MECHANISM OF THE OXIDATION OF KETONES IN THE PRESENCE OF COMPLEXES OF COPPER WITH o-PHENANTHROLINE IN ALKALINE MEDIA

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Complexes of copper with o-phenanthroline (Phen) in alkaline media are active catalysts of the liquid-phase oxidation of lower aliphatic alcohols and methyl ethyl ketone (MEK) to acids at 30-50°C in aqueous and in water–alcohol solutions [1-3]. With the goal of establishing the mechanism of the oxidation of ketones, we have investigated the influence of conditions on the composition of the products of the oxidation of cyclohexanone (CH) and have compared the oxidizability of various ketones in the presence of complexes of copper with Phen in the present work.

EXPERIMENTAL

Ketones [cyclohexanone (CH), α-tetralone, 3-heptanone, MEK, 2-pentanone, 5-methyl-3-heptanone, methyl isopropyl ketone, acetophenone, and acetone] were passed through a column of activated Al_2O_3 for removal of traces of hydroperoxides before the experiment.

Oxidation was conducted in the presence of complexes of copper with Phen of various compositions. Since the stability constants of the complexes of Cu(II)•nPhen (n = 1, 2, 3) are sufficiently large, the catalyst was prepared by mixing a solution of $CuCl_2$ and Phen directly in the reaction vessel. A mixture of water and propanol (1:1 by volume) was used as the solvent and the usual volume of the solution was 10 ml.

The total oxidation rate was measured by the absorption rate of O_2 on a manometer with an automatic maintenance of O_2 pressure. The P_{O_2} for most of the experiments was 100 kPa.

For analysis of the products, the reaction was stopped by neutralization of the medium, passing CO_2 through the solution. Cyclohexanone and 1,2-cyclohexanedione (CHD) were analyzed without additional treatment of the sample. For analysis of the acids contained in the sample, the solvent and the neutral products were preliminarily removed by evaporation of the sample in vacuum. The dry residue, containing a mixture of salts of organic acids, was dissolved in an aliquot of water and the solution was acidified with 2 N H_2SO_4 to a pH ~1.

The concentration of reaction products and CH was determined by GLC. Chromaton N-AW-DMCS with 15% silicone DC-550 (0.2-0.3 mm) of the "Chemapol" company, a column length of 120 cm, Ar as the carrier gas, 170°C, and a flame-ionization detector were used for the analysis of CH and CHD, adipic acid, 1-hexanal-6-carboxylic acid (aldehydic acid), and o-phenylenediamine. Polysorb-1 (0.5-0.8 mm), a column of length of 3 m, He as the carrier gas, 140°C, and a katharometer were used for the GLC analysis of low-molecular-weight acids.

The oxidate was subjected to vacuum distillation for identification of CHD. The last fraction, distilling at 150°C, contains CHD and traces of CH. The qualitative reaction to α-diketones was used to detect CHD in the solution [4]. The fraction after its treatment with o-phenylenediamine forms a residue which is poorly soluble in water. A raspberry colored dioxime, which is insoluble in water, forms upon the addition of hydroxylamine hydrochloride and $NiCl_2$ to the aqueous solution of the fraction and heating the solution. A condensation reaction with o-phenylenediamine was used for the quantitative determination of CHD. The amount of CHD was determined by GLC according to the amount of used o-phenylenediamine. The peak corresponding to CHD disappears on the chromatogram with the oxidation of CHD in the presence of $Ca(OH)_2$ and complexes of copper with Phen. Adipic acid (~40%) is formed in the solution, calculated on the converted CHD. The α-keto acid can be formed as a by-product of the oxidation of CHD. A method of further oxidation is used for identification of the aldehydic acid. The peak belonging to this compound completely disappears on the chromatograph upon oxidation of the calcium salt of the probable aldehydic acid [50°C, water–alcohol

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solution containing 0.2 g $Ca(OH)_2$ in 10 ml solution], and adipic acid is formed. The analyzed compound is not a hydroxy acid since the stoichiometry of the absorbed O_2 (1:0,5) corresponds to the reaction

$$HCO(CH_2)_4COOH + 0{,}5O_2 \rightarrow HOOC(CH_2)_4COOH$$

The stoichiometry of the consumption of O_2 must be 1:1 for oxidation of the hydroxy acid.

