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Effect of the Polarity of the Medium on the Decomposition of Cumyl Hydroperoxide and Cumene Autoxidation in the Presence of Cu(II)-Acetylacetonate

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The effect of the polarity of the medium on the rate and the course of cumyl hydroperoxide (CHP) decomposition at 60°C in the presence of copper acetylacetonate [$Cu(acac)_2$] as catalyst was investigated with the help of the radical-type inhibitor *N*-phenyl-2-naphthylamine (PNA). The influence on the oxidation rate of a mixture of cumene and nitrobenzene under analogous conditions was also studied. It was shown that the effect of $Cu(acac)_2$ on the decomposition of CHP is different from that of $Co(acac)_2$ catalyst investigated previously. Whereas $Co(acac)_2$ leads to the formation of free radicals only, a molecular course of the CHP decomposition was also observed in the presence of $Cu(acac)_2$. The values of the initial rates of the decomposition of CHP (W_{in}^{CHP}) and of the consumption of PNA (W_{in}^{PNA}) decrease with increase of the dielectric constant of the medium. However, the ratio between these rates remains independent of the change of the polarity of the medium. This fact shows that the dielectric constant does not affect the direction of the decomposition of CHP to molecular and to radical products.

INTRODUCTION

The catalytic activity of the acetylacetonates of various metals for oxidation of organic compounds has been considered in a number of investigations (*1–15*). In the cases when Co(II)-acetylacetonate was used as catalyst, it was shown that the decomposition of the hydroperoxides proceeded mainly to free radicals (*15*, *18*). A number of investigations reviewed by Zaikov *et al.* (*23–25*) have studied the effect of the medium on autoxidation processes in the liquid phase. The effect of the medium on decomposition of hydroperoxides and on autoxidation of hydrocarbons in the presence of metal acetylacetonates has not been studied until our recent investigation (*18*) and one reported by Matienko *et al.* (*26*).

We have previously studied the effect of the polarity of the medium on the decomposition of cumyl hydroperoxide (CHP) in the presence of $Co(acac)_2$ (*18*). It was established that a change of the polarity of the medium influences neither the initial rate of hydroperoxide decomposition, nor the direction.

The purpose of the present paper is to study the effect of the polarity of medium on the rate and direction of the decomposition of CHP in the presence of Cu(II)-acetylacetonate, which differs from $Co(acac)_2$ both with respect to the metal atom and steric structure.

EXPERIMENTAL

The investigation was performed by methods described in detail in our former work (*18*). $Cu(acac)_2$ was recrystallized from chloroform, air-dried, and then dried

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for 8 hr in a high-vacuum apparatus under a pressure of 1 N/m^2. CHP was purified by recrystallization of its sodium salt and subsequent distillation of the hydroperoxide obtained. The concentration of CHP was followed iodometrically by titration of 0.5-ml samples in chloroform/acetic acid solution with 0.1 N sodium thiosulfate solution. The concentration of N-phenyl-2-naphthylamine (PNA) was determined spectrophotometrically, analogously to the previous study (*18*). Nitrobenzene, benzene, and cumene were purified by standard methods. During the experiments superpure nitrogen, 99.999%, was bubbled through the reaction mixture. The oxidation of cumene was carried out as previously (*18*).

RESULTS

The decomposition of CHP was performed in nitrobenzene at 60°C in a nitrogen atmosphere. The initial concentration of CHP ranged from 4.5 to $7.2 \cdot 10^{-2}$ mol/liter, whereas those of the catalyst ranged from $1.5 \cdot 10^{-4}$ to $1.1 \cdot 10^{-2}$ mol/liter. Figure 1 shows the dependence of the initial rate of decomposition of CHP-($W_{\text{in}}^{\text{CHP}}$) on its initial concentration. As is seen in the figure, a linear relationship is established in the range of concentrations studied, and unlike the analogous system employing $Co(acac)_2$ as a catalyst, the Michaelis-Menten relationship is not observed, i.e., in this case the relationship is first order with respect to the hydroperoxide. Figure 2 shows the dependence of $W_{\text{in}}^{\text{CHP}}$ on the initial concentration of $Cu(acac)_2$. The dependence does not reflect a definite mathematical relationship, and it includes two lines sharply differing in slope. The data given in the same figure show that the order of the reaction with respect to the catalyst changes with increasing catalyst concentration. There are two possible explanations for this phenomenon. Either the mechanism of the reaction depends on the concentration of the catalyst, or the increase of the concentration of the catalyst may lead to the formation of larger associated species, which are catalytically less active.

