Composition catalysts of ethylbenzene oxidation based on bis(acetylacetonato)nickel(II) and phase transfer catalysts as ligands

2*. Quaternary ammonium salts

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New composition catalysts based on bis(acetylacetonato)nickel(II) and ammonium salts, R_4NBr (Me_4NBr, n-$C_{16}H_{33}Me_3NBr$) for selective oxidation of aromatic hydrocarbons to the appropriate hydroperoxides have been introduced. It is demonstrated that the rate, selectivity, and degree of conversion of ethylbenzene to α-ethylphenylhydroperoxide in this case are significantly higher than those observed for monodentate and macrocyclic ligands used as activating additives. The data obtained are in good agreement with the suggestion that the selective catalyst is formed in the course of ethylbenzene oxidation as a result of regioselective interaction of dioxygen with the γ-carbon atom of the acetylacetonate ligand controlled by R_4NBr.

Key words: oxidation, homogeneous catalysis, composition catalysts, bis(acetylacetonato)nickel(II), dioxygen, phase transfer catalysts.

It was recently established that quaternary ammonium salts R_4NX can play two different roles in various catalytic reactions in water-organic systems. These salts can act not only as catalysts of phase transfer, but also R_4NX salts are often directly involved in the catalytic reaction itself. Thus, for example, in reactions of the oxybromination of aromatic compounds a lipophylic ammonium salt transfers H_2O_2 into the organic phase. At the same time, since it is a Lewis acid it forms $R_4NBr(Br_2)_n$ or $R_4NBr(HBr)_n$ adducts thus activating Br_2 or salts of HBr for electrophilic attack on the aromatic ring.[2] In the catalytic oxidation of styrene to benzaldehyde by hydrogen peroxide in water — organic solvent systems ammonium salts completely transfer H_2O_2 and the catalyst (Ru, Pd) into the organic phase by forming hydrogen bonds. Moreover, complex formation affects the properties of the catalyst by changing its activity (rate and selectivity of the reaction).[3] In the oxidation of p-xylene in a water — organic system in the presence of $CoBr_2$ and R_4NBr the catalytically active species are complexes of $CoBr_2$ with R_4NBr.[4]

We used the ability of quaternary ammonium salts to form complexes with compounds of metals of variable valency to design catalytic systems based on bis(acetylacetonato)nickel(II) for selective oxidation of aromatic hydrocarbons.

It is known that in hydrocarbon solvents quaternary ammonium salts form complexes with strong hydrogen bonds, $R_4N^+(X...HOCMe{=}CHCOMe)^-$, in which the acetylacetone is completely enolized.[5]

Previously we found that the increase in the efficiency of $Ni(acac)_2$ in the oxidation of alkylarenes to hydroperoxides in the presence of the ligands D with electron donor properties is due to the following sequence of events: activation of the CH-methine bond of the acetylacetonate ion because of complexing of D with $Ni(acac)_2$, addition of molecular O_2 to this bond and subsequent transformation of the complexes formed into new catalytic species.[6] We expected the same regioselective addition of oxygen to the acetylacetonate ligand of the Ni-complex in the presence of R_4NX, because different electrophilic reactions in $R_4N^+(X...HOCMe{=}CHCOMe)^-$ complexes are known to occur at the CH-methine bond of acetylacetone.[5]

Experimental

Ethylbenzene was oxidized in the presence of $Ni(acac)_2$, and additions of tetramethylammoniumbromide (Me_4NBr) and cetyltrimethylammoniumbromide (CTAB) at 120°C.

The analysis of the products, the experimental data processing, and the conditions of the oxidation of ethylbenzene were essentially the same as those described in communication 1.[1]

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*For communication 1 see Ref. 1.

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The UV spectra of $Ni(acac)_2$ and $Fe(acac)_3$ were recorded on a "Specord UV-VIS" spectrophotometer in H_2O and $CHCl_3$.

Results and Discussion

As can be seen in Fig. 1, *a* (curves *1* and *2*) oxidation of ethylbenzene in the presence of $Ni(acac)_2$ and Me_4NBr additives is characterized by a much higher percentage of PEH than the reaction catalyzed by $Ni(acac)_2$. Together with PEH, AP, MPC, and P are formed.* In this case $[PEH]+[AP]+[MPC]+[P] = [PEH]+\Sigma[P] = \Delta[RH]$. A considerable increase in the induction period of phenol accumulation is observed (Fig. 1, *d*).