DISCUSSION OF RESULTS

Optimum pH values of the medium (~12) for the oxidation of MEK in the presence of complexes of copper with Phen can be obtained by the use of $Ca(OH)_2$ as the base [3], whose limited solubility in a water–alcohol medium also allows carrying out the oxidation at a constant pH value up to the depths of conversion of the substrate. Therefore, we used $Ca(OH)_2$ as the base in the present work. Paraffin and aromatic hydrocarbons (decane, cumene, ethylbenzene) and also monoolefins (cyclohexene) are practically unoxidized in alkaline media in the presence of complexes of copper with Phen. Cyclopentadiene, which, as is known, easily forms carbanions under the action of bases, is oxidized at high rates in alkaline media. Aliphatic alcohols (methanol, ethanol, propanol) are oxidized only in nonaqueous media. Methanol, having the smallest pK_a value (~16), is oxidized at the highest rates [5]. Ketones are oxidized at even higher rates in water–alcohol solutions in the presence of $Ca(OH)_2$ and complexes of copper with Phen.

The dependence of the oxidizability of the compounds under investigation in the presence of complexes of copper with Phen on their strucutre conforms well with the assumption of the participation of carbanions in the limiting stage of the process.

The activation energy (E_a) of the oxidation of CH in a system of water, propanol, $CuCl_2$ ($5 \cdot 10^{-4}$ mole/liter), Phen ($1.5 \cdot 10^{-2}$ mole/liter), and $Ca(OH)_2$, measured by the initial rate of the absorption of O_2, is equal to 13 kcal/mole and is close to the E_a for the oxidation of CH in an alkaline medium by chloramine-T (9.7 kcal/mole) [6]. By the analogy with [6] one can assume that the rate of oxidation of cyclohexanone in our case is also limited by the rate of formation of carbanions, which explains the correlation between the "oxidizability" of organic compounds and the pK_a values.

From the kinetic curves of the absorption of O_2 during the oxidation of various ketones (Fig. 1) it is evident that CH is oxidized at the greatest rate and acetophenone, methyl naphthyl ketone, methyl isopropyl ketone, and acetone at the smallest rates. For acetophenone and acetone the pK_a values are equal to 19 and 20, respectively, while the pK_a for CH is 16.7 [7]. The rate of absorption of O_2 during oxidation of cyclopentadiene (pK_a = 15 [5]) is triple the rate of oxidation of CH. Polymeric substances are formed as oxidation products in the latter case.

Only AcOH is formed during the oxidation of MEK; formic and propionic acids are practically absent (Table 1). Evidently, in an alkaline medium MEK is not able to form carbanions with the charge on the primary C atom. The difficulty of deprotonization of the CH_3 group probably also causes the low oxidizability of acetophenone, methyl naphthyl ketone, and acetone. During the oxidation of MEK by chloramine-T in an alkaline medium the CH_3 group is also not affected, since diketone is the only oxidation product of MEK in this case [8], which indicates the low concentration of carbanions with the charge on the primary C atom.

The rate of oxidation of ketones and other organic compounds in alkaline media depends both on the ability of the substrate to form carbanions and also on the activity of these carbanions. Thus, benzaldehyde, acetylacetone, and phenol, which are characterized by high acidity of O–H and C–H bonds and are capable of forming stable carbanions under the action of a base, are slowly oxidized in our conditions. The low nucleophilicity of the carbanions which are formed in this case evidently determines the small rate of their reaction with O_2.

