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The *p*-dichlorbenzene oxidising dechlorinating in the presence of copper (II) complexes and nitrogen (II, IV) oxides in the ultrasonic field

Abstract. The results of oxidising dechlorination in solution CuCl2–TBP–HCl–NaNO2–O2–H2O in an ultrasonic field kinetics research are presented in the article. Influence of all system components, influence of modulation frequency and time of the ultrasound exposition is studied and quantitatively described. It is shown that in the presence of ultrasound the system redox potential increases by 200 mV, the binuclear copper(II) complex formation constant increases by one order at smaller (approximately by one order) acidity of the solution.

Keywords: oxidation, dechlorination, p-dichlorbenzene, catalyst, ultrasound, kinetics, mechanism.

Introduction

The action of ultrasonic waves to chemical reactions was revealed for the first time in 1927. The number of the publications devoted to the studying of reactions considerably changing the rate or the direction in the ultrasonic field increases every year. In relation to influence of acoustic vibrations sonochemical reactions can be divided on two groups: one of them are accelerated in an ultrasonic field, but can pass also at its absence although with smaller rate, and others do not proceed absolutely without influence of ultrasonic vibrations. For the actualization of both groups of reactions are applied high- (2-10 MHz), mid- (20-100 kHz) and low-frequency (2-10 Hz) vibrations.

Not only the rate of homogeneous catalytical reactions increases but also the number of catalytical cycles increases under the influence of ultrasound. The ultrasound is one of the factors influencing on catalytical activity of the ferrum(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrinchloride (Fe(TDCPP)Cl) in homogeneous system where reaction of cyclohexanol formation from cyclohexane proceeds on the classical mechanism of hydroxylation with the participation of iodosylbenzene: PhIO is restored to iodobenzene oxidising the Fe(TDCPP)Cl with the result that catalytically active particles of the ferrum(IV)oxoporphyrin radical are formed which immediately hydroxylate the cyclohexane [1]. Optimum conditions of reaction are gathered up: [Fe(TDCPP)Cl] = $3\text{-}10^{-4}$ $mol{\cdot}l^{-1}$ in 1,2-dichloroethane, ultrasonic stirring at 273K in plenty of PhIO. The ultrasound allows to reach extraordinary high exit of the cyclohexanol (96%) and more than to double (from 45 to 96) number of reaction cycles. The catalyst Fe(TDCPP)Cl operating in an ultrasonic field may be considered as good biosimilar model. It is the stable, steady and selective catalyst allowing to receive the cyclohexanol as the sole product.

The number of catalytical cycles with the participation of the water-soluble rhodic catalyst of the alkenes hydroformylation considerably increases under the influence of an ultrasonic field (35-40 kHz). The number of such cycles at the reception of aldehydes in the water solution containing the carbon monoxide and hydrogen in the ratio 1:1 at the pressure 2.5 MPa and also to hex-1-en and rhodic complex $HRhCl(CO)[P(C_6H_4SO_3H)_3]_3$ amount 11,34 under the influence of ultrasound whereas it is equal 3.24 in the conditions of mechanical stirring with a speed 500 $r{\cdot}min^{-1}$.

Thusly, the ultrasound is capable to accelerate a number of homogeneous catalytical reactions, changing their mechanisms in certain cases, and to raise stability of homogeneous catalysts [1].

It is shown for the first time *on the example* *of paradichlorobenzene (p-DCB)* that *p*-DCB catalytical oxidizing dechlorinating is possible to implement in an ultrasonic field at the presence of nitrogen (II-IV) oxides and complex compounds of copper.

Experiment

The process was studied in the static conditions in the kinetic mode using the isothermal device supplied by the potentiometric device consisting of platinum and calomel half-element. The reaction rate was watched by the oxygen absorption rate in the system *p*-DHB–TBP–HCl–CuCl–$NaNO_2$–O_2–H_2O.

The reaction products was defined spectrophotometrically and quantitatively determined by the known technique. The received results have shown that the sole product of the *p*-dihlorbenzene oxidising dechlorinating in the studied conditions is *p*-benzoquinone.