Additions of the macrocyclic ether 18C6 under the described conditions of the oxidation of ethylbenzene act in a way similar to Me_4NBr.[1] However, in the former case phenol appears immediately, although the rate of its accumulation is considerably lower than in presence of $Ni(acac)_2$ only.

Figure 2, *a* gives the plots of the selectivity of the oxidation of ethylbenzene to PEH ($S = [PEH]/\Delta[RH] \cdot 100\%$) versus the degree of conversion of ethylbenzene ($C = \Delta[RH]/[RH]_0 \cdot 100\%$) in the presence of $Ni(acac)_2$ (curve 1) as well as $Ni(acac)_2$ with Me_4NBr (curves *2*—*4*). It can be seen that in the presence of $Ni(acac)_2$ the selectivity of oxidation (*S*) is 90 % at $C = 4$ %, whereas in the presence of Me_4NBr the maximum selectivity of

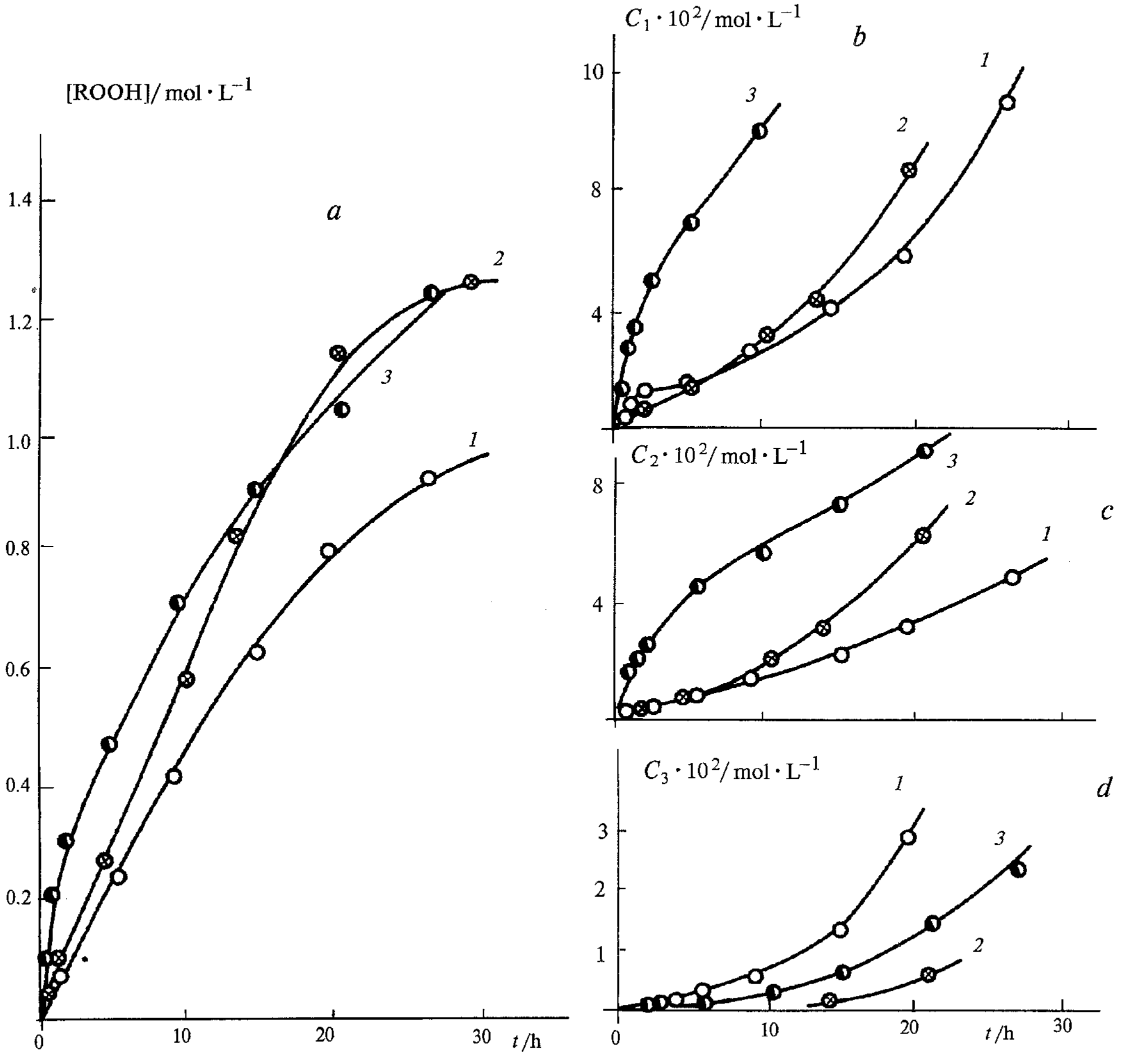

Fig. 1. Kinetic curves of the accumulation of HPE (*a*), AP (*b*), MPC (*c*), P (*d*) in the oxidation of ethylbenzene in the presence of $1.5 \cdot 10^{-4}$ mol L^{-1} of $Ni(acac)_2$ (*1*) and additions of Me_4NBr (*2*) and $n\text{-}C_{16}H_{33}Me_3NBr$(*3*). $[R_4NBr] = 1 \cdot 10^{-3}$ mol L^{-1}. C_1 is concentration of acetophenone, C_2 is concentration of methylphenylcarbynol, C_3 is concentration of phenol.

