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

L. I. Matienko, L. A. Mosolova, and I. P. Skibida*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 938 2156

The addition of the macrocyclic polyether 18-Crown-6 (18C6) increases the selectivity of oxidation of ethylbenzene to α-phenylethylhydroperoxide (PEH) in the presence of $Ni(acac)_2$. The initial oxidation rate, selectivity and degree of conversion of ethylbenzene to PEH are greater than those catalyzed by $Ni(acac)_2$ only. The efficiency of the macrocyclic ligand as an activator of $Ni(acac)_2$ exceeds that of monodentate donor ligands. The high selectivity of the process is due to both the "primary" $Ni(acac)_2 \cdot 18C6$ complexes and the products of their transformation in the course of oxidation. The mechanism of ethylbenzene oxidation catalyzed by $Ni(acac)_2 \cdot 18C6$ complexes is discussed.

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

In our previous studies[1—3] we demonstrated that the selectivity of the oxidation of aromatic hydrocarbons to hydroperoxides in the presence of homogeneous catalysts based on metals of variable valency could be greatly improved by introducing donor molecules into the system, which can form monodentate complexes with metal ions. Investigation of the mechanism of these catalytic systems revealed that the high selectivity of the oxidation of ethylbenzene to hydroperoxide in the presence of $Ni(acac)_2$ and donor additives (D) is caused by the formation of the mixed ligand binuclear complex $Ni_2(acac)(OAc)_3 \cdot D$ in the course of oxidation. Cyclic polyether 18-Crown-6 (18C6) and polyethylenglycols (PEG) exhibit a similar modifying action on the oxidation of ethylbenzene in the presence of bis(acetylacetonato)cobalt(II).[4]

In present study the efficiency and mechanism of the composition catalyst $\{Ni(acac)_2 + 18C6\}$ in the oxidation of ethylbenzene are investigated.

Experimental

Ethylbenzene was oxidized in the presence of $Ni(acac)_2$ and 18C6 at 120°C. Ethylbenzene and its oxidation products, such as methylphenylcarbinol (MPC), acetophenone (AP) and phenol (P), were analyzed by GLC according to the procedure given in Ref. 1; the PEH concentration was determined iodometrically.

As shown earlier, in the region of low $Ni(acac)_2$ concentrations (1.10^{-4}—1.10^{-3} mol · L^{-1}) rather high selectivity of the oxidation of ethylbenzene to PEH (90%) was observed, although there was a very low degree of conversion (C = 2—4%). The addition of monodentate donor ligands (HMPA) does not have a substantial effect on the selectivity or yield of hydroperoxide under these conditions.[2] For this reason, to estimate the possible increase in the degree of conversion of ethylbenzene to hydroperoxide and the selectivity of oxidation in the presence of the macrocyclic polyether, the initial $Ni(acac)_2$ concentration was $1.5 \cdot 10^{-4}$ mol · L^{-1} in all experiments.

Spectra of $Ni(acac)_2$ were recorded with a Specord UV-VIS spectrophotometer in the UV region for aqueous solutions in the presence of 18C6 and *N*-methyl-2-pyrrolidone (MP).

The initial rates of the reaction (W^0) were calculated by the procedure in Ref. 5, allowing us to determine W^0 with an accuracy of ±5%.

Results and Discussion

The addition of 18C6 does not influence the qualitative composition of the products of ethylbenzene oxidation catalyzed by $Ni(acac)_2$ at 120°C, however, it does significantly change the ratio of the products. The content of PEH increases and the rate of phenol accumulation decreases significantly. The kinetics of MPC and AP accumulation are practically invariant. In this case the balance of products is always fulfilled:

$$[PEH] + [MPC] + [AP] + [P] = [PEH] + \Sigma[P] = \Delta[RH]$$

As can be seen from Fig. 1, when 18C6 is added the initial rate of ethylbenzene oxidation increases greatly and at the ratio $[18C6]:[Ni(acac)_2]$ = 1:1 the initial rate is 4—5 times greater than that in the absence of 18C6.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1406—1411, August, 1994.

