to tenths of a percent, although being markedly higher than the amount of phenol formed), as to consider their effect on the rates of both the main and the side reactions from the standpoint of a substantially varying composition of the reaction medium (continuum).

It cannot be positively asserted whether aldehydes (such as formaldehyde, acetaldehyde, propionaldehyde, and benzaldehyde) and organic acids (formic, acetic, propionic, and benzoic, respectively), that are formed in the course of cumene oxidation, are actually inhibitors, or if they only serve as retarders of the hydroperoxide formation reactions, because to date this subject matter has not been studied to a sufficient extent. This question becomes even more difficult in view of the knowledge that, for example, benzaldehyde accelerates the hydroperoxide formation rate [4], while weak organic acids, such as acetic and propionic acids, are assumed to have almost no effect thereon (it should be noted, though, that the latter assumption is very tentative, and requires a deeper investigation). On the contrary, aldehydes and strong organic acids are definitely known to act in a similar manner to a phenol inhibitor, in that they noticeably slow down the hydroperoxide formation rate and, simultaneously, accelerate the rate of by-product formation. Therefore, the effect of these newly-formed impurities on radicals $R^\bullet$ and $RO_2^\bullet$ is almost the same as that of phenol: all of them act in the two opposite directions, decelerating and accelerating the respective reactions.

Based on the data illustrated in Fig. 3 [1] and Fig. 10, it would be rather inappropriate to consider phenol as a weak inhibitor, despite the relatively small value of relationship k_7/k_2 [2]. However, the consideration of phenol (and of other compounds having a similar effect) as an inhibitor in its own right raises reason-able doubts, because phenol does not only retard reactions (1)–(3), (21), but also accelerates side reactions (4), (15), (19), (22). The same is true for the so-called retarders, which also, in a similar manner to inhibitors, affect radicals $R^\bullet$ and $RO_2^\bullet$ in the opposite directions of decelerating and accelerating respective reactions. Therefore, the mechanisms that both inhibit and accelerate reactions occurring with participation of radicals $R^\bullet$ and $RO_2^\bullet$, are likely to be different for $[R^\bullet + In]$, as opposed to $[RO_2^\bullet + In]$. However, regardless of the above explanations, the existing terms “inhibitors” and “retarders” still appear to be rather ambiguous. Moreover, the term “reaction retarders” is not classified either *per se*, or in conjunction with their similarity to, and/or difference from, inhibitors. For this reason, the existing definitions of reaction inhibitors and retarders (the latter including aldehydes, acids, etc.) probably require additional clarification, for example by way of differentiating them in accordance with their specific effect on radicals $R^\bullet$ and $RO_2^\bullet$. However, this clarification should only provide certain additions and amendments to, and by no means result in a complete revision of, the existing classical postulates that define the term “inhibitors”, as are set forth in [2, 13, 19, 20]:

1. “…inhibitors are substances that, being present in minor concentrations of 0.01% to 0.1%, are able to terminate a chain process.”

2. “The action of inhibitors… may only be understood in the light of the chain theory, and in particular is based on the assumption that an inhibitor reacts with chain-leading free radicals, thereby terminating oxidation chains.”

3. “The decelerating impact of an inhibitor, referred to as inhibitor efficiency,… is determined by the speed of interaction between peroxide radicals and inhibitor molecules.”

4. “… a lower process temperature and a slower rate of chain initiation correspond to a stronger decalerating effect of an inhibitor.”

5. “… inhibitors (including phenols, …) react with $RO_2^\bullet$ with formation of radicals $InO^\bullet$ and ROOH molecules…, while a formed phenoxy radical is nonreactive and thus incapable of continuing the chain.”

In fact, the complete list of classical postulates may actually be more diverse than the above five items compiled by the author of this article. However, the possible incompleteness of these items cannot diminish the obvious fact that the abovementioned contradicttions and ambiguities must be eliminated therefrom, so as to provide a more appropriate and accurate approach to defining the terms “inhibitor” and “retarder” of a reaction in a manner that would be uniform and clear for every researcher.