The primary products of the oxidation of all ketones in our conditions are acids (see Table 1). Aldehydic acid and CHD (Fig. 2), being the only reaction products in the initial stages, are formed along with adipic acid during the oxidation of CH. The amount of aldehydic acid is negligible. The relationship of the concentrations of adipic acid and CHD weakly depends on the concentrations of the catalyst and CH. Aldehydic acid is formed, in our opinion, during catalytic hydration of CHD

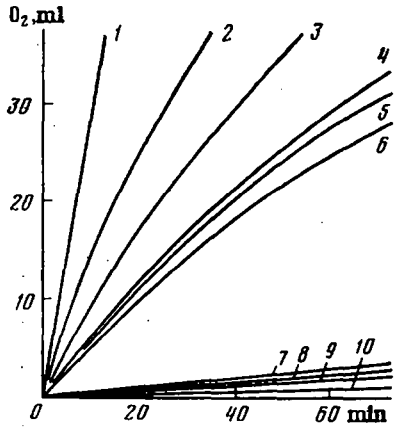


Fig. 1

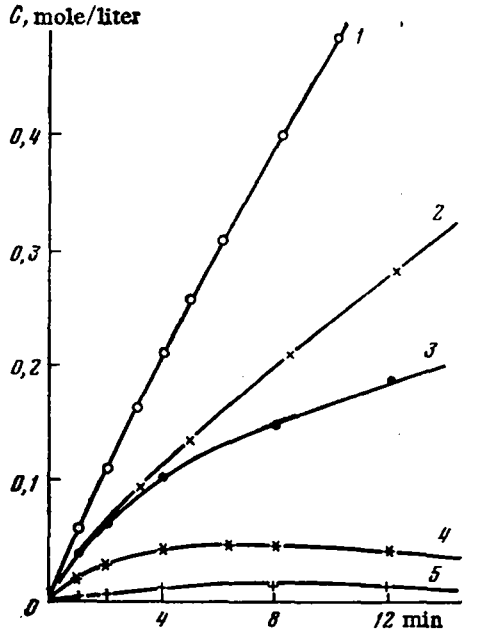


Fig. 2

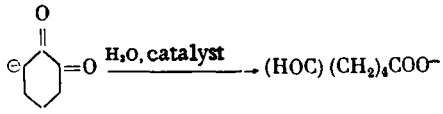
Fig. 1. Kinetic curves of the absorption of oxygen during the oxidation of ketones: 1) cyclohexanone; 2) α-tetralone; 3) 3-heptanone; 4) methyl ethyl ketone; 5) 2-pentanone; 6) 5-methyl-3-heptanone; 7) methyl isopropyl ketone; 8) methyl naphthyl ketone; 9) acetophenonone; 10) acetone. $[CuCl_2] = 2.5 \cdot 10^{-3}$, [Phen] $= 7.5 \cdot 10^{-3}$ mole/liter, 5 ml H_2O, 5 ml hempa, 5 mmole ketone, 50°C, 0.1 g $Ca(OH)_2$, P_{O_2} = 100 kPa.

Fig. 2. Kinetic curves of the absorption of oxygen (1), the consumption of $Ca(OH)_2$ (2), and the accumulation of adipic acid (3), CHD (4), and aldehydic acid (5) during the oxidation of cyclohexanone. $[CuCl_2] = 2.5 \cdot 10^{-3}$, [Phen] $= 1.5 \cdot 10^{-2}$, [CH] = 1 mole/liter, 5 ml H_2O, 5 ml 1-propanol, 50°C, P_{O_2} = 100 kPa.

TABLE 1. Accumulation of Acids in the Process of the Oxidation of Aliphatic Ketones, $[CuCl_2] = 2.5 \cdot 10^{-3}$ mole/liter, [Phen] $= 7.5 \cdot 10^{-3}$ mole/liter, 5 ml H_2O, 5 ml propanol, 5 mmole ketone, 0.2 g $Ca(OH)_2$, 50°C, P_{O_2} = 100 kPa

Ketone	$W_{O_2} \cdot 10^5$, mole/liter·sec	ΔO_2 mmole	Time,* min	HCOOH	CH_3COOH	EtCOOH	Total acid†
				mmole			
3-Heptanone	6,6	2,4	70	–	0,3	0,23	2,7
2-Butanone	4,7	2,6	120	–	2,0	–	2,7
3-Methyl-2-butanone	4,0	2,4	150	–	0,6	0,17	2,7
5-Methyl3-heptanone	3,2	2,8	130	–	0,34	0,17	2,7
Acetone	0,1	1,0	200	0,03	0,05	–	

*The time is indicated corresponding to the complete neutralization of the solution (with the exception of acetone), i.e., to the formation of 2.7 mmoles of acid.
†Calculated on the formation of a monobasic acid.



since upon evaporation of alkaline solutions of the reaction products in the presence of complexes of copper with Phen practically all of the CHD is converted to aldehydic acid.