In the study on the effect of the polarity of the medium a nitrobenzene-benzene mixture was used analogous to that used before (*18*). Table 1 presents the initial rates of decomposition of CHP and of consumption of PNA, employed in the system with a view to avoiding the induced decomposition of CHP. By the consumption of the radical inhibitor, traced spectrophotometrically, we assessed the directions of decomposition of the hydroperoxide to

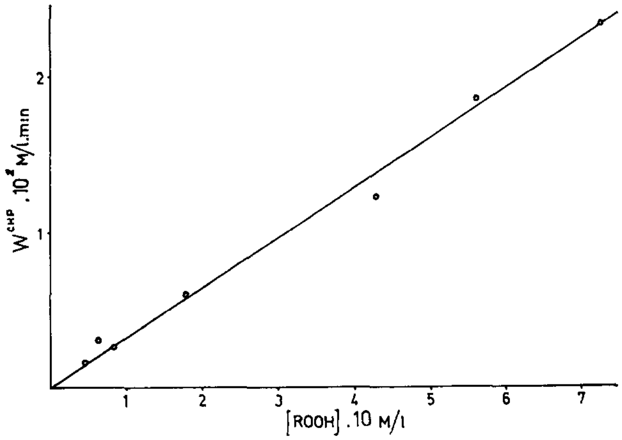


FIG. 1. Dependence of the initial rate of decomposition of CHP on its initial concentration in nitrobenzene at 60°C; $Cu(acac)_2$, $3.14 \cdot 10^{-3}$ mol/liter.

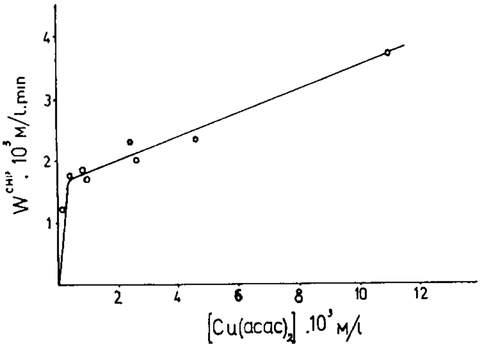


FIG. 2. Dependence of the initial rate of decomposition of CHP on the initial concentration of $Cu(acac)_2$ in nitrobenzene at 60°C; CHP, $8.8 \cdot 10^{-2}$ mol/liter.

TABLE 1

Decomposition of CHP at 60°C[a]

Ratio nitrobenzene: benzene	$W_{in}^{CHP} \cdot 10^3$ mol/liter min		$W_{in}^{PNA} \cdot 10^3$ mol/liter min
	Under nitrogen	Under oxygen	
1:0	2.10	2.44	1.93
3:1	2.32	—	1.60
1:1	2.61	—	2.53
1:3	3.18	—	2.74
0:1	4.18	—	4.08

[a] $Cu(acac)_2$, $2.5 \cdot 10^{-4}$ mol/liter; PNA, $3.3 \cdot 10^{-2}$ mol/liter.

molecular products or free radicals. It is seen from the table that with the increase of the polarity of the system, the rate of decomposition of CHP and the consumption of the inhibitor (W_{in}^{PNA}) decrease, remaining commensurate in value. The decomposition of CHP does not proceed to complete consumption, i.e., in the course of time the catalytic activity of the catalyst decreases significantly and the decomposition of the hydroperoxide ceases completely (Fig. 3). It was established experimentally that the quantity of hydroperoxide decomposed per mole of catalyst depends on the ratio between the initial concentration of the hydroperoxide and the concentration of the catalyst. The results given in Fig. 8 show that the relationship is linear. The same figure presents also the effect of PNA on the quantity of hydroperoxide decomposed.

During the decomposition of CHP in the presence of $Cu(acac)_2$ in nitrobenzene, formation of dark-colored crystals with a mp 311°C was observed, with the following elemental analysis: Cu, 26.9%; C, 48.1%; H, 2.44%.