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*PEH is α-phenylethylhydroperoxide, AP is acetophenone, MPC is methylphenylcarbynol, P is phenol, ΣP is AP+MPC+P, RH is ethylbenzene.

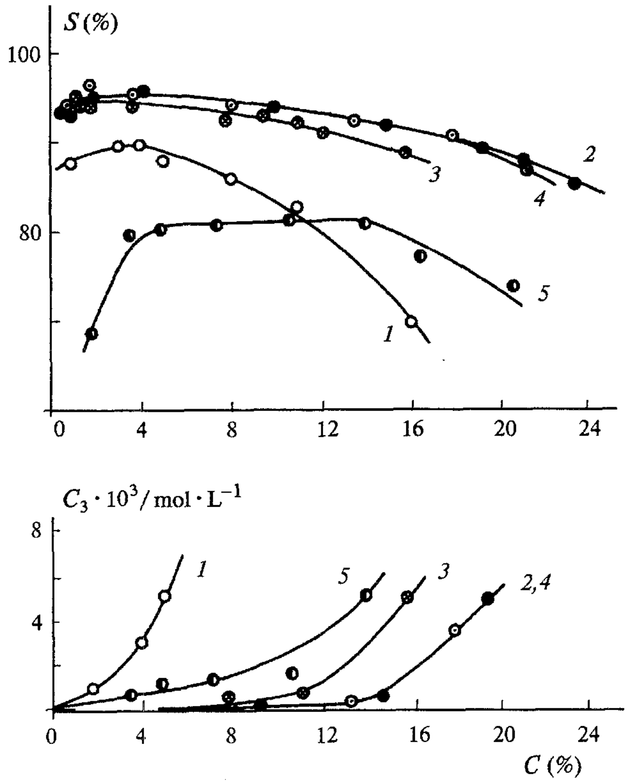

Fig. 2. Dependence of the selectivity (*a*) and concentration of phenol (*b*) in the oxidation of ethylbenzene catalyzed by $Ni(acac)_2$ (*1*) and the catalytic system {$Ni(acac)_2+R_4NBr$} (*2—5*) on the degree of conversion of ethylbenzene (*C*) at various concentrations of Me_4NBr: *2*, $0.5 \cdot 10^{-3}$; *3*, $1.0 \cdot 10^{-3}$; *4*, $2.0 \cdot 10^{-3}$ mol L^{-1}; and n-$C_{16}H_{33}Me_3NBr$: *5*, $1.0 \cdot 10^{-3}$ mol L^{-1}. $[Ni(acac)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1}. C_3 is concentration of phenol.

oxidation 90 % < $S \le 95$ % is reached more quickly (at C = 2—3 %) and remains at the same level almost to $C \approx 19\%$. The catalytic activity of a system for oxidizing ethylbenzene to PEH (if the selectivity S is not lower than 90 %) can be estimated by the value of parameter $\bar{S} \cdot C$, where $\bar{S}$ (%) is the mean selectivity of the system at S > 90 %, and C (%) is the degree of conversion at which S = 90 %. As can be seen from Table 1, the system {$Ni(acac)_2+Me_4NBr$} is more efficient than {$Ni(acac)_2$+18C6} and {$Ni(acac)_2$+HMPA}.