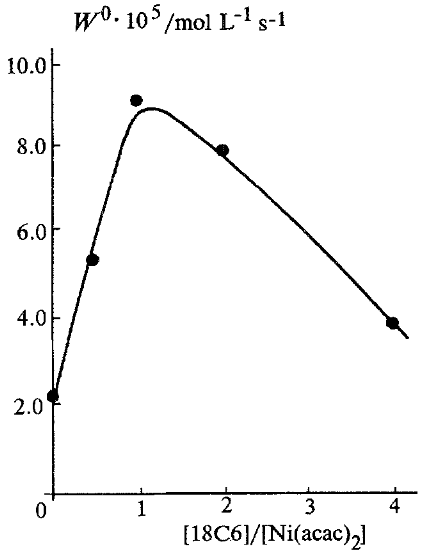


Fig.1. Dependence of the initial rate of catalyzed ethylbenzene oxidation in the presence of the catalytic system $\{Ni(acac)_2 + 18C6\}$ on the ratio of [18C6] to $[Ni(acac)_2]$.

The highest oxidation selectivity of hydroperoxide formation $S_{max} = [ROOH]/\Delta[RH]$ in the presence of the $\{Ni(acac)_2 + 18C6\}$ catalytic system is as great as 97% (Fig. 2, *a*), whereas in the presence of $\{Ni(acac)_2 + HMPA\}$ the maximum selectivity of RCOOH formation does not exceed 90%.[3] If there is 18C6 present, the selectivity of oxidation $S \geq 90\%$ is maintained up to ~16% conversion of ethylbenzene(compared with 4% for HMPA).

As in the case of HMPA, the decrease in selectivity that accompanies the increase in the degree of ethylbenzene conversion, is due to the evolution of heterolytic reactions of PEH degradation in the system and the accumulation of a significant amount of phenol (Fig. 2, *b*) as a by-product of the reaction.

In spite of the fact that 18C6 is comparatively easily oxidized by the radical chain mechanism,[6] the increases in W^0 and the selectivity of oxidation are not related to the additional initiation of the reaction by 18C6. In the absence of $Ni(acac)_2$ an autocatalytic evolution of the process is observed, whose initial rates are one order of magnitude lower; the selectivity of PEH formation equals 85% in the beginning of the reaction and falls drastically as the degree of ethylbenzene conversion increases.

Obviously, the effects observed are caused mainly by the formation of complexes between 18C6 and $Ni(acac)_2$, as was shown earlier for $Co(acac)_2$. Although the affinity of crown ethers for "soft" ions of transition metals is rather weak, the possibility of the formation of complexes of $Ni(NO_3)_2$, $NiCl_2$ with 18C6 (composition: 2:1 and 1:1)[7,8] was proved by means of IR-, NMR-, ESP-, and mass spectroscopy.