The experiments on the oxidation of cumene and its nitrobenzene mixtures employing identical cumene hydroperoxide and $Cu(acac)_2$ concentrations and performed at the same temperature as in the cases of the decomposition of the hydroperoxide (Fig. 4) lead to contrary results. With an increasing polarity of the medium the rate of oxidation of reactant cumene

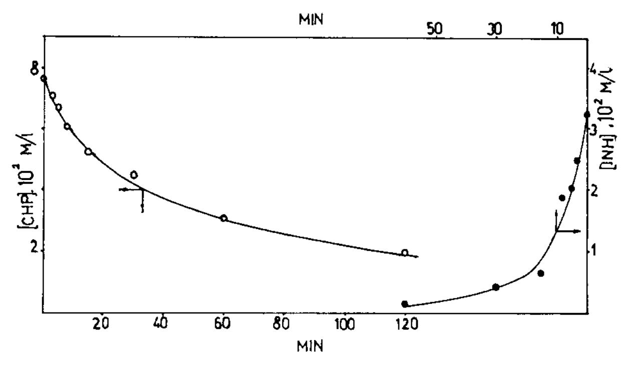


FIG. 3. Decomposition of CHP in benzene at 60°C in the presence of $Cu(acac)_2$, $4.57 \cdot 10^{-3}$ mol/liter; CHP, $8.8 \cdot 10^{-2}$ mol/liter; PNA, $3.25 \cdot 10^{-2}$ mol/liter.

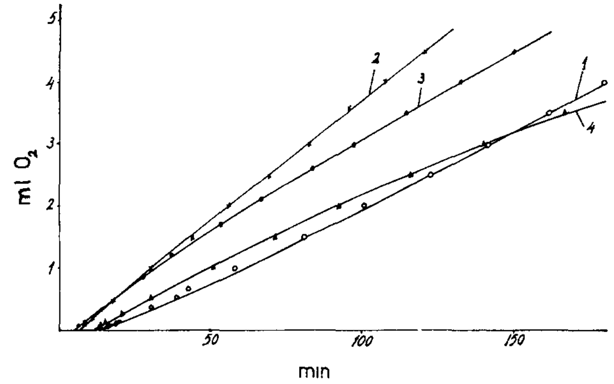


FIG. 4. Oxidation in the presence of $Cu(acac)_2$, $2.48 \cdot 10^{-4}$ mol/liter; CHP, $8.8 \cdot 10^{-2}$ mol/liter; $t = 60°C$. 1, cumene; 2, cumene:nitrobenzene in a ratio of 3:1; 3, in a ratio of 1:1; 4, in a ratio of 1:3.

related to 1 mol of cumene increases (Table 2). A linear dependence of the rate of oxidation (W_0^{max}) on the concentration of cumene is established (Fig. 5). The dependence of the initiation rate (W_i) on the cumene concentration can be seen in Fig. 11.

DISCUSSION

First-order kinetics are obeyed during the first 60 min (Fig. 6). The reaction then changes its order with respect to CHP, which shows that some secondary (additional) processes take place and the initial mechanism changes.

The results from Fig. 2 reveal that the increase of the concentration of $Cu(acac)_2$ to $5 \cdot 10^{-4}$ mol/liter leads to a sensitive change of the maximum rate of decomposition of CHP. The increase of the concentration of the catalyst above this value causes a fivefold decrease of the coefficient of increase of the reaction rate. The effect is attributed to the possibility of association of $Cu(acac)_2$, which has been proved in the case of $Co(acac)_2$ (*19*, *20*). Obviously, the nonassociated $Cu(acac)_2$ shows a higher catalytic activity for the decomposition of CHP as compared to the associated catalyst. Therefore, it can be concluded that if a possibility of maintaining $Cu(acac)_2$ in nonassociated form is found, its catalytic activity will be increased. The poisoning of the catalyst during the reaction of decomposition of

TABLE 2

Oxidation of Cumene at 60°C[a]

Ratio nitrobenzene: benzene	$W_0^{max} \cdot 10^6$ mol of O_2/liter sec	$W_0^{max} \cdot 10^6$/ mol of cumene
3:1	4.13	2.30
1:1	5.51	1.53
1:3	6.20	1.15
0:1	3.63	0.51

[a] $Cu(acac)_2$, $2.5 \cdot 10^{-4}$ mol/liter; CHP, $8.8 \cdot 10^{-2}$ mol/liter.