The influence of Me_4NBr on the kinetic relationships of the oxidation of ethylbenzene in the presence of $Ni(acac)_2$ apparantly indicates the formation of catalytically active complexes between $Ni(acac)_2$ and Me_4NBr.

The observed increase in the selectivity S and the degree of conversion of ethylbenzene in the presence of $Ni(acac)_2+Me_4NBr$ is not connected with the catalytic action of free Me_4NBr. It is known that ammonium salts can catalyze the oxidation of hydrocarbons by activating molecular oxygen.[7] However, in the present case the catalytic activity of R_4NBr does not play a considerable role, since the relationships of the oxidation of ethylbenzene in the presence of only Me_4NBr differ from those catalyzed by the {$Ni(acac)_2+Me_4NBr$} system. At the beginning of the reaction a period of auto-acceleration is observed, whose initial rate $W^0 = 2 \cdot 10^{-6}$ mol$(L \cdot s)^{-1}$ is a factor of 10 lower than the initial rate of oxidation in the presence of either $Ni(acac)_2$ or the composition catalyst. The selectivity of oxidation to PEH, which is the highest at the beginning of the reaction (S = 95—97 % at C = 3%), quickly decreases during the transformation of ethylbenzene.

Table 1. Value of the parameter $\bar{S} \cdot C$ in the oxidation of ethylbenzene in the presence of $Ni(acac)_2$ and activating additives D ($[Ni(acac)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C)

D	D·10³/mol L⁻¹	Y = $\bar{S} \cdot C$
HMPA	1.0	360
18C6	0.3	1009.5
	0.15	1466.3
Me_4NBr	0.5	1796.2
	1.0	1464.4
	2.0	1665.8

The thermal decomposition of R_4NBr is not likely to play a considerable role either, because it takes place mainly in a basic medium. Also, the possible products of decomposition are amines, olefins, and alkyl bromides, which have no catalytic activity.[4]

The influence of an ammonium salt on the catalytic activity of $Ni(acac)_2$ depends on the structure of the radical R of the ammonium cation. Thus, additions of cetyltrimethylammoniumbromide (CTAB) decrease the maximum selectivity of the oxidation of ethylbenzene to PEH down to 80—82 % (Fig. 2, *a*). The initial rate of accumulation of PEH is higher than that of the reaction catalyzed by the {$Ni(acac)_2+Me_4NBr$} system (Fig. 1, *a*). However, at the same time the initial rate of the accumulation of by-products of the reaction, *viz.*, AP and MPC, significantly increases (Fig. 1, *b*, *c*). The induction period on the kinetic curve of the formation of phenol is shorter than that of the reaction catalyzed by the {$Ni(acac)_2+Me_4NBr$} system, but longer than that of the reaction catalyzed by $Ni(acac)_2$ (Fig. 1, *d*).

The dependence of the selectivity of the reaction on the structure of the radical R of the ammonium cation in the oxidation of styrene to benzaldehyde by hydrogen peroxide in the presence of Ru or Pd salts and R_4NX additives was explained by the difference in the catalytic activity of Ru or Pd complexes with quaternary ammonium salts.[3]

The formation of catalytically active complexes between $Ni(acac)_2$ and R_4NBr is additionally confirmed by the extreme character of the plots of the initial rates of the oxidation of ethylbenzene in the presence of $Ni(acac)_2$ versus $[R_4NBr]$ when $[Ni(acac)_2]$ = const, as was done for 18C6.[1]