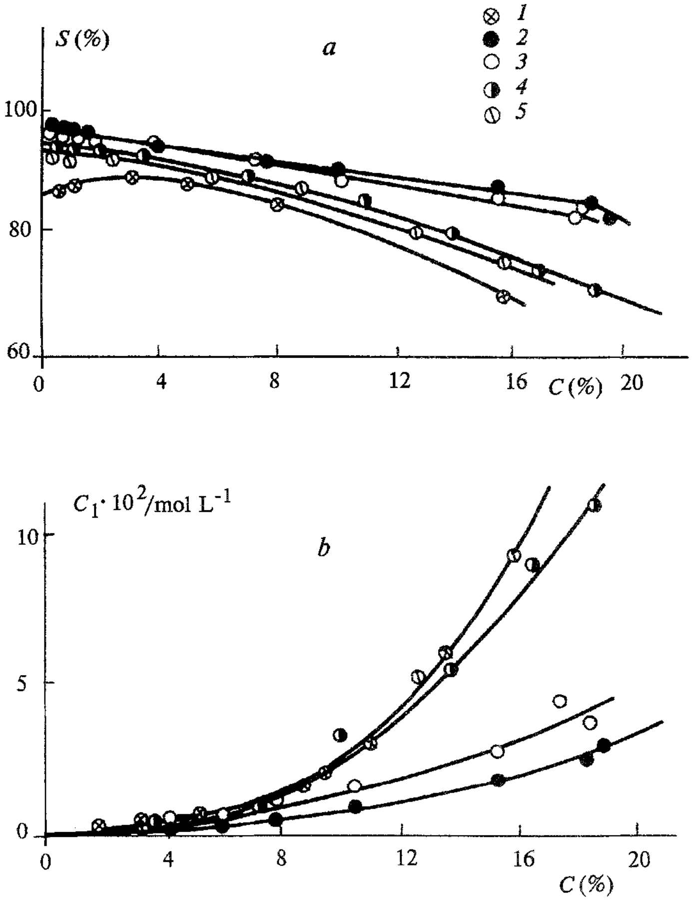


Fig.2. Dependence of the selectivity (*a*) and phenol content in products (*b*) during ethylbenzene oxidation catalyzed by $Ni(acac)_2$ (*1*) and $\{Ni(acac)_2 + 18C6\}$ (*2—5*) on the degree of ethylbenzene conversion: $[Ni(acac)_2] = 1.5 \cdot 10^{-4}$ mol·L^{-1}, $[18C6] = 1.5 \cdot 10^{-4}$ (*2*), $3 \cdot 10^{-3}$ (*3*), $7.5 \cdot 10^{-5}$ (*4*), $6 \cdot 10^{-4}$ mol. ·L^{-1} (*5*), 120°C.

The formation of a complex between 18C6 and $Ni(acac)_2$ in our system is confirmed by comparison of UV spectra of the initial components and their mixtures. As can be seen from Fig. 3, when an aqueous solution of 18C6 is added to the $Ni(acac)_2$ solution a decrease in absorption intensity of the acetylacetonate ion $(acac)^-$ and a short-wave shift of the adsorption maximum (spectra *1—3*)* take place. A similar change in the intensity of the $(acac)^-$ absorption band is observed in the absorption spectrum of bis(acetylacetonato)nickel(II) when it is coordinated with a monodentate ligand, *viz.*, *N*-methyl-2-pyrrolidone (spectrum *4*). Evidently, the formation of a complex between $Ni(acac)_2$ and 18C6 does not lead to displacement of the acetylacetonate ligand from the inner coordination sphere of Ni(II), because otherwise the short-wave shift of the absorption band should be accompained by a significant increase in the absorption of the solution at $\lambda = 275$ nm, which corresponds to the absorption maximum of acetylacetone

---

*Ligands 18C6 and MP do not exhibit any absorption bands in the region considered.

Table 1. Rates of accumulation of products of ethylbenzene oxidation at the beginning of the reaction (W^0) and during oxidation ($\bar{W}$), estimated rates of chain termination ($W^0{}_t$) and chain propagation ($W^0{}_p$).

$c \cdot 10^4$/mol $\cdot$ L^{-1}		$W \cdot 10^6$/mol $\cdot$ L^{-1} $\cdot$ s^{-1}					
Ni(acac)$_2$	18C6	$W^0{}_{ROOH}$	$W^0{}_{AP+MPC}$	$W^0{}_t$	$W^0{}_p$	$\bar{W}_{ROOH}$	$\bar{W}\Sigma_P$
1.5	—	21.0	2.7	0.3	2.4	11.0	1.3
1.5	3.0 (1 : 2)	77.0	3.0	3.0	—	15.0	2.6
1.5	1.5 (1:1)	85.0	2.9	3.6	—	15.0	2.5
1.5	0.8 (2 : 1)	51.0	2.8	1.3	1.7	13.0	3.0
1.5	6.0 (1:4)	42.0	2.4	1.0	1.4	13.0	2.9
—	—	—	—	—	—	10.0	6.3

(spectrum *5*). The possibility of complex formation between 18C6 and K(acac) without displacement of acetylacetone from the coordination sphere of the metal ion was shown earlier.[9]

In the oxidation of alkylaromatic hydrocarbons in the presence of mixed ligand complexes $ML_n \cdot D$ (ML_n is compound with variable valence metal D is donor ligand) the dependence of the selectivity of hydroperoxide (*S*) formation on the degree of conversion of the hydrocarbon (*C*) usually has an extremal form.[1—3] In this case the selectivity of hydroperoxide formation depends greatly on the activity of the catalyst in the reaction of hydroperoxide degradation. In the course of oxidation, *S* increases due to the transformation of $ML_n \cdot D$ complexes to new catalytic particles, which are less efficient in the catalytic degradation of ROOH.