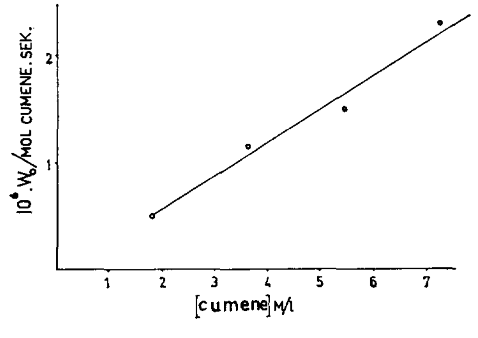


FIG. 5. Dependence of the maximum rate of oxidation per mole of cumene on the concentration of cumene; $t = 60°C$; $Cu(acac)_2$, $2.48 \cdot 10^{-4}$ mol/liter; CHP, $8.8 \cdot 10^{-2}$ mol/liter.

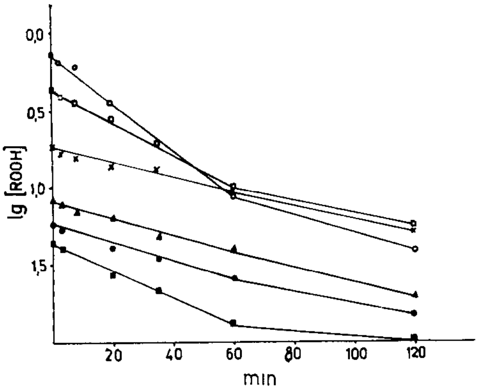


FIG. 6. Transformation of the kinetic curves for decomposition of CHP in nitrobenzene at 60°C in the presence of Cu(acac)$_2$, $3.14 \cdot 10^{-3}$ mol/liter, and PNA, $3.35 \cdot 10^{-2}$ mol/liter.

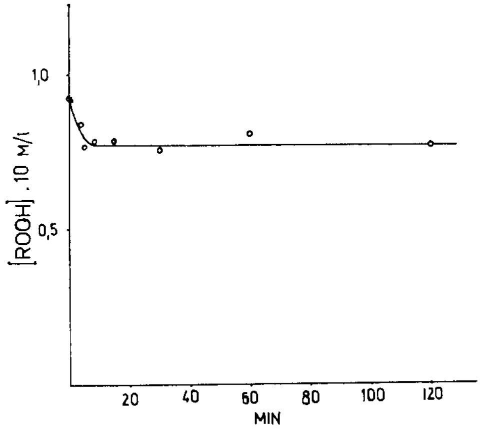


FIG. 7. Decomposition of CHP in nitrobenzene at 60° in the absence of PNA; Cu(acac)$_2$, $2.48 \cdot 10^{-4}$ mol/liter.

CHP is observed analogously as with Co(acac)$_2$. It should be noted that in the absence of PNA, Cu(acac)$_2$ decomposes a small amount of the initial hydroperoxide and is readily poisoned (Fig. 7). Besides this, the results from the decay of CHP in the simultaneous presence of PNA and Cu(acac)$_2$ (Figs. 7 and 8) show that the decomposed amount of hydroperoxide is approximately equal to the sum of the moles of PNA and the moles of CHP which are decomposed by Cu(acac)$_2$ in the absence of PNA. These facts demonstrate the activating effect of PNA, as observed during decomposition of CHP in the presence of phthalocyanines (*21*). The