TABLE 2. Rates of the Accumulation of Adipic Acid and the Consumption of CHD and Aldehydic Acid ($[CuCl_2] = 2.5 \cdot 10^{-3}$ mole/liter, $[Phen] = 1.5 \cdot 10^{-2}$ mole/liter, [CH] = 1 mole/liter, 0.2 g $Ca(OH)_2$, 50°C, P_{O_2} = 100 kPa)

Time, min	Concentration, mole/liter		Rate, mole/liter·sec		
	CHD	aldehydic acid	accumulation of adipic acid ($\cdot 10^4$)	consumption of CHD ($\cdot 10^5$)	consumption of aldehydic acid* ($\cdot 10^6$)
2	0,03	0,0027	4	3,2	2,2
4	0,04	0,009	2,6	4,5	7,4
8	0,05	0,010	2,1	3,0	8,2

*Calculated from data of Figs. 2 and 3.

With the goal of establishing the path of the formation of adipic acid, its accumulation rate was compared with the rates of consumption of aldehydic acid and CHD.

The absorption of O_2 during the oxidation of aldehydic acid is well described by the first-order expression (Fig. 3). Determined by the dependence of W_0 on the concentration of aldehydic acid, $k = (8.2 + 0.8) \cdot 10^{-4}$ sec^{-1} ($[CuCl_2] = 2.5 \cdot 10^{-3}$, $[Phen] = 1.5 \cdot 10^{-2}$ mole/liter, 0.1 g $Ca(OH)_2$ (10 ml solution)). The initial rate of oxidation of CHD to adipic acid under these same conditions and [CHD] = 0.05 mole/liter (the maximum CHD concentration reached in the experiments amounts to $2.5 \cdot 10^{-5}$ mole/liter·sec). From Table 2 it is evident that rates of consumption of CHD and aldehydic acid are practically two times slower than the rate of accumulation of adipic acid. Consequently, practically all of the adipic acid is formed directly from CH, passing the stage of the formation of intermediate products.

During oxidation of CH, and also other ketones, practically all of the copper is found in the oxidized state (+2). However, if in the course of oxidation the stirring is stopped and the diffusion of O_2 in the solution is hindered, then the complex of Cu(I) with Phen quickly begins to accumulate, which possesses high activity in the reaction of the oxidation of ketones at a pH >9. A very high absorption rate of O_2 is observed in the first moment upon using $[Cu(Phen)_2]^+$* as the original catalyst. After 5-10 sec from the conversion of practically all of the copper to Cu(II), the rate of absorption of O_2 coincides with that observed using $[Cu(Phen)_2]^{2+}$ as the original catalyst. The complex of Cu(I) with Phen is stable at a pH of 12 in the absence of a ketone in the water–alcohol solution.

The oxidation of ketones conforms to a first-order expression with respect to the concentration of the ketone and $[Cu(II)(Phen)_2]^{2+}$, the oxidation rate increases with an increase in the pH of the medium. An increase in the activity of the carbanion in the presence of the catalyst is dependent on the bonding of it with the copper–phenanthroline complex [3]. Since Cu(I) is a stronger electron donor than Cu(II), the carbanion in the complex of Cu(I) can react with O_2 at high rates, which also causes a high oxidation rate in the presence of $[Cu(Phen)_2]^+$.

