React. Kinet. Catal. Lett., Vol. 19, No. 3–4, 263–266 (1982)

UNUSUAL SELECTIVITY OF ALCOHOL OXIDATION BY OXYGEN IN AQUEOUS ALKALINE SOLUTIONS OF COPPER PHENANTHROLINE COMPLEXES

V. P. Tretyakov, G. P. Zimtseva, E. S. Rudakov and A. V. Bogdanov

Institute of Physical Organic and Coal Chemistry, Donetsk, USSR

Received August 5, 1981
Accepted November 27, 1981

In aqueous alkaline solutions copper phenanthroline complexes catalyze the oxidation of primary alcohols and cyclohexanol to carboxylic acids at 333–373 K and P_{O_2} = = 0.2–0.4 MPa. Unlike in radical-chain and metal-complex oxidation, secondary and acyclic alcohols are not oxidized in these conditions.

В водных щелочных растворах фенантролиновые комплексы меди катализируют окисление первичных спиртов и циклогексанола в карбоновые кислоты при температурах 333–313 К и давлении кислорода 0,2–0,4 МПа. Вторичные ациклические спирты не окисляются в этих условиях в отличие от радикальноцепного и металлокомплексного окисления.

In the presence of copper phenanthroline complexes and strong bases primary (CH_3OH, C_2H_5OH, C_3H_7OH) and secondary (iso-C_3H_7OH) alcohols are oxidized by oxygen at 303–318 K and P_{O_2} = 0.1 MPa /1/. CH_3OH produces formaldehyde and formic acid. Methyl alcohol-benzene mixture (1 : 1 vol.) absorbs oxygen more rapidly as compared with methanol without benzene additives /2/. The addition of water sharply decreases the rate of oxidation of methanol by oxygen catalyzed by copper phenanthroline complexes in basic media. Oxygen absorption completely ceases when the water concentration in the aqueous methanol solution reaches 20 M /2/.

We have found that in more severe conditions (333–373 K, P_{O_2} = 0.2–0.4 MPa) the copper phenanthroline catalyzed oxidation of alcohols by oxygen also takes place in aqueous alkaline solutions and the selectivity is unusual

The reaction was studied in a 30 cm^3 shaken temperature-controlled glass reactor modified to operate at pressures of up to 0.4 MPa. Oxygen absorption was recorded according to the volume variations under the piston of a 20 cm^3 glass syringe connected with the reactor by a capillary tube. The syringe piston was loaded with a weight

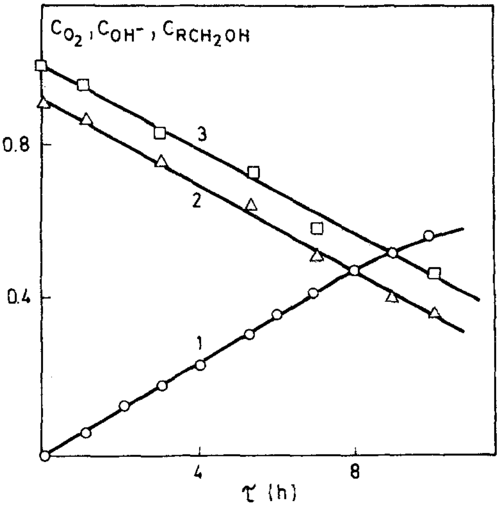

Fig. 1. Oxidation of ethyl alcohol by oxygen, T = 370 K, P_{O_2} = 0.32 MPa. [$CuCl_2$] = 1 x 10^{-2}, [o-phen] = 2 x 10^{-2} M. 1. Oxygen consumption (mol) per 1 l of solution – C_{O_2}; 2. Variations in NaOH concentration (M) – C_{OH^-}; 3. Variation of ethyl alcohol concentration (M) – C_{RCH_2OH}

corresponding to the internal pressure. Kinetic measurements were carried out on a modified setup with a U-shaped manometer as a measuring unit, which separates the reactor from a buffer vessel filled with oxygen.

Alcohol concentrations after the experiments were determined by the GLC method. Carboxylic acids were identified by GLC and paper chromatography techniques. The yields of acids were found using GLC and the titration of solution samples with 0.1 M sulfuric acid.

Initial concentrations of alcohols, alkali and catalyst in the solutions were ranging within 0.1–1.0, 0.1–1.0 and 1 x 10^{-3}–1 x 10^{-2} M, respectively, at the ratio Cu(II) : O-Phen = 1 : 2.