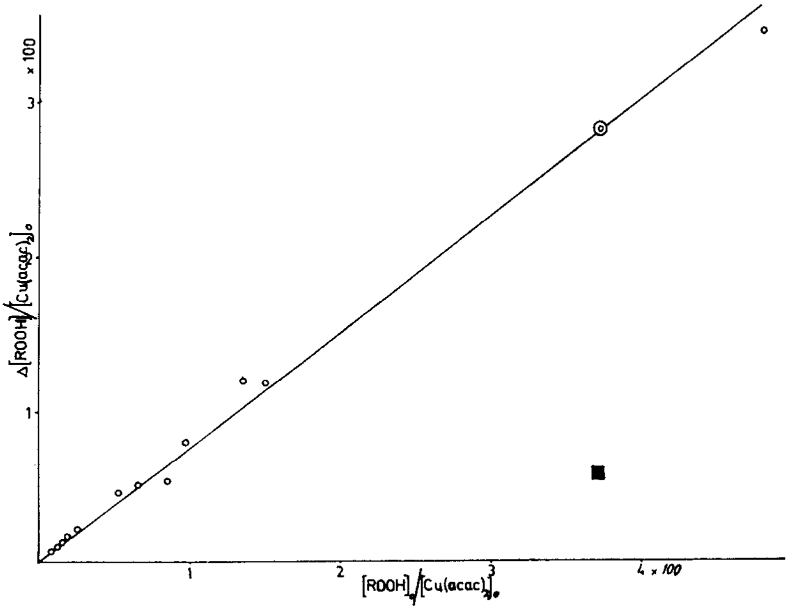


FIG. 8. Dependence of the ratio between the quantity of CHP decomposed and the initial concentration of the catalyst on the ratio of the initial concentrations. Additional data: ■, without PNA; ⊙, in presence of PNA.

observed effect of activation by PNA could be explained by the ability of PNA to form a complex with Cu(acac)$_2$ and in this way to facilitate the interaction of the catalyst and the hydroperoxide, and at the same time the poisoning of the catalyst is impeded.

The decomposition of the hydroperoxide continues until PNA is present in the system (Fig. 3). After its consumption the catalyst is poisoned probably forming a stable complex with the products of the decomposition. This fact may be one of the reasons for the absence of the influence of oxygen on the rate of the decomposition of CHP (Table 1), since it is evident that at a higher temperature the complex between Cu(acac)$_2$ and oxygen will be less stable than its complex with PNA or with the products of the decomposition.

By comparison the correlation between the initial rate of decomposition of CHP and that of consumption of PNA (characterizing the rate of formation of the products of the free radicals) we considered the possibility of a partial regeneration of CHP during the interaction of free peroxide radicals with the inhibitor. The results are shown in Table 1. They show that when Cu(acac)$_2$ is used as catalyst, molecular decomposition of CHP is observed (consumption of almost 50% of the hydroperoxide by molecular decomposition takes place), whereas in the presence of Co(acac)$_2$ all of the hydroperoxide decomposes to free radicals (*18*).

On increasing the dielectric constant of the solution, the rate of decomposition of CHP decreases without changing the ratio in the rate of decomposition to molecular and radical products. This shows that the activated complexes in both directions are less polar than the initial complexes of the reacting catalyst and reactant molecule, and second, the ratio of the reactivities of the activated complexes does not change with changing the polarity of medium.

The difference in the ratio between the rates of molecular and radical decomposition observed in the presence of Co(acac)$_2$ and Cu(acac)$_2$ can be interpreted in term of the difference between the diffusion constants of the radical leaving the cage of the solvent and the constant of the inner cell recombination. The difference in the ESR spectra of Cu(acac)$_2$ in benzene and nitrobenzene observed by us supports the concepts given in our previous work (*18*) and experimentally proved elsewhere (*19, 20*) concerning the presence of "adsorbed" free RO$^\cdot$ and RO$_2^\cdot$ radicals on the molecule of the catalyst. It can be assumed that in the presence of Cu(acac)$_2$ a solvent–catalyst activator system is observed, which forms a common cell and the rate of diffusion of the radicals will also depend on the strength of the RO–Cu(acac)$_2$–PNA bond.

The spectrum taken in nitrobenzene corresponds to that described by Gersmann and Swalen (*27*), whereas in benzene an intense broad line appears in the spectrum, and the shape of the lines and their widths differ considerably from those in nitrobenzene.

The data from Fig. 5 show that the maximum rate of oxidation depends linearly on the concentration of the hydrocarbon which shows that the equation of Tobolsky *et al.* (*28*) in our case is not followed. This result shows that together with the decomposition of hydroperoxide another initiation of the oxidation of cumene through the activation of oxygen by Cu(acac)$_2$ exists. The rate of initiation effected by Cu(acac)$_2$ and in the presence of PNA decreases with increasing the polarity of the solvent, whereas the rate of initiation increases upon cumene oxidation accomplished without PNA. The values of W_i were calculated taking into account the corrected values for $k_p/k_t^{0.5}$ and the effect of the polarity on this value (*18*). This contradiction is explained by weakening of the effect of association of the molecules of the catalyst, as compared to those of the hydroperoxide.