In the course of the oxidation of ethylbenzene in the presence of $Ni(acac)_2 \cdot 18C6$ complexes, the selectivity of PEH formation is the greatest at the beginning (up to $C = 2$—4%), when its value reaches $S = 95$—97%.

A significant decrease in the oxidation rate is observed at $C > 2$—4% (Table 1, $\bar{W} = \bar{W}_{ROOH} + \bar{W}\Sigma_P$). The selectivity of the reaction remaines high (not less than 90%) up to $C = 16\%$. The selectivity of the process appears to be caused by the initial complexes as well as by the products of their conversion during the reaction.

As is evident from Table 1, when the ratio [Ni(acac)$_2$]:[18C6] = 1:1 the initial rate of PEH accumulation $W^0{}_{ROOH}$ is increased 4-fold, whereas the initial rates of AP and MPC accumulation practically do not differ from $W^0{}_{(AP+MPC)}$ in the absence of 18C6.

By analogy with the data published in Ref. 1, one can propose that the coordination of the macrocyclic ligand 18C6 with Ni(acac)$_2$ leads to enhancement of the catalyst activity during chain generation apparently due to the activation of molecular oxygen.

The transition of Ni(II) to the high-spin state as a result of its coordination with macrocyclic polyether makes possible the interaction between Ni(II) and triplet O_2, promoting its transition to the active $O_2^{\bullet -}$ form. O_2 is known to form rather stable adducts with {Ni(II)-azacrown ether}.[10] For this reason the suggestion mentioned above, that coordination of macrocyclic ether with Ni(II) complex would lead to activation of molecular oxygen, seems to be quite probable.

At the same time, the complexes of Ni(acac)$_2$ with 18C6 are apparently inactive in the decomposition of hydroperoxide at the central Ni atom. This results in a decrease in the rate of ROOH decomposition and an increase in the rate of its accumulation.

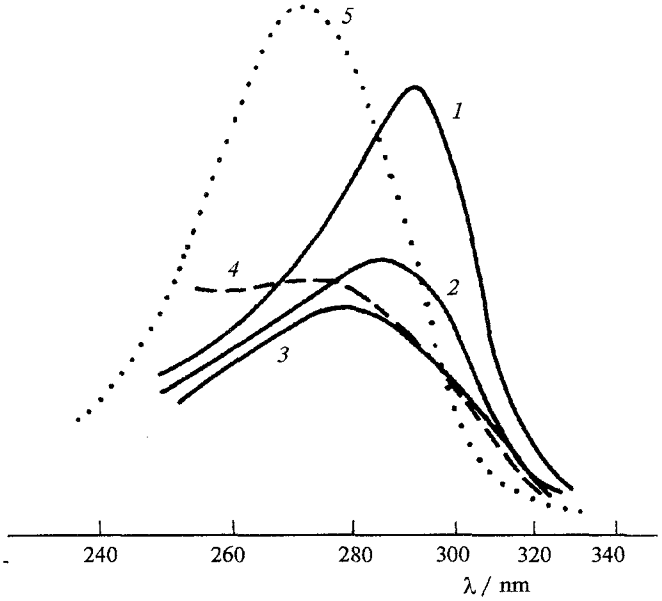


Fig.3. Electron absorption spectra of aqueous solutions: *1*, Ni(acac)$_2$; *2,3*, {Ni(acac)$_2$ + 18C6}; *4*, {Ni(acac)$_2$ + MP}; *5*, Hacac. [Ni(acac)$_2$] = $1 \cdot 10^{-4}$, [18C6] = $2 \cdot 10^{-4}$ (*2*), $1 \cdot 10^{-3}$ (*3*), [MP] = $1 \cdot 10^{-1}$, [Hacac] = $1.9 \cdot 10^{-6}$ mol $\cdot$ L^{-1}, 20°C.