The laboratorial installation for research of sonochemical reactions is presented in [2].

Results and discussion

In the studied conditions (20-60°C), modulation frequency 60-200 kHz, at using of air instead of oxygen and in the absence of natrium nitrite as the nitrogen oxides donor the nitrogen oxides concentration in the solution amount $\sim 10^{-6}$-10^{-7} mol/l and is insufficient for the realisation of *p*-DHB oxidising dechlorinating process.

In the gas phase over the solution nitrogen oxides NO and NO_2 appear which was identified IR-spectrophotometrically, using Specord–7-25 by intensive absorption bands (cm^{-1}): NO_2 (749, 1318, 1617), NO (1880) and N_2O (2190, 2220). The increasing of bands intensity characteristic for NO_2 and the fall of NO bands intensity corresponds to the increasing of oxygen absorption rate on conversion curves and to the redox potential increasing in the solution. The given fact allows to assume that autocatalytic character of curves is conditioned by the occurrence of NO_2 as a result of HNO_2 disproportionation and NO oxidation by oxygen to NO_2.

$$2HNO_2 \rightarrow NO_2 + NO + H_2O$$

$$2NO + O_2 \rightarrow NO_2$$

The basic part of the process carries at constant NO_2 content in the gas phase and invariable redox potential. This fact allows to assume that *p*-dihlorbenzene oxidising dechlorinating catalysis is linked with this particle. The redox potential value is in the interval 0,6-1,1V, at that $d\varphi/da(H_3O^+) > 0$, $d\phi / dC_{HNO_3} > 0$, $d\phi / dC_{CuCl_2} > 0$, $d\phi / dC_{CuCl} < 0$. Thereunder potential of an electrode for the studied systems can be presented in the form:

$$\varphi = 1{,}09 + \frac{RT}{F}\ln\frac{[NO_2]\cdot[H^+]}{[HNO_2]} = 0{,}54 + \frac{RT}{F}\ln\frac{[Cu^{2+}]}{[Cu^+]}$$

The increasing of sodium nitrite concentration in the solution *p*-DCB–TBP–HCl–CuCl–$NaNO_2$–O_2–H_2O leads to the increasing of oxygen absorption rate W_{O_2} and quantity of the absorbed oxygen Q_{O_2}; the correlation $C_{HNO_3} / Q_{O_2} = 4$ corresponds to the stoichiometry of the reaction:

$$4HNO_2 + O_2 \rightarrow 4NO_2 + 2H_2O$$

The increasing of modulation frequency in the interval from 0 to 150 kHz leads to increasing of oxidation rate and maximum shift on curve $Wo_2 = f(Qo_2)$ to the axis of ordinates and the maximum disappears absolutely at the frequency more than 125 kHz (figure 1a). The increasing of modulation frequency leads to the increasing both initial and stationary redox potentials on the potentiometric curves. IR-spectra testify that intensity of absorption bands characteristic for NO_2 (743, 1318, 1617) increases and decrease for NO (1880) with the frequency increasing. The results of the ultrasonic irradiation (at 150 kHz) time influence to the *p*-dihlorbenzene oxidising dechlorinating rate in the solution are received. Optimum time of the ultrasonic irradiation is 40 minutes (figure 2).