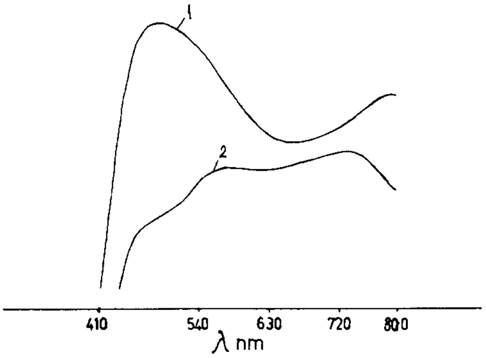
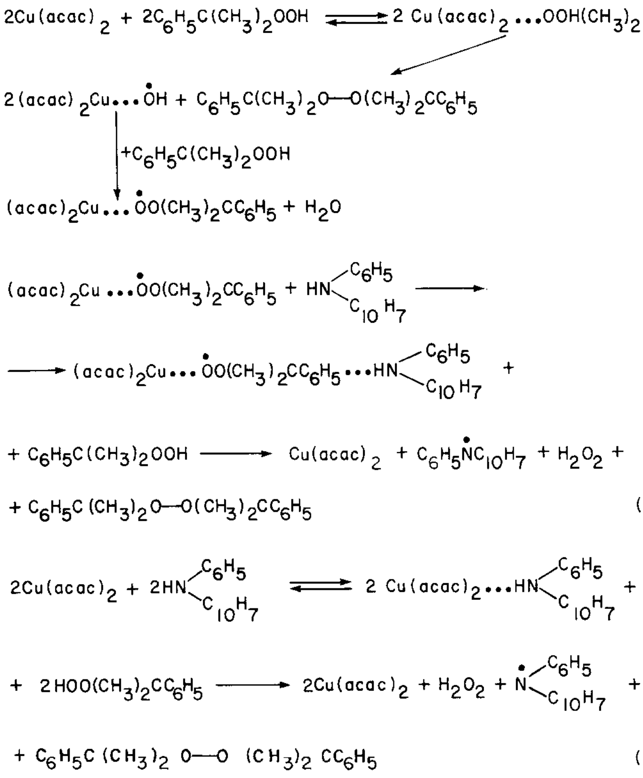


FIG. 9. Visible spectra of solution after 24 hr: 1, $Cu(acac)_2$ in ethanol; 2, $Cu(acac)_2$ in ethanol with PNA.

On the other hand, in polar solvents the effect of linking $RO^{\cdot}$ and $RO_2^{\cdot}$ to $Cu(acac)_2$ will disappear which will facilitate the diffusion of the radicals in the solvent volume.

It is seen in Fig. 10, curve 3, that at 20°C and with concentrations of CHP of $2.5 \cdot 10^{-1}$ mol/liter and of $Co(acac)_2$ of $2.5 \cdot 10^{-3}$ mol/liter, the signal of $RO_2^{\cdot}$ with g-factor 2.015 appeared. With $Cu\cdot(acac)_2$ the signal of $RO_2^{\cdot}$ radicals was not observed. This result is in accordance with our experimental data concerning the existence of extensive molecular decomposition of hydroperoxide in the presence of $Cu(acac)_2$. The most probable explanation of this phenomenon is that the free alkoxy and peroxy radicals which were produced recombined in the cage of the solvent. The absence of a signal from these radicals shows too that their interaction with the radical acceptor is carried out through a common complex of the radical inhibitor and the catalyst, since the inhibitor concentration decreased during the reaction.

Taking into account the above facts and considerations, the decomposition of CHP in the presence and in the absence of PNA and nitrobenzene as a solvent can be represented by the following scheme:



$$2Cu(acac)_2 + 2C_6H_5C(CH_3)_2OOH \rightleftarrows 2\,Cu(acac)_2\cdots OOH(CH_3)_2CC_6H_5$$

$$2(acac)_2Cu\cdots\dot{O}H + C_6H_5C(CH_3)_2O{-}O(CH_3)_2CC_6H_5 \qquad (1)$$

$$\Big\downarrow{+C_6H_5C(CH_3)_2OOH}$$

$$(acac)_2Cu\cdots\dot{O}O(CH_3)_2CC_6H_5 + H_2O$$

$$(acac)_2Cu\cdots\dot{O}O(CH_3)_2CC_6H_5 + HN{<}^{C_6H_5}_{C_{10}H_7} \longrightarrow$$