Thus, when $2.4 \cdot 10^{-3}$ mol $\cdot$ L^{-1} of 18C6 is added to a solution containing $1.2 \cdot 10^{-3}$ mol $\cdot$ L^{-1} of Ni(acac)$_2$ and $8.9 \cdot 10^{-2}$ mol $\cdot$ L^{-1} of ROOH the rate of PEH degradation at 120°C drops almost 30-fold (from $3.4 \cdot 10^{-4}$ (without 18C6) to $1 \cdot 10^{-5}$ mol $\cdot$ L^{-1}).

The relationships observed can be accounted for within the framework of a radical chain mechanism of the reaction as confirmed by the following calculation.

The expression for PEH accumulation may be written as:

$$W^0_{\mathrm{ROOH}} = k_2[\mathrm{RH}][\mathrm{RO_2^{\bullet}}] - W_\mathrm{d}$$

If the reaction is catalyzed by Ni(acac)$_2$ the rate of PEH* degradation (W_d) at the initial time is two orders of magnitude lower than the rate of its accumulation (see Table 1). For this reason, W_d can be assumed to be close to zero.

Therefore, the equation for the rate of chain termination is derived as:

$$W_\mathrm{t} = k_6[\mathrm{RO_2^{\bullet}}]^2 = k_6 \left(\frac{W^0_{\mathrm{ROOH}}}{k_2[\mathrm{RH}]} \right)^2 \qquad (1)$$

In the case of catalysis by the system {Ni(acac)$_2$ + 18C6} these conditions may be assumed to be realized since, as we have shown, the addition of 18C6 reduces the rate of PEH degradation catalyzed by Ni(acac)$_2$ 30-fold, and quadratic chain termination is likely to be the only reaction of AP and MPC formation.

$$2\ \mathrm{RO^{\bullet}_2} \rightarrow \mathrm{R'{=}O} + \mathrm{ROH} + \mathrm{O_2}$$

Using the data of Table 1 and Eq. (1) one can conclude that the rates of the chain termination reactions actually coincide with the rates of MPC and AP formation ($W^0_{\mathrm{AP+MPC}}$) at least for two ratios of concentrations [Ni(acac)$_2$]:[18C6] = 1:1 and 1:2.

When the reaction is stabilized by RO$^{\bullet}$ radicals the obtained ($W^0_{\mathrm{AP+MPC}}$) values are equal to the rates of chain generation as a result of RH and O$_2$ interaction. In the calculation[12] the following values of the constants and concentrations of hydrocarbons were used: $k_2 = 23.6$ L $\cdot$ mol^{-1} $\cdot$ s^{-1}, $k_6 = 1.9 \cdot 10^7$ L $\cdot$ mol^{-1} $\cdot$ s^{-1}, [RH] = 8.2 mol $\cdot$ L^{-1}.

When the ratio [Ni(acac)$_2$]:[18C6] is equal to 2:1 or 1:4, the experimental values of the rates $W^0_{\mathrm{AP+MPC}}$ are nearly twice as large as the calculated rates (W^0_t) (Table 1).

At these ratios, the discrepancy between W_t and $W^0_{\mathrm{AP+MPC}}$ may be accounted for the formation of AP and MPC not only as a result of the reaction of chain termination but also as a result of chain prolongation (W_p):

$$\mathrm{RO_2^{\bullet}} \xrightarrow{\mathrm{cat}} \mathrm{R'{=}O\ (ROH)} + \mathrm{R^{\bullet}} \qquad (2)$$

At a low concentration of the catalyst, by-products of the reaction seem to form in the prolongation reaction and in the chain termination reaction. The participation of Ni(acac)$_2$ in the reaction of chain prolongation is supported by the stability of the ratio of the rates of AP and MPC accumulation at the rate of ROOH accumulation at t → 0, as well as by the existence of a linear relationship between W_p and Ni(acac)$_2$ in the range of concentrations [Ni(acac)$_2$] = $(1.5\text{—}10) \cdot 10^{-4}$ mol $\cdot$ L^{-1} (Fig. 4).