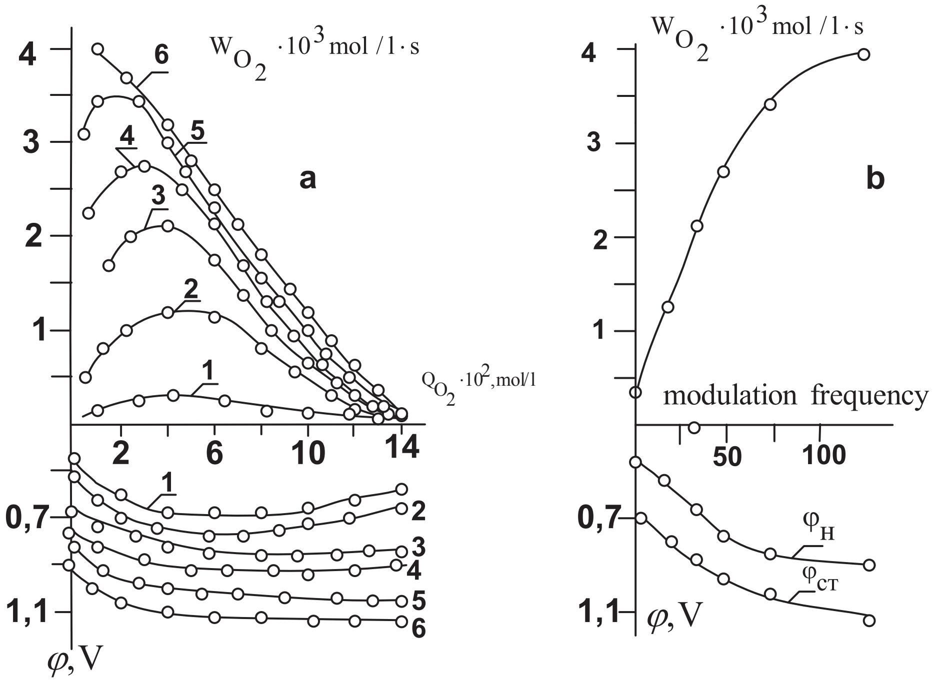

Figure 1 – The *p*-dihlorbenzene oxidizing dechlorinating in the ultrasonic field
T = 323K, P_{O_2} = 1 atm., a, b: C_{NaNO_2} = 2,0·10^{-3} mol/l, C_{CuCl} = 1,3·10^{-3} mol/l, $C_{p-DCB} = 1{,}2 \cdot 10^{-1}$ mol/l, C_{HCl} = 0,5 mol/l

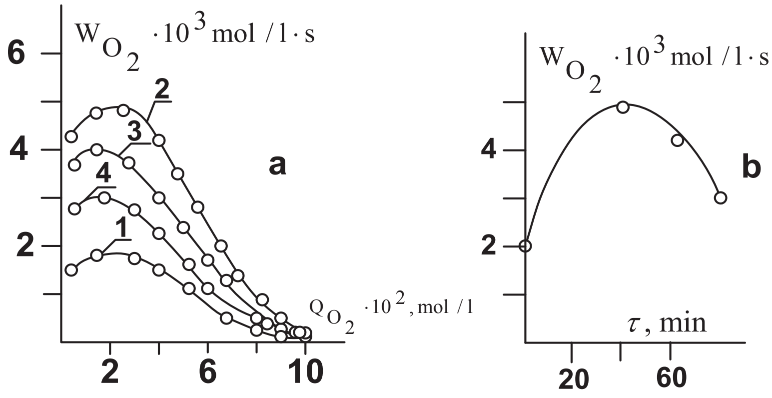

Figure 2 – The *p*-dihlorbenzene oxidizing dechlorinating in the ultrasonic field
T = 333K, P_{O_2} = 1 atm., modulation frequency 60 kHz
a, b : C_{NaNO_2} = 2,0·10^{-1} mol/l, C_{CuCl} = 1,8·10^{-3} mol/l, C_{HCl} = 0,6 mol/l, $C_{п-ДХБ} = 1{,}0 \cdot 10^{-4}$ mol/l,

The dependence of oxygen absorption rate on is described by the equation of the second order (figure 3a, b)