$$\longrightarrow (acac)_2Cu\cdots\dot{O}O(CH_3)_2CC_6H_5\cdots HN{<}^{C_6H_5}_{C_{10}H_7} +$$

$$+ C_6H_5C(CH_3)_2OOH \longrightarrow Cu(acac)_2 + C_6H_5\dot{N}C_{10}H_7 + H_2O_2 +$$

$$+ C_6H_5C(CH_3)_2O{-}O(CH_3)_2CC_6H_5 \qquad (2)$$

$$2Cu(acac)_2 + 2HN{<}^{C_6H_5}_{C_{10}H_7} \rightleftarrows 2\,Cu(acac)_2\cdots HN{<}^{C_6H_5}_{C_{10}H_7} +$$

$$+ 2HOO(CH_3)_2CC_6H_5 \longrightarrow 2Cu(acac)_2 + H_2O_2 + \dot{N}{<}^{C_6H_5}_{C_{10}H_7} +$$

$$+ C_6H_5C(CH_3)_2\,O{-}O\,(CH_3)_2CC_6H_5 \qquad (3)$$

FIG. 10. ESR spectra: 1, $Cu(acac)_2$ in cumene; 2, $Cu(acac)_2$ in nitrobenzene; 3, $Co(acac)_2$ in cumene with CHP.

Reaction (1) is assumed to proceed through an intermediate complex with CHP in the absence of PNA, as is proved by Fig. 7. However, the results from the experiments show that the equilibrium is strongly shifted to the left, i.e., the reaction does not obey the Michaelis–Menten relationship (Fig. 1).

Reactions (2) and (3) take into account the activating effect of PNA. These interactions are supported experimentally by the electronic spectra taken in the

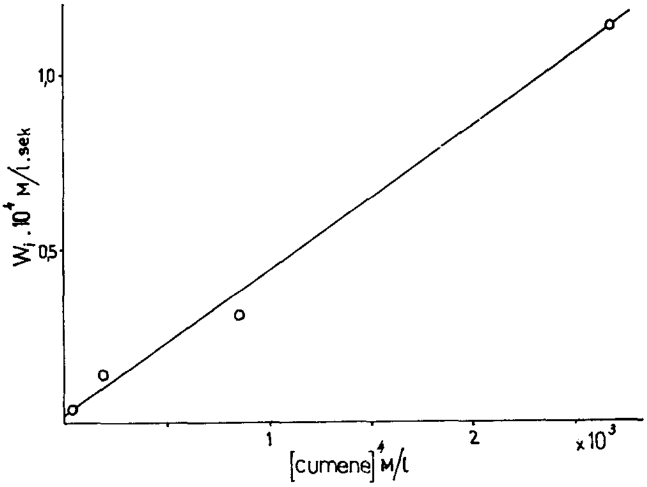


FIG. 11. Dependence of the initial rate of oxidation on the concentration of cumene: $t = 60°C$; $Cu(acac)_2$, $2.48 \cdot 10^{-4}$ mol/liter; CHP, $8.8 \cdot 10^{-2}$ mol/liter.

visible region (Fig. 9), which show that when a mixture of $Cu(acac)_2$ and PNA with concentrations of $2.48 \cdot 10^{-4}$ and $3.25 \cdot 10^{-2}$ mol/liter, respectively has stayed in a solution of alcohol at room temperature, the spectrum is considerably changed.

The gas chromatographic analysis of the products of decomposition of CHP shows traces of cumyl alcohol and acetophenone, which allows us to conclude that dicumylperoxide is the basic product of decomposition, as suggested in our earlier work (*18*).

The crystalline product with a melting point of 311°C isolated in our experiments is assumed to be a modification of the catalyst (its basic form probably).

The low stoichiometric coefficient of the decomposition of the hydroperoxide in the presence of $Cu(acac)_2$ ($\sim$40) in comparison with $Co(acac)_2$ ($\sim$130) shows that the reactions which result in the decomposition of the catalyst and its removal from the reaction system as a crystal product play a very significant role.

Taking into consideration the results from the analysis of the precipitated dark crystals formed in the process of cumene hydroperoxide decomposition, which contain a great amount of copper and have a melting point different from that of $Cu(acac)_2$, we can propose structures similar to the forms with $Co(acac)_2$ discussed by Prikril *et al.* (*19*).

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