6. The differences between certain postulates of the classical oxidation theory and the concepts formulated as a result of the reported research, with respect to cumene (applicable to both Article I [1] and this Article II). The classical theory of hydrocarbon oxidation is based on the following inherent and crucial ideas, as is noted in [2, 13, 19, 20]:

(1) The oxidation reaction, under the conditions of air bubbling through the oxidized product, is completely promoted by oxygen (O_2^{liquid}) dissolved in the liquid phase represented by the oxidized products;

(2) Gaseous oxygen (O_2^{gas}) at the liquid–gas interface does not affect oxidation at all;

Oxidation is contemplated as a purely homogeneous process;

(4) Oxidation must be carried out in a kinetic regime, where 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;

(5) Oxidation is described by the simplified equation: $W = k_1[R^\bullet][O_2]$, where W is the rate of oxygen absorption, and k_1 is the rate constant of the reaction between $R^\bullet$ and O_2^{liquid};

(6) A variation in pressure causes a proportional (linear) change in the concentration of dissolved oxygen in the liquid phase, which in turn predetermines a proportional (linear) change in the oxidation reaction rate;

(7) A deviation from a linear trend of reaction rate, with an increase in pressure, is explained by a shift in rate-limiting stage from the reaction between $R^\bullet$ and O_2^{liquid} to the reaction involving $ROO^\bullet$ and the hydrocarbon to be oxidized (RH);

(8) An increase in the concentration of hydroperoxide being the source of radicals $ROO^\bullet$ and $RO^\bullet$, and of their transformations, as well as relative variations in the rate constants of reactions between ROOH and $R^\bullet$ and of transformations of radicals $RO_2^\bullet$ with formation of ROOR, cause selectivity losses: the magnitude of selectivity declines with a rise in the degree of cumene conversion and in the concentration of hydroperoxide;

(9) "In application to all reaction classes, substances that, being present in minor concentrations of 0.01 to 0.1 wt %, are able to terminate a chain process are referred to as inhibitors" [2, 13].

In the light of the results of the direct test runs described herein above, as well as of the data reported in [3–5], a set of fundamental distinctions from the nine classical postulates listed above, in application to cumene oxidation, may be formulated:

1. The oxidation reaction proceeds by two independent paths: cumene oxidation by oxygen (O_2^{liquid}) dissolved in the liquid phase represented by the oxidized products (non-selective reaction path); and cumene oxidation by gaseous oxygen (O_2^{gas}) at the liquid–gas interface (selective reaction path).

2. Gaseous oxygen (O_2^{gas}) at the liquid–gas interface makes a significant, and under certain conditions even prevailing, contribution to the formation of hydroperoxide.

3. Oxidation is not a purely homogeneous process, but it should be considered as a process comprising a combination of homogeneous and heterophase pathways: (a) a homogeneous path that takes place in the liquid phase under the influence of O_2^{liquid}; and (b) a heterophase path that proceeds at the liquid–gas interface under the influence of O_2^{gas}.

4. Cumene oxidation, within all of the ranges of process conditions available in commercial operation, when air is fed in excess, occurs: (a) in a kinetic regime, with respect to O_2^{liquid}, because the rate of oxygen transfer from the gas phase into the liquid phase is significantly higher than the rate of oxygen expenditure in chemical reactions; and (b) in a diffusion regime, with respect to O_2^{gas}.

5. Bubble-type cumene oxidation is described by the equation: $W_{\text{total}} = W_1^{\text{gas}} + W_1^{\text{liquid}}$, where W_1^{gas} varies as a function of k_1^{gas}, $[O_2^{\text{gas}}]$, and of the liquid–gas interface area, while W_1^{liquid} is subject to the equation: $W = k_1[R^\bullet][O_2]$.

6. A variation in pressure causes: (i) a change in the relationship between the reactions promoted by O_2^{gas} and O_2^{liquid}, and (ii) a variation in the amount of inhibitors (In/InH/retarders of the hydroperoxide formation reaction) formed in the liquid phase; a combined effect of factors (i) and (ii) predetermines a non-linear trend of the hydroperoxide formation reaction rate when pressure or cumene conversion rate increases.

7. A deviation from a linear trend of reaction rate, with an increase in pressure, is not caused by a shift in the rate-limiting stage, but is rather determined: (i) by a change in the relationship between the quantities of hydroperoxide formed by the two independent reaction paths (i.e., through O_2^{gas} and O_2^{liquid}), and (ii) by the amount of hydroperoxide expended into by-products under the effects of O_2^{liquid}, inhibitors, and process temperature.

8. The magnitude of selectivity does not so much depend on the concentration of hydroperoxide being the source of radicals, nor on relationships between the rate constants of reactions between ROOH and radicals $R^\bullet$ and of transformations of radicals $RO_2^\bullet$ with formation of ROOR, but more on the concentration of inhibitors in the oxidized products, which in fact has a significant impact on the relationships $[R^\bullet]/[In]$ and $[ROO^\bullet]/[In]$ and, therefore, on the amounts of hydroperoxide and by-products formed in the process.

9. Inhibitors and retarders are chemical substances that, being present in minor concentrations of 0.001 to 0.5 wt %, are able, directly or indirectly, either through

chemical reactions with radicals or by any other path, to decrease the concentration of radicals $R^•$, and to correspondingly decelerate the rate of hydroperoxide formation, while simultaneously accelerating the rate of conversion of radicals $ROO^•$ into $R^•$ and then into ROH, i.e., into the by-products of hydrocarbon oxidation.