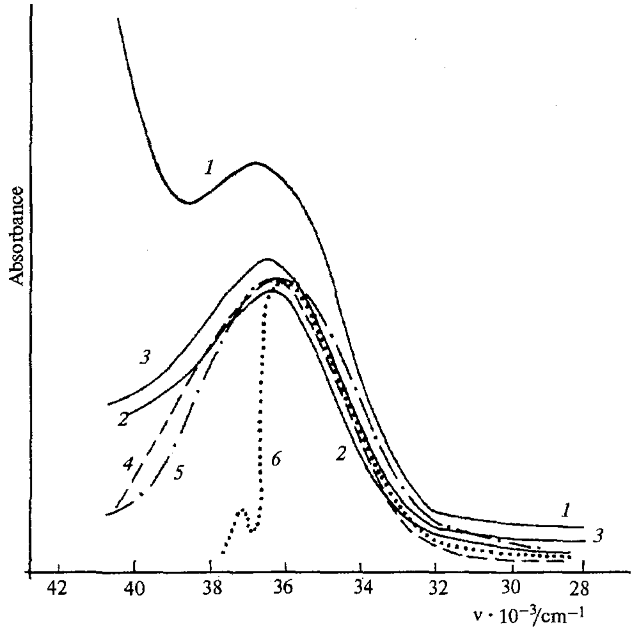

Fig. 3. Absorption spectra of solutions: *1*, $Fe(acac)_3$ ($2.2 \cdot 10^{-5}$), *2—6*, $Fe(acac)_3+R_4NX$: *2*, Me_4NBr ($2.3 \cdot 10^{-3}$), *3*, $n\text{-}C_{16}H_{33}Me_3NBr$ ($2.3 \cdot 10^{-3}$); *4*, Bu_4NBr ($2.4 \cdot 10^{-3}$); *5*, Bu_4NI ($2.0 \cdot 10^{-3}$); *6*, $Et_3C_6H_5NCl$ ($2.6 \cdot 10^{-3}$ mol L^{-1}), 20°C (spectra were recorded using R_4NX solutions as a reference).

The maximum values of the rates are $W^0 = 3.1 \cdot 10^{-5}$ mol(L s)$^{-1}$ for {$Ni(acac)_2+Me_4NBr$} system and $W^0 = 8.8 \cdot 10^{-5}$ mol(L s)$^{-1}$ for the {$Ni(acac)_2$+CTAB}. These values are ≈1.4 and 4 times higher, respectively, than W^0 of the reaction catalyzed by $Ni(acac)_2$ alone. The maximum values of W^0 do not depend on the nature of R_4NBr and are observed at $[R_4NBr] = 1 \cdot 10^{-3}$ mol/L, which corresponds to the formation of the 1:1 complex.

The formation of a complex of R_4NBr with $Ni(acac)_2$ might occur by coordination of the Br^- anion at the fifth coordination site of the Ni ion. The axial coordination of R_4NBr can be seen from the analysis of the electronic absorption spectra of aqueous solutions of $Ni(acac)_2$ in the presence of Me_4NBr and CTAB. A decrease in the absorption intensity and a shift of the $(acac)^-$ ligand band to the higher energy region are observed. Similar changes in the $Ni(acac)_2$ spectrum were observed in the case of $SnCl_2$ coordination.[8] Axial coordination of $SnCl_2$ through the Cl^- anion was confirmed by X-ray diffraction analysis.

The formation of complexes between $CoBr_2$ and R_4NBr was proved by means of absorption spectrometry (the visible part of spectrum). The formation of ion pairs between ammonium cations and the complex mononuclear anions $CoBr_3^-$ and $CoBr_4^-$ has been proposed.[4]

Along with inner sphere coordination of the ammonium cation with the acetylacetonate ion, outer sphere coordination is possible too. We demonstrated the possibility of outer sphere coordination of R_4NBr with β-diketonates of metals of variable valency, using complexes of $Fe(acac)_3$ in the presence of various R_4NX as examples.

In the UV spectrum, tris(acetylacetonato)iron(III) exhibit an intense absorption band at $\nu = 37 \cdot 10^3$ cm^{-1} ($CHCl_3$) of the π—π* transition of the conjugated cycle of the acetylacetonate ion[9] (Fig. 3). In the presence of the salts Me_4NBr, $n\text{-}C_{16}H_{33}Me_3NBr$ (CTAB), $(C_2H_5)_4NBr$, $(C_2H_5)_3C_6H_5NCl$, Bu_4NI, and Bu_4NBr a decrease in the intensity and a bathochromic shift of the absorption maximum to $\nu = 36 \cdot 10^3$ cm^{-1} ($\Delta\lambda \approx 10$ nm) are observed. Such a change in the spectrum indicates the influence of R_4NX coordinated in the outer sphere on conjugation in the ligand. Similar changes were observed in the spectra of Fe(III) chelates containing CF_3 and C_6H_5 substituents in a chelate ring of the β-diketonate complex.[9] The bathochromic shift of absorption maximum was also observed in spectra of fluorine-containing β-diketonates of Ba and Ca.[10] It is also impossible to eliminate a slight influence of the π-system of the halide atom. This influence is corrobo-