The formation of a complex between Ni(acac)$_2$ and 18C6 results in inhibition of the chain prolongation reaction (Table 1). At the ratios [Ni(acac)$_2$]:[18C6] = 1:1 and 1:2, W_p = 0, evidently due to steric hindrances to the coordination of RO$_2^{\bullet}$ radicals by the catalytically active complexes Ni(acac)$_2$ $\cdot$ 18C6 and Ni(acac)$_2$ $\cdot$ (18C6)$_2$.

At the ratio [Ni(acac)$_2$]:[18C6] = 2:1 the increase in the chain prolongation rate (Table 1) seems to be accounted for by assuming that in this case part of the Ni(acac)$_2$ is not bound to 18C6. The increase in the rate of chain prolongation (W_p) when the concentration of 18C6 is 4 times greater than that of [Ni(acac)$_2$] is likely to be associated with the increased probability of coordination of the RO$_2^{\bullet}$ radical with the metal ion as a result of opening of the acetylacetonate chelate ring. Axial coordination of electron donor ligands is known to

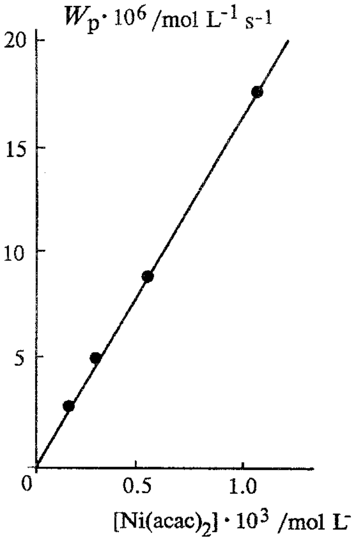


Fig.4. Dependence of the rate of chain prolongation (*2*) on the catalyst concentration in ethylbenzene oxidation reaction by Ni(acac)$_2$, 120°C.

---

*The rate of PEH degradation at the beginning of the reaction was estimated according to the formula:[1]

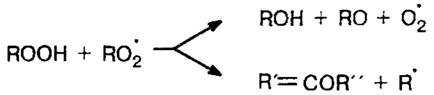
$$W_\mathrm{d} = \frac{k_\Sigma K_\Sigma [\mathrm{Ni(acac)_2}] \cdot [\mathrm{ROOH}]}{1 + K_\Sigma[\mathrm{ROOH}]} = 1.3 \cdot 10^{-7}\ \mathrm{mol \cdot L^{-1} \cdot s^{-1}}$$

at K_Σ (the equilibrium constant[1] of Ni(acac)$_2$ $\cdot$ ROOH complex formation) = 21 mol $\cdot$ L^{-1}; k_Σ (the rate constant of complex degradation) = 0.398 s^{-1} and [ROOH]^0 = $1 \cdot 10^{-4}$ mol $\cdot$ L^{-1}.

increase the probability of chelate cycle opening.[13] We have shown that at the ratio $[18C6]:[Ni(acac)_2] = 140:1$ the drop in the absorption intensity of the acetylacetonate ring is accompanied by the appearance of an absorption band at $\lambda = 270$ nm, which can be assigned to a monodentate O-linked acetylacetonate ligand.[13]

In the reaction of ethylbenzene oxidation in the range of $C = 2-16\%$ the reaction rate $\overline{W} = \overline{W}_{ROOH} + \overline{W}_{\Sigma P}$ is a constant that is not dependent on [18C6], it is five times lower than the initial rate $W_o = W^0_{ROOH} + W^0_{AP+MPC}$ and coincides with the noncatalytic oxidation rate.

It may be assumed that in the reaction catalyzed by the $\{Ni(acac)_2 + 18C6\}$ system the increase in selectivity of ethylbenzene oxidation in comparison with noncatalyzed oxidation ($S_{noncat} << 80\%$) is related to the inhibition of chain radical degradation of PEH:



(3)

The change in the rate and mechanism of the formation of the oxidation product is obviously due to transformation of the initial complexes $Ni(acac)_2 \cdot (18C6)_n$ ($n = 1, 2$) into new catalytically active particles, as we have shown earlier for monodentate donor ligands D. This modification occurs by activation of the CH-methine bond $(acac)^-$ with respect to the electrophilic addition of oxygen.[3]

Crown ethers are known to catalyze the electrophilic addition of acetylacetonate ions to the γ-carbon atom.[14] Therefore, it is quite possible that $Ni(acac)_2 \cdot (18C6)_n$ complexes transform into $Ni_x(acac)_y(AcO)_z \cdot (18C6)$ particles as a result of the regioselective addition of oxygen to the γ-carbon atom of the acetylacetonate ligand of the nickel complex controlled by the macrocyclic polyether.