Oxidation of hydrocarbons of different structures is well-known to be characterized by the same major regularities, and to generally follow the same mechanisms [2, 11–13, 19, 20]. Based on this common knowledge, it can be reasonably assumed that the principal distinctions from the classical liquid phase oxidation notions, that have been established in the application to cumene oxidation, and that include the discovery of the process occurrence by two independent reaction paths (i.e., through O_2^{gas} and O_2^{liquid}), and of the responsibility of inhibitors for the formation of by-products, may turn out to be similar for other hydrocarbons as well.

It should be noted that the assumptions of the classical oxidation theory are based on studies that were carried out under necessarily low degrees of conversion of oxidation feed, without in-depth analysis of both the quantitative and qualitative compositions of resulting oxidation products, and under relatively mild operating conditions, where the contributions of other relevant factors (such as by-products and inhibitors/retarders of reaction rates) may be neglected. However, appreciably more severe conditions imposed in a commercially practiced oxidation process (and in particular, in a process of cumene oxidation), and a markedly higher degree of cumene conversion, lead to a significant deviation of the observed regularities from the classical notions, or even to an apparent conflict therebetween.

In particular, if cumene oxidation had occurred in accordance with the classical assumptions listed in items (1) through (9) above, there would have been no opportunities for substantial improvement of the design of a commercial hydroperoxide production process and its selectivity, with the hydroperoxide formation reaction proceeding exclusively by the essentially non-selective path (through O_2^{liquid}) [5]. However, the gained experience of commercial implementations of state-of-the-art technologies for cumene oxidation has actually confirmed the opposite case – in particular, that an imposed shift of the cumene oxidation reaction towards the O_2^{gas} path, by means of enlarging the interface area, increases both reaction rate and selectivity value, thus simultaneously providing a conclusive proof of the oxidation occurrence by two independent reaction paths, promoted by O_2^{gas} and O_2^{liquid} [21].

It is no less important to state that the postulated deviations from the classical oxidation assumptions, established for cumene, are only relevant as an appropriate adjustment, based on the direct experimental evidence, of certain important aspects of the otherwise very elegant classical theory of oxidation. These deviations clarify certain challenges and contradictions that existed in the classical theory, but that could not be explained earlier. Finally, the results of the research disclosed above, provide a solid ground for identifying the direction for future improvement of the performance of commercial cumene oxidation processes, and may even prove to be useful for commercial oxidation processes using other hydrocarbons as the feed.

Summarizing the study results discussed above, a number of final conclusions may be formulated as follows:

1) Direct experimental evidence of the occurrence of cumene oxidation under the influence of O_2^{gas} at the liquid–gas interface, and of a substantial contribution brought by this reaction path to the formation of cumene hydroperoxide as a desired product, has been provided.

2) The cumene oxidation reaction conducted in the air bubbling regime, 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}).

3) The magnitude of selectivity of cumene oxidation occurring at the gas–liquid interface under the influence of O_2^{gas}, is in significant excess over the selectivity of cumene oxidation driven by O_2^{liquid} in the liquid phase.

4) A growth in the concentration of inhibitors has a major impact on the relationships between the concentrations of radicals and inhibitors (e.g., $[R^•]/[In]$ and $[ROO^•]/[In]$), thereby causing a deceleration of hydroperoxide formation and an escalation in the formation of by-products within the entire studied range of the degree of cumene conversion, which ultimately results in a loss of oxidation selectivity and prevents a further increase in the degree of cumene conversion.

5) A state of an oxidation process described by the condition of $([R^•] \& [RO_2^•]) \ll [In]$, causes the hydroperoxide concentration to reach its limit value (corresponding to the case of $d[CHP]/dt = 0$), followed by a

decline in hydroperoxide concentration (d[CHP]/$dt < 0$) with an increase in cumene conversion rate.

Pre-removal of inhibitors from the oxidation reaction mixture allows an appreciable acceleration of the hydroperoxide formation rate, a marked increase in the cumene conversion rate and selectivity value, and overcoming of the relatively small limiting value of hydroperoxide concentration.

For bubbling-type cumene oxidation, which occurs by both reaction paths (i.e., through O_2^{gas} and O_2^{liquid}), a set of fundamental distinctions from the classical postulates have been provided, which are relevant as an adjustment of certain aspects of the classical theory and as provision of an insight into certain occurrences and regularities relating to the high degrees of cumene conversion, which were not earlier studied under the framework of the classical theory.

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