Table 2. Dependence of the rates of accumulation of products of ethylbenzene oxidation in the beginning of the process (W^0) and during the oxidation ($\overline{W}$) in the presence of {$Ni(acac)_2+R_4NBr$} on the nature of the radical R.

R_4NBr	$[R_4NBr] \cdot 10^3$ / mol L^{-1}	$W^0_{ROOH} \cdot 10^5$ / mol L^{-1} s^{-1}	$W^0_{AP+MPC} \cdot 10^6$ / mol L^{-1} s^{-1}	$\overline{W}_{ROOH} \cdot 10^5$ / mol L^{-1} s^{-1}	$\overline{W}_{\Sigma P} \cdot 10^6$ / mol L^{-1} s^{-1}	$W^0_p \cdot 10^6$ / mol L^{-1} s^{-1}
—	—	2.1	2.7	1.1	1.3	2.4
Me_4NBr	0.5	2.7	2.2	1.9	2.0	2.7
	1.0	2.9	1.8	1.5	1.7	1.1
	2.0	2.3	2.6	1.7	1.3	2.3
$n\text{-}C_{16}H_{33}Me_3NBr$	1.0	6.1	27.0	1.5	2.7	25.0

Note. W_{ROOH} is the rate of accumulation of PEH, $\overline{W}_{\Sigma P}$ is the rate of accumulation of AP, MPC, P; W_p^0 is the calculated rate of the reaction of chain elongation. $[Ni(acac)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C.

rated by the small shift of the absorption band of the system {$Fe(acac)_3$+Bu_4NI} (spectrum *5*) with respect to the absorption line of {$Fe(acac)_3$ + Bu_4NBr} (spectrum *4*).

The change in the conjugation in the chelate ring of the acetylacetonate complex, when R_4NBr is coordinated in the outer coordination sphere of the metal, can be caused by participation of the oxygen atoms of the acetylacetonate ion in the formation of coordination bonds with the ammonium ion or hydrogen bonds with the alkyl substituents of the ammonium ion. Thus, for example, it was established that the absorption band of phenol associated with the π—π^* transition experiences a bathochromic shift of 500 cm^{-1} due to formation of hydrogen bonds with dioxane.[11]

As can be seen from Table 2, in the oxidation of ethylbenzene in the presence of {$Ni(acac)_2$+R_4NBr} a decrease in the reaction rate is observed in all cases ($\bar{W} = \bar{W}_{ROOH} + \bar{W}_{\Sigma P}$). In the case of catalysis by the {$Ni(acac)_2$+Me_4NBr} system this occurs mainly because of the decrease in the rate of accumulation of PEH. When the reaction is catalyzed by {$Ni(acac)_2$+CTAB} the reaction rate decreases because of a decrease in the rate of accumulation of PEH (≈4-fold) and the accumulation of products $W_{\Sigma P}$ by about one order of magnitude. The selectivity of PEH formation increases in this case from 93 at the initial stages to 95—97 % ({$Ni(acac)_2$+Me_4NBr}) and from 70 to 82 % ({$Ni(acac)_2$+CTAB}). The observed relationships confirm the hypothesis about transformation of [$Ni(acac)_2$ · R_4NBr] complexes. This transformation can be a result of electrophilic regioselective attack of O_2 on the γ-carbon atom of the acetylacetonate ligand controlled by the ammonium salt. Due to the favorable combination of the electronic and steric factors there is a high probability of formation of the structure [$Ni_x(acac)_y(OAc)_z$ · R_4NBr](P*),[6] which is a more selective catalyst of the oxidation of ethylbenzene to PEH than [$Ni(acac)_2$ · R_4NBr] complexes. The significant increase in conversion while maintaining high selectivity (not less than 90%) may be accounted for by higher stability of P* complexes to complete oxidation to nickel acetate. The formation of nickel acetate causes a sudden drop in the selectivity of the catalytic oxidation of ethylbenzene to PEH[6] due to outer sphere coordination of R_4NBr and steric difficulties in the regioselective oxidation of the $(acac)^-$ ligand.