It is known that O_2 is activated in processes of liquid-phase oxidation through the formation of peroxide compounds, i.e., by means of the transfer of two electrons on the O_2 molecule. The reaction of the coordinated carbanion A^- with O_2 is possible during oxidation of carbanions in our experiments according to the reaction

$$[Cu^{n+}(Phen)_2 \cdot A^-] + O_2 \rightarrow [Cu^{(n+1)+}(Phen)_2 \cdot AO_2^{2-}]$$

in which O_2 obtains one electron the carbanion, and the second from the Cu^{n+} ion. It is evident that in such a reaction the Cu(I) complex can be more active, since the conversion of Cu(I) to Cu(II) proceeds much easier than the conversion of Cu(II) to Cu(III).

The $[Cu(II)(Phen)_2 \cdot AO_2^{2-}]$ can be oxidized further to adipic acid or CHD according to the scheme

$$[Cu(II)(Phen)_2 \cdot AO_2^{2-}] \xrightarrow{Cu(I),\ O_2} 2[Cu(II)(Phen)_2]^{2+} + (CH_2)_4(COOH)_2 \text{ (Adipic Acid)} \quad (1)$$

$$[Cu(II)(Phen)_2 \cdot AO_2^{2-}] \rightarrow [Cu(I)(Phen)_2]^+ + C_6H_8O_2 \text{ (CHD)} \quad (2)$$

*The complex $[Cu(Phen)_2]^+$ was accumulated by means of reduction of Cu(II) in the reaction medium in an Ar atmosphere.

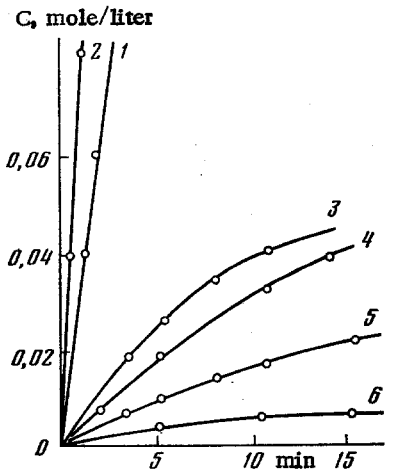


Fig. 3

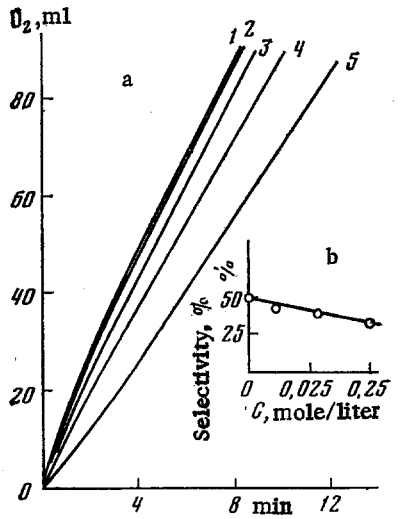


Fig. 4

Fig. 3. Kinetic curves of the accumulation of adipic acid (1) and the absorption of oxygen during the oxidation of 1.0 mole/liter cyclohexanone (2), 0.05 mole/liter CHD (3), and 0.085 (4), 0.034 (5), and 0.018 mole/liter (6) aldehydic acid. The conditions are given in Fig. 2.

Fig. 4. Kinetic curves of the catalytic oxidation of cyclohexanone (a) without introduction (1) and with introduction at the start of the reaction of 0.2 g adipic acid (2) and CHD in concentrations (mole/liter): 0.01 (3), 0.028 (4), and 0.05 (5). The dependence of the selectivity of the formation of adipic acid (b), calculated on the absorption of O_2, on the concentration of CHD, introduced at the start of the reaction; ΔV_{O_2} is 100 ml. The conditions are given in Fig. 2.

The second copper ion can take part in reaction (2). Analogously, the formation of acid with participation of complexes of divalent copper can be accomplished according to the scheme

$$\{Cu(II)(Phen)_2 \cdot A^-]^+ + O_2 \rightarrow [Cu(III)(Phen)_2 \cdot AO_2^{2-}] \xrightarrow{Cu(II)} 2[Cu(I)(Phen)_2]^+ + (CH_2)_4(COOH)_2 \quad (3)$$

Since the conversion of Cu(II) to Cu(III) is difficult as compared with the conversion of Cu(I) to Cu(II), the conversion of cyclohexanone according to reaction (3) evidently limits the process.