Unlike in non-aqueous media /1/, when the oxidation of alcohols in aqueous alkaline solutions is catalyzed by copper phenanthroline complexes, oxygen is absorbed without an induction period. The rates of consumption of oxygen and alcohol coincide at the initial portions of the kinetic curves and are equal to the accumulation rate of the respective carboxylic acid anions (Fig. 1). The reaction stoichiometry fits the equation

$$R\text{–}CH_2OH + OH^- + O_2 = RCOO^- + 2H_2O,$$

Table 1

Oxidation of alcohols by oxygen catalyzed by copper phenanthroline complexes in alkaline aqueous solutions at 370 K, $P_{O_2} = 0.32$ MPa; $[CuCl_2] = 1 \times 10^{-2}$, [o-phen] $= 2 \times 10^{-2}$ M

Substrate (RCH_2OH)	[RCH_2OH] (M)	[NaOH] (M)	$W \times 10^{6\,a}$ ($mol\ l^{-1}\ s^{-1}$)	Reaction time (h)	Conversion of RCH_2OH(%)	Ratio of reacted components $O_2 : RCH_2OH : NaOH$
CH_3OH	1.0	1.0	3	6	10	1 : 1 : 1
C_2H_5OH	1.0	1.0	17	9	55	1 : 1 : 1
C_3H_7OH	1.0	1.0	67	0.5	10	1 : 1 : 1
C_3H_7OH	1.0	1.0	67	2	33	5 : 3 : 5
iso-C_3H_7OH	1.0	1.0	0	4	0	–
C_4H_9OH	0.4	0.5	50	4	50	2 : 1 : 2
sec-C_4H_9OH	1.0	1.0	0	4	0	–
tert.-C_4H_9OH	1.0	1.0	0	4	0	–
iso-C_4H_9OH	0.4	0.6	30	3	–	–
cyclo-$C_6H_{11}OH^b$	0.25	0.3	25	2.5	36	2 : 1 : 2

[a] W is the oxidation rate, the amount of O_2 (mol) consumed in the linear section of the kinetic curve by one liter of the solution per second; O_2 is not consumed without catalyst.

[b] Without catalyst ($[C_6H_{11}OH] = 0.25$, $[NaOH] = 0.3M$, $P_{O_2} = 0.32$ MPa, 370 K), $W = 1 \times 10^{-6}$ mol l^{-1} s^{-1}.

where R is a primary alkyl group or H. Data on the oxidation of alcohols are listed in Table 1. Methyl alcohol is oxidized to formic acid. Ethyl alcohol is selectively oxidized to acetic acid up to 55% conversion. The oxidation of n-propyl and butyl alcohols is selective only at low conversions (up to 20%). At higher extents of oxidation of butyl alcohol (50%) a mixture of butyric and propionic acids is formed. The oxidation product of cyclohexanol is adipic acid. At 36% conversion of the alcohol the ratio of the reacted components is O_2 : cyclohexanol : NaOH = = 2 : 1 : 2, which coincides with the stoichiometry of adipic acid formation. Without catalyst and at 370 K, cyclohexanol is slowly oxidized mainly to CO_2.

The reactivity of alcohols increases in the series: $CH_3OH\ (1) < C_2H_5OH\ (6) < C_3H_7OH\ (22) < \text{iso-}C_4H_9OH\ (43) < C_4H_9OH\ (83) < C_6H_{11}OH\ (100)$.

In the same conditions iso-C_3H_7OH, sec-C_4H_9OH and tert-C_4H_9OH are not oxidized. This selectivity of the oxidation of primary and secondary alcohols seems unusual. Other systems demonstrate a normal type of the selectivity: $CH_3OH < C_2H_5OH < \text{iso-}C_3H_7OH < \text{sec-}C_4H_9OH$, e.g. when alcohols are oxidized by palladium salts in aqueous solution /3/, and when radical-chain oxidation by oxygen takes place /4/.

The available data are insufficient to establish the reaction mechanism. The inertness of the CH group of the secondary alcohols $(CH_3)_2CHOH$ and $CH_3(C_2H_5)CHOH$, as compared with the CH_2 group of the primary alcohols, could be attributed either to steric hindrance or to a four-electron reaction mechanism /5/. But the high oxidation rate of the secondary alcohol (cyclohexanol) is at variance with this interpretation. However, in the case of cyclohexanol, which is also oxidized by oxygen in alkaline solutions without catalyst, an alternative oxidation mechanism is possible.

REFERENCES

1. W. Brackman, C. I. Gaasbeek: Recl. Trav. Chim., Pays-Bas, *85*, 242 (1966).
2. O. N. Emanuel, A. M. Sakharov, I. P. Skibida: Izv. Akad. Nauk SSSR, Ser. Khim., *12*, 2692 (1975).
3. I. V. Kozhevnikov, V. E. Taraban'ko, K. I. Matveev: Kinet. Katal., *21*, 940 (1980).
4. E. T. Denisov, N. I. Mitskevich, V. E. Agabekov: Mechanisms of the Oxidation of Oxygen-Containing Compounds in Liquid Phase, p. 26. Nauka i Tekhnika, Minsk 1975.
5. A. E. Shilov, A. A. Shteinman: Kinet. Katal., *14*, 149 (1973).