The greater selectivity of ethylbenzene oxidation in the presence of complexes of $Ni(acac)_2$ with Me_4NBr (S = 97%) at the beginning of the process (C = 0—4%) in comparison with catalysis by $Ni(acac)_2$ (S = 85—90%) may be accounted for by the increase in the activity of the complexes in the reaction of chain initiation and by the decrease in their activity in the reaction of chain propagation, $RO_2^{-\bullet}$ + cat → products.

As in Ref.1, the calculated rates of chain termination (W_t^0) were compared with values of W^0_{AP+MPC} obtained experimentally using the assumption that the homolytic decomposition of HPE can be neglected in comparison to the rate of its formation (S of the process is higher than in case of $Ni(acac)_2$ catalysis). The difference in W_t^0 and W^0_{AP+MPC}, as in the preceding work,[1] can be accounted for by participation of the catalyst in chain propagation (W_p^0).

It can be seen from Table 2 that the minimum value of W_p^0 is observed at [Me_4NBr] = $1 \cdot 10^{-3}$ mol/L, which corresponds to the formation of the complex [$Ni(acac)_2$ · Me_4NBr] in a 1:1 ratio. As [Me_4NBr] increases further W_p^0 increases too; at [Me_4NBr] = $2 \cdot 10^{-3}$ mol/L the latter reaches the value of W_p^0 observed in the presence of $Ni(acac)_2$ only.

The observed effects are similar to those observed before.[1] It is evident that in this case in the process of Me_4NBr coordination (in the inner and in outer spheres) steric hindrances to coordination of $RO_2^\bullet$ with the metal ion can appear (W_p^0 drops). If [Me_4NBr] is rather large, the probability of opening of the chelate ring of the $(acac)^-$ ion increases and coordination of the radical $RO_2^\bullet$ with the metal center becomes possible (W_p^0 increases).

It follows from the data of Table 2 that replacing one CH_3 radical with n-$C_{16}H_{33}$ in the quaternary ammonium cation results in a significant decrease in the selectivity of the reaction at the beginning and at the later stages of the process. In this case the selectivity of the reaction is even lower than that in case of $Ni(acac)_2$ catalysis.

A tenfold increase in the rate of the accumulation of products W^0_{AP+MPC} over that found with $Ni(acac)_2$ catalysis is observed. However, the rate of accumulation of PEH (W^0_{ROOH}) increases only threefold.

The calculated value of W_p^0 in the case of catalysis by complexes [$Ni(acac)_2$ · CTAB] is ten times higher than W_p^0 in the case of $Ni(acac)_2$ catalysis. The simultaneous formation of AP and MPC in the reaction of chain propagation during the interaction of [$Ni(acac)_2$ · CTAB] with radicals $RO_2^\bullet$ (not from ROOH) is confirmed by the fact that the ratio of the accumulation rates W_{AP}/W_{ROOH} and W_{MPC}/W_{ROOH} at t—0 differs from 0.

As can be seen from the spectra in Fig. 3 replacing the radical Me in the R_4N^+ cation with the radical n-$C_{16}H_{33}$ results in weakening of the outer sphere coordination of the quaternary ammonium salts with the acetylacetonate ligand. Apparently, the possibility of coordination of the $RO_2^\bullet$ radical with the metal ion increases. In addition to this, it is possible that simultaneously the donor activity of the central metal ion increases. This would promote the coordination of the radical $RO_2^\bullet$ and molecular oxygen (increase W_p^0 and W^0_{ROOH}).

As for non-catalytic oxidation of ethylbenzene in the presence of quaternary ammonium salts Me_4NBr or CTAB, the sudden drop in the selectivity S of PEH formation even at the very initial stages of the reaction (S <95% at C >3%) is related to the acceleration of the decomposition of ROOH due to the formation of complexes with hydrogen bonds ROOH...$Br^{-}N^{+}R_4$.[12] At the same time the activity of R_4NX in the decomposition of ROOH does not depend on the structure of the ammonium cation but depends only on the nature of the halide ion.

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