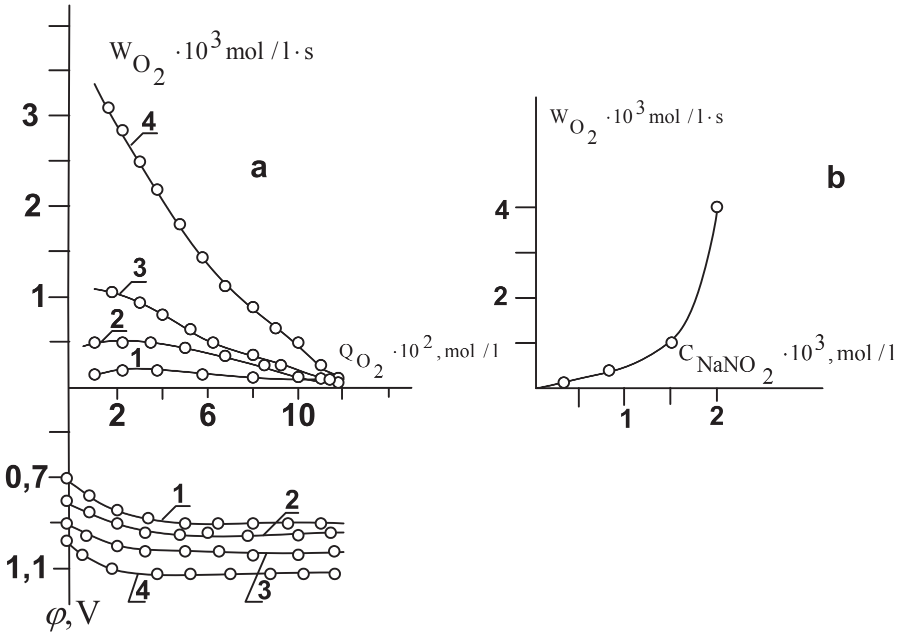

Figure 3 – The *p*-dihlorbenzene oxidizing dechlorinating in the ultrasonic field. T = 333K, P_{O_2} = 1 atm., modulation frequency 60 kHz, irradiation time 40 min.

a, b: $C_{CuCl} = 2{,}4 \cdot 10^{-3}$ mol/l, $C_{HCl} = 0{,}4$ mol/l, $C_{p\text{-}DCB} = 1{,}0 \cdot 10^{-4} \text{mol/l}$, $W = k \cdot C^2_{HNO_2}$ at 333K, k = $1{,}0 \cdot 10^3$ l/mol·min

The received value k by two order more than the similar value presented for the reaction in the absence of ultrasound.

The copper(II) chloride concentration influence to oxygen absorption rate and quantity of the absorbed oxygen in the process of *p*-dihlorbenzene oxidising dechlorinating is studied in the C_{CuCl2} interval from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ mol/l and C_{HCl} from $1 \cdot 10^{-1}$ to $7 \cdot 10^{-1}$ mol/l (figure 4).

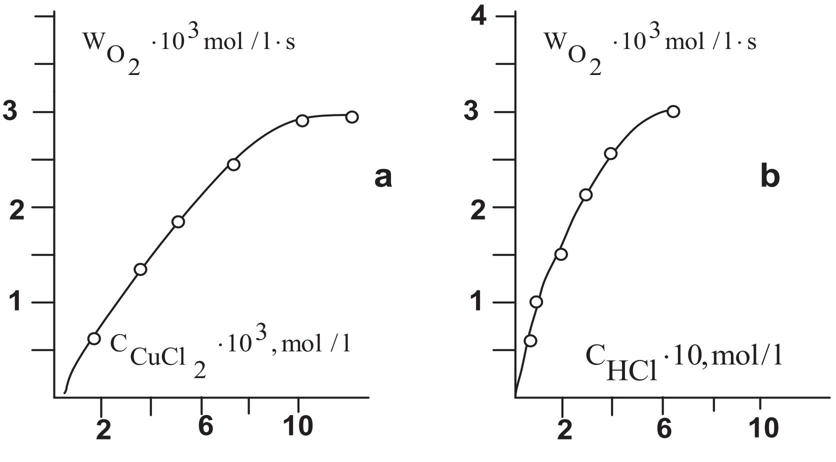

Figure 4 – The *p*-dihlorbenzene oxidising dechlorinating in the ultrasonic field T = 333K, P_{O_2} = 1 atm., modulation frequency 60 kHz, irradiation time 30 min.

a, b: $C_{NaNO_2} = 2{,}0 \cdot 10^{-3}$ mol/l, $C_{p\text{-}ДХБ} = 1{,}0 \cdot 10^{-1} \text{mol/l}$

The results demonstrate that fact that selectivity of process does not change in the studied C_{CuCl_2} interval. The quantity of the absorbed oxygen remain constant and corresponds to the stoichiometry of nitrobenzoquinone reception from *p*-dihlorbenzene**.**

The dependence of oxygen absorption rate in the solution *p*-DCB–TBP–HCl–CuCl–$NaNO_2$–H_2O from initial concentration of copper chloride is described by the equation

$$W_{O_2} = \frac{k_1 \cdot C_{CuCl} \cdot \alpha_2}{1+\alpha_2 \cdot C_{CuCl}},$$

where α – the constant of equibalance

$$CuCl_2^- + CuCl_2^- \xleftrightarrow{\alpha_2} Cu\text{–}Cl\text{–}Cu + Cl^- \quad (7)$$

at 333K, $\alpha = 6.5 \cdot 10^2$ l/mol, $k = 3.75 \cdot 10^2$ l/mol·min.

Thus, redox potential of the system CuCl–$NaNO_2$– HCl–*p*-DCB increases on ~200 mV in the presence of ultrasound, at the same mechanism of oxidising dechlorinating without ultrasound the copper(II) binuclear complex formation constant increases approximately by an order even at smaller (approximately by an order) acidity of the solution.

References

1 Sulman M.G. The influence of the ultrasound on catalytical processes. – M: Successes of chemistry, 2000. – Vol. 69, №2 – P. 178-189.

2 Есенова А.А., Ильяс Р.У., Шакиева Т.В., Елубай М., Емельянова В.С. Влияние ультразвука на кинетику окисления диоксида серы кислородом в присутствии закрепленных на полиакриловую кислоту комплексов кобальта и никеля // Вестник КазНУ. Серия химическая. – 2008. – №1 (49). – С. 168-172.

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Ультрадыбыстық өрісте азот (II, IV) оксиді мен мыс (I, II) комплекстерінің қатысуымен п-дихлорбензолды тотықтыра дехлорлау

Мақалада п-дихлорбензолды CuCl2–ТБФ–HCl–NaNO2–O2–H2O ерітіндіде ультрадыбыстық өрісте тотықтыра дехлорлау кинетикасын зерттеудің нәтижелері көрсетілген. Жүйедегі барлық компоненттердің әсері мен модуляция жиілігі және ультрадыбыстың экспозиция уақыты анықталып көрсетілді. Ультрадыбыстың қатысында жүйенің сұрыптаушылығы өзгермейді, тотығу-тотықсыздандыру потенциалы 200мВ дейін өседі, ерітіндіде Cu2+концентрациясы жоғарылайды, сондықтан дехлорлау процесінің жылдамдығы да жоғарылайды. Ерітіндінің қышқылдығы төмен болғанда (бір есе) мыс (II) биядролық комплексінің түзілу константасы бір есеге өсетіні термодинамикалық есептер арқылы көрсетілген.

Түйін сөздер: тотығу, дехлорлау, п-дихлорбензол, катализатор, ультрадыбыс, кинетика, механизм.

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Окислительное дехлорирование *п*-дихлорбензола в присутствии комплексов меди (II) и оксидов азота (II, IV) в ультразвуковом поле

В статье представлены результаты исследования кинетики окислительного дехлорирования п-дихлорбензола в растворе CuCl2–ТБФ–HCl–NaNO2–O2–H2O в ультразвуковом поле. Изучено и количественно описано влияние всех компонентов системы, влияние частоты модуляции и времени экспозиции ультразвука. Показано, что в присутствии ультразвука селективность процесса не меняется, редокс-потенциал системы возрастает на 200 мВ, в растворе возрастает концентрация Cu2+, и как следствие возрастает скорость дехлорирования. Термодинамические расчеты показали, что константа образования биядерного комплекса меди (II) возрастает на порядок при меньшей (примерно на порядок) кислотности раствора.

Ключевые слова: окисление, дехлорирование, п-дихлорбензол, катализатор, ультразвук, кинетика, механизм.