Along with reaction (3) the reaction products could be formed through the intermediate formation of the radical A•, coordinated by a copper ion. The reduction of Cu(II) to Cu(I) must limit such a process

$$[Cu(II)(Phen)_2]^{2+} \xrightarrow{A^-} [Cu(I)(Phen)_2 \cdot A^{\cdot}]^+ \begin{cases} \xrightarrow{O_2} [Cu(I)(Phen)_2 \cdot AO_2^{\cdot}] \xrightarrow{Cu(II)} 2[Cu(I)(Phen)_2]^+ + C_6H_{10}O_2 & (4) \\ \xrightarrow{Cu(II)} 2\,|\,Cu(I)(Phen)_2]^+ + \text{Products} & (5) \end{cases}$$

However, the rate of reduction of Cu(II) to Cu(I) in an anaerobic medium [reaction (5)] is 50 times less than the rate of oxidation of CH and, consequently, the conversion of Cu(II) to Cu(I) cannot limit the oxidation reaction. It could be possible to assume that the conversion of Cu(II) to Cu(I) is accelerated through the participation of O_2 in the limiting stage. In this case one would expect the dependence of W_{O_2} on P_{O_2} in a large range of P_{O_2} change. In our case, W_{O_2} ceases to depend on $[O_2]$ at $P_{O_2} > 20$ kPa. Consequently, such a reaction cannot introduce a significant contribution to the total oxidation rate.

Accumulation of CHD leads to an increase in the reduction rate of Cu(II) to Cu(I), which could lead to acceleration of the oxidation. In reality, W_{O_2} falls with an increase in the

depth of the reaction according to the accumulation of CHD. Additions of CHD to the original mixture noticeably decrease the absorption rate of O_2 and the selectivity of the formation of adipic acid does not influence the oxidation rate. The observed inhibition effect is evidently connected with a modification of the catalyst in the presence of CHD, which is indicated by the disappearance of the bands in the absorption spectra of the solution which are characteristic for complexes of copper with Phen. The direction of the reaction is changed in the presence of the modified catalyst. It is possible that radical processes, leading to the formation of bifunctional products, begin to play a role.

CONCLUSIONS

1. In alkaline media, complexes of copper with o-phenanthroline catalyze the oxidation of organic compounds which are capable of forming carbanions. The oxidation rate is determined by the concentration and nucleophilicity of the carbanions.

2. The sequence of the formation of the oxidation products of cyclohexanone in the presence of complexes of copper with o-phenanthroline in alkaline media is established and a mechanism for the process is suggested.

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INFLUENCE OF THE SOLVENT ON THE KINETICS OF THE REVERSIBLE RECOMBINATION OF 2-ARYLINDAN-1,3-DIONYL RADICALS

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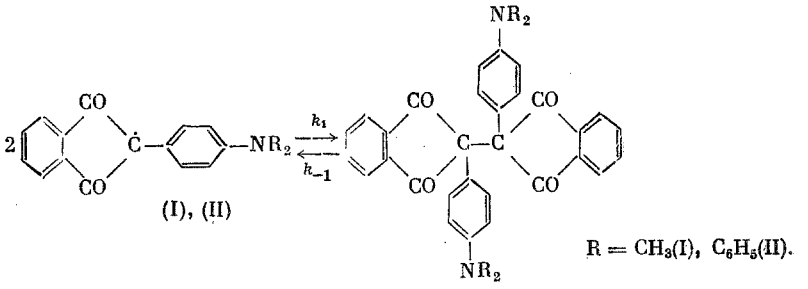
UDC 541.12.038,2:541.127:541.515

One is able to separate the effects which are dependent on the viscosity of the solvent and those dependent on specific solvation [1] as a result of research of the influence of the solvent on the kinetics of rapid radical reactions. So, during the reversible recombination of 2-(4'-dimethylaminophenyl)indan-1,3-dionyl (I) and 2-(4'-diphenylaminophenyl)indan-1,3-dionyl (II) radicals [2]



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