The drop in selectivity when $C > 16\%$ coincided with a significant increase in the rate of phenol accumulation (Fig. 2), which can be attributed to the complete oxidation of the mixed ligand complex $Ni_x(acac)_y(AcO)_z \cdot (18C6)$ to nickel(II) acetate, which is an efficient catalyst of PEH heterolysis.

Thus, in the present study we established that the selectivity of the oxidation of ethylbenzene to PEH in the presence of the complexes $Ni(acac)_2 \cdot 18C6$ and $Ni(acac)_2 \cdot (18C6)_2$ is higher than that of catalysis by $Ni(acac)_2$ complexes with monodentate electron donor axial ligands.

References

1. L. A. Mosolova, L. I. Matienko, Z. K. Mayzus, *Izv. AN SSSR, Ser. khim.*, 1981, 731 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, 612 (Engl.Transl.)].
2. L. A. Mosolova, L. I. Matienko, *Neftekhimiya,* 1985, **25**, 540.
3. L. A. Mosolova, L. I. Matienko, I. P. Skibida, *Kinetika i kataliz,* 1987, **28**, 479, 484 [Kinet. and Catals, 1987, **28** (Engl. Transl)].
4. L. I. Matienko, L. A. Mosolova, I. P .Skibida, *Kinetika i kataliz,* 1990, **30**, 1377 [*Kinet. Catal.*, 1990, **30** (Engl. Transl.)].
5. R. W. Wilkinson. *Chemistry and Industry,* 1961, Sept.2, 1395.
6. M. N. Nazarov, M. V. Kochinashvili, E. M. Kuramshin, S. A. Kotlyar, *Tezisy VI Vsesoyuznoi konferentsii po okisleniyu organicheskikh soedinenii v zhidkoi fase, Proceedings of VI All-Union conference on the organic compounds oxidation in liquid phase,* L'vov, 1986, 56 (in Russian).
7. A. Knochel, J. Kliems, J. Ochler, and G. Rudolf, *Inorg. Nucl. Chem. Lett.,*1975, **11**, 787.
8. D. Devos, J. Van Daalen, A. C. Knegt, Th. C. Van Heyningen, L. P. Otto, M. W. Von, A. Y. M. Wigsman, and W. L. Driessen, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1319.
9. C. Diche, C. Pascard-Billey, C. Cambillay, and G. Bram, *J. Chem. Soc. Chem. Commun.*, 1977, 183.
10. E. Kimura and R. Nachida, *J. Chem. Soc. Chem. Commun.*, 1984, 499.
11. L. A. Mosolova, L. I. Matienko, I. P. Skibida, *Kinetika i kataliz,* 1988, 29, 1078 [*Kinet. Catal.*, 1988, **29** (Engl. Transl.)].
12. N. M. Emanuel, E. T. Denisov, Z. K. Mayzus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi fase, Chain reactions of hydrocarbons oxidation in liquid phase.* Nauka, Moscow, 1965, 375 (in Russian).
13. O. V. Burlakova, *Pyataya konferentsiya molodykh uchenykh VUZ'ov Irkutskoi obl., chast' 1. Fifth conference of young scientists of Irkutsk region colleges,* part 1: Theses of reports. Irkutsk University, 1987, 124 (in Russian).
14. E. Demlov, Z. Demlov, *Phase transfer catalysis,* Mir, Moscow, 1987, 485 [E. V. Dehmlow, S. S. Demhlow, *Phase transfer catalysis*, Verlag Chemie, Weinheim, 1983].

Received February 8, 1994;
in revised from March